



Jürn W. P. Schmelzer, Gerd Röpke, and Vyatcheslav B. Priezzhev (Editors)









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Nucleation Theory and Applications

JÜRN W. P. SCHMELZER, GERD RÖPKE, AND VYATCHESLAV B. PRIEZZHEV (EDITORS)



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The present book consists of contributions directed to the analysis of first- and second-order phase transitions from both experimental and theoretical points of view. They have been presented and discussed in the course of the research workshops «Nucleation Theory and Applications» organized at the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research in Dubna, Russia, in the period from 2009 to 2011. The volume of the proceedings supplements results published in three former conference proceedings in the years 1999, 2002, 2005 and 2009 also in Dubna and two monographs with overview lectures published by WILEY-VCH in 1999 and 2005 as well as in a series of monographs by the participants. In the present proceedings, the spectrum of different topics includes experimental investigations of thermodynamic properties of matter (in thermodynamic equilibrium and non-equilibrium states including glasses), nucleation-growth phenomena and their theoretical interpretation, the theoretical analysis of the course of first- and second-order phase transitions, the discussion of principal problems of the thermodynamic description of clusters, molecular-dynamic analyses of phase equilibria and clustering phenomena, and a variety of applications.

Теория нуклеации и ее применения / Под ред. Ю. Шмельцера, Г. Рёпке, В. Б. Приезжева. — Дубна: ОИЯИ, 2011. — XIII, 483 с.

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В сборнике представлены результаты экспериментального и теоретического анализа фазовых превращений первого и второго рода, которые докладывались и обсуждались на рабочих совещаниях «Теория нуклеации и ее применения», проходивших в Лаборатории теоретической физики им. Н. Н. Боголюбова Объединенного института ядерных исследований в 2009–2011 гг. Эти результаты дополняют обзор результатов, опубликованных в четырех предыдущих томах серии, вышедших в свет в 1999, 2002, 2005 и 2009 гг. в Дубне, двух монографиях, выпущенных в 1999 и 2005 гг. издательством WILEY-VCH, и в ряде монографий участников. Сборник состоит из 25 глав, в которых отражены результаты экспериментального анализа свойств веществ (в термодинамически равновесных и неравновесных состояниях, включая стекла), процессов нуклеации и роста кластеров новых фаз и теоретическая интерпретация этих данных, общий теоретический анализ фазовых превращений первого и второго рода, обсуждаются принципиальные вопросы термодинамического описания кластеров, молекулярно-динамического анализа фазовых равновесий и процессов агрегации, а также рассматриваются разнообразные применения теории.

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Preface

... wir wollen froh sein, wenn wir in unserer Lage und geschichtlichen Entwicklung in Europa Mächte finden, mit denen wir auf keine Art von Konkurrenz der politischen Interessen angewiesen sind, wie das zwischen uns und Russland bisher der Fall ist ..., wenn nicht liberale Dummheiten oder dynastische Missgriffe die Situation fälschen.

Otto von Bismarck

Чернобыль - трагедия и моей жизни тоже. Я ощущаю это каждую секунду.

Когда катастрофа произошла, и я узнал, что там натворили, чуть на тот свет не отправился. Потом решил немедленно уйти с поста президента Академии наук, даже обратился по этому поводу к М. С. Горбачеву. Коллеги останавливали меня, но я считал, что так надо. Мой долг, считал я, все силы положить на усовершенствование реактора...

Но я покривил бы душой, если бы согласился с мнением, что теперь атомную энергетику развивать не надо и все АЭС следует закрыть.

Отказ человечества от развития атомной энергетики был бы для него губителен. Такое решение не менее невежественно и не менее чудовищно, чем тот эксперимент на Чернобыльской АЭС, который непосредственно привел к аварии.

Анатолий П. Александров

The present book consists of contributions devoted to the analysis of first- and second-order phase transitions and the glass transition both from experimental and theoretical points of view. They have been presented and discussed in the course of the research workshops *Nucleation Theory and Applications* held in Dubna, Russia, in the yearly meetings in April 2009-2011. Hopefully, the results will be of use also for other colleagues engaged in similar problems.

The programs of the workshops and the list of participants are given in the appendix. In the appendix, also the content of the first four volumes of the proceedings, covering the periods from 1997-1999, 2000-2002, 2003-2005, and 2006-2008 is reprinted as well as the content of two monographs with overview lectures published by WILEY-VCH in 1999 and 2005. In addition, a list of some other monographs published by participants of the workshops is given there as well. The cover pages of most of these books are given at the cover pages of the present volume. They give some interesting insight into the topics of discussion for about a period of fifteen years, now.

The general aim of these meetings was and is [i.] to bring together a number of leading scientists in the field of the theoretical description and experimental investigations of first- and second-order phase transformations of the member countries of the Joint Institute for Nuclear Research, of Germany and beyond; [ii.] to discuss recent developments in this field with particular emphasis on the work done in the different groups invited; [iii.] to establish and/or tighten direct cooperation links; [iv.] to carry out research on common research projects; [v.] and to check whether the experimental facilities available at the Joint Institute for Nuclear Research in Dubna can be utilized for an experimental investigation of the kinetics of phase transformation processes in different systems of interest. These aims could be fully realized, again.

The workshops could not have been organized without the financial support of a number of organizations and institutions. Further funding was required, of course, to obtain the results which are presented and discussed in the workshop. Some of the sponsoring organizations, we would like to express our particular gratitude, are (in alphabetic order): (i.) Brazilian State of São Paulo Research Foundation; (ii.) Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) Germany (via Research projects, the TRANSFORM and Heisenberg-Landau programs); (iii.) DESY Hamburg, Germany; (iv.) Deutsche Forschungsgemeinschaft (DFG) (via Research projects, travel, conference and publication grants); (v.) Deutscher Akademischer Austauschdienst (DAAD); (vi.) Helmholtz-Gemeinschaft Deutscher Forschungszentren; (vii.) Leibniz Institute for Tropospheric Research, Leipzig, Germany, for additional funding of publications; (viii.) QSIL Langewiesen, Germany; (ix.) Russian Foundation for Basic Research (RFBR). To all above cited organizations and those not mentioned explicitely, we would like to express our sincere thanks, as well as to all colleagues who helped us in the organization of the workshops. In particular, we would like to express our thanks here to V. I. Zhuravlev, G. G. Sandukovskaya, and E. N. Rusakovich.

It is a particular pleasure to publish the present book in 2011 which has been declared as the German-Russian Science Year. As noted by Mrs. Annette Schavan, Federal Minister of Research and Education, "Such a year of science highlights the diversity of German-Russian cooperation in education and research". We intend with the present volume to give a contribution to the reflection of such diversity.

In the preparation of the spectrum of activities connected with the German-Russian Science Year, bilateral intergovernmental consultations reaffirmed the strategic partnership in education, research and innovation. In line with such strategic statements, it is planned to continue the research workshops also in the next years. The respective information will be given at the homepage **http://theor.jinr.ru** of the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research and via Email. For questions, please contact us [preferably via Email: juern-w.schmelzer@uni-rostock.de (J. W. P. Schmelzer)].

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1 Introductory Remarks

Doctrina multiplex, veritas una.

Inscription written at the front of the main building of the University of Rostock

Wenn es nur eine Wahrheit gäbe, könnte man nicht hundert Bilder über dasselbe Thema malen.

Pablo Picasso

¹Ob die Kälte die Ursache für die Sterngestalt beim Schnee ist? Wahrlich, ohne echtes Wissen ist das Leben tot.

Johannes Kepler

The present book contains overviews on lectures which have been presented at the Research workshops *Nucleation Theory and Applications* in Dubna in the last three years (2009-2011). In accordance with the general line of organization of these workshops, they represent either an account of the work which has been performed independently by colleagues from the different groups invited or they contain results worked out in the last years during the research workshops and in between them in the framework of different common projects. Thus, the presence of the same authors in several contributions is obviously unavoidable in order to give some account of the results of the common work.

Of course, neither all contributions presented nor all of the results obtained in the common research can be included in one book. In the appendix, the programs of the workshops are given in order to allow one to obtain some more general overview and to give also the possibility to establish direct contacts to the respective colleagues. In addition, also the content of volumes 1-4 of the proceedings is reprinted giving an account on the work performed earlier. It is one of the most pleasing results of the workshops that the number of direct contacts in the network of cooperation links has been again increased considerably. Hopefully, this book can facilitate further advances in this respect.

In the present proceedings, the spectrum of topics includes direct experimental investigations both of thermodynamic properties of matter (in thermodynamic equilibrium and non-equilibrium states including glasses) and nucleation-growth phenomena and their interpretation, the theoretical analysis of the course of first- and second-order phase transitions, the discussion of principal problems of the thermodynamic description of clusters and a variety of applications. In particular, I would like to mention the spectrum of contributions devoted to phase formation processes in nuclear matter and their analogies and differences to phase formation in the other more conventional fields of applications. Hereby, contributions are included (at the status of preprints), again, which have been submitted in an appropriate form till the end of the workshop 2011 or some finite time afterwards.

In the absolute majority of cases (but not in all), the results reported, and presented now here, have been approved by the participants. Thus, it was decided, as at the last times, not to establish some kind of final

¹A continuation and extension of this discussion by Kepler is given in Chapter 2 and at the end of the book.

refereing system in order to allow one a rapid publication of the proceedings. This way, except some minor editorial changes, to bring the contributions into the same form and to remove obvious misprints in the original manuscripts, no changes have been made in the course of preparation of this book for publication. It is believed that the presentation of even different points of view may stimulate the further discussion (and will be more useful) until, finally, some agreement can be reached. Thus, the responsibility for the content of the papers is retained, again, totally with the authors. They have to bear up both the honor for their results and the possible risk.

Due to the support from the host institution, the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research (JINR), the workshops could be carried out under nearly perfect conditions. Finally, I would like to note that it was a real pleasure, again, to prepare this volume for publication. I acknowledge herewith the perfect cooperation with Alexander S. Abyzov (in addition to the common work, for his help in the preparation of the figures, if it was required).

It is also a particular pleasure to express my thanks to Dr. Jörg Möller for the figures on the cover page illustrating different phenomena of ice formation. The interpretation of them is given by him as follows:

Ephemeral cosmos

The known is finite, the unknown infinite, as Shakespeare put it. If you think you know everything about nucleation and crystal growth, you are recommended to take a close look at snow first. Sometimes you may find tiny bubbles, sometimes flat empty spaces, inside snow flakes. You will see a plethora of different shapes, but you would probably not expect to see even color. Still, in one of the pictures shown, one sheet of air in a flake is so thin that it reflects some light in reflection so the crystal appears green. You see individual displays perfect symmetry, to the minutest detail. You also see, occasionally, flakes that are virtually identical, but most are as different as you might imagine. A perfect symmetry often includes the exact location of each individual tiny bubble, of which you may find dozens or more in one crystal. Some express dentritic growth, others do not. Most flakes show rotational 6-fold symmetry of all of their features, others show such symmetry in terms of external shape, but have no apparent symmetry of any kind internally. Most flakes of 6-fold rotational symmetry show mirror symmetry about 6 respective planes (all of which cut in the axis of rotational symmetry) - but some of those with dendrites do not, giving a partial spiral appearance. Still others appear to have grown in pairs, starting from a common plane of mirror symmetry. And then, some are completely irregular, others having grown in different directions, like from the center of a tetrahedron towards its corners, at completely different rates ... and in a few moments, they are all gone for good! As though they never existed! All of those in all the pictures taken together – just barely enough to feed a thirsty sparrow.

Finally, I have to note that for known technical reasons, the printed version of the proceedings is available as black & white copies. In a number of cases, the contributions are prepared by the authors submitting colored versions of the figures. The respective colored versions of the chapters (and of course also all other chapters) are available as pdf-files from the authors or the editor (juern-w.schmelzer@unirostock.de). We will try to make the pdf-file of the proceedings available also via the homepage of the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research. Last but not least, I would like to express my gratitude to the colleagues of the Publishing Department of the Joint Institute for Nuclear Research for the final perfect completion of the work.

2 Hast Thou Entered into the Treasures of the Snow? (JOB, 38:22) *Gyan P. Johari*

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¹Man löst keine Probleme, indem man sie aufs Eis legt.

Winston Churchill

They are hexagons, those snowflakes in the storm,

² Johannes Kepler wrote with his characteristic exactness, disputing the shape of snowflakes depicted in woodcuts by Olaus Magnus, the archbishop of Uppsala. But Robert Finch saw a snowflake romantically,

I have watched each flake, hesitant narcissus, Float into visible fragrance on the sight. Effect of Snow.

Like the flowers of genus narcissus – and the star of David – most snowflakes are six-cornered. But when infra-red radiations of the Sun preferentially melt a snowflake's core and it recrystallizes, it changes to a multi-petalled form, enveloping a drop of water in a large sphere of its vapor. Then, it looks like a sunflower, which John Tyndall discovered in the snows of the French Alps. You can occasionally find a Tyndall flower in the snow on your automobile's windshield, or produce one by irradiation.

In polarized light, a snowflake looks colorful, like an image in a kaleidoscope. But, unlike the kaleidoscope image which can be reproduced, no two snowflakes are found to be identical, as more than 5000 photomicrographs published by Wilson Bentley, by Dobrowolska, who also wrote articles on their shapes, and by Nakaya, have convinced us. Bentley spent nearly half a century photographing snowflakes in the New England mountains during the early days of photography, using a hand-made camera and a portable stand made from wood.

In our crystalline winter, children at play catch a snowflake in their hand and then try to observe it closely, but in vain. After it has soft-landed on their woolen mitts, they look at it keenly holding their breath to prevent it from melting.

The shape of an airborne snowflake depends upon the weather conditions. It may be a dendritic sixcornered star, an approximately flat hexagon, a composite of seven hexagons, a blunted triangle, a six-sided rod or simply a distorted sphere. These shapes, which are depicted by ten symbols, are produced when micron-sized water droplets in the atmosphere crystallize, tending to achieve perfection in symmetry but not attaining it. During their leisurely fall – and occasional rise – through the winter air, snowflakes can merge to produce a variety of other shapes and grow or ablate as they pass through air of varying humidity.

Floating in the rarified atmosphere at high altitudes, snow flakes refract and disperse light, and thus form the colored halos, pillars, arcs and circles around the Sun in an orderly array. Occasionally, they lead to brilliant and fiery events. On smashing against or by sweeping over an aircraft's wings and fusilage, snow flakes produce St. Elmo's fire on the leading surfaces and illuminate the trailing edges of the wing tips. In turbulent clouds, their contact with supercooled water droplets causes electrical discharges, which produce the cloud-to-cloud and the cloud-to-ground lightening. No snowflake has a perfect symmetry.

¹Added by Jürn W. P. Schmelzer

²Gyan P. Johari, a Fellow of the Royal Society of Canada, is Professor Emeritus of Materials Science and Engineering at McMaster University, Hamilton, Canada. He once did research on ice and glaciers. Part of this text is excerpted from his lecture given at the Ottawa Glaciology Society meeting of May 1983.

2 Hast Thou Entered into the Treasures of the Snow? (JOB, 38:22)

But human designs can achieve almost perfection in symmetry: The Order of Canada's insignia is an idealized snowflake, in the shape of a perfectly symmetrical six-pointed star, precisely as in the sketches of Robert Hooke in the 17th century, and in the woodcuts of Olaus Magnus a century earlier.

Nor does it have a perfect arrangement of its atoms. The hydrogen atoms of its water molecules change positions with time giving it a different arrangement once every few microseconds, and the arrangement of the water molecules in its crystal is marred by flaws. Under the names of proton disorder, point defects, dislocations and stacking faults, these flaws cause snowflakes to rapidly recrystallize and ultimately meta-morphize into solid ice. Under certain temperature and humidity conditions, large crystals formed in the intermediate stages of this metamorphosis produce loosely-packed layers separated by very large inter-layer shear planes of lower crystal density. When the weight of snow above such planes has increased and the potential energy of the top layer has reached near the limit of its structural stability, a mechanical shock dislodges the meter-thick layers above the shear planes. This initiates an avalanche.

Snow accumulated over thousands of years, its successive layers turning to ice, has produced glaciers and permanent ice covers in the Earth's polar regions and on the highest mountains in the tropics. Eruption of volcanoes has deposited traces of ash and dust between the layers and thus provided markers for geological dating of the ice cores drilled from these regions. The temperature of snow formation determines the oxygen-16 to oxygen-18 isotope ratio, and measurements of this ratio in slices of ice cores drilled from glaciers calibrated with the dates of volcanic eruptions have helped determine the climatic conditions of the past. An ice sample core of 950 meters contains the climatic history of 46 500 years.

Under the pressure of overlying layers, ice can trap methane, ethane and other small molecules. In time, pressure and temperature conditions transform the (ice-hydrocarbon mixtures) hexagonal arrangement of water molecules containing channels, like honeycombs stacked in alignment, to an arrangement of close-fitting cages of molecular dimensions. Small hydrocarbon molecules become confined in these cages, and the new structure formed is known as ice clathrate. Remaining a solid at a few degrees above 0°C under pressure, ice clathrates are found buried underground in the permanent frost regions of the Earth, and at the bottom of northern seas. When the pressure is removed they decompose into ice and the hydrocarbon gas is released. Ice clathrates comprise one source of natural gas in Russia.

Although ice is hard to the fall of a person, and brittle to the blow of an axe, it is soft to the continuous pull of gravity, which makes glaciers flow like rivers – faster at the top than near their beds, and faster in the center than at their sides. Glaciers cover 10% of the land area of the Earth and store 75% of the world's freshwater. Radio waves penetrate ice and this helps in determining the depth of the permanent ice covers. In some regions in the Antarctic, ice is found to be up to 4200 meters deep; the weight of ice has depressed the land in others. Snow and ice have all but buried the Royal Society mountains in Antarctica.

Flowing like extremely slow rivers, glaciers ultimately reach the ocean. Here, they plunge into it, or else extend on the ocean's surface as an enormous, strain-bearing, 100-meter to 800-meter thick tongue of ice, lifted and lowered by the tides twice a day. After this tongue has reached a certain expanse and strain, the abrupt force of the high waves fractures it into icebergs. This is the calving of a glacier, which has been found to produce up to 80 kilometer long icebergs. Directed by the ocean currents and continuously shifted by the Coriolis force, the icebergs travel majestically toward lower latitudes.

Cooke's 1772-1775 voyage put the Antarctic ice on the map. But Coleridge's words (Ancient Mariner) put it in our imagination,

And now there came both mist and snow, And it grew wondrous cold: And ice, mast high came floating by ...

The ice was here, the ice was there, The ice was all around ...

Showing only 10% of their size and appearing like white castles on the deep blue ocean, icebergs scour the bottom of the ocean and tumble, and ultimately melt away. Nothing else wanes so slowly or totally in its majesty. Edwin Pratt (The Titanic) extols their power in these words:

The gray shape with the paleolithic face Was still the master of the longitudes ...

To Dante, ice was something to be found at the center of the Earth and only after passing the center of gravity, he and his guide could leave the region of ice. To him, ice is at the bottom rung of Hell. But Thomas Mann's young engineer, Hans Castorp (Magic Mountain), finds the knowledge and the wisdom, the consecration, while lost in the snows. You will find it in the chapter called Snow, where Hans Castorp lost on the perilous heights dreams his dream of humanity, Mann later comments. And, Leslie Orgel (1966) showed that adenine, one of the four constituents of the genetic code in the DNA molecule, is produced when a dilute solution of ammonia, carbon dioxide and hydrogen cyanide freezes and the electrical forces on the ice surface facilitate the chemical reaction, thereby suggesting that the chemical constituents of life could have evolved in the ice laden regions. Quelques arpents de neige (Candide) is Voltaire's derision of the cause of the war between France and Britain to gain control of Canada. Contrast that with Kipling's much latter reconciliation with Canada as still Our Lady of the Snows!

Who would not remember Hans Christian Andersen's **Snow Queen**, her castle's walls of driven snow, its great hall paved with ageless ice and lit by the aurora borealis; the little boy Kai being carried off in a snow storm by the Snow Queen in her horse-driven sleigh; his child friend Gerda searching for him and, after a long and perilous journey, finding him sitting in the great hall arranging pieces of ice into a pattern to express Eternity, and no pattern satisfying him; her warm tears of joy melting the ice about his heart, and she finally leading him home where roses are in bloom. The book of Habakkuk says:

Behold ye among the heathen, and regard, and wonder marvellously...

3 Structural Order Parameters, Relaxation and Crystallization Jürn W. P. Schmelzer Institute of Physics, University of Rostock, 18051 Rostock, Germany

НЕЗАБУДКИ

У незабудок пятерная симметрия, Частица неба в каждом лепестке, И пять лучей, потерянных Россией, Пребудут вечно в маленьком цветке.

Звезда уволена за архаичность, А серп и молот — за примитивизм. И взят орёл — раздвоенная личность, Он, точно, не зовёт нас в коммунизм.

Пьют мужики от недостатка веры, А может быть, причина и в другом... Бог с ней, с политикой. Нам, староверам, Позвольте быть с голубеньким цветком.

Поддержит он природное хотенье Жить по себе в содружестве людей. Пусть будет это милое творенье Звездою малой родины моей.

Владимир П. Скрипов

Abstract

A brief analysis of the spectrum of problems in the application of the basic ideas of classical nucleation theory to crystallization processes in glass-forming melts is given. It covers the analysis of the properties of critical clusters (whether they are widely identical to the properties of the evolving macroscopic phases or not) and the resulting from the respective assumptions consequences with respect to their sizes and the work of critical cluster formation, the question whether the viscosity or the effective diffusion coefficients determines the kinetics of crystal formation and growth (the possible decoupling of diffusion and viscosity) or whether this process is realized by alternative mechanisms not studied in detail so far, the problem of the determination of the size of the structural units entering the expressions both for crystal nucleation and growth, and the problem to which extent the thermodynamic and kinetic properties of glass-forming melts can be considered as a function of the actual thermodynamic state parameters of the systems under consideration. Applying the structural order parameter approach as developed be De Donder, it is shown that the dependence of the properties of glass-forming melts on prehistory (or the dependence on the structural properties) can be given a definite quantitative interpretation.

3.1 Introduction

The theoretical concepts underlying the description of crystal nucleation and growth processes have been developed in its basic premises already 80-90 years ago. In a variety of cases, the resulting from such attempts classical methods of description of nucleation, the classical nucleation theory (CNT) and the classical theory of crystal growth, supply us with a satisfactory description of the respective processes, however, in a not much less or even larger number of cases severe deviations between the predictions of theory and experiment are observed. By this reason, related problems remain to be widely discussed and are analyzed in detail in the attempts to resolve the problems of deviations of theory and experiment. The present paper is devoted to the description of some overview on current problems in this respect and possible ways of their resolution continuing the previously performed analysis [1, 2, 3, 4, 5, 6, 7, 8, 9] (see, e.g., also [10, 11]).

3.2 Some Spectrum of Problems in the Application of Basic Ideas of the Theory of Crystal Nucleation and Growth to Experiment

3.2.1 State Parameters of the Critical Clusters and Work of Critical Cluster Formation

One of the basic characteristics of the crystal nucleation-growth processes is the steady-state nucleation rate, J, describing the number of supercritical clusters formed per unit time in a unit volume. It can be expressed generally as

$$J = J_0 \exp\left(-\frac{W_c}{k_B T}\right) \,. \tag{3.1}$$

Here W_c is the work of critical cluster formation, it is equal to the minimum change of the appropriate thermodynamic potential of the ambient glass-forming melt required to form a cluster of critical size capable to further deterministic growth, k_B is the Boltzmann constant and T the absolute temperature. Provided the state of a cluster has to be described by more than one parameter – e.g. the number of particles of different components – as it is usually the case in glass crystallization, the critical cluster corresponds to a saddle point of the appropriate thermodynamic potential, here (for given external pressure and temperature) of the Gibbs free energy, G. An example is shown in Fig. 3.1.

Provided the system evolves into the new phase via the saddle point (dark line in the right-hand side part of Fig. 3.1), then according to Gibbs classical approach to the description of thermodynamically heterogeneous systems [12] the properties of the critical clusters are determined via the following set of equations:

$$(p_{\beta} - p_{\alpha}) + \sigma \frac{dA}{dV_a} = 0 , \qquad \mu_{j\alpha} = \mu_{j\beta} , \qquad T_{\alpha} = T_{\beta} .$$
(3.2)

Here σ is the interfacial tension, p is the pressure, Ω is the chemical potential, A is the surface area and V_{α} is the volume of the cluster of the new phase. The subscripts α specify the parameters of the cluster phase while the subscript β refers to the parameters of the ambient melt. For spherical clusters with a radius R, the first of equations Eq. (3.2) goes over into the conventional Young-Laplace equation, $p_{\alpha} - p_{\beta} = 2\alpha/R$.

The bulk parameters of the critical clusters are determined in Gibbs approach by equality of the chemical potentials of all components and equality of temperature in the considered different phases. Applying this set of equations one comes to the conclusion that the properties of the critical clusters should be widely identical to the properties of the newly evolving macroscopic phases. By this reason, one can model then the thermodynamic driving force for nucleation and growth processes by a Taylor expansion of the chemical potential difference at the melting temperature. In such approximation, the temperature dependence enters the description only via the difference between actual temperature, T, and melting temperature, T_m , i.e. via

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Figure 3.1: Change of the Gibbs free energy, ΔG , in dependence on the radius, R, or the number of particles, n, in the crystal cluster formed in the ambient melt. On the left side, the common picture is shown when one parameter is sufficient for the description of the state of the cluster. On the right hand side, it is assumed that the cluster consists of two different components, n_1 and n_2 . The dark curve shows the path of evolution via the saddle. This is the path which is usually supposed to be the main path of evolution to the new phase. The light line indicates the evolution via a ridge of the thermodynamic potential. $W_c = \Delta G_c$ is the value of ΔG at the saddle point.

the difference $(T - T_m)$ and the fixed for a given value of pressure entropy of melting. Of course, assuming that the bulk properties of the critical clusters are the same as the properties of the respective macroscopic phase, one could also use direct measurements in order to derive expressions for the driving force. The underlying this procedure assumption is, however, in general not true, as shown by computer simulations, alternative theoretical approaches and experimental results. The bulk properties of the critical clusters – and, as a consequence, also their surface properties – deviate from the properties of the evolving finally macroscopic phases.

The respective failure of the classical Gibbs theory can be removed in the framework of the generalized Gibbs approach. It replaces above given relations, Eqs. (3.2), by the following set of equations:

$$(T_{\alpha} - T_{\beta})s_{\alpha} + (p_{\beta} - p_{\alpha}) + \sigma \frac{dA}{dV_{\alpha}} + \sum_{j=1}^{k} \rho_{j\alpha}(\mu_{j\alpha} - \mu_{j\beta}) = 0 ,$$

$$(\mu_{j\beta} - \mu_{j\alpha}) = \frac{3}{R} \left(\frac{\partial\sigma}{\partial\rho_{j\alpha}}\right)_{\{\rho_{j\beta}\}, T_{\beta}} ,$$

$$(T_{\beta} - T_{\alpha}) = \frac{3}{R} \left(\frac{\partial\sigma}{\partial s_{\alpha}}\right)_{\{\rho_{j\beta}\}, T_{\beta}} .$$
(3.3)

Here s is the entropy volume density and ρ_i are the particle volume densities of the different components. These equilibrium conditions coincide with Gibbs' expressions for phase coexistence at planar interfaces, i.e., for large cluster sizes $(R \to \infty)$, or when, as supposed in Gibbs' classical approach, the surface tension is considered as a function of only one of the sets of intensive state variables of the coexisting phases, either of those of the ambient or of those of the cluster phase. In such limiting cases, Gibbs' equilibrium conditions Eqs. (3.2) are obtained as special cases from Eqs. (3.3).

The application of Eqs. (3.3) allows one to determine the properties of the critical clusters in an alternative to Gibbs classical method way. The results of such analysis show that the properties of critical clusters deviate as a rule considerably from the properties of the evolving bulk phases. Experimental data verifying this result in the analysis of crystal nucleation and growth processes are given in Refs. 2 and 3 and

3 Structural Order Parameters, Relaxation and Crystallization

in [13, 14]. In addition, also the estimates for the size of the critical clusters may lead to different results as compared with the classical Gibbs approach.

Both in the classical and generalized Gibbs approaches (we assume here in both cases that the surface of tension is chosen as the dividing surface), the work of critical clusters formation is given by the relation

$$W_c = \frac{1}{3}\sigma A . aga{3.4}$$

Accounting for the possible deviations of the bulk properties of the critical clusters and their sizes, it can be shown that the classical Gibbs approach overestimates as a rule the work of critical cluster formation and underestimates the steady-state nucleation rates. Such account is easy to perform for condensation and boiling, where the density of the bubbles may vary continuously. Similarly, the processes can be described quantitatively for segregation processes in solutions where the concentration of the components in the cluster phase may vary continuously as well. In application to crystal formation, the proper account of the "degree of crystallinity" of the crystal precursors and its incorporation into the thermodynamic properties of the evolving clusters seems to be a problem which is much less studied and understood.

3.2.2 Passage via the Saddle Point versus Ridge Crossing

In applying Eq. (3.1) it is assumed that the evolution path to the newly evolving phase proceeds via the saddle of the thermodynamic potential hypersurface. However, in principle, also a passage via a ridge may be possible and preferred by some kinetic reason even if it refers to a higher potential barrier to be overcome [15, 16]. This problem has been discussed in detail also in a recent own paper (Ref. 8) for the case of segregation in solutions by solving numerically the set of kinetics equations describing nucleation and cluster growth and employing the generalized Gibbs approach for the description of the thermodynamic aspects of cluster formation and growth. According to mentioned analysis, deviations of the preferred evolution path from the trajectory passing the saddle occur for states in the vicinity of the classical spinodal curve both for metastable and unstable initial states. Here the system prefers to form localized density and/or composition fluctuations of finite value instead of spatially entended fluctuations with low changes of density and/or composition.

With respect to crystallization, the situation is partly different. According to the analysis by Skripov and Baidakov [17, 18] there is no spinodal in congruent melt crystallization, i.e., if the compositions of the melt and the crystal phase coincide. By this reason, one can expect that in these cases the evolution to the new phase will proceed as a rule via the saddle point. Moreover, in the analysis of segregation processes in glass-forming melts it turns out that the most significant deviations from the classical picture occur in the vicinity of the spinodal curve. By this reason, for the mentioned cases, when the spinodal is absent, the behavior can be expected to be well-described by classical terms, however, the discussed already above problem - as fas as to critical crystal clusters the macroscopic properties may be assigned to - remains open. However, in the general case crystallization is accompanied by changes in the composition and the generalized Gibbs approach has to be utilized to model the respective processes.

The problem discussed in this subsection has a further consequence: if in computer simulations a passage via a potential barrier is observed, the respective barrier does not correspond necessarily to the saddle point. It can refer also to a ridge and in such cases, above equations cannot be utilized to compute thermodynamic properties referring to the critical clusters.

3.2.3 Decoupling of Diffusion and Viscosity

As discussed in detail in Refs. 5 and 7 (c.f. also [19, 20]), primarily the kinetic pre-factor J_0 in Eq. (3.1) is determined by the diffusion coefficient of the basic units in the melt undergoing crystallization. For one-component systems, we may write (c.f. Refs. 5 and 7)

$$J = \sqrt{\frac{\sigma}{k_B T}} \left(\frac{D}{d_0^4}\right) \exp\left(-\frac{W_c}{k_B T}\right).$$
(3.5)

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3.2 Basic Ideas of the Theory of Crystal Nucleation and Growth to Experiment

Replacing the diffusion coefficient, D, by the viscosity, η , via the Stokes-Einstein equation,

$$D = \frac{k_B T}{d_0 \eta} , \qquad (3.6)$$

we get the commonly employed relation

$$J = \frac{\sqrt{\sigma k_B T}}{d_0^5 \eta} \exp\left(-\frac{W_c}{k_B T}\right) \,. \tag{3.7}$$

However, the replacement of the diffusion coefficient by viscosity is already questionable for one-component systems (due to the possible decoupling of diffusion and relaxation), it becomes even more questionable for crystallization processes in multi-component systems, where an effective diffusion coefficient, D_{eff} , determines primarily the nucleation-growth process, being a function of the partial diffusion coefficients, D_i , of the independently diffusing components in the melt and their molar fractions, x_i , both in the melt and in the evolving crystal phase (see Refs. 5 and 7 for more details).



Figure 3.2: Illustration of the difficulties one is confronted with in solving the problem of theoretical description of crystal nucleation and growth processes.

The effective diffusion coefficient is given by the following relation:

$$\frac{1}{D_{eff}} = \sum_{i=1}^{k} \frac{\nu_{i\alpha}^2 \left[1 + \left(\frac{D_i^*}{D_i}\right) \left(\frac{d_\alpha}{d_\beta}\right) n^{1/3} \right]}{D_1^* x_{i\beta}} \,. \tag{3.8}$$

Here d_{α} and d_{β} are parameters describing the average size of the independently moving particles in the melt and the crystal cluster phase, D_i and D_i^* are the partial diffusion coefficients of the respective components in the bulk of the melt and near to the interface melt-crystal, $x_{i\beta}$ are the molar fractions of the different components in the ambient melt and $\nu_{i\alpha}^2$ is given by $\nu_{i\alpha}^2 = x_{i\alpha} + n(dx_{i\alpha}/dn)$, where n is the total number of particles in a crystal cluster. D_{eff} is the effective diffusion coefficient which plays the role of D in Eq. (3.7) for multi-component crystal nucleation.

A detailed estimate of the magnitude of the error one introduces by the replacement of the effective diffusion coefficient via viscosity is believed to represent a highly interesting problem, however, as it seems it is hardly possible to realize such analysis for a wide class of systems due to the limited knowledge of the respective parameters (c.f. also [21]).

3.2.4 Size of the Structural Unit

In Eqs. (3.5) and (3.7), the size parameter d_0 enters having for one-component systems the meaning of the size of the structural unit moving independently in the liquid and being responsible for crystallization. The question arises in this respect how such size parameter has to be defined in the cases that crystallization proceeds in a multi-component system. In Ref. 7 this problem has been analyzed in detail.

Provided the process of crystallization is realized via an independent motion of several components, then this parameter has to be defined as the average size of the independently moving components. This result holds true both for the description of nucleation and the description of growth processes.

3.2.5 Alternative Mechanisms of Crystallization

In the book by Skripov and Faizullin (Ref. 18) one can find the following statement: *the transition from the liquid to the fcc-crystal and back cannot be accomplished by just small (of atomic size) shifts in the positions of single atoms: for such transitions a significant part of atoms should be moved by a distance of about one atomic spacing.* It follows that these processes cannot be interpreted via above sketched kinetic mechanisms of crystal nucleation and growth being based on the consideration of the more or less independent motion of the single particles of the different components of the glass-forming melt. Similarly, Leko [22] connects in his comprehensive analysis of crystallization of quartz glass the respective processes with bond switching. As it seems, a detailed specification of the kinetic pre-factor J_0 for both these mechanisms of crystallization is not performed so far.

3.2.6 Dependence of the Properties of Glass-forming Melts on Prehistory

The proper account of the circle of problems sketched above is already a hard task comparable with the problems of supply of raw material for glass melting as sketched in Fig. 3.2. In Fig. 3.3, typical relations are shown between glass transition temperature T_g (for conventional cooling rates) and the temperature T_{max} where the maximum of the steady-state nucleation rate is reached. It is evident that the maximum of the steady-state nucleation rate is reached. It is evident that the properties of the ambient glass-forming melt in order to determine correctly the thermodynamic driving force of the process of crystallization and the surface energy term.

The typical behavior of the density of glass-forming systems in vitrification is shown in Fig. 3.4. The density increases with decreasing temperature but its values depend not only on the thermodynamic state parameters but also on cooling rate or, in more general notations, on the prehistory, i.e., the way how the glass-forming melt was brought into the respective state. In order to describe the respective behavior in thermodynamic terms, one has to introduce, at least, one additional order parameter denoted here as ξ and representing the free volume of the melt under consideration. The change in time of this additional order parameter can be described for isothermal conditions as

$$\frac{d\xi}{dt} = -\frac{1}{\tau(p, T, \xi)} \left(\xi - \xi_e\right).$$
(3.9)

Here τ (p, T, ξ) is the characteristic relaxation time, depending on pressure, temperature and the structural order parameter. It can be shown (c.f. [23] and in detail the Appendix) that such relaxation equation can easily reproduce the often observed relaxation behavior of the form $\xi \propto t^{1/2}$ and can give a key to the

theoretical understanding of the stretched exponential relaxation kinetics. In Eq. (3.9), ξ_e is the equilibrium value of the structural order parameter.



Figure 3.3: Dependence of the steady-state nucleation rates for $\alpha - \text{Li}_2\text{O} 2\text{SiO}_2$ on temperature as obtained by different authors (left, c.f. Ref. 1) and (right) the relation between the temperature of maximum nucleation rate and glass transition temperature for a large class of glass-forming melts [24].

For given cooling and heating rates, q = (dT/dt), Eq. (3.9) can be transformed into a relation describing the change of the order parameter with temperature. The solution of this equation for constant cooling and heating rates results in the dependencies demonstrated in Figs. 3.4 and 3.5.



Figure 3.4: Typical dependence of the density of glass-forming melts on temperature in cooling (here shown for a borosilicate glass [25], left side). On the right hand side this behavior is interpreted qualitatively employing one structural order parameter [26] connected with the free volume of the system under consideration.

Since the structural order parameter is a function of pressure and temperature and of the prehistory of the melt, also the thermodynamic properties of the melt depend on the same set of parameters. It follows as a consequence that the thermodynamic state parameters of the crystal cluster in the ambient phase are, as a rule, dependent on prehistory as well. Once the bulk properties depend on prehistory, also the surface properties have to depend on prehistory. Consequently, the kinetics of crystal nucleation and growth is affected, in general, by prehistory and may proceed, in particular, in a different way for cooling and heating processes.

In above considerations, the order parameter is assumed to have the same value in the whole system. However, the intensity of fluctuations in the glass transition range is as a rule higher as compared to systems in thermodynamic equilibrium. In the glass transition range, local fluctuations are not damped out since the



Figure 3.5: Left: Dependence of the structural order parameter on temperature in cooling-heating processes performed with the same absolute value of the rates of change of temperature. Right: Dependence of the characteristic relaxation time on temperature for cooling and heating processes (for the details see Ref. 23).

system is in a non-equilibrium state. A particular experimental realization of such peculiarity consist in the "fluctuation flashes" in heating observed and discussed in detail by Porai-Koshitz and coworkers (see Ref. 27 for an overview).

Since the thermodynamic state parameters are dependent on the structural order parameter, the kinetic parameters have to depend, in general, on the structural order parameter(s) as well. For the case discussed here, the dependence is demonstrated in Fig. 3.5 (right side) obtained by similar computations as the ones resulting in Fig. 3.5 (left side).

Employing in this way the order parameter concept for the description of glass-forming melts, the discussion of the dependence of the crystal nucleation and growth processes on the structure of the glass-forming melts (see e.g. [28]) can be given a quantitative basis. In this treatment, structural properties are considered as additional parameters not determined uniquely by the conventional thermodynamic state variables like mole number, pressure and temperature but by additional parameters which can be changed independently, in addition. Such approach is possible only if the system is out of equilibrium and treated respectively by introducing additional structural order parameters. As a consequence, in such cases, in order to derive the nucleation and growth rates, one has to determine the bulk and surface properties as well as the kinetic parameters not only in dependence on mole numbers, pressure and temperature but also in dependence on the (set of) structural order parameters depending, in general, on prehistory (e.g., cooling and heating rates). A more extended analysis of the sketched here circle of problems will be given in a forthcoming paper [29].

3.3 Conclusions

A spectrum of partly resolved and partly unresolved problems is discussed arising in the application of the classical theories of nucleation and growth to experiment, In particular, in order to treat nucleation processes in glass-forming melts, as a rule, the prehistory of the system under consideration has to be properly taken into account in addition to the spectrum of factors governing the crystallization process if the prehistory can be neglected. The account of the prehistory or the structure of the system can be performed in the framework of the structural order parameter approach as developed by De Donder and discussed in application to the description of glass-forming systems in detail in Ref. 23 and cited there papers. Such effects are considered as particularly important in the analysis of ultra-fast nano-calorimetry at cooling and heating rates in the range between 10^{-4} K/s up to 10^{5} K/s [30, 31]. A detailed analysis of the possible effect of prehistory on the kinetics of crystal nucleation and growth is planned to be performed in near future.

3.4 Appendix: Some Comments on the Relaxation Kinetics of Glass-Forming Melts

3.4.1 Introduction

In order to describe appropriately the glass transition, relaxation processes and the state of the resulting glass, at least, one additional order parameter has to be introduced into the description of glass-forming systems [32, 33, 34, 35, 36, 37, 38, 39]. Here we consider the case that one structural order parameter $\tilde{\xi}$ is sufficient for the description of relaxation processes [1, 26, 40, 41, 42]. In stable and metastable equilibrium states, the order parameter is a function of the two independent state parameters, i.e., $\tilde{\xi}^{(e)} = \tilde{\xi}(p, T)$. At given values of pressure and temperature, the relaxation behavior can be expressed as

$$\frac{d\tilde{\xi}}{dt} = -\frac{1}{\tau(p,T,\xi)} \left(\tilde{\xi} - \tilde{\xi}^{(e)}\right) .$$
(3.10)

In order to simplify the notations, we will use in the following derivation instead of $\tilde{\xi}$ the dimensionless reduced quantity

$$\xi = \frac{\tilde{\xi} - \tilde{\xi}^{(e)}}{\tilde{\xi}^{(e)}} . \tag{3.11}$$

In such definition, the equilibrium state the systems eventually tends to correspond to $\xi(t \to \infty) = 0$.

Employing the methods of thermodynamics of irreversible processes, in preceding analysis it was demonstrated that the kinetics of relaxation for the case of existence of only one structural order parameter ξ can be written in the form (cf. Eqs. (3.10) and (3.11), [1, 40])

$$\frac{d\xi}{dt} = -\frac{1}{\tau(p,T,\xi)}\xi .$$
(3.12)

Here p is the pressure, T the temperature and ξ the order parameter defined in such a way that it approaches zero for the metastable or stable equilibrium states corresponding to the respective values of temperature and pressure. In a first approximation, one could suggest to replace the characteristic relaxation time $\tau(p, T, \xi)$ by the Maxwellian relaxation time $\tau_0(p, T)$ depending only on pressure and temperature but not on the order-parameter. Such approximation would lead to the simplified equation

$$\frac{d\xi}{dt} = -\frac{1}{\tau_0(p,T)}\xi\tag{3.13}$$

and an exponential relaxation behavior of the order parameter given by

$$\xi(t) = \xi(0) \exp\left(-\frac{t}{\tau_0}\right) . \tag{3.14}$$

However, already more than 150 years ago, R. and F. Kohlrausch were aware (cf. [40]) that such simple relaxation law, as given by Eq. (3.14), is not sufficient for the description of relaxation processes in glass-forming melts (somewhat later this point was reaffirmed also already by Tool [43]), replacing them (in above notations) by dependencies of the form

$$\frac{d\xi}{dt} = -\frac{\psi(\xi)}{\tau_0(p,T)}\xi\tag{3.15}$$

or

$$\frac{d\xi}{dt} = -\frac{\varphi(t)}{\tau_0(p,T)}\xi .$$
(3.16)

3 Structural Order Parameters, Relaxation and Crystallization

Employing different assumptions for the dependencies of either $\psi(\xi)$ on ξ or $\varphi(t)$ on t, different relaxation laws can be obtained, for example, Kohlrausch's stretched exponent formula (for $\varphi(t) \propto 1/t^n$ with n < 1; for more details see [40])

$$\frac{\xi}{\xi(0)} = \exp\left\{-\left(\frac{t}{\tau_K}\right)^{\beta}\right\} , \qquad \beta = 1 - n , \qquad \tau_K = \tau_0 (1 - n)^{1/(1 - n)} . \tag{3.17}$$

This equation was proposed to use in the description of relaxation of glass-forming melts by Rekhson and Mazurin [44, 45], it turned out to be a very useful method of description but has - as mentioned by Mazurin - not found a theoretical foundation so far (for alternative approaches of theoretical foundation involving, however, certain ad hoc assumptions [46] see [47, 48, 49]).

In order to establish the type of dependence $\varphi = \varphi(t)$ or $\psi = \psi(\xi)$ in above equations, one can - as one possible approach - develop statistical mechanical models of relaxation processes appropriate for the desired classes of systems under consideration. Alternatively, one can start with Eq. (3.12) and try to find out which kind of relaxation behavior one may expect making only very general assumptions in the analysis of this relation. In such approach, one can either understand the origin why certain classes of relaxation laws have been turned out appropriate in describing relaxation or suggest dependencies eventually capable for a detailed description. The analysis of this second approach is the aim of this note extending the work performed in our previous paper [40].

3.4.2 Analysis

In the analysis of Eq. (3.12) we assume (i.) that $\tau(p, T, \xi)$ can be expanded into a Taylor series with respect to the structural order parameter ξ and (ii.) that in the limit $\xi \to 0$ Eq. (3.13) holds, i.e., $\lim_{\xi\to 0} \tau(p, T, \xi) = \tau_0(p, T)$. Introducing a dimensionless time scale $t' = t/\tau_0$, Eq. (3.12) can be written then as

$$\frac{d\xi}{dt'} = -\frac{1}{1+a_1\xi + a_2\xi^2 + a_3\xi^3 + \dots}\xi, \qquad t' = \frac{t}{\tau_0(p,T)}.$$
(3.18)

Here $a_i = a_i(p,T)$ are the (dimensionless) expansion coefficients of $\tau(p,T,\xi)$ at $\xi = 0$. Eq. (3.18) leads to

$$\left(\frac{1}{\xi} + a_1 + a_2\xi + a_3\xi^2 + a_4\xi^3 + \dots\right)d\xi = -dt'.$$
(3.19)

Integration in the limits $(\xi(0), \xi(t'); 0, t')$ yields

$$\left(\ln\xi + a_1\xi + \frac{a_2}{2}\xi^2 + \frac{a_3}{3}\xi^3 + \dots\right)\Big|_{\xi(0)}^{\xi(t')} = -t'.$$
(3.20)

In general, knowing the expansion coefficients, $\xi(t')$ can be determined from Eq. (3.20).

However, in the particular cases that one of the terms in Eq. (3.19) respectively Eq. (3.20) dominates, we get some spectrum of particular simple differential equations and solutions

$$\frac{d\xi}{\xi} = -dt', \qquad \xi(t') \cong \xi(0) \exp(-t'), \qquad (3.21)$$

$$a_k \xi^{k-1} d\xi = -dt', \qquad \xi(t') \cong \left\{ \xi^k(0) - \frac{k}{a_k} t' \right\}^{1/k}, \qquad k = 1, 2, \dots.$$
 (3.22)

As a particularly important special case, we get for k = 2 the result $\xi \cong (t')^{1/2}$.

3.4 Appendix: Some Comments on the Relaxation Kinetics of Glass-Forming Melts

Let us now consider the particular case that the relaxation behavior is governed by the term containing the expansion coefficient a_j with j = k + 1. According to Eq. (3.22), the dependence $\xi(t)$ for this mode is given by

$$\xi(t') \cong \left\{ \xi^{j}(0) - \frac{j}{a_{j}} t' \right\}^{1/j} .$$
(3.23)

In the course of time, the term containing the expansion coefficient a_k may replace it since ξ is decreasing with time. The differential equation of this mode, we can write as

$$\frac{a_k \xi^k}{\xi} d\xi = -dt' \qquad \text{or} \qquad \frac{d\xi}{\xi} = -\frac{1}{a_k \xi^k} dt' . \tag{3.24}$$

Replacing $\xi(t)$ on the right hand side by its solution for the case j = k + 1 (cf. Eq. (3.23)), we obtain

$$\frac{d\xi}{\xi} = -\frac{1}{a_k \left(\xi^{k+1}(0) - \left(\frac{k+1}{a_{k+1}}\right)t'\right)^{k/(k+1)}} dt' \,. \tag{3.25}$$

In other words, we arrive at Kohlrausch (or Jenckel-type cf. Eq. (3.17) and [40]) relaxation equations where the parameters n = k/(k+1) and $\beta = 1 - n$ will have the values

$$n = \frac{1}{2}, \qquad \beta = \frac{1}{2} \qquad \text{for} \qquad k = 1, n = \frac{2}{3}, \qquad \beta = \frac{1}{3} \qquad \text{for} \qquad k = 2, n = \frac{3}{4}, \qquad \beta = \frac{1}{4} \qquad \text{for} \qquad k = 3...$$
(3.26)

Let us suppose now that the term a_{k+1} is very small, then the relaxation behavior governed by the term in the expansion with j = k + 2 may go over into a behavior governed by the term a_k and the respective differential equation. Instead of Eq. (3.25) we get then

$$\frac{d\xi}{\xi} = -\frac{1}{a_k \left(\xi^{k+2}(0) - \left(\frac{k+2}{a_{k+2}}\right)t'\right)^{k/(k+2)}} dt' \,. \tag{3.27}$$

Instead of Eq. (3.26), we have then

$$n = \frac{1}{3}, \qquad \beta = \frac{2}{3} \qquad \text{for} \qquad k = 1, n = \frac{1}{2}, \qquad \beta = \frac{1}{2} \qquad \text{for} \qquad k = 2, n = \frac{3}{5}, \qquad \beta = \frac{2}{5} \qquad \text{for} \qquad k = 3...$$
(3.28)

This analysis can be extended to even higher numbers of eventually missing terms in the expansion of τ . In general, we would have then (for $a_k \neq 0$, $a_{k+1} = \ldots = a_{j-1} = 0$, $a_j \neq 0$)

$$n = \frac{k}{k+j}, \qquad \beta = 1 - n = \frac{k}{k+j}.$$
 (3.29)

The respective differential equation would read

$$\frac{d\xi}{\xi} = -\frac{1}{a_k \left(\xi^{k+j}(0) - \left(\frac{k+j}{a_{k+j}}\right)t'\right)^{k/(k+j)}} dt'$$
(3.30)

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with the general solution

$$\ln\left(\frac{\xi(t')}{\xi(0)}\right) = \frac{a_{k+j}}{ja_k} \left\{ \left[\xi^{k+j}(0) - \left(\frac{k+j}{a_{k+j}}\right)t'\right]^{j/(k+j)} - \xi^j(0) \right\}$$
(3.31)

3.4.3 Discussion

The approach predicts that, in addition to the exponential decay, near to equilibrium, relaxation may be governed in intermediate stages by laws of the form $\xi(t') = (\xi^k(0) - (k/a_k)t')^{1/k}$. Such kind of relaxation behavior was already distinguished by Kauzmann [50] and recently reconfirmed to dominate the dielectric α process in viscous organic liquids [51]. In addition, it allows one to understand the origin of stretched exponential type relaxation processes, it gives estimates of the coefficient β in agreement with experimental findings ($0.3 \le \beta \le 0.75$).

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4 Explosive Cavitation in Superheated Liquid Argon and Argon-Helium Solutions

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Френкель был физиком-теоретиком.

Этим самым я хочу подчеркнуть, что он интересовался прежде всего и главным образом тем, что происходит в реальных объектах,

и применявшиеся им математические средства обслуживали его физику, а не наоборот,

как это иногда случается с представителями современного поколения ученых.

Справедливость подобного утверждения, можно сказать, засвидетельствована каждой страницей его книги о жидкостях. Он спрашивает: «Что же происходит в действительности и как это можно объяснить?» - и задается этим вопросом именно так, а отнюдь не в форме:

«Вот изящная теория; годится ли она? Эксперименты же, вероятно, ошибочны, если они ей противоречат».

Nevill F. Mott

Abstract

The kinetics of explosive boiling-up of liquid argon and argon-helium solutions has been investigated at negative pressures created by the reflection of a compression pulse 3-5 μ s long from the free surface of a liquid by the method of liquid pulse heating on a thin platinum wire (with a rate of temperature increase of about 1 K/ μ s). The limiting superheats T_* (stretches p_*), the effective nucleation rate J_* and the derivative $(d \ln J/dT)_{T=T_*}$ have been determined by experimental data on the thermal perturbation of a wire probe and the results of solution of the problem on the initial stage of explosive boiling-up of a liquid. It has been found that the dissolution of helium results in a decrease of the cavitation strength of argon. The experimental data are compared with homogeneous nucleation theory. Satisfactory agreement between data of experiment and theory with the use of the capillarity approximation in the latter is found, although limiting stretches (superheats) attained by experiment are nevertheless systematically lower than calculated ones.

4.1 Introduction

The liquid phase can exist, as a metastable one, also at negative pressures. There are no fundamental differences between a superheated ($p \ge 0$) and a stretched (p < 0) liquid. Spontaneous boiling-up and cavitation at temperatures sufficiently far away from absolute zero should be described by the classical nucleation theory connecting this process with thermal fluctuations [1].

Extensive experimental material has been accumulated by now on the limiting superheats [2-5] and the cavitation strengths [6-15] of liquids of different chemical nature. As distinct from a superheated liquid, where the discrepancy between theory and experiment in the superheat temperature is equal to units and fractions of Kelvin [2,5], limiting stretches registered in experiments, by the data of many authors [6-11], are usually tens and even hundreds of times smaller than the theoretical values. The discrepancy between theory and experiment is usually explained by the imperfection of the contact of the liquid with the internal parts of the walls of the measuring chamber and the presence of dissolved gases and solid suspended particles on the walls and in the liquid volume. In this respect, cryogenic liquids are sufficiently pure. Many foreign gases in them are frozen out and can be easily detached by filtering. The good, close to complete, wettability of solid bodies by cryogenic liquids does not allow vapor cavities to exist on the inner walls of a vessel for a long time.

In studying the cavitation strength of cryogenic liquids use was made of both quasi-static [6-10] and dynamic [12-15] methods. Meissner et al. [6,7] investigated the cavitation strength of nitrogen and superfluid helium in metal bellows. In experiments on He II no abrupt cavitation effect was discovered. The authors of [7] conclude that even if a negative pressure was realized in He II, its value did not exceed – 0.03 MPa. Beams [8] investigated the breaking strength of nitrogen, oxygen, argon and helium by creating inertia loads in U – shaped glass tubes immersed in a Dewar vessel with the liquid under investigation. A pressure of the limiting stretch $p_* \simeq -1.2$ MPa was achieved for liquid argon at a temperature T = 85 K, whereas the homogeneous nucleation theory gives $p_* \simeq -19.0$ MPa. The cavitation strength of liquid helium was also investigated by the methods of spouting [9], osmotic pressure [10], and acoustic methods [11].

The results presented in [6-10] most likely point to heterogeneous cavitation in cryogenic liquids. All attempts to remove from the system possible completed and easily activated boiling sites failed. The idea of realization of homogeneous cavitation in He II based on the ideal wettability of practically all solid materials by this substance did not prove its value either. The authors of subsequent papers [12-15] adopted a strategy for the achievement of homogeneous nucleation in a stretched liquid not by means of removing possible cavitation centers from it, but at the cost of neutralization of heterogeneous nucleation in the phase-transition shock regime. For this purpose, use was made of combined pulse methods of generation of negative pressures and liquid superheat [12], and also focused acoustic fields [13-15], which made it possible to separate the cavitation zone from the transducer walls and to considerably reduce its volume. The method of focusing of acoustic fields was used for investigating the cavitation strength of liquid helium in references [13-15]. The results are in satisfactory agreement with the classical homogeneous nucleation theory.

The present paper gives the results of investigating the kinetics of explosive boiling-up of liquid argon and argon-helium solutions at negative pressures. Use was made of an approach based on the combination of two methods: pulse stretching with the reflection of a compression wave from the liquid free surface and pulse liquid superheat on a thin platinum wire [12]. This approach made it possible to realize a shock boiling-up regime, at which the main contribution to evaporation is made by bubbles of fluctuation origin, and to achieve nucleation rates $J = 10^{22} - 10^{23} \text{ s}^{-1}\text{m}^{-3}$ in a tensile-stressed liquid. At positive pressures limiting superheats for liquid argon had been measured earlier [16,17].

The structure of the paper is as follows. Section 4.2 describes the method of investigation and the experimental setup, presents briefly the theory of the method. Section 4.3 presents the results of the experiments and compares the data obtained with homogeneous nucleation theory. Section 4.4 contains the discussion and conclusions.

4.2 Experimental Setup and Measurement Procedure

The schematic diagram of the measuring chamber is given in Fig. 4.1. Liquid argon 1 ($V \approx 70 \,\mathrm{cm^3}$) is in vapor-liquid equilibrium at a temperature T = 107 K in a cylindrical chamber 44 mm in diameter. The height of the liquid column in the chamber is 40-50 mm. The chamber bottom is a duralumin membrane (3), which is 0.8 mm thick. At a discharge of a low-inductance capacitor (5) into a spiral coil (4) pressed to the membrane a pressure pulse 3-5 μ s long is generated. The front of the pulse is less than 1 μ s, the amplitude is up to 15 MPa. A negative-pressure pulse in the liquid is generated when a compression pulse is reflected from the liquid-vapor interface. The pressure of the stretch in the reflected wave is determined by the expression

$$p_{-} = p'' + p_{+}k , \qquad (4.1)$$

where p'' is the gas or vapor pressure above the surface of the liquid, p_+ is the pressure in the compression wave, k is the reflection factor calculated by the formula

$$k = \frac{\omega'' - \omega}{\omega'' + \omega} \,. \tag{4.2}$$

Here $\omega'' = \rho''c''$, $\omega = \rho c$ are the gas and the liquid acoustic impedances, respectively, c'', c, ρ'' , and ρ are the sound velocity and the density in vapor and liquid, respectively. Since far from the critical point $\omega \gg \omega''$, k < 0. The dependence of the pressure amplitude in a compression pulse p_+ on the voltage of the capacitor supply was determined in calibration experiments with the help of a pulse pressure transducer. The calibration experiments were conducted in the range of temperatures (100-140K) and pressures under investigation. The error of determination of pressure in a stretching pulse is 5 %.



Figure 4.1: Schematic diagram of the measuring chamber: (1) liquid under investigation, (2) platinum wire, (3) duralumin membrane, (4) spiral coil, (5) low-inductance capacitor.

The liquid is superheated on a thin platinum wire 2 with a diameter of 20 μ m and a length of 10 mm located at the center of the chamber and immersed in the liquid to a depth of 3-5 mm. The wire is heated by rectangular current pulses 15-25 μ s long with an amplitude of 5-10 V at a rate of temperature increase of about 1 K/ μ s. The heating pulse and the stretching pulse reflected from the liquid free surface are synchronized in such a way that the liquid boiling-up takes place at the moment of passing of the maximum of a negative-pressure pulse through the wire. The wire is included in a measuring bridge circuit. The temperature of the wire probe is determined by its electrical resistance with an error not exceeding 2 %.



Figure 4.2: Oscillogram of an electric signal of boiling-up of liquid argon on a platinum heater at pressure p = -2.0 MPa. The delayed sweep of the oscillograph with respect to the beginning of a heating pulse is equal to 15.0 μ s. An arrow shows the beginning of intense fluctuation nucleation $t = t_*$.

In the absence of boiling-up, the wire temperature T(t) increases monotonically with the rate $\dot{T} \simeq \text{const}$ up to the moment of attainment of the conditions of intense fluctuation nucleation, when the thermal regime of the wire changes abruptly. When the liquid boiling-up begins, a short-lived temperature perturbation, $\theta(t)$, appears on the curve of the time dependence of the temperature of the wire, T(t), being heated. The absolute value is $|\theta(t)| \ll |T(t)|$. Therefore the signal of boiling-up is preliminarily separated with the help of a special filter and then delivered to the entrance to an oscillograph (Fig. 4.2).

We consider a simplified variant of solution of the problem on a thermal signal in the wall-evaporation regime, whose detailed analysis is given in [18, 19]. Owing to the good wetting of platinum with liquid argon, and also to the fact that the superheated wall layer is thin and the contribution of completed centers is small, bubbles originate by the homogeneous nucleation mechanism. The homogeneous nucleation rate depends on the liquid temperature T(t, x), which in its turn is a function of the time t and the distance to the heater wall x. The logarithm of the fluctuation nucleation rate J(t, x) with good accuracy is a linear function of the temperature [20], therefore in a wide temperature range we can employ the approximation

$$J(t,x) = J_n \exp\left[(T(t,x) - T_n) G_T \right] , \qquad G_T = \frac{d \ln J}{dT} = \text{const} ,$$
(4.3)

where J_n is the nucleation rate at the temperature of fixation, $T_n \equiv T(t_n, 0)$.

Bubbles come into being in a thin wall layer, therefore along with J it is convenient to introduce the surface rate of fluctuation nucleation I at the heater temperature $T(t) \equiv T(t, 0)$ calculated by the formula

$$I(T(t)) = \int_{0}^{\infty} J(t,x)dx = J(T(t)) \left[G_T \left| \frac{\partial T(t,x)}{\partial x} \right|_{x=0} \right]^{-1} .$$

$$(4.4)$$

4.2 Experimental Setup and Measurement Procedure

The temperature gradient near the heater is given by the formula [21]:

$$\frac{\partial T\left(t\right)}{\partial x}\bigg|_{x=0} = -2\frac{T_n - T_\infty}{\sqrt{\pi a t_n}} , \qquad (4.5)$$

where a is the liquid thermal diffusivity, T_{∞} is the temperature far away from the heater.



Figure 4.3: Microphotographs of explosive boiling of a liquid on bubbles of fluctuation origin at a heating rate of 1 K/ μ s: a) Z(t) is 0.05, b) Z(t) is 1. The exposure time is 0.05 μ s, p = -4.5 MPa.

In experiments on liquid explosive boiling-up at negative pressures on thin filament heaters bubbles at the stage of a considerable thermal perturbation prove to be strung on a filament like "beads" (Fig. 4.3 b). It is explained by the high rate of the bubble growth in a stretched liquid. At a negative pressure the bubble growth is retarded by the inertia of the surrounding liquid (Rayleigh's theory), therefore the rate of increase of the bubble radius is a constant equal to

$$\dot{R} = \sqrt{\frac{2(p''-p)}{(3\rho)}} \,. \tag{4.6}$$

Every bubble "dries" a part of the wire as long as its diameter d. Consequently, the condition of validity of the "bead" model may be written as follows:

$$I\left(T\left(t\right)\right) \cdot \pi d^{3} < \dot{R} . \tag{4.7}$$

According to this condition, in the time of the bubble growth to a size equal to the wire diameter no new bubbles arise. In the experimental results presented here the condition Eq. (4.7) is fulfilled at pressures lower than -2 MPa. The time of the bubble transformation into a "bead" is 0.05-0.5 μ s.

The part of the wire length covered with bubbles is found by integrating "dry" spots with respect to the time of their origination:

$$Z(t) = 2\pi d \int_{0}^{t} I(T(\tau)) \cdot \dot{R} \cdot (t-\tau) d\tau$$

$$= 2\pi \frac{\dot{R}d}{\left(G_{T}\dot{T}\right)^{2}} I(T(t)) \left[1 - \left(1 + G_{T}\dot{T}t\right) \exp\left(-G_{T}\dot{T}t\right)\right].$$

$$(4.8)$$

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From here on the count of time begins with the time fixation $t_n = t_* - 1\mu s$.

With growth and contact with the wire probe the bubbles envelop the heater surface and perturb the heat flow from the wire. Eq. (4.8) makes it possible to calculate the nucleation rate J(T(t)) at the instant of registration of explosive boiling-up t_* for a chosen value of $Z(t) = Z_*$. The value of G_T required for calculating J(T(t)) by Eq. (4.8) is determined from the condition of proportionality at the initial stage of boiling-up of the temperature signal $\theta(t)$ (Fig. 4.4) and the nucleation rate J(t). Such proportionality is substantiated by a thermal physics calculation [18]. In experiments, the signal of explosive boiling-up is separated by a special filter, which transforms the temperature by the formula $\theta(t) = T(t + \delta t) - T(t)$, where the delay time is $\delta t = 0.2 \ \mu$ s. From the relation $\theta(t, 0) \propto J(t)$ and Eq. (4.3) follows the formula

$$G_T = \dot{T}^{-1} \frac{\partial \ln \theta \left(t, 0 \right)}{dt} \,. \tag{4.9}$$

The correctness of Eq. (4.9) is tested by the condition of independence of the quantity G_T from the time of development of boiling-up at its initial stage.



Figure 4.4: Oscillogram of a thermal signal in the initial stage of explosive boiling-up for an argon-helium solution at p = -3.9 MPa, $\dot{T} = 0.8$ K/µs (solid line). The dotted line shows calculation at $G_T = 7$.

The error of determination of the effective nucleation rate by the procedure described above does not exceed one order and is mainly caused by the uncertainty of the value of Z_* set in calculations by Eq. (4.8). A typical photograph of the explosive boiling-up of a liquid on a wire is presented in Fig. 4.3. The thermal perturbation is most pronounced at the instant the wire is fully covered with a vapor "coat". Therefore in calculations the nucleation rate Z_* was taken equal to unity. The temperature of intense fluctuation nucleation T_* was also registered at that instant. Under changes of time t_* in the range from 15 to 25 μ s, the temperature of intense fluctuation nucleation T_* does not change practically. This fact is explained by the strong temperature dependence of the nucleation rate and is an additional argument in favor of the fluctuation mechanism of nucleation.

From Eqs. (4.3) – (4.8) it follows that the effective thickness of the wall layer, which makes the main contribution to nucleation, in experimental conditions is equal to $10^{-6}-10^{-7}$ m, the characteristic time of boiling-up is 10^{-7} s, the nucleation rate in this case is equal to $10^{22}-10^{24}$ s⁻¹m⁻³. Such high values of

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the nucleation rate are ensured by realization of the shock boiling-up regime. In this regime, evaporation is mainly ensured by bubbles of fluctuation origin [2-4].

In the experiments with solutions, the saturation of liquid argon with helium was realized at a pressure of 2.04 MPa. The establishment of concentration equilibrium in the chamber was controlled by the static pressure and the temperature of the limiting superheat of the solution. The constancy of the value of the attainable-superheat temperature, which in the process of saturation varied from 138.7 K to 136.1 K pointed to the completion of the gas dissolution. The process of helium dissolution was intensified by passing pressure pulses with an amplitude up to 5 MPa through the solution. When an inverted wave returned to the bottom of the chamber, at the membrane surface one could observe an intense formation of cavitation bubbles, which facilitated the agitation of the liquid.

4.3 Experimental Results. Comparison with Homogeneous Nucleation Theory

Experiments were performed on argon of high purity (99,998%). All in all, there were three series of measurements. Every series was conducted on different heaters with a new portion of argon in the measuring chamber. Experimental data on the attainable-superheat temperature for liquid argon at positive and negative pressures are presented in Fig. 4.5. At a temperature of 110 K the value of the limiting stretch $\Delta p_* = p_s - p$ was 10 MPa.



Figure 4.5: Boundary of attainable stretches of liquid argon (dots), saturation line p_s , spinodal p_{sp} . Dots of different types refer to experiments employing different wire probes. Dashed lines show the results of calculation of the limiting stretch by the homogeneous nucleation theory (Eqs. (4.11)–(4.13)) for two values of the nucleation rate: the upper line refers to $J = 10^{20} \text{ s}^{-1}\text{m}^{-3}$, the lower line to $J = 10^{25} \text{ s}^{-1}\text{m}^{-3}$, C is the critical point.

The boundary of essential instability of the liquid phase (spinodal) is determined by the condition [2]

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 , \qquad (4.10)$$

where v is the specific volume of the liquid. The spinodal of liquid argon is approximated in [3, 22] by the results of measuring the (p, v, T)-properties in stable and metastable states (Fig. 4.5). At a pressure p = -10 MPa the spinodal temperature $T_{sp} \simeq 116.5$ K, which is 6.5 K higher than the superheat temperature achieved in the experiment.

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On the spinodal, a homogeneous system loses its reducing reaction to mechanical or thermal perturbations whatever small they are. However, even before the attainment of this boundary in a metastable liquid, owing to fluctuations during the thermal motions of a collective of interacting particles, there may appear nuclei of the competitive phase. These nuclei initiate a phase transition if their size exceeds a certain critical value. Then the growth of a new phase is accompanied by a decrease of the thermodynamic potential $\Delta \Phi$.

In classical nucleation theory, the boiling-up of a superheated (stretched) liquid is treated as the Brownian motion of bubbles in the one-dimensional space of their sizes with the potential field $\Delta \Phi = W(R)$. The maximum value of the potential barrier $W_* = \Delta \Phi_*$ corresponds to the formation of a critical nucleus of radius R_* . In the stationary case the nucleation rate, i.e. the number of viable $(R > R_*)$ nuclei forming in a unit volume in unit time is determined by the expression [1]

$$J = \rho_n B \exp\left(-G\right) \,, \tag{4.11}$$

where ρ_n is the particle number density of a metastable liquid, $G = (W_*/k_BT)$ is the Gibbs number, the work of formation of a critical nucleus W_* referred to the average energy of the thermal motion per degree of freedom, B is the kinetic factor which takes into account the dynamics of the bubble growth.

For the work of formation of a critical bubble we have

$$W_* = \frac{2}{3}\pi R_*^3 \left(p_*'' - p \right) = \frac{16}{3}\pi \frac{\sigma^3}{\left(p_*'' - p \right)^2} , \qquad (4.12)$$

where σ is the surface tension at the critical bubble – metastable liquid interface, p''_* is the pressure in a critical bubble.

The problem on cavitation in a nonvolatile, inertialess, high-viscosity liquid was solved by Zeldovich [1]. Later this particular case of nucleation was considered by Kagan [23]. By the data of [1, 23], we have

$$B = \frac{3}{8\pi R_*^2 \eta} \left(\sigma k_B T\right)^{1/2},\tag{4.13}$$

where η is the liquid viscosity. If the dynamics of a near-critical bubble is determined by the liquid evaporation rate, at positive and low negative pressures [23]

$$B = \frac{3}{3-b} \left(\frac{2\sigma}{\pi m}\right)^{1/2},$$
(4.14)

where m is the molecular mass, $b=1-(p/p_*'')=2\sigma/R_*p_*''\;$.

At a fixed nucleation rate J, Eqs. (4.11)-(4.14) determine the value of the limiting liquid stretch p_* (the boundary of attainable stretches). Calculations by formulas of the homogeneous nucleation theory presuppose a knowledge of substance properties in stable and metastable states. Such information for liquid argon has been taken from [3, 24, 25].

The kinetic factor B in Eq. (4.11) depends only very slightly on temperature and pressure as compared with the exponential factor. According to Eq. (4.13) at a pressure of -10 MPa and a temperature of 110 K, the value of B is equal to $1.35 \cdot 10^9 \text{s}^{-1}$; at p = 2.5 MPa and T = 140 K, the value of the kinetic factor is $1.18 \cdot 10^8 \text{s}^{-1}$. The numerical values of the factor B obtained by Eq. (4.13) at T = 140 K are approximately an order smaller than those obtained by Eq. (4.14). The very strong dependence of the nucleation rate Eq. (4.11) on the exponent makes such differences in the evaluation of the coefficient B insignificant, i.e. attainable-superheat temperatures in this case differ by no more than one tenth of Kelvin.

The results of calculating limiting superheats for liquid argon by the homogeneous nucleation theory (Eqs. (4.11)-(4.13)) for two values of the nucleation rate $J = 10^{20} \text{s}^{-1} \text{m}^{-3}$ and $J = 10^{25} \text{s}^{-1} \text{m}^{-3}$ are shown as dashed lines in Fig. 4.5. The calculations were performed in a macroscopic approximation, i.e. it was assumed that the surface tension of critical bubbles σ did not depend on their size and was equal to the value at the planar interface σ_{∞} [25].

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4.3 Experimental Results. Comparison with Homogeneous Nucleation Theory

With decreasing temperature and increasing liquid stretch, the radius of a critical bubble decreases. In liquid argon at $(T/T_c) = 0.95$ (T = 143 K), where T_c is the temperature at the critical point, and $J = 10^7 \text{s}^{-1} \text{m}^{-3}$ the radius of a critical bubble is 6.4 nm, and at $J = 10^{25} \text{s}^{-1} \text{m}^{-3}$, R_* is equal to 3.5 nm. If $(T/T_c) = 0.6$ (T is then equal to 90 K), at the indicated values of the nucleation rate the radii of critical bubbles are 1.4 and 0.9 nm, respectively. At temperatures far from the critical one the vapor density is low, so critical bubbles in a stretched liquid do not practically contain any gas phase.

Allowance for the size effect (dependence $\sigma(R_*)$) in the homogeneous nucleation kinetics results in increasing value of $G_T = d \ln J/dT$. If at a pressure p = -3 MPa and $J_n = 10^{25} \text{s}^{-1} \text{m}^{-3}$ the value of G_T calculated by the homogeneous nucleation theory in a macroscopic approximation is $\approx 5 \text{ K}^{-1}$, allowance for the size effect in the framework of the van der Waals capillarity theory [5] gives $G_T \approx$ 6.5 K^{-1} . The values of G_T calculated by Eq. (4.9) from the conditions of optimum description of the beginning of the signal of explosive boiling-up have an error of about 20-25%. Such large values of the error are mainly connected with the high level of noise (Fig. 4.4). For p = -2MPa and $T_* = 125.8$ K we have $J_* = 3 \cdot 10^{23} \text{s}^{-1} \text{m}^{-3}$, $G_T = (7.0 \pm 1.0) \text{K}^{-1}$. For p = -3 MPa and $T_* = 126.8$ T we have $J_* = 6 \cdot 10^{22} \text{s}^{-1} \text{m}^{-3}$, $G_T = (5.5 \pm 1.0) \text{ K}^{-1}$. Thus the data obtained, confirming the general principles underlying the homogeneous nucleation theory, do not allow us yet making an unambiguous conclusion in favor of presence or absence of the effect of the curvature of the bubble-liquid interface on the kinetics of argon explosive boiling-up at negative pressures.



Figure 4.6: Cavitation strength of an argon-helium solution Eq. (4.1) and pure argon Eq. (4.2). The dashed lines show results of calculations by homogeneous nucleation theory (Eqs. (4.3)–(4.5)) for $J = 10^{22} \text{ m}^{-3} \text{s}^{-1}$, the upper – an argon-helium solution, the lower – pure argon. $p_s^{\text{Ar}-\text{He}}$, p_s^{Ar} – lines of phase equilibrium for an argon-helium solution and for argon, p_{sp}^{Ar} – argon spinodal, C – argon critical point.

Limiting superheats of solutions with the helium content equal to 0.31 mol% have been measured in the pressure range from +2 to -8 MPa. The nucleation rates realized in experiment lie in the interval $J = 10^{21} - 10^{23} \text{m}^{-3} \text{s}^{-1}$. The results of the measurements are presented in Fig. 4.6. Ibid one can see experimental data on the cavitation strength of pure argon. Helium dissolution leads to a decrease in the cavitation strength and the temperature of argon superheat. At a pressure p = -5 MPa the shift in the

limiting-superheat temperature is approximately 3.5 K, and in pressure it reaches 2 MPa.

Experimental data have been compared with calculations via Eqs. (4.11)-(4.13). In them the peculiarities of nucleation in a solution are mainly allowed for via the parameters σ and p_s . Calculations by Eqs. (4.11)–(4.13) were made in a macroscopic approximation – the surface tension at the vapor bubble– metastable solution interface was assumed to be equal to its value at a planar interface. The properties of an argon-helium solution required for calculation were taken from [22, 26-28]. The results of calculating of limiting strength at $J = 10^{22} \text{ m}^{-3} \text{s}^{-1}$ are presented in Fig. 4.6. Given ibid are theoretical values of the limiting strength for pure argon. Within the experimental error, experimental results agree with homogeneous nucleation theory. However, limiting stretches (superheats) achieved by experiment are systematically lower than calculated ones. Besides, the values of the derivative G_T obtained in the course of experiments are somewhat higher than those calculated by formulae of homogeneous nucleation theory in a macroscopic approximation. As is shown in [5], it is just this kind of disagreement between experiment and classical homogeneous nucleation theory that should be observed if the latter does not take into account the size effect, i.e. the dependence $\sigma(R_*)$. To reconcile data of theory and experiment on limiting stretches (superheats), it is necessary to assume that the surface tension of a critical bubble $\sigma(R_*)$ is 5-10 % smaller than at a flat interface. Owing to the weak temperature and pressure dependence of the pre-exponential factor in Eq. (4.11) the derivative G_T is determined by the temperature dependence of the Gibbs number, i.e. $G_T \simeq dG/dT$.

4.4 Conclusion

Under certain conditions, liquids can tolerate considerable tensile stresses at both static and dynamic conditions. Stress release results from the formation of vapor or gas bubbles inside the liquid. Homogeneous nucleation determines the lower boundary of the liquid cavitation strength, which at temperatures below $0.85-0.9 T_c$ is located in the region of negative pressures. The characteristic size of a bubble and the vapor density in it decrease when moving along this boundary from the region of positive into the region of negative pressures. Critical bubbles in a highly stretched liquid prove to be practically empty. All this creates a number of difficulties both in an experimental investigation of homogeneous cavitation at negative pressures and in the interpretation of results obtained in the framework of the classical nucleation theory.

The small sizes of critical bubbles make a liquid extremely sensitive to the smallest inhomogeneities both inside it and on the surrounding walls. The absence of a vapor phase in a bubble complicates the description of its growth both in the framework of the classical scheme of successive acts of evaporation and condensation and in the context of the hydrodynamic approach based on the use of local thermodynamic quantities. The classical homogeneous nucleation theory is formulated for small supersaturations when $G = (W_*/k_BT) \gg 1$ and the macroscopic description of new-phase nuclei is legitimate. The possibility of using for bubbles of radius 1-2 nm, which corresponds to three or four intermolecular distances in the liquid, the same value of surface tension as at a flat interface is far from being evident. In investigations of spontaneous cavitation at negative pressures not only the revealing and the study of fine effects, for instance, such as the size effect, are of interest, but also a detailed verification of the classical nucleation theory in its macroscopic version.

In experiments on explosive cavitation in liquid argon homogeneous conditions of nucleation were attained both by decreasing the time of the liquid stay under a negative pressure by means of generation of a short pulse stretch and by reducing the volume of the cavitating liquid by heating a thin liquid layer near the surface of the shock boiling-up regime, at which the disturbance of continuity is mainly caused by bubbles of fluctuation origin. A boiling-up signal, whose transducer is the wire heater, carries information on the liquid limiting superheat temperature T_* , the nucleation rate J_* and its temperature dependence G_T . Since in experiments on explosive cavitation it is difficult to vary the nucleation rate within considerably large limits, the value of the derivative G_T is an important argument in substantiating the homogeneous mechanism of nucleation and analyzing the fine nucleation effects.

The realization of the explosive cavitation method presented in this paper made it possible to register

4.4 Conclusion

the limiting superheat temperature for argon with an error ± 0.5 K at an uncertainty in pressure of about 5%. The nucleation rate corresponding to this superheat temperature was registered with an accuracy of one order. This accuracy was sufficient for stating a satisfactory agreement between experimental data and the classical homogeneous nucleation theory in a macroscopic approximation. The discussion of fine effects in nucleation is beyond the scope of this analysis. Values of G_T calculated by the homogeneous nucleation theory in a macroscopic approximation of G_T from experimental data on the explosive boiling-up signal. To reduce the error of measuring G_T to 2-3%, it is necessary to increase the sensitivity of the setup measuring section by one order. The work in this direction will be continued.

The dissolution of a gas in a liquid leads to changes in its properties. With an interface a free-volatile component is usually adsorbed in the interfacial layer, causing the pressure to decrease. Thus, the dissolution of 0.5 mol% of helium in liquid argon at the normal-boiling temperature increases the saturation pressure by 7 MPa [28] and decreases the surface tension by 10% [26]. The surface tension and the vapor pressure are the main quantities that determine the work of formation of a nucleus and, consequently, the nucleation rate.

In experiments on the kinetics of explosive cavitation in an argon-helium solution a decrease in the cavitation strength of liquid argon was revealed when helium was dissolved in it. The dissolution of 0.31 mol% of helium in argon at a temperature of $0.75T_c$ (113 K) reduces its cavitation strength by 2 MPa. This result is in good agreement with classical homogeneous nucleation theory. The latter fact indirectly points to the establishment of an equilibrium composition of the vapor–gas mixture in a critical bubble and adsorption equilibrium at the solution–critical bubble interface.

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5 The Main Silica Phases and Some of their Properties

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The beginning chemist might predict that silicon, having the same external electron structure as carbon, will form two oxides – SiO and SiO₂, both gaseous; further, that SiO, like CO, will be stable at high temperatures but will disproportionate at lower temperatures into SiO₂ and Si (as does CO into CO₂ and graphite). Why is he so nearly right about SiO and so completely wrong about SiO₂?

Robert B. Sosman

Abstract

The presented chapter gives a review of historical and modern aspects of investigation of the structure and properties of silica - one of the most abundant substances on Earth. Silicas are substances with the same chemical formula, SiO₂, but different structures. The variety of crystal forms of silicas seems to be unique; they vary from loose clathrasils to the built of tetrahedral units proper silicas such as quartz and cristobalite and to very dense high pressure phases built of SiO₆-octahedrons. Specifics of the crystal structures, formation conditions and abundance in nature are discussed. Special attention is given to quartz and some of its properties such as the existence of right and left quartz, its anisotropy; uncommon thermal expansion and the underlying it mechanism; the phenomena accompanying the $\alpha - \beta$ -inversion – opalescence and appearance of incommensurate phases in a very narrow temperature interval; and pressure induced amorphization, and so on. Physico-chemical problems of hydrothermal synthesis of quartz single crystals are also discussed. Some relatively new phenomena, pressure induced transformations in amorphous silica and/or polyamorphism, are briefly reviewed as well. The electronic structure of silica is analyzed; its specific features explain the multiformity of silicas as well as their unexpectedly high reactivity and the negative thermal expansion coefficients of high-temperature polymorphs of proper silicas built of SiO₄-networks.

5.1 Introduction

Nothing is something

The concept of zero is said to be a great finding of ancient Indian mathematicians. Just in the 9^{th} century they have comprehended that nothing is something. If we want to fill something, we should provide ourselves with an appropriate void. To have a void is to have something. Thus, zero in a number shows that we have no unities in a given number position, but it also shows us that the number contains this position.

A similar situation is found in chemistry. Atoms with empty outer orbitals have more possibilities for chemical bond formation than atoms with the same electronic configuration but without empty orbitals. Presence of empty d-orbitals in silicon atoms imparts to silicon dioxide a number of specific features which are absent for carbon dioxide although carbon is the nearest analogue of silicon. This "chemical void" can be partially filled and involved in orbital hybridization. As a result, we get such properties as an extraordinary

glass forming ability of silica; a great number of polymorphs for this elementary glass forming substance; ability to form five-coordinated complexes contrary to pronounced tetravalence of silicon; ability to form easily activated complexes resulting in an unexpectedly high reactivity at very low temperatures. The latter property together with ability to catalysis leads to high-temperature phases (like quartz and cristobalite) growth from solutions at 300°C or even at 100°C. Finally, involving empty *d*-orbitals in hybridization in the long run leads to zero thermal expansion of SiO₄ tetrahedrons.

On my experience, reasons of the listed and some other features of silica are often remaining incomprehensible for specialists in glass science because these reasons lie in a quite far field. In the presented review, I try to discuss some spectrum of the interesting properties of silica and, when it is possible, to supply an explanation. I also wanted to tell about some amazing investigations performed fifty or more years ago, very prolonged and laborious and very precise, which apparently could not be executed in full detail in a similar way presently. In this chapter, I mainly use materials of the monographs [1] and [2] as a starting point.

5.2 Specific Features of Silica Resulting from the Electronic Structure of Silicon

5.2.1 Specific Features of Silica Compounds and Differences to Chemical Analogs: Silicon and Carbon

There exist in nature a great diversity of silicon compounds. After carbon, silicon forms the largest number of compounds with other elements. On the one hand, this is a result of silicon position, similar to carbon, in the main sub-group of the IV group of the Periodic System and is determined by the same factors that provide such a wide spectrum for carbon compounds. However, the latter statement is true only partly, and the author of the Periodical System of elements, D. I. Mendeleev, was the first who emphasized sharp distinctions in CO_2 and SiO_2 properties [4]. The great number of carbon compounds results also from closeness in C–C, C–O and C–H bonding energies (Table 5.1). As a result, these bonds spring up with approximately equal probability.

Table 5.1: Average bonding energies (kJ/mol) for some bonds of carbon and silicon [1].

Bond	X			
	С	Si		
X-X	346	222		
Х–О	358	452		
X–H	413	318		

As opposed to this, bonding energy for the bond Si–O considerably exceeds Si–H bonding energy and two times surpasses Si–Si bonding energy (Table 5.1). Therefore the basis of silicon chemistry is made up not from usual for carbon chains –X–X–X– but chains –Si–O–Si–O–Si–. Only a small number of silicon compounds may be considered as an analogue of organic compounds of carbon. All three types of the bonds (X–X, X–H and X–O) are nearly equal with respect to their energy advantage in carbon chemistry, but in silicon chemistry there is the alone energy advantageous type of the bond (X–O) therefore a less number of compounds is known for silicon than for carbon. At the same time, silicon compounds have specifics that make them unique among other classes of compounds. Silica is really unique by abundance of its polymorphic modifications; structural multiformity of silicates is great indeed and by far exceeds the variety of carbon compounds.

The difference between the chemical analogues, C and Si, is not only quantitative but qualitative, too. The highest coordination number for carbon is four; but for silicon, it can reach five and six. The valence



Figure 5.1: Interior tetrahedral O-Si-O and exterior inter-tetrahedron Si-O-Si angles.



Figure 5.2: Histograms for the Si–O–Si angle distribution established for different compounds: a) silicates (468 angle values); b) polymorphs of silica (80 angle values) [1]. Arrows mark the tetrahedral angle.

angle of oxygen in organic compounds of R–O–R type (where $R = CH_3$, C_2H_5 and others) is equal to tetrahedral angle 109°28′ and it seems that the same should be valid for the similar Si–O–Si angle (Fig. 5.1) whether the Si–O bond can be considered as mainly ionic or mainly covalent. In actual truth, in silica, silicates and organo-silicon compounds the angle discussed changes over wide limits 120–180°.

5 Silica Phases and Some of their Properties



Figure 5.3: The effect of temperature and cation size on the Si–O–Si angle of double-layered aluminasilicates: *a*) $Ba[Al_2Si_2O_8]$ above 570°C; *b*) $Ba[Al_2Si_2O_8]$ below 570°C; *c*) $Ca[Al_2Si_2O_8]$. Open points refer to Ba or Ca cations, solid points to Si and Al atoms.

As it is seen from Fig. 5.2 constructed according to the most precise measurements of Si–O–Si angles in silicates, the value of 139° is of frequent occurrence. For the angles of pure silica polymorphs, the most frequent value is even higher, 147°. Compounds with the tetrahedral Si–O–Si angle, 109°28′, do obviously not exist among silicas and silicates! Moreover, the valent Si–O–Si angles in silicas and silicates vary not only from structure to structure, but for every given structure, they can change over rather wide limits with temperature or under chemical substitution in solid solutions (Fig. 5.3). This distinguishing feature is not inherent for carbon-oxygen compounds; the valent C–O–C angle is rigid and differs only sligthly from tetrahedral angle. One more specific feature of silicon compounds is the too large difference between the Si–O bond length calculated from the covalent Si and O radiuses (1.83 Å) and the bonds established experimentally, in particularly the average for silicas and silicates bond length (1.62 Å).

The origin of the mentioned above and some other features of silica compounds such as the variety in mechanisms of chemical reactions, catalytic character of silica glass crystallization and chemical reaction with silica participation, specifics of some physical properties such as thermal expansion results from the electronic structure of the silicon atom and some peculiarities of its interaction with oxygen. These topics will be addressed in the next section.

5.2.2 Electron Structure of the Silicon Atom and its Interaction with Oxygen

The configuration of the valence shells of carbon and silicon atoms seems to be the same, s^2p^2 . A transformation of the valence shells takes usually place at chemical compound formation. In an excited state, the atom has one *s* and three *p* electrons at the outer shell (Fig. 5.4), which form four identical sp^3 hybrid orbitals. Silicon atoms in the ordinary four-valent state use just these tetrahedral directed bonds with an angle of nearly 109°. Overlap of $3sp^3$ orbitals of silicon with 2p orbitals of oxygen forms a chemical bonding of σ -type that is the bond with maximal overlapping of electronic density on the line connecting Si and O atoms. These four hybrid sp^3 orbitals are quite stable and thus of primary importance for silicon chemistry. The major part of silicon compounds is constructed from SiO₄ tetrahedrons; they are the main constructional element of silicas, silicates and organosilicons.

However, there is a very significant difference in the valence shells of carbon and silicon: silicon has five vacant d-orbitals that are absent in the outer shell of carbon. Linus Carl Pauling was the first who understood that vacant place differs from absent one and in his famous book "The Nature of the Chemical Bond" put forward an idea of 3d-orbitals participation in the chemical bonding of silicon with electronegative atoms (oxygen, for example) to explain the difference in silicon and carbon chemistry and numerous discrepancies in prospective and experimentally established properties of the silicon bonds. Electronegative substitute of silicon increases its positive effective charge and promotes contraction of diffusive 3d-orbitals, which become energy commensurable with 3s and 3p-orbitals and thereby enhance valent capabilities of silicon. According to modern concepts based on manifold experimental evidences, 3d-orbitals of silicon are involved in π -bond formation together with an unshared p-electron pair of electronegative substitute



Figure 5.4: Electron shells of carbon and silicon in an exited state.

(oxygen), i.e. $(p_{\pi}-d_{\pi})$ -coupling. Furthermore, formation of additional σ -bonds is possible, too, by $3sp^3d$ and $3sp^3d^2$ hybridization.

Let us briefly discuss the consequences of the occurrence of these two additional types of bonding for the case of silicon-oxygen interaction because they are of high importance for silicon chemistry. A detailed review and analysis of the available literature data one can find in the monograph [1] for X-ray investigations and in [2] for the chemical approach.

5.2.3 Consequences of π -Bonding in Silica

The availability of π -bonding in SiO₄ tetrahedrons is confirmed clearly by the mentioned above difference between the calculated and experimentally measured single Si-O bond length. The bond length is 1.83 Å for the covalent model and contracts to 1.76 Å with due regards for the partially ionic character of the bond, but according to X-ray analysis the true length value varies in 1.59-1.63 Å limits for different forms of silica with tetrahedral coordination. Such large contraction of the bond indicates strong π -bonding inside SiO₄ group and increasing in the bond order because of a shift of an unshared p-electron pair of oxygen atom to one of the empty d-orbitals of silicon. Besides the bond contraction, π -bonding leads to reduction in the dipole moment of Si-O bonds, decreasing of the effective positive charge of silicon to +2 and a negative charge of oxygen to -1. The availability of additional $(p_{\pi} - d_{\pi})$ -bonding can also explain the more acid character of silanols in comparison with carbinols, the higher Si-O bond energy (419-494 kJ/mol) as compared with more dipolar C-O bond (358 kJ/mol) as well as the absence or significant weakening of donor-acceptor ability of siloxane (Si-O-Si) bond in siloxanes and polysiloxanes. Participation of both unshared electron pairs of oxygen of bridging Si-O-Si bond in $(p_{\pi} - d_{\pi})$ -bonding effects upon the valent Si-O-Si angle and leads the last to its increasing (Fig. 5.2). Valent Si-O-Si angles are not rigid but have a considerable flexibility because of diffusivity and different orientation of the five 3*d*-orbitals of silicon resulting in π -bond formation for just any spatial location of oxygen atoms. This feature appears to explain the large number of polymorphic modifications of silica with different types of packing of SiO₄ tetrahedrons. Clear correlations between Si-O-Si angles and Si-O distances may be observed for a given crystal structure, but they are not always comparable for different modifications. The approaching of the valent Si-O-Si angle to a value of 180° is not typical for silica modifications and occurs only in individual structural positions of high-temperature cristobalite and coesite.

Thus, π -bonding manifests itself quantitatively in Si-O bond contraction and strengthening as a result

of increasing in the bond order, the latter varying in silicas and organosilicon compounds over limits from 1.2 to 1.5. The most suitable for π -bonding are d_{xy} , d_{xz} and d_{yz} orbitals, which are directed at 45° angle to the (x, y, z)-axes. Maximal overlapping of the electron clouds is located in this case out of the line connecting Si and O atoms. An interesting consequence of the latter fact is consided below in the paragraph devoted to thermal expansion of quartz. Another consequence is the very high tendency of silica melt to glass formation. SiO₂ is the most famous glass former, its analogue in the periodic system GeO₂ is less known but comparable in glass formation tendency as distinct from CO₂ which was produced in amorphous silica-like state only recently and under very high pressure [5]. The inter-tetrahedron Si-O-Si angle in quartz glass varies from 120 to 180° with the most probable value of nearly 144°.

5.2.4 Increase in Silicon Coordination Number as a Result of *s-p-d*-Hybridization

Five vacant *d*-orbitals of silicon may be used apart from the Si-O strengthening by π -bonding for formation of additional directed σ -bonds with strongly electronegative atoms like fluorine, oxygen or nitrogen. In this case, silicon coordination number increases to five and six.

Presently a number of quite stable at ambient condition compounds is known in which the five-coordinated state of silicon was established by X-ray single crystal investigations. For some other compounds, groups [SiA₅] with five-coordinated silicon were established by spectroscopy and chemical methods. In these compounds, the first coordination sphere of silicon contains at least one strongly electronegative atom besides oxygen. These groups form because of $sp^3d_{z^2}$ -hybridization, and the coordination polyhedron of silicon is represented usually by a slightly distorted trigonal bipyramid. For ideal $sp^3d_{z^2}$ -hybrid orbital (and trigonal bipyramids), the valent X-Si-X angle is equal to 120°.



Figure 5.5: Dependence of average values for three X-Si-X angles on X-Si-Y and X-Si-Y' angles.

Fig. 5.5 demonstrates the interrelation between average values for three X-Si-X angles in 15 refined crystal structures involving five-coordinated silicon and average values of X-Si-Y and X-Si-Y' angles (where Si-Y is the shortest and Si-Y' is the largest distance between the Si atom and apical ligands [6]). The point 1 in the picture relates to forsterite Mg₂[SiO₄] with distorted tetra-coordination of silicon; point 2 - the ideal tetrahedral sp^3 -hybridization in a hexagonal close-packed lattice with the angle of 109°28'; 17 –

the ideal $sp^3d_{z^2}$ -hybridization. The experimental data for compounds with five-fold silicon fall on two lines passing through ideal tetrahedral and trigonal bipyramidal positions. Thus, there is a more or less continuous change from sp^3 - to $sp^3d_{z^2}$ -hybridization and participation degree of $3d_{x^2-y^2}$ - and $3d_{z^2}$ -orbitals of silicon in its bonding with ligands increases in this row; correlations between interatomic distances d(Si-A)and corresponding angles confirm this conclusion [6].





Six-fold coordination of silicon appears due to sp^3d^2 -hybrid orbitals formation directed to octahedron vertexes. It may be formed at ambient conditions in silicates with the general formula $M_rSi_sO_t$ containing Si–O–M bonds and if electronegativity of the M-atom is sufficiently high as it takes place for C, H, P or F. Two polymorphic modifications of silicon pyrophosphate SiP₂O₇ are the examples of stable at ambient condition compounds with SiO₆ octahedrons. Among compounds with Si(OH)₆ groups there is the mineral thaumasite [7] which was found also in industrial concretes. However, the major part of compounds with six-coordinated silicon is stable only under high and super-high pressure; a list of the compounds together with the structural information one can find in [1]. The most famous example is stishovite, one of high-pressure modification of SiO₂ (Fig. 5.6). Involving six relatively large oxygen atoms in the coordination sphere of relatively small silicon atom is aided by ultrahigh pressures (16-18 GPa) because of the necessity to overcome strong electrostatic repulsion of oxygen. The Si-O bonds inside octahedrons of stishovite are taken to be predominantly covalent, four shorter bonds (0.1716 nm at Fig. 5.6) being $(p - d)_{\pi}$ -bonded to some extent and two longer bonds (0.1872 nm) being single.

Polymerization of silicic acid in water solutions also leads to increasing in coordination number of silicon. For example, Mitzyuk and coauthors showed in a series of X-ray studies reviewed in [2] that average coordination number of silicon with respect to oxygen in hydrogels of polysilicic acid changes from 4.5 to 5.8 in dependence on water content and degree of the gelskeleton ageing. A similar situation is found in methanol-replaced gels. The fact was explained by donor-acceptor complexes formation between water or methanol molecules and silicon atoms and confirmed by IR spectroscopy data. Thus, high-coordinated silicon complexes can be easily formed at ambient conditions.

It is well known that the larger the atom is in size, the higher can be its coordination number because of deminution in Coulomb repulsion of ligand atoms. Germanium is larger than silicon and has vacant d-orbitals, too, and easily forms GeO₆ octahedrons at atmospheric pressure. Stishovite can exist at atmospheric pressure and was found in small amounts in nature but only in meteorite craters where it was formed by percussion metamorphism produced at meteoric impact.

5.2.5 Implication of *s-p-d*-Hybridization for Chemical Reactions and Physical Transformations of Silica

The possibility of silicon atom to form s - p - d hybrid orbitals in addition to the main four-valent sp^3 bonds is of decisive importance for chemical reactions with silicon participation and explains an extreme sensibility of silica phase transformations to the presence of minor additions of some substances. There are many evidences demonstrating that chemical processes with participation of silica phases such as dilution or growth from solution passes through formation of five- or six-coordinated activated complexes. A detailed literature review and further references can be found in the monograph [2], here we only briefly summarize the main specific features of these processes.

Every physical or chemical transformation of silica goes through switching of \equiv Si-O-Si \equiv bonds which are the main structural element for all types of silicas as well as silicates. The bond is especially inert, and its decomposition is a limiting stage for dilution or polymerization of silica in water; the hydrolysis mechanism is catalytic and depends on different agents present in water. In neutral and alkaline medium, the process is accelerated by OH⁻ and in acid medium by H⁺ and F⁻ ions. Presence of some salts in water solutions accelerates silica dilution at pH=2-4 and higher because of nucleophilic anions attack in the row $F^- >$ SO²⁻₄ >Cl⁻. Ability of siloxane bond Si-O-Si to heterolytic decomposition in presence of these agents was repeatedly verified for organosilicon compounds, too, and the process always goes with formation of intermediate five-fold complexes. Redistribution of electronic density in \equiv Si-O-Si \equiv groups promotes to heterolytic decomposition of Si-O bonds. Actually, the oxygen atom of the water molecule forms a donor-acceptor bonding with the attacked silicon atom, lowers its positive effective charge and weakens ($p_{\pi} - d_{\pi}$) coupling in Si-O bond. As a result, an electrophilic attack of a hydrogen atom of H₂O molecule to bridging oxygen is facilitated and siloxane bond breaks with formation of strongly hydroxylated products.

In the presence of OH^- ions in water solution, they apparently take part in initial stages of silica dilution with intermediate activated complex formation:

$$= Si-O-Si = + OH + O^{-}-Si = + OH + O^{-}-Si$$

Activated complex

The intermediate activated complexes are not durable and easily decompose with \equiv Si-O⁻-anions formation; the latter can participate in the back reaction. In dependence on pH, nature and state of the medium, they may be deactivated to a variable degree and thereby regulate the rate of dilution.

In acid solution, the process of silica dilution goes apparently with formation of intermediate activated complexes with closed chain. In the case of weakly dissociable hydrofluoric acid, the bond decomposition goes according to the following scheme:

$$H-F$$

$$:= Si-O-Si = \rightarrow = Si-OH + F-Si =$$

It is easy to see that one of the silicon atoms in the four-centered activated complex is five-coordinated. Strong acids like HCl and H_2SO_4 also form closed-chain complexes but with water molecules. The more detailed regularities of water solubility of quartz and influence of different agents will be discussed in the section devoted to hydrothermal synthesis.

5.3 Phases of Silica and Their Properties

Hydrothermal crystallization of quartz is also a complicated process depending on a large number of parameters. Acidity of the growth medium and presence of salt additions act on quartz growing rate in addition to temperature and pressure. Ability of siloxane bonds to five-folded activated complex formation underlies in the basis of these catalytic activity. In manufacturing environment of hydrothermal synthesis, the desired temperature/pressure conditions assure immediate quartz formation from water solution, but at lower values of these parameters, the process goes through intermediate phases. The nature of crystallizing phases including clathrasils, their stability and forming sequence also depend on acidity or alkalinity of the medium and the nature of salt additions, all other factors being the same.

As we have seen before, the five-fold activated complexes are different for the different mediums; they stimulate formation of clathrasils with different structures, silica-X and silica-Y (see the next part for details). It is significant that silica-X changes with environment, in particular with the nature and state of the medium. Different types of silica-X and their forming conditions as well as crystallization paths of silica in water solutions for different temperature/pressure conditions are described in detail in [2]. It was especially shown that temperature resistant silica phases like cristobalite and quartz can be formed in water solutions as a result of reconstructive transformations of other crystalline phases at 100-300°C and even at room temperature. Taking into consideration the high strength of Si-O bond and the fact that it is the only type of bonding in silica, it seems impossible. Nevertheless formation of activated complexes sharply reduces the energy barrier for the transformations and makes them possible.

Crystallization of silica and silicate glasses takes place along comparable lines. According to our evidence, cristobalite and quartz can be produced in sodium silicate glasses of appropriate compositions immediately above the glass transition region, at 540°C. The alkali ions play here a role of the transformation catalyst. Hence, silicate glasses have intrinsic catalysts in their structure that provoke siloxane bond splitting followed by high-temperature phase (like quartz or cristobalite) crystallisation at relatively low temperatures. In silica glass, this role passes to impurities. An extremal sensitivity of silica glass crystallization to mode of production and experiment conditions as well as non-repeatability of crystallization results (this is true not only for coefficients of kinetic dependencies but for the dependence character, too) has been systematically studied and explained by Leko & Komarova (see, for example, [9, 10, 11, 12, 13, 14]) as a result of trifling fortuitous pollutions. In superpurity silica glass any trifling admixture or pollution are beyond competition as catalysts and play a decisive role in crystal nucleation and growth. Kinetic dependencies, which are really intrinsic for silica glass, can be obtained only in special conditions described by the mentioned above authors.

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The word "Silica" denotes a substance with chemical formula SiO_2 . It is the most abundant substance on the Earth. Nearly 58% of the lithosphere consists of bonded SiO_2 , and 12% of this silica is found in form of separate rocks as quartz, chalcedony, and opal and so on. Silica is unique among natural and artificial compounds because of a wide variety of different modifications. The major part of them has long been known as minerals, but development of high pressure technique brought about the creation of a number of dense forms of silica, both crystalline and amorphous. Different authors give different lists of silica polymorphs, which exist at quite special condition such as different gas or liquid environment, its acidity and pressure. The phase diagram for pure SiO_2 under normal conditions is in doubt and there is no final set of proper silica phases.

We consider here some problems of compact silica. Dispersed forms of silica are a separate and very special subject, which we do not touch upon in this paper. All compact crystalline as well as amorphous silicas have three-dimensionally connected networks except for fibrous silica-W, and all silica networks except for the three densest ones are built from SiO_4 tetrahedrons connected by their vertexes. Silica phases and compounds are amazing substances in many respects. Let us take a look at these phases, their structures, abundance in nature and some properties (Tables 5.2 and 5.3).

Mineral name	Modifi- cation	Crystal system	Z	Т, °С	Density, g/cm ²	Typical structural elements of crystal lattice [2]
Zeolite H-ZSM5		orthorhombic	96	room	1.79	Large cavities
Melanophlogite 46[SiO ₂]·6[N ₂ ,CO ₂]·2[CH ₄ ,N ₂]		cubic	46	room	1.95	Large cavities 0.5 and 0.65 nm
Fibrous silica-W (oxide_Si)		orthorhombic	4	room	1.97	Chains of SiO ₄ tetrahedrons bonded by edges
Zeolite theta-1		orthorhombic	24	room	1.97	Large cavities
Lechatelierite (silica glass)		disorded	_	room	2.201	Continuous three- dimensional cristobalite-like network from tetrahedrons
Tridymite	high	hexagonal	4	>420	2.19	Layers of 6- membered rings in
		hexagonal	8	220	2.21	(0001) plane
	medium		24	105-180	2.23	
	low*	rhombic	48	room	2.25- 2.27	Layers of 6- membered oval rings in (001) plane
	\mathbf{low}^\dagger	rhombic	64,160	room		
	low [‡]	rhombie	320	room		
Cristobalite	high	cubic	8	248	2.19	Layers of 6- membered rings of tetrahedrons in (111) plane
	low	tetragonal	4	28	2.32	Layers of 6- membered rings of tetrahedrons in (101) plane

Table 5.2: Symmetry, calculated crystallographic density and number Z of $SiO_{4/2}$ tetrahedrons in the unit cell for the main silica crystal phases (according to [1, 2, 15, 16]). Data for the high modifications have been got at different temperatures; hence they should be compared with the low temperature data with caution (the last reference is the largest on-line mineral database and mineralogy reference website on the internet). In the table they are marked with grey color ((1) Meteorite low-tridymite, (2) natural low-tridymite, (3) volcanic low-tridymite).

5.3.1 Dense Octahedral Silicas: High Pressure Phases

Three densest phases of silica are constructed from SiO₆ octahedrons. One of this phases is the quite famous **stishovite**, has been describe in the previous section (Fig. 5.6). The second phase, **seifertite**, is the densest and hardest polymorph of silica so far found in nature, with the scrutinyite (α -PbO₂) type structure. The mineral was named after Friedrich A. Seifert (born 1941), founding Director of the Bayerisches Geoinstitut, Universität Bayreuth, Germany, for his seminal contributions to high-pressure geoscience. The phase was predicted in 2007 by the metadynamics method [17]. It was found in 2008 [18] as lamellae occurring together with dense silica glass lamellae in composite silica grains in the heavily shocked Martian meteorite Shergotty. It was inferred that seifertite was formed by shock-induced solid-state transformation of either

Mineral name	Modifi- cation	Crystal system	Z	T, °C	Density, g/cm ²	Typical structural elements of crystal lattice [2]
Keatite		tetragonal	12	room	2.50	Spiral 4-membered chains around quadric axis
Moganite	high	orthorhombic	12	1354	2.56	left- and right- handed threefold spirals
	low	monoclinic	12	room	2.62	left- and right- handed threefold spirals
Quartz	high	hexagonal	3	575	2.54	Spiral chains around hexagonal axis
	low	trigonal	3	22	2.655	Spiral chains around triple axis
Coesite		monoclinic	16	room	2.95	Chains of 4- membered rings of feldspar type
Stishovite		tetragonal	2	room/1 atm	4.28	Rutile-like structure built from SiO ₆ octahedrons bonded by edges
Seifertite		orthorhombic	4	room	4.29- 4.30	α-PbO ₂ -like structure built from SiO ₆ octahedrons

 Table 5.3:
 Continuation of Table 5.2



Figure 5.7: Projection of structure of melanophlogite to the plane (001).

tridymite or cristobalite on Mars at an estimated minimum equilibrium shock pressure in excess of 35 GPa. With respect to the density the mineral corresponds to density of the last solid layer which is situated above

the liquid Earth core. The mineral was also intergrown in some grains with minor stishovite and a new (third) **unnamed monoclinic dense silica polymorph** constructed from SiO_6 with a ZrO_2 -type structure.

5.3.2 Clathrasils: Friable Silica Phases

All silica phases built of tetrahedrons may be divided into two groups, the proper silicas and filled silicas or clathrasils [1]. The proper silicas like quartz, cristobalite, keatite and coesite can be formed from pure SiO_2 in proper temperature/pressure conditions. Clathrasils can not be formed without presence of some organic or inorganic molecules. Low-molecular forms of silicic acid condense around the guest molecules, the latest being not cations but neutral compounds which organize silica framework around themselves and playing the role of seeds in the crystallization process. The guest molecules appear to be locked inside polyhedral cavities (cages) of the framework and a form of the cage is determined by size and form of the guest molecule. In some cases organic guest molecules may be deleted out by burning, the residuary skeleton being pure SiO_2 and keeping its stability (zeolites). In other cases the structure collapses after the guest molecules removal (melanophlogite).

A common chemical formula of **melanophlogite** is $46\text{SiO}_2 \cdot 2\text{M}^{12} \cdot 6\text{M}^{14}$, where M^{12} and M^{14} are guest molecules in 12- and 14-hedral cages consequently. Possible M^{12} guests are N_2 , Kr, Xe, CH₄; possible M^{14} guests are N_2 , $N_2\text{O}$, CO₂, Kr, Xe, CH₃NH₂ [1], as well as S and water [2]. A structure of the cubic silica framework of melanophlogite is presented in Fig. 5.7 (according to [2]). Melanophlogite is a rare mineral; it is found as a sublimation product at fumaroles near volcanoes. After prolonged air curing (during 30 years) in natural weathering conditions melanophlogite loses its structure stabilizing organic molecules and water and turns into cristobalite. Melanophlogite turns black under heating because of burning-out of organic guest molecules but keeps the cubic silica structure until 900 °C and then is gradually transformed into cristobalite above this temperature. Because of its open cage-like molecular structure, melanophlogite is sometimes considered as a relative of zeolites which we do not consider here because zeolites are a very special type of crystals. Nevertheless inasmuch as the Database MINCRYST [15] included two of them in the list of silicas, we present some information on them in Tables 5.2 and 5.3 in one row with melanophlogite to demonstrate typical properties of clathrasils – their low density and friable unwieldy structure with large number of SiO_{4/2} tetrahedrons per the unit cell (Z).

5.3.3 Exception: Fibrous Silica

Main crystalline silica phases are presented in Tables 5.2 and 5.3 in ascending order of density for low temperature modifications. Many of them occur in nature and all of them have their individual mineral names because of the great importance of silicas for people. The clathrasils begin the table and octahedral silicas finish it; the usual tetrahedral silicas are placed in between them. The only exception is a strange phase which is placed among clathrasils because of its low density but does not belong to this family of silicas because of its low Z and relatively simple structure. This is fibrous **silica-W** with a structure



Figure 5.8: The two-element chain isolated chain in structure of silica-W

constructed by chains of SiO₄ tetrahedrons bonded by the edges (Fig. 5.8). It was synthesized in a laboratory [19] and falls out on its structure of all other tetrahedral silicas which are built from tetrahedrons bonded by corners. Silica-W is formed by oxidation of gaseous SiO, either directly by O₂ or through disproportionation according to the equation $2SiO=SiO_2+Si$. The structure is isotypic with SiS_2 and $SiSe_2$, both of which

are fibrous. The phase is unstable at atmospheric conditions because it absorbs water and converts into amorphous hydrated silica [3].

5.3.4 Proper Silicas

Among pure tetrahedral silicas there are five modifications with topologically different frameworks – coesite, keatite, quartz, moganite and cristobalite. Tridymite has the same topology of layers as cristobalite. As we will see later, it can be considered as filled silica. Brief characteristics of the phases are presented in the central part of Tables 5.2 and 5.3.



Figure 5.9: Phase equilibrium diagram for SiO₂ polymorphs.

Three of the most far-famed silicas, quartz, cristobalite and tridymite, have high and low temperature polymorphs but in the scientific literature there is no general rule for their designation. In physical chemistry high temperature modifications should be named α -phases because these phases can be established with high reliability whereas some probability always exists to find a new modification at low-temperatures. Physical chemists name these low-temperature phases as β , γ , δ and so on. On the contrary, geologists name α -phase that modification which they can take in their hands, i.e. the low temperature modification. It is necessary to say that $\alpha - \beta$ transformations of quartz, cristobalite and tridymite are completely reversible and it is practically impossible to quench their high temperature phases at atmospheric conditions. It means that there is no chance for geologist to face in nature with high temperature modifications of these silicas. To avoid a muddle with the α and β modifications, in the modern literature it is accepted to name silica polymorphs as high and low.

Thermodynamic parameters of the main silicas remain up to now the subject of constant and persistent discussions. Tridymite takes here a special place because it always contains some impurities and cannot



Figure 5.10: Density dependence of refraction indices for silica modifications.

be form from quartz and cristobalite in 'dry' condition. The phase diagram constructed employing the suggestion that tridymite does not belong to proper silicas is presented in Fig. 5.9 according to [2]. The more traditional version based on the famous Fenner's diagram and including tridymite one can find for example in [20]. To our opinion, not quartz but cristobalite is the only stable silica phase at atmospheric conditions and its field should be prolonged down along the abscissa. The phase equilibriums of silicas however are not the subject of this paper and we will return to this theme in a paragraph on tridymite only for a brief discussion.

The dependence of the refractive indexes on density for silicas is linear (Fig. 5.10, according to [2]) as for natural as well for synthetic modifications. Let us briefly consider the main crystalline tetrahedral silicas.

5.3.5 The Main Crystalline Tetrahedral Silicas

Quartz

Ancient Greeks knew quartz and named it "cold similar ice", i.e. $\kappa\rho\nu\sigma\tau\alpha\lambda\lambda\sigma\zeta$ that sounds as 'crystallos'. Thus, quartz as the most ambient terrestrial mineral with its striking regular faceting and transparency gave its name for designation of solids at all. For its contemporary name quartz owed Bohemian mines of the XIV century. They named gob and nonmetallic minerals as *Querz*, and in contrary to the ancient Greece quartz have got its special name from the collective name of a large class of minerals. Quartz is the most widespread mineral in the earth's crust after feldspars. Quartz is ubiquitous in nature; it enters into the composition of sedimentary and igneous rocks, as well as crystalline slates. It is also an important constituent of vein and mineral deposits of various origin. Because of its high hardness and low solubility

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quartz accumulates as sands and pebbles. It seems that quartz needs oxygen for its formation, and it is very rare on planets devoid of atmosphere like Moon and Mars or meteorites [2, 21]. According to modern data quartz does not form at the normal pressure in absence of impurities including water [2] which stabilize its structure.



Figure 5.11: Plane (0001) projection of high (a) and low (b) quartz structure.

A crystal structure of quartz is very well presented and explained at the interesting web-site **The Quartz Page** [22], therefore we do not stop here on this question in detail but mention only main features of quartz structures, high and low (Fig. 5.11). In the next section, which is devoted especially to quartz properties, we present some specific features of it.

The network structure of quartz (as well as of cristobalite and tridymite) with SiO_{4/2} tetrahedrons bonded by their vertexes is quiet flexible and its high-low $(\beta - \alpha)$ transition occurs without structure reconstruction but only due to mutual turn and rotation of the tetrahedrons. Thus, the structures of the both quartz polymorphs are very similar, but the symmetry of the high-temperature form is higher. Along the *c*-axis, which is perpendicular to the plane of the figure, the quartz structure is built from continuous helixes of tetrahedrons. Fractional numbers on the tetrahedrons at Fig. 5.11 show their heights inside the unit cell in fractions of the *c*-parameter. The helixes form relatively large channels (about 2 nm crosswise) penetrating the quartz structure. Small cations like H⁺, Li⁺ or Na⁺ can enter the channels for compensation of negative charge and thereby enlarge the unit cell parameters of quartz. Entry of large foreign atoms in quartz structure results in formation of so-called defect-channels with cross-section of 0.02-0.05 micrometers [2]. The defect-channels go perpendicular or parallel to the optical axis of quartz and are important for physical properties of quartz. Impurities inside the defect-channels begin to move under electric field and provide quartz conductivity [23, 24].

The inversion temperature of quartz (temperature of $\alpha - \beta$ or low-high transition) is close to 573°C; impurities in natural samples vary it slightly within $\pm 2^{\circ}$ C, but for synthetic quartz a temperature deviation of the inversion point may reach 35°C.

Moganite

This novel silica polymorph has first been described in 1976 [25], in volcanic rocks of the Mogan formation on Gran Canaria islands, Spain. It later turned out to be identical with **lutecite**, a so-called length-slow chalcedony type that was commonly found in chalcedony. Moganite is always intergrown with cryptocrys-talline quartz to form chalcedony [26]. During some time the both names, moganite and lutecite, were used in crystallographic literature, but now moganite is the conventional name of the mineral.

A review of early investigations of moganite crystal structure together with molecular dynamics simulations is given in [27]. The structure of moganite was repeatedly analyzed [28, 29, 30]. Moganite crystallizes in monoclinic crystal system in contrast to trigonal low-quartz, nevertheless their structures are much alike (Fig. 5.12, compare with Fig. 5.11b), distorted six-membered canals go along one of the axis in both struc-



Figure 5.12: Crystal structure of low moganite in the plane (011). The six-membered canals go along *a*-axis.

tures. Unlike quartz, moganite features alternating fragments of both left- and right-handed threefold spirals cut by (011) plains. As a result, closed four-membered rings are presented in moganite, and the unit cell dimension doubles along the corresponding axis of quartz structure [27].



Figure 5.13: X-ray patterns of quartz and moganite according to PCPDFWin database.

Structural similarity of quartz and moganite results in their morphological and radiographic similarity

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which make difficulties for their diagnostics. Thus, similar to quartz crystallites in chalcedony, moganite is intensely twinned according to the Brazil law and forms rocks morphologically similar to quartz [26]. A certain similarity in X-ray patterns of moganite and quartz is also evident (Fig. 5.13). Positions of the strongest peaks are very close, and there is some correspondence in the positions of other significant peaks, but peaks split or have satellites in the pattern of lower symmetric moganite. Together with morphological similarity of the rocks, this difficulty of X-ray identification seems to be the reason why moganite has been identified as an individual silica polymorph only in the modern time.

A careful X-ray examination of more than 150 specimens of fine-grained quartz varieties from around the world has revealed that more than 10% and as much as 80% of the silica in many samples is actually moganite [31]. The large amount of moganite (>30%) was found in charts from arid, alkaline environments may resurrect length-slow silica as an indicator of evaporitic regimes, and the absence of moganite in weathered and hydrothermally altered silica samples may be a useful measure of fluid-rock interaction. The amount of moganite seems to decrease with time as it is slowly converted into chalcedony, and agates older than approximately 100-150 million years seem to be almost void of it [26]. On the other hand recent experiments [32] established that at pressure 100 MPa moganite is a low temperature polymorph of low quartz stable for kinetic rather then for thermodynamic reasons.

Moganite has a high-temperature orthorhombic β -modification, the crystal structure determination has been performed in [30] for 1354°C. Molecular dynamics (MD) simulations for high-pressure conditions [27] showed that moganite at 300 K has to exhibit two crystal-crystal phase transformations, at about 5 and 21 GPa, and these high-pressure forms appear to be the most stable phases among quartz family of silica in the temperature range from 100 to 1100 K and the pressure range from 0 to 30 GPa. Raman spectroscopy study of an anomalous behavior of moganite during pressure induced transformation was investigated in [33]. Comparison of natural and MD simulated moganite structures permits to suggest that natural moganite is a high-pressure phase existing between 5 and 21 GPa and conserving as a metastable phase at normal conditions. The MD simulated orthorhombic phase which is stable at normal conditions and up to 5 GPa seems to be close to the high-temperature modification of natural moganite.

Tridymite

We already discussed a serious objection against the opinion that tridymite is a pure silica. It is based on the impossibility to produce tridymite without stabilizing impurities or water. In this respect very impressive results were obtained by Flörke [34]. He tried the experiment of electrolyzing the foreign oxides out of a disk of tridymite with direct current at 1200 and 1350 °C. The final product at the anode proved to be pure silica but in form of cristobalite while tridymite still persisted at the cathode, where the other oxides had accumulated. A similar experiment at 1050 °C yielded a mixture of quartz and cristobalite at the anode. Flörke concluded that tridymite has no place on the equilibrium diagram of pure silica.

Another fundamental argument against tridymite ranking to pure silica polymorphs was provided by methods of physical chemistry. Holmquist [35] investigated phase equilibriums in the high-silica regions of Li_2O-SiO_2 , Na_2O-SiO_2 and K_2O-SiO_2 systems. He found that tridymite is a binary incongruently melting phase containing between 0.5 and 1 % of a metal oxide which has at the diagrams its own separate field of existence divided from pure silica (cristobalite) with two-phase region. This conclusion is quite radical and does not give place for doubts of the foreign nature of tridymite - but only for those who knows the phase rule.

Our own experiments gave a similar result [36]; a reductive schema of phase equilibriums in the sodiumsilicate system according to these data is presented at Fig. 5.14. It was found that tridymite is the only equilibrium phase existing in a concentration range 1.75-2.5 wt. % Na₂O and over a temperature range of 900-1250°C. In this region the X-ray pattern of tridymite uninterruptedly changes with concentration and reflects continuous change in the structure of tridymite. Over a concentration range 0.6–1.75 Na₂O tridymite coexists with cristobalite. In this region, the amount of tridymite changes from 100 % to negligible parts with reduction in sodium oxide content; amount of cristobalite simultaneously increases. Existence of the two-phase region (Tr + Cr in the picture) with gradual transition from tridymite to cristobalite shows that



Figure 5.14: Phase equilibriums in the silica-rich part of $Na_2O - SiO_2$ system. Tr s.s. means the single-phase region of tridymite solid solution.



Figure 5.15: The idealized layer in the structure of high-tridymite.

tridymite cannot be a pure silica phase but it is a binary (or foreign multi-component) phase and the structure of it has to change with nature and content of impurities. It is necessary to emphasize that concentration limits in the diagrams in [35] and in Fig. 5.14 are given by synthesis without taking alkalis volatilization into account. The real boundaries of the single-phase field of tridymite are located much closer to pure silica than they were presented in the diagrams discussed.

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An example of changes in the tridymite structure with nature and amount of the other components in its composition we can find in Tables 5.2 and 5.3. Tridymite presented differ in amount of Z per unit cell as a consequence of difference in their origin and therefore in the chemical composition. The other result of structural variety of tridymites is the strange fact that up to now nobody knows how many polymorphs it has [2, 3, 37].

In the structure of hexagonal high temperature tridymite there are plane layers parallel to the (0001) crystallographic plane (Fig. 5.15). In vertical direction layers are bonded by tetrahedrons vertexes directed towards each other. The layers alternate as ABAB... (hexagonal packing). In the ideal structure there are two such layers per unit cell, but in some natural samples the unit cell can consist of ten and more distorted layers alternating as ABCBA, DBCBD and so on.



Figure 5.16: Projection of the low-cristobalite structure to the plane (001) (left) and (100) (right).

All described properties of tridymite show that it is a binary compound with a very low content of cations (alkali or others) and it may be considered as cation-filled silica. The tridymite position in Tables 5.2 and 5.3 between the typical clathrasils and the proper silicas is in good correspondence with this attribution. Tridymite is quite rare as an individual mineral. It is commonly found as three twinned plates that intersect each other at an angle of $35^{\circ}18'$ (see photo at The quartz page [22]); its name is related to this peculiarity.

Cristobalite

Cristobalite was found for the first time at the end of XIX century during microscopic investigation of rocks from *San Cristobal deposit* in Mexico. It exists in two polymorphic forms presented in Tables 5.2 and 5.3 which can convert one into another without frame reconstruction but owing to rotation of tetrahedrons SiO_4 . The structure of the low-temperature tetragonal modification is presented in Fig. 5.16. Structure of the high-temperature cubic modification contains plane layers parallel to (111) and constructed from six-membered rings of tetrahedrons. These layers are exactly the same that high-tridymite contains in crystallographic plane (001) (Fig. 5.15) but in cristobalite the layers alternate as three-step cubic close packing ABCABC... instead of double-step hexagonal close packing in tridymite. This specific feature gives the opportunity for intergrowing of cristobalite and tridymite structures. According to the layers alternation the crystal can be mainly cristobalite or mainly tridymite; in some cases it may be impossible to distinguish one from another [2]. Such hybrid forms are not rare in nature and the name cristobalite-tridymite opals (opal-CT, the other mineral name is **lussatite** [20]).

The temperature of $\alpha - \beta$ inversion of cristobalite is rather sensitive to disordering in its structure. Wellordered cristobalite undergoes an abrupt transition at 270 °C, a hysteresis being almost absent. Structure



Figure 5.17: Perspective projections of the substance of structural interstices of quartz (a), cristobalite (b) and silica glass (c).

disorder reduces the inversion temperature of cristobalite to 130 $^{\circ}$ C and broadens its temperature hysteresis [38]. Flörke mentioned that in opals the inversion temperature can be reduced to 60-100 $^{\circ}$ C [39].

Low density of cristobalite and close examination of its structure shows that its framework is relatively friable in comparison with quartz. The most obvious illustrative example of this difference is provided by the substance of structural interstices of quartz and cristobalite calculated by molecular dynamics method [40] (Fig. 5.17). As we can see from the picture a volume of structural interstices in cristobalite mediates between quartz and quartz glass. Quartz is much more dense substance than cristobalite but nevertheless it contains structural interstices along its c-axes. Thus it was supposed that these substances having flexible frames with sufficient structural interstices can be converted into much more dense tetrahedral modifications. This modification was really obtained by Coes [41] and afterwards was named coesite.

Coesite

It was shown that the best initial substance for coesite synthesis is amorphous silica which is being completely converted into coesite for 1 hour at T=580°C and P=3GPa. In the field of its stability (Fig. 5.9) coesite can be produced from different forms of silica including quartz. It was also produced by shock compression of natural and artificial quartz-containing porous materials. According to the phase diagram (Fig. 5.9), coesite should be transformed into quartz after pressure relief, but it exists in metastable state under ambient conditions. Under atmospheric pressure and temperature below 1100°C coesite is not being transformed into quartz during long time, but at 1700°C it is being directly converted into cristobalite.

A reason of coesite stability in the metastable region is in its specific crystal structure with SiO_4 tetrahedrons associated not in six-member but in four-member rings (Fig. 5.18). The structure of coesite is a three-dimensional net with the four-member rings of tetrahedrons which are parallel to (010) and (001) planes. Infinite chains of the four-member rings do not incorporate with each other within their planes but connect together through equivalent chains in overlying and underlying layers. One of the four-member rings of overlying layer is presented in Fig. 5.18 (the filled tetrahedrons).

After laboratory discovery of coesite, it was found in the nature, in the famous Barringer Meteor Crater, which was produced by a large meteorite impact in Arizona desert (history and geology of the crater are presented on the Site of the Barringer Crater Company [42]). Later coesite was found in many young meteorite craters and now it is considered as the indicator of a recent in geological sense meteoric explosion. In young craters coesite may account for about 40 % of the total silica content but in ancient craters its amount does not exceed hundredth parts of percent. It was also found in diamond kimberlite pipes of Yakutia and South Africa.



Figure 5.18: Chains [Si₄O₁₁] in plane (010) in coesite structure.

Intermediate Phases

Hydrothermal synthesis of quartz from amorphous silica proceeds quickly and up to the end at high temperatures (300-600°C) and pressures (50-400 MPa) but at lower temperatures the process goes much slower and passes through formation of intermediate crystal phases. These phases may be of two types, pure silicas and cation-filled phases like the already discussed melanophlogite, tridymite or opal-CT. Some other cation-filled phases forming during quartz synthesis are denoted as **silica-X** and **silica-Y**. They have no constant composition because it changes with the nature and concentration of cations in the hydrothermal solution; nevertheless their X-ray patterns have clear specific features, which permit to identify each of the phase and confidently resolve their subsorts like silica-X1 and silica-X2 [32].



Figure 5.19: Content of silica phases in dependence on time during their transformations in hydrothermal condition [2]: 1) amorphous silica; 2) silica-X2; 3) cristobalite; 4) quartz.

A detailed investigation of physico-chemical properties of silica-X and silica-Y and the necessary conditions for their formation has been performed in [2]. Fig. 5.19 illustrates temperature changes in hydrothermal transformations of amorphous silica in alkaline medium at saturated vapor pressure. We see that two silica phases of very high thermodynamic stability, quartz and cristobalite, can form at relatively soft conditions, at comparatively low temperature and pressure. The path of quartz formation passes through origination and decay of intermediate phases, and metastable silica-X2 is much more stable here than cristobalite.



Figure 5.20: Intermediate phases of hydrothermal transformation of amorphous silica into quartz in alkaline solutions [2] at moderate temperature and pressure (a) and in relatively pure water solutions at higher temperature and pressure (b). Arrows in ovals show the direction of operating parameter increase.

Two minerals close to silica-Y, **magadiite** $(Na_2Si_{14}O_{29}11H_2O)$ and **kenyaite** $(Na_2Si_{22}O_{41}(OH)_86H_2O)$, are described in the Mineralogy Database [43] including the structure of magadiite. The minerals named by the place of their origin – the soda Magadi lake in Kenya where the transformation of amorphous silica into quartz takes place in natural conditions. The described above clathrasil melanophlogite can also form as an intermediate phase in natural conditions. Possible diagrams for transformation of amorphous silica into quartz in alkaline mediums and at moderate temperature/pressure conditions are presented in Fig. 5.20a. In relatively pure mediums and at higher temperatures and pressures the reaction goes through proper silica phases – cristobalite and denser **keatite** (Fig. 5.20b).

Keatite

Keatite is medium in its density between cristobalite and quartz (see Tables 5.2 and 5.3). It was first produced in 1954 by P. P. Keat [44] during hydrothermal synthesis of quartz in alkaline solutions but till now it is not found in nature (the Quartz Page suggests that it may be found in stratospheric dust particles). Keatite can be obtained as an intermediate product in a large number of hydrothermal reactions. It forms over the temperature range 380-585°C and pressure from 30 to 120 MPa in the systems SiO_2-H_2O [45] and $Al_2O_3-SiO_2-H_2O$ [46]. The structure of keatite is built from coupled by vertices tetrahedrons similar to the main silica phases like quartz, cristobalite, tridymite or coesite but in contrast to them the SiO_4 -tetrahedrons in keatite are not crystallographically equivalent.

There are two sorts of tetrahedrons in the keatite structure (Fig. 5.21). Eight of 12 tetrahedrons in the unit cell are in the general positions and form di-ortho-groups which make 4-fold helixes along the c-axis (the darker tetrahedrons in the figure), as opposed to four other tetrahedrons (the lighter ones) which place in the partial positions at 2-fold axes and join the 4-fold helixes among themselves in endless wollastonite



Figure 5.21: The plane (001) projection of keatite structure.

chains along the z-axis. Under heating up to 430° C keatite has negative thermal expansion due to its contraction along the z-axis. Keatite fully transforms into cristobalite when calcinated in air at 1620° C during 3 hours [2].

5.3.6 Amorphous Silica

The natural silica glass has its own mineral name, **lechatelierite.** It forms by rapid cooling of molten silica and occurs as so-called fulgurites at places where a lightning has struck into quartz sand. The high temperatures cause the quartz sand to melt along the branched and irregular path of the lightning through the sand. Simultaneously, the molten quartz is pushed away from the lightning because of the repelling forces between the charged particles. As a result, hollow tubes of silica glass form [47]. Lechatelierite can also be found at impact craters of meteorites.



Figure 5.22: Fulgurites of lechatelierite with approximate size 150-200 mm (a, the rare photo has been taken from The Quartz Page) and typical products from quartz glass (b).

An exterior of the mineral (Fig. 5.22a) seams to be radically different from commercial quartz glasses (Fig. 5.22b) but they are the same material with the density 2.20 g/cm³ and similar structure. At Fig. 5.10 the point of lechatelierite falls exactly onto the common line of crystalline silicas and coincides with the point of artificial silica glass.



Figure 5.23: The scheme of anomalies in water and *a*-silica.

The structure of artificial silica glass is now well known owing to both experimental and simulation methods; therefore we do not consider it in this paper. It should be only emphasized that although silica glass is usually produced by quartz melting and often designated as quartz glass it has cristobalite-like structure. Designations a-silica or a-SiO₂ without any interpretation or specification meets in the literature currently; they denote compact amorphous silica such as molten quartz glass or CT-opal.

There is a certain parallelism between water and a-silica. They both have similar anomalies of properties, the scheme of anomalies according to [48] and [49] is presented at Fig. 5.23. The latter reference is a very interesting review of more then 70 anomalies of water; literature on anomalous properties of a-silica is presented in [50]. The anomalies appear as a hierarchy of effects with different bounds. The 'structural' bounds indicate where water and a-silica are more disordered when compressed; the 'diffusion' or dynamic bounds indicate where diffusion increases with density, and the 'density' or thermodynamic bounds show where there is a temperature of the maximum density. All phenomena above-listed were first discovered and investigated for water and only then were carried over to amorphous silica with a sole exception: in vitreous state silica is known in the nature from time immemorial; vitreous water was found in the nature only in the modern time – in meteorites, and probably vitreous water is a matter of nuclei of comets.

In addition to the mentioned anomalies both water and *a*-silica have transformations in liquid state referred to as polyamorphism. This effect we will study in the next section.

5.3.7 Polyamorphism

Polyamorphism is a relatively new term denoting for liquids a phenomenon similar to polymorphism in crystalline solids. We have to admit the fact of existence of liquids and amorphous solids with the same composition but with different densities and therefore with different structures. Discovery of a high-density modification of water [51] introduced into common use in scientific community the idea of polyamorphism [52, 53, 54].

Refractive indexes for silicas built of tetrahedrons are linearly proportional to their densities (Fig. 5.10). A significant change in the density or in the refractive index is a convincing indicator of the structure change.


Figure 5.24: Changes in the refractive index value in the process of crystalline quartz melting (according to [37]).



Figure 5.25: The relative volume change (a) and bulk modulus (b) for silica glass under pressure buildup and release (according to [58]). The arrows show the direction of pressure changes. The breaks in the curves correspond to heating from 290 K to 545 K and backwards. Solid lines are the glass compression at 290 K.

As pointed out above, a standard silica glass has cristobalite-like structure; its density is approximately 2.201 g/cm³ and the refractive index is the smallest for glasses, $n_D = 1.459$. Quartz is denser than the glass

(Tables 5.2 and 5.3) and its refractive index is higher, $n_D = 1.544$ for ordinary rays (quartz is birefringent).

Fig. 5.24 presents a partially melted peace of quartz. The sample was heated at 1700°C for a few hours and then was quenched. The refractive indexes were measured for the residual quartz (from the right) and for a vitreous band at its edge (from the left). This simple experiment has been produced in the sixties of the last century and brought out clearly that a denser form of silica glass exists. Really, the refractive index of the just melted glass immediately adjacent to the crystalline part of the sample is very close to that of quartz. Immediately after melting, the structure of the melt is quartz-like and only in a few hours it is transformed into a usual cristobalite-like glass with the corresponding refractive index. The experiment went unnoticed and only modern success in high-pressure investigations together with intensive and widely reviewed study of dense forms of water stimulated specialists in silica glass to recognize its polyamorphism.



Figure 5.26: Phase diagram for *a*-silica polyamorphism below crystallization temperatures (*a*) and the thermodynamic phase diagram and hypothetic diagram for liquid SiO₂ (*b*) (according to [58]).

In the sixties of the last century it was also established that fast neutron irradiation produces a significant change in the structure of silica glass and at a dose of the order of 10^{20} per cm² the initial glass completely transforms into so-called metamict phase. The mentioned dose leads also to amorphization of crystalline quartz with formation of the metamict phase, too. A brief review of early investigations of the metamict phase in context of the discussion on existence of liquid-liquid transformations one can find in [55]. The findings of modern Raman scattering investigations indicate that concentration of three- and four-member rings of tetrahedrons in the irradiated glass increases with the dose that is an enhancement of coesite-likeness of the structure [56]. It is known, that all glasses have a universal form of the low-frequency Raman boson peak [57] and on this point the metamict phase is really a glass in spite of excess of a free

5.4 Quartz and Some of Its Properties

volume produced in a explosive-like interaction between neutrons and the substance. In [56] it was also demonstrated that the maximum of the low-frequency Raman spectrum (boson peak) shifts with an increase in the irradiation dose, and the medium-range order size decreases from 25 Å for the initial glass to 19 Å for the sample subjected to irradiation at a maximum dose.

A considerable list of references on the amorphous-amorphous transition and densification of silica glass is presented in [50] together with MD simulation study, as well as in an experimental study of dense modifications of a-SiO₂ [58]. Two types of a-silica densification are established at present. One of them takes place at room temperature under pressures 12-40 GPa. Investigations of the glass structure, Raman and Brillouin scattering and MD simulation showed that this transformation goes with change in silicon atom co-ordination from 4 to 6 and represents the analogue of quartz-stishovite transformation. The second type of silica glass densification occurs at lower pressures, 8-10 GPa at room temperature, but its regularities and nature involve difficulties in interpretations. Here we present a brief review of *in situ* experimental study of the latter type of transformation according to [58] to give an indication of this relatively new phenomenon.

The volume of glassy a-SiO₂ was measured upon compression to 9 GPa at high temperatures up to 730 K and at both pressure buildup and release (Fig. 5.25). It was established that the residual densification of a-SiO₂ after high-pressure treatment was due to an irreversible transformation accompanied by a small change in the volume directly under pressure. The bulk modulus of the new amorphous modification was appreciably higher (80% more than its original value), giving rise to residual densification as high as 18% under normal conditions for densification at 700 K (for densification temperature 545 K at Fig. 5.25 the residual densification is 12%). It was shown that the transformation pressure shifted to a lower pressure of about 3-4 GPa with a rise in temperature up to the crystallization interval. Heating of the dense silica glass with the rate 20 K/min at normal pressure showed a reverse transformation into the low-density phase at 1000-1100 K. The studied before densification of a-SiO₂ from above 9 GPa at normal temperature was demonstrated to be a manifestation of the same phase transformation accompanied by tetrahedral rearrangement similar to quartz-coesite transition.

The authors of [58] made a conclusion about the existence of at least two pressure-induced phase transitions accompanied by structure rearrangement in a-SiO₂. They suggested a nonequilibrium phase diagram for a-silica (Fig. 5.26a). The hatched gaps correspond to the straight and forward transitions between the usual cristobalite-like silica glass (LI) and the densified tetrahedral coesite-like glass (LII). The blank gaps correspond to transitions between tetrahedral LII phase and octahedral stishovite-like phase (LIII). The solid lines limit the straight transitions, the dashed lines – the forward ones. Phase diagrams for SiO₂ transformations in the solid and liquid states are compared at Fig. 5.26b.

Similar baric transformations are known for many glasses, in particular for another famous glass-former oxide, B_2O_3 [59]. The measurements of the relative volume change under compression together with the structure investigations and computer simulations reveal the basic features of the phase transitions in B_2O_3 glass. Similar to *a*-silica, both direct and reverse transitions are smeared in pressure. Analogous results were obtained for *a*-GeO₂ [60], too.

5.4 Quartz and Some of Its Properties

Ancient Greeks knew quartz and named it "cold similar ice", i.e. $\kappa\rho\nu\sigma\tau\alpha\lambda\lambda\sigma\zeta$ that means a crystal. Thus, quartz as the most ambient terrestrial mineral with its striking regular faceting and transparency gave its name for designation of solids at all. By its contemporary name quartz is obliged to Bohemian miners of the XIVth century. They named gob and nonmetallic minerals as *Querz*, and in contrast to the ancient Greece, quartz have gotten its special name from a collective name of the large class of minerals.

Quartz is the most widespread mineral in the earth's crust after feldspars. Quartz is ubiquitous in nature; it is a part of sedimentary and igneous rocks, as well as crystalline slates. It is also an important constituent of vein and mineral deposits of the various origin. Because of its high hardness and low solubility quartz accumulates as sands and pebbles.

The general information on quartz properties with links to other databases on quartz is presented in

[61]; the full-length explanation of physical and chemical basic of the quartz properties one can find on The Quartz Page [22]. Here we review in more detail some of the properties being of considerable importance for practice but little known especially regarding their physical nature.

5.4.1 Enantiomorphism of Quartz

Absence of planes and a center of symmetry among symmetry elements of low-quartz gives it a possibility to form right as well as left handed structures which are mirror equal or enantiomorphic. L3 axes of quartz are polar because chains of tetrahedrons form spirals along these axes with right or left screw. Crystals of right and left quartz are different in their crystallographic form (Fig. 5.27) and they differ from each other in some physical properties, too.



Figure 5.27: Habits of left and right handed quartz.

Plane of polarization rotates clockwise in right quartz and anticlockwise in left one. Right and left quartzes differ in their etch figures, in percussion patterns on crystal face (11 0), in patterns of Brazilian twin seams; but they are indistinguishable of each other in constants of their thermal, electrical and optical properties (except rotation of plane of polarization).

5.4.2 Twins (Zwillinge) in Quartz

The Great encyclopedia of Kyrill and Methody defines twins as regular joins of two similar crystals in which one crystal differs from the other with a mirror-reflection plane, or with turn around a symmetry axis or with reflection in an inversion center. A joint plane in the twin is not a phase boundary because the structure turn or reflection takes place at this plane without bond breaking.

Twins may be different in nature. Growth twins form by coalescence or reciprocal intergrowth of crystals, but the mechanism of these processes remains incompletely comprehended. Transformation twins arise under structure transformation during polymorphic transitions. For example, when hexagonal highquartz transforms under cooling into trigonal low-quartz, some parts of the structure may be turned through 180° relatively to each other around the L_3 axis and form so-called Dauphiné twins which are very typical for quartz. Deformation twins arise under mechanical loading of a crystal during plastic deformation. Twins of this kind appear only in crystals with hindered sliding deformation, quartz and tiff being striking



Figure 5.28: Twinning boundaries revealed by etching a basal plane (0001) (perpendicular to L_3 axis): a) according to the Brazilian law; b) according to the Dauphiné law.

examples. An ordinary pressure by a knife blade on an edge of the tiff rhombohedron shifts a part of the crystal into a twinning position.

Problems of quartz twinning were systematically studied in the course of 30 years by E. V. Tzinzerling and then described in a very interesting monograph [62]. She began to work under the direction of the famous Russian crystallographer A. V. Shubnikov and realized his idea of artificial transformation of a twinned quartz crystal into single crystal and back. In the subsequent text of this section we briefly review her main results.



Figure 5.29: A scheme of twinning of Dauphiné type under a shifting force according to A. V. Shubnikov: a) lowquartz structure in projection on the basis plane (0001); b) a Dauphiné twin in low-quartz. An arrow shows the direction of the force action. "Grey" atoms keep their positions, "white" and "black" atoms are moved.

Twinning laws are especially multiform for quartz because of its enantiomorphism, which represents capability to form irreducible right and left crystals. Besides the mentioned Dauphiné twins¹, Brazilian² and Japanese³ twinning laws are abundant in quartz⁴ (Fig. 5.28). From the optical point of view twinned

¹Dauphiné twins consist of an aggregate of two right or two left quartz crystals with parallel L_3 axes.

²Brazilian twins represent joins of right and left quartz crystals with antiparallel L_3 axes.

³Japanese twins are twins of growth. Axes [0001] of separate crystals are inclined to each other at an angle of 84°34'.

⁴The typical view of Japanese and Dauphiné twins in quartz as well as many other kinds of twins is accessible at the site "Twins in the world of crystals" (in Russian)

quartz is a single crystal and may be used in optical industry but it is not convenient for electronics if the twins contained are Dauphiné or Brazilian. Electrical axes are antiparallel in components of these types of twins. If the twin contains 50% in area extent of one and 50% of other twin components, the total piezoelectric effect of the crystal is zero. Free from twins conditioned single crystals are infrequent for quartz and therefore quite expensive but just these crystals are needed for electronics.



Figure 5.30: Effect of the double low-high-low inversion on Dauphiné twins in quartz: a) a pattern of the initial twins on the quartz plate; b) a curtain pattern on the same plate after retwinning procedure. Size of the plate is $25x22 \text{ mm}^2$.

Artificial twinning and untwinning (transformation of a quartz crystal with twins into the single crystal) is possible only for Dauphiné twins, for other types with non-parallel twin axes untwinning is equivalent to destruction of the crystal. At the process of Dauphiné twinning, the atoms rearrange in twin position inside the unit cell and without macroscopic displacement of crystal matter (Fig. 5.29).

As a consequence of the laborious investigations Tzinzerling brought out clearly that twinning as a result of any kind of mechanical deformation as well as a result of only thermal action on the crystal or of voltage failure is a mechanical phenomenon by its nature. The difference is only in origin of the shifting strain: an outside force or internal stresses in the crystal as a result of anisotropy of quartz thermal expansion. The latter is maximal just below the $\alpha\beta$ inversion point, from 573 to 550°C, and remains significant until 300°C. Retwinning occurs readily in this temperature interval, it was pointed out, in quartz crystals even during some technological procedure following with heating like a brazing at a sputtered metal layer. Investigators noted a random character of thermal retwinning patterns. Tzinserling showed that the system in the twinning pattern becomes evident only for pure crystals, free from impurities, inclusions and internal cracks. She discovered the method to free ill-conditioned quartz crystals from twins by double low-high-low temperature inversion with following slow cooling. As a result crystals with a twin affection of 50 % in area extent and with zero piezoelectric effect converted into predominantly single crystals with only 12 % of twins concentrated at the edges of the quartz plates. The typical form of twins after this retwinning procedure is presented at Fig. 5.30 and received the name "curtain". Making of "curtains" has some similarity with single crystal growing: a moderate temperature gradient is necessary together with careful and slowly heating and cooling in the vicinity of the inversion point. After the retwinning procedure, edges of the "curtains" should be carefully deleted by a polishing and as the result the piezoelectric ability of the quartz plate is completely recovered.

The first successful experiments of Dauphiné twins elimination from quartz by torsional deformation

http://files.school-collection.edu.ru/dlrstore/16774b92-93f0-80a6-2d02-aed3a1c1784e/48-51_01_2003.pdf

were performed in [63, 64] simultaneously with the author of [62]. The latter author showed that all types of Dauphiné twins independently of their origin, defects and patterns can be untwinned into single crystals by a multiple prolonged and enlarged loading together with a subsequent heating. However quartz with impurities keeps the memory about its initial twins. After complete untwinning by torsional deformation, quartz crystals restore the initial twins with faithfully copy of former twin boundaries if they undergo low-high-low transformation. These works provided a possibility to create the industrial untwinning of quartz crystals.

5.4.3 Anisotropy of Quartz

A variety of physical properties shows a sharp anisotropy for quartz crystals predominantly in directions which are parallel and perpendicular with the major axis L_3 [65]. The anisotropy shows up not only in structural but in all vectorial properties such as thermal, mechanical, optical, electrical and so on. Durability of quartz is maximal and thermal expansion is minimal in L_3 direction because the structure is harder in this direction than in perpendicular one. Table 5.4 (according to [62, 66]) gives an indication of anisotropy for some physical properties of quartz.

Physical property	in parallel with L_3	perpendicular to L_3	
Thermal expansion at 40° C, K ⁻¹	$7.81 \cdot 10^{-6}$	$14.19 \cdot 10^{-6}$	
Electroconductivity, Ohm ⁻¹ m ⁻¹	2.50	0.16	
Resistivity at 20°C, Ohm·cm	$1 \cdot 10^{14}$	$2 \cdot 10^{16}$	
Thermal conductivity at 0°C,	0.0325	1.0173	
cal/(cm·s·K)			
Refractive index, n_D	1.553	1.544	
Breaking point, kg/cm ²			
compressive	28020	27380	
tensile	1210	930	
bending	1790	1180	
Hardness, dyn/cm ²	$22.5 \cdot 10^9$	$30.2 \cdot 10^9$	

Table 5.4: Anisotropy of some properties of quartz.

Quartz possesses a very low positive birefringence. The optical axis in quartz corresponds to the L_3 axis of the unit cell, so there is no birefringence when light passes the crystal from tip to tip. The maximum birefringence occurs when the light passes perpendicular to the optical axis. Light that passes the crystal along the L_3 axis will also not be split into two rays of opposite polarization [67].

5.4.4 Thermal Expansion of Quartz

Many people do not distinguish quartz and quartz glass and properties of the glass which is more known for users, arrogate also to crystals. It is a widespread opinion that quartz has a very low thermal expansion coefficient and can be easily heated to high temperatures and quenched from them without appearance of mechanical stress. This is true not for quartz but for silica glass which has a thermal expansion coefficient about 1/18th of that of ordinary glass. This uncommon property permits one to use silica glass for chemical glassware production.

Common Features of Thermal Expansion of Solids

Near to room temperature quartz has a thermal expansion coefficient that is only slightly lower than that of ordinary glass but at higher temperatures the thermal expansion of quartz becomes very unusual. The reason is the following.

5 Silica Phases and Some of their Properties



Figure 5.31: Potential energy of interaction between two atoms for the case of anharmonic oscillations in dependence on the distance between the atoms. Here r_o is the equilibrium atom position at zero temperature; $x_1, x_3, x_3...$ are the mean atom positions at temperatures $T_1 < T_2 < T_3...$

For most of the solids their thermal expansion is determined by the skewness of the atomic potentials resulting in anharmonicity of lattice thermal vibrations (Fig. 5.31, [68]). A coefficient of anharmonicity γ is defined by the third derivative of the potential energy. The linear thermal expansion coefficient α is directly proportional to γ , and their signs coincide. Thermal expansion of crystalline solids is usually anisotropic; a typical example is presented at Fig. 5.32. Both parameters are given at the same scale. We see that magnesite becomes longer at heating predominantly along the *c*-axis and almost not at all expands along the *a*-axis. If we cut out a ball of a single crystal of such a material and heat it, the ball will change its form and transform into an ellipsoid in correspondence with the thermal expansion coefficients along each of the crystal axes.

A parabolic law gives usually a good interpolation for thermal expansion of solids resulting in the constant α . In some cases the structure of solids is such that at heating it contracts in one direction and expands in others, similar to an elastic band, but in doing so its volume increases with temperature.

Specific Features of Thermal Expansion in Low Quartz

The sketched above consideration was made to describe the usual thermal expansion and to appreciate the uncommon thermal behavior of quartz [69, 70, 71] which is presented at Fig. 5.33. As we can see, the thermal behavior of the low and high modifications of quartz are radically different and the both are far from the standards described in the previous section. The parabolic law does not hold for fitting of the low-quartz thermal expansion.

It is known that after a correct fitting the experimental points are located in a random manner on both sides of the approximating curve. An improper approximation leads to an alternation of groups of the experimental points lying on one and on other side of the curve. The parabolic law gives just this case of approximation. A proper approximation for the low-quartz expansion is a power function with a fractional index and a vertex in the point of the high-low inversion:

$$a_{low} = a_{high} + k_a (T_{cr} - T)^{\eta}$$
 $c_{low} = c_{high} + k_c (T_{cr} - T)^{\eta}$,

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Figure 5.32: Temperature changes of the unit cell parameters of magnesite MgCO₃.

where a_{low} , c_{low} and a_{high} , c_{high} are the unit cell parameters of the low and high phases, correspondingly; k_a and k_c are coefficients, T_{cr} is the inversion temperature and η is the fractional index which may be considered as pointing to an order of the transition: 1/2 for first order and 1/3 for second order. Both indexes give comprehensible approximation, but need use of some adjustable parameters. In the case of $\eta = 1/2$ an appropriate approximation can be achieved by correcting the inversion temperature, $T_{cr}^* = T_{cr} + \Delta$, with a value of the temperature lag Δ about 7-9°C. As we shall see later, this approach corresponds to a first order transformation although the opinion to treat it as a second order transformation is rather widespread.

The proportions of the unit cell of quartz changes with temperature (Fig. 5.34) since the *a*-axis lengthens quicker than the *c*-axis. From room temperature to 500°C, c/a value changes linearly but above 500°C the slope of the plot increases. The latter fact shows a specificity of the thermal expansion process in low-quartz in a relatively wide vicinity of the transformation. In high-quartz changes in the c/a proportions are very small but quite measurable.

Thermal Expansion of High Quartz

It is obvious from Fig. 5.33 that both parameters of high-quartz decrease at heating, with constant $\alpha_a = -3.8 \cdot 10^{-7} \text{ K}^{-1}$ and $\alpha_c = -1.31 \cdot 10^{-6} \text{ K}^{-1}$, therefore, its volume decreases too, that is high-quartz is compressed at heating. Such a phenomenon meets rather seldom and needs an explanation.

Linear Thermal Expansion Coefficient of Quartz

Temperature change of both linear thermal expansion coefficients is presented at Fig. 5.35 according to [69]. At negative temperatures both $\alpha(T)$ for low-quartz can be considered linear but above zero the rate of their change begins to increase and above 450 - 500°C grows up critically at approach to the high-low inversion temperature at 573°C and reaches rather high values.

At change of temperature thermal expansion occurs almost instantly; in these conditions such behavior of the thermal expansion coefficient near the inversion point results in a frequent fracture of the samples and underlies a thermo-crushing method. In this method quartz flinders are heated up to 900-1000°C and then

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Figure 5.33: The unit cell parameters of high purity standard polycrystalline quartz in dependence on temperature [69]. The break in the interpolated curves corresponds to the $\alpha - \beta$ inversion point.

dropped into water. A violent contraction of quartz below the inversion point and presence of temperature gradient in depth of flinders bring about their destruction.

Our X-ray experiments with thin single-crystal plates will be describes later; in these experiments temperature slowly varied around the inversion temperature over $3-5^{\circ}$ interval. As a result about every second plate has burst because of the small temperature gradient along the plates. For comparison - a red hot silica glass rod can be dipped into water without cracking. It is also known that clays involving quartz sand crack at heating up to 575° C but not far from this temperature. Quartz is not used for refractory production; cristobalite and tridymite have jumps of the volumes at high-low transformation, which are comparable with that of quartz, but their thermal expansion coefficients have no critical behavior in the vicinity of the transformations and this is sufficient in order that products from them are not destroyed at the transformation.

The Nature of Thermal Expansion of High and Low Quartz

We know that the quartz structure is built up from only one type of structural units, namely tetrahedrons SiO_4 connected by vertexes. X-ray structural analysis allows one determining co-ordinates of each atom in the unit cell and permits to follow temperature changes of a single tetrahedron. The high-temperature modification of quartz belongs to the highest crystal system, hexagonal, and tetrahedrons in that structure are regular, with equal Si-O bonds. Low-temperature quartz belongs to lower trigonal system, and under the action of the crystal field skewness the tetrahedrons are distorted. Two of four Si-O bonds in each tetrahedron have one length and two others - another. Fig. 5.36 shows how tetrahedral Si-O bonds change



Figure 5.34: Temperature dependence for the lattice parameters ratio, c/a, for low and high quartz according to [69]. Solid dots: low-quartz, open dots: high quartz.



Figure 5.35: Temperature dependencies of linear thermal expansion coefficients of quartz along the *a*-axis (α_a) and *c*-axis (α_c). Above 600°C, α_a virtually coincides with an abscissa axis on the scale of the figure.

with temperature.

In low quartz both types of bonds, Si-O1 and Si-O2, behave in the same way – they contract with temperature. At heating from room temperature up to the high-low inversion at 573°C the Si-O1 bond decreases for 1.1% and Si-O2 for 1.6%. At approach to the point of transformation, the rate of contraction of tetrahedrons increases, whereas the structure, which is built from these tetrahedrons, steadily expands. It is obvious that the thermal expansion of low-quartz comes from a rearrangement of tetrahedrons. In the inversion point the bond lengths Si-O1 and Si-O2 become equal. At the further heating we observe in high quartz only a very slow contraction of regular tetrahedrons with the thermal expansion coefficient of the



Figure 5.36: Temperature dependence of Si-O bonds in quartz tetrahedrons [72].

order of $-1.2 \cdot 10^6 \text{ K}^{-1}$ which is suitable for explanation of the thermal expansion in high quartz.



Figure 5.37: Projection of right handed high-quartz structure onto the (x, y)-plane and perpendicular the *c*-axis directed on the onlooker. The figures in the circles show the relative height of the Si-atoms above the (x, y)-plane. The tilt axes d_1 , d_2 and d_3 are indicated.

Let us consider a geometric model explaining the mechanism of thermal expansion in low-quartz (Fig. 5.37, [73]) in suggestion that the tetrahedrons are regular as is the case of high-quartz. All lengths in

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the model are dimensionless and given in units of the *a*-axis in the high-phase. Then the lattice constants in the high temperature phase are:

$$a = 1$$
, $c = 2\sqrt{3}R$, $R = \frac{\sqrt{3}}{2}\frac{1}{1+\sqrt{3}}$

R being the Si-O distance. Vertical displacements of tetrahedrons in Fig. 5.37 (numbers in the circles) are also given in the same units. For "regular" quartz (regular SiO₄ tetrahedrons) there is no open parameter in the high-phase except for a scaling factor. As the authors [73] wrote, "the conditions of rigid and connected tetrahedra leave only one way to produce the low temperature phase from this structure. This is the simultaneous tilt of the tetrahedra around the three axes d_{1-3} ... Because of tetrahedra being linked, this "tilt operation" shortens the dimensions (*a*, *c*) of the unit cell."

A simple geometrical consideration allows one to formulate the structure of "regular" low-quartz in terms of only one parameter – the tilt angle δ . In particular, for the unit cell parameters of low-quartz the authors got the following expressions:

$$a = 1 - 2R(1 - \cos \delta)$$
, $c = 2\sqrt{3R}\cos \delta$.

The unit cell parameters of low-quartz do not depend on the sign of the tilt angle δ but the atomic coordinates do, and the δ -sign determines the kind of Dauphiné twin. Checking the validity of the tilt model for "regular" quartz by comparing these equations to the relevant experimental result at room ($\delta = 16.3^{\circ}$) and at 600°C ($\delta = 0$, above the phase transition) shows a surprisingly good agreement (Table 5.5).

Table 5.5: Comparison of tilt model of "regular" quartz with experiment. By convention the *a* parameter of high-quartz is taken as unity.

Variables	25°C		600°C	
	Exp.	Model	Exp.	Model
a	0.9831	0.9745	1.0 (fixed)	1.0 (fixed)
<i>c</i>	1.0813	1.0539	1.0921	1.0981



Figure 5.38: Comparison of experimentally determined tilt angle δ with expected temperature dependence of δ on the basis of a Landau type expansion for the free energy [73].

The authors [73] considered the tilt angle δ as the order parameter. They proposed the analytical form of $\delta(T)$ assuming a free energy expansion of the Landau type to be valid and suggesting that the highlow transition is of first order. As Dauphiné twins are energetically equivalent, only even powers enter in the expansion of the tilt angle δ . The authors also obtained an equation for calculating the angle δ from X-ray structural data. Combining the results they calculated that a jump of the tilt angle at the transition temperature has to be 7.3° (Fig. 5.38). A temperature lag for the developed model was estimated as 10°C that is close to the lag derived for approximation of the unit cell parameter by a power function with a fractional index $\eta = 1/2$.

The Origin of Thermal Contraction of the Tetrahedrons

The nature of thermal contraction of the XO_4^{n-} tetrahedral ions are well explained in [74] with the significant title "Role of 3*d*-orbitals in π -bonds between (a) silicon, phosphorus, sulfur, or chlorine and (b) oxygen or nitrogen". As the author writes, "two strong π -bonding molecular orbitals are formed with the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of X and the appropriate $2p\pi$ and $2p\pi'$ -orbitals". The author illustrates the electron structure of the tetrahedral ion with the help of handmade models (Fig. 5.39) Thermal expansion of these orbitals results in increasing their overlapping and growth in the bond order. The bonds become stronger and shorter at heating.



Figure 5.39: On the left – overlap of $X(d_{x^2-y^2})$ with oxygen $2p\pi$ in XO_4^{n-} ; on the right – overlap of $X(d_{z^2})$ with oxygen $2p\pi$ [74].

It is obvious from [74] that not only silicon but also its neighbors in the third group of the Periodical System can create tetrahedral structures with similar properties, although some tetrahedral ions are much more complicated as compared with SiO_4 tetrahedron. Today the list of tetrahedral ions is much more extended. In particular a quartz-like structure of $AIPO_4$ expands at heating in the low-phase and has almost constant volume in the high phase [75]; hence aluminum and phosphorus should be added to the list (a) and (b) of [74], correspondingly. Specific features of high-low transitions in quartz and quartz-like $AIPO_4$ are similar, too [76].

Contraction of SiO_4 tetrahedrons takes place not only in quartz but in all silicas, for example in cristobalite (Fig. 5.40). We see again that when relative displacements of tetrahedrons are exhausted the structure loses its ability to expand. The mechanism of thermal expansion of low-cristobalite is described in [77] together with a review of cristobalite-like structures constructed of tetrahedrons and showing a similar type of the thermal expansion.



Figure 5.40: Thermal expansion of low and high cristobalite [78].

Low-quartz and low-cristobalite have "corrugate" structures; a straightening of them provides their thermal expansion at heating in spite of absence of the expansion of the "constructive bricks" – tetrahedrons. A structure of silica glass is loose (Fig. 5.17c) with a minimal corrugation. As a result, relative tilts of the tetrahedrons at heating are insignificant and the thermal expansion depends on the inherent thermal expansion of the tetrahedrons or rather on its absence.

5.4.5 High-Low or $\alpha - \beta$ -Transformation in Quartz

To the high-low transition in quartz the attention of researchers is directed to intensively within the last sixty years and to less extent even considerably earlier [79, 80] because it is accompanied by very specific phenomena and anomalies [81, 82, 83, 84, 85, 86, 87]. The literature on this question is numerous; it seems that it is the most intensively investigated phase transformation at all. Nevertheless, new investigations lead to new questions. Here we make only a very brief review of some aspects of the transition.

Order of the High-Low Transition in Quartz

A lambda-like behavior of the second derivatives of the thermodynamic potentials, what thermal expansion coefficient is, is typical for the second order transitions. Other properties of this kind (such as the heat capacity [88], and elastic modulus and light scattering (Fig. 5.41)) gave rise to the firm opinion that highlow transformation in quartz is of a second order still in the fifties of the last century. Nevertheless not lambda-like trend of the second derivatives is a decisive criterion of a second order transition but also the absence of a jump of the first derivatives and in the first place of the volume.

In the sixties the powder diffraction study [88] seem to allow one to suggest that the unit cell parameters of quartz undergo a jump at the inversion point but this conclusion could be easily disputed because of deficient accuracy of temperature measurement and insufficient number of measurements in the transformation region. To avoid these problems a special method has been developed [69, 91], the so-called X-ray radiography with oscillating temperature. Temperature on the sample varied continuously around the inversion temperature within the limits $\pm 2^{\circ}$ C. If the crystal structure uninterruptedly changes with temperature, the measured 2θ values of the selected reflection should be distributed normally in the narrow temperature interval because of accidental errors. If the function $2\theta(T)$ has a break inside the limits of the temperature

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Figure 5.41: Temperature dependencies of elastic modulus perpendicular to the optical axis of quartz (a, [89]) and scattered light (b, solid dots - heating; open dots - cooling [90]).

variation, two nearly normal distributions of 2θ should be registered. The reflections $214 (2\theta \approx 95^{\circ} \text{ at } \text{Cu}_{K_{\alpha}} \text{ radiation})$ and $231 (2\theta \approx 104^{\circ})$ have been measured for quartz powder approximately hundred times everyone, the result is presented at Fig. 5.42. Two separate distributions of the 2θ angle frequency are observed



Figure 5.42: Bar graphs for 2θ values of quartz reflections 214 and 231 in the inversion point. The left distributions belong to high-quartz, the right ones – to low-quartz.

for both reflections. In both cases a forbidden band is found for 2θ , for the reflection 321 it reaches a value which is larger than the width of the 2θ distributions.

A similar investigation was carried out for a single crystal of quartz. The reflection 060 ($2\theta \approx 150^{\circ}$) was measured nearly fifty times with the similar result; for such remote reflection a distance between the peaks of the high- and low-quartz distributions reaches 0.8°. In no experiments it has been registered any reflection within the forbidden bands. We observe here a jump of the structural parameters of quartz during high-low inversion, thus this is a first order transformation. The unit cell volume jump, calculated by using these data, is only 0.6%. This value is significantly smaller than the volume jump (2.5–5%) which can be

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found for the quartz inversion in the literature because the latter relates to a "destructive" part of thermal expansion. Real jump of the volume is small, but it does exist. Investigations performed by other sensitive methods also confirm the first-order character of the transformation [92, 93].

Transitional Opalescence

Molecular light scattering in transparent solids has been first discovered in 1928 by the Soviet physicists G. S. Landsberg and L. I. Mandelstam and first it was revealed and investigated just in crystalline quartz. At room temperature, molecular light scattering in quartz is very low, about 10^{-7} of the incident light intensity. Intensity of molecular light scattering in quartz linearly increases with temperature up to 450°C (Fig. 5.41b) and then begins to rise critically when the high-low inversion temperature approaches [90]. In the latter work performed in 1956-1957, the high-temperature optical chamber has been designed with temperature gradient in the direction of the incident light beam from 0.03 to 0.1°/mm and with the vertical gradient of 0.01°/mm. In this condition, the authors have observed, as they have thought, a "critical" opalescence in quartz in very narrow temperature quartz lies on one side of the nebulous band and high-quartz – on another side. Under continuous heating the opalescent band moves from the hot side of the chamber to the low one.



Figure 5.43: Photographs of opalescence in quartz with horizontal temperature gradient of 1 (*a*) and 0.03 (*b*) degree/mm. White dashed lines show the direction of the incident light beam. The exposition time was one second; the width of the opalescence zone at the photo (*a*) is 0.5 mm, in (*b*) – 3 mm; light scattering by the nebulous band in the direction of observation is by a factor of $1.4 \cdot 10^4$ more intense than at room temperature or in high-quartz at 600°C.

The described phenomenon is reversible and can be repeated as many times as one wants until the crystal is destroyed. The authors [90], following an independent theoretical consideration [94], concluded that the presence of the narrow nebulous band between two polymorphous modifications of quartz does not leave any possibility to interpret the low-high inversion in quartz as a first order transition. They supposed that the observed phenomenon is light scattering on optical inhomogeneities produced by thermal fluctuations.

Since then the transitional opalescence in quartz was studied repeatedly [95, 96, 97]. Intensity of the transitional opalescence depends on lattice defects, the size and form of which can be diagnosed relying on frequency and angle dependencies in the opalescence region [98]. A quality control method for piezoelectric quartz was suggested based on intensity measurement of isofrequency light scattering at $\alpha - \beta$ phase transition [99]. The idea that the opalescence in quartz is originated by thermal density fluctuations was not confirmed by later investigations. The opalescence is not a dynamic but static phenomenon, the optical inhomogeneities are invariable in time and space [98, 100, 101] and produced by so-called incommensurate phase [95, 102] (the latter work is a review with the indicative title: "The α - <incommensurate phase> $-\beta$ transition of quartz: a century of research on displacive phase transitions"). A suggestion of irregular Dauphiné microtwinning as a reason of the opalescence was developed, too [62, 100].

Incommensurate Phase

Figure 5.44 schematically presents formation of an incommensurate or modulated phase (in the literature it may be designated as IC or inc) in a crystal [103]. In modulated phases, the atoms are slightly displaced from their lattice positions following a periodic law. A superposition of two or three displacement waves can coexist in the crystal. In the case of a single wave, the modulated phase is referred to as 1q, if two or three waves coexist the modulated phases are denoted as 2q and 3q, respectively. When the ratio of the lattice parameter of the modulated phase to the modulation wavelength is an irrational number, this phase is termed incommensurate. However, since the exact value of the actual ratio is unknown, it is usually represented in the form of an irreducible fraction such as 20/41 in [104].



Figure 5.44: Superstructure formation in the model two-dimensional crystal: a) the normal phase with the unit cell parameter a; b) the commensurate phase with the doubled parameter in one of the directions; c) the incommensurate phase, a period of the displacement wave is incommensurate with the unit cell parameter.

In dielectric crystals, the modulated phase arises from the high-symmetry commensurate (normal) phase due to a phase transition, which "is caused by the disappearance of the acoustic mode with a wave vector lying within the first Brillouin zone" [104]. In quartz upon cooling the following sequence of phase transformations is observed: normal phase (high-quartz) $\rightarrow 1q \rightarrow 3q \rightarrow$ commensurate phase (low-quartz) [104, 105]. It was shown that the incommensurate phase near the $\alpha - \beta$ transition point in quartz is improper ferroelastic and should be split into domains [106]. On an electron microscope image of the domains one can see, for example, in [101], a review of simulation methods for the sequence of transformations presented in [104] as well as the author's simulation of the domain structures formation at the different stages of the inversion. Acoustic and light scattering anomalies observed in the IC phase are qualitatively consistent with the ferroelastic nature [106].

5.4.6 Pressure-Induced Amorphization of Crystalline Silica

After discovery of pressure amorphization of ice, the crystalline-to-amorphous transformations in the solid state became the subject of intensive study (see the review [107]). It was established [108] that quartz and coesite transform to amorphous solids at 25-35 GPa and 300 K, as well as other materials with quartz-type structure like $Si_{0.56}P_{0.44}O_{1.56}N_{0.44}$ or AlPO₄-GaPO₄ [109]. The phenomenon was confirmed by molecular dynamics simulations [110] and a similar behavior was predicted for cristobalite [111]. It was also shown that melting is the physical phenomenon responsible for pressure-induced amorphization and that the structure of a "pressure glass" is similar to that of a very rapidly $(10^{13} \text{ to } 10^{14} \text{ K/s})$ quenched thermal glass.

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5.5 Hydrothermal Synthesis of Quartz

The basic principles of single crystal growth were repeatedly expounded; one can find them, for example, in books of R. A. Laudise [113, 114] together with a description of the hardware implementations. The monographs [112, 113, 114] have been employed in writing of this part.

Hydrothermal synthesis is a special case of solution growth. This method is used if solubility of a growing crystal phase is too low. The main ways to raise it are addition of an appropriate mineralizator and temperature and pressure increase. Many minerals were formed in such conditions in the Earth interior by very low growth rate from water solution at high temperature and pressure. The most abundant mineral formed by this way is quartz. That is the reason why geologists were the first who began to experiment on hydrothermal synthesis of quartz to understand how it could be formed on Earth.

5.5.1 Brief History

K. Schaufheutl and independently H. de Senarmont first grew microscopic crystals of artificial quartz from water solutions in the middle of 19th century. These works as well as the subsequent ones had a mineralogical task to explain natural quartz formation; therefore, the authors were quite satisfied with small size of crystals. In 1880-1881 brothers Pierre and Paul-Jacques Curies discoved direct and inverse piezoelectric effect for quartz (see also [65] for details of the phenomenon) and some other non-central symmetrical crystals. It permitted to use quartz for transformation of electric signals to sound and back. However for this purpose quartz crystals should be large, perfect and free of twinnings. Thus interest to artificial crystals production arose because the natural crystals with necessary properties are very rare. The first large quartz single crystals were grown on seeds only in 1905-1909 by G. Spezia. His single crystals were produced from sodium silicate solution with addition of NaCl and after five-month experiments had nearly 2 cm length along the *c*-axis.

Radio engineering expansion brought very soon to insistent need in large quartz single crystals. Massive defect-free crystals were necessary to develop systems for frequency stabilization by means of piezoelectric quartz resonators. In the thirties of the last century, systematic efforts were directed at development of a method suitable for commercial production of piezoelectric quartz. R. Nacken in Germany succeeded in growing of relatively large crystals (up to 5 g) in isothermal conditions (400°C) with silica glass powder as a feed material. Solubility of silica glass is an order of magnitude higher than of crystalline quartz; hence the solution was supersaturated with respect to quartz and growth was possible. It seems that the process of glass solution with subsequent transfer of the dissolved silica to a seed may proceed until the glass exhausts and large crystals may be produced by this way. Unfortunately, quartz grew not only on the seed but on the glass, too. Crystallization stopped dissolution of the glass, and cyclical renewal of the feed material made crystal quality worse. Nevertheless, these first experiments showed that free of twinning quartz can grow relatively fast on high-quality single-crystal seed. The largest crystals synthesized by Nacken reached 2 cm after 90 days. Hence, the task of artificial growing of piezoelectric quartz was solvable in principal.

World War II gave an impulse to advancement of radio industry. After the war, strong attempts were made to find a way for industrial synthesis of piezoelectric quartz in UK, USA and USSR. At the end of the forties it became evident the Nacken's method has no perspective at many points. The most important of them is that the method should not be isothermal. The English scientists W. Wooster and L. A. Thomas were the first who showed the principal possibility to produce large enough quartz crystals by continuous transfer of matter from a feed material to the seed under temperature drop conditions. This work had a profound impact in further industrial development of hydrothermal synthesis of quartz.

In the USA the "Bell Telephone" has achieved the most considerable success. In 1956, the general procedure for synthetic piezoelectric quartz was laid down and the industrial production was organized by "Western Electric". They started up in 1958 with a pilot plant in Massachusetts and soon to a considerable degree satisfied with quartz the requirements of radio-electronic industry. Independently, T. Sawyer made a major contribution in development of the temperature drop method. In 1956, he organized his own firm "Sawyer research production" and began to produce high-quality quartz crystals.

Japan has no own deposits of natural piezoelectric quartz. An electronics firm "Toyocom" was one of the first, which was interested in creation of independent source of raw materials. In 1955, the firm began with experimental investigation in piezoelectric quartz synthesis and already in 1960 mass-production of large crystals has been organized.

In the USSR, A. V. Shubnikov undertook his first exploring work on quartz synthesis in 1939. After the war this work was resumed in the Institute of Crystallography of the Academy of Science of the USSR. In the beginning of the fifties, a new Scientific Research Institute for piezoelectric raw materials ("VNIIP") was created together with a pilot shop in Alexandrov city not far from Moscow. Later the institute was renamed as "VNIISIMS" – All-Union Scientific Research Institute for synthesis of mineral raw materials. In 1957, the first production regulation for piezoelectric quartz synthesis at a serial plant was elaborated, and the industrial production of synthetic quartz was started in 1961-1962.

5.5.2 Temperature Drop Method

The method consists in creation of some temperature difference between dissolution and crystallization chambers and is useable if the material solubility in a working medium changes with temperature. As a rule, solubility of quartz in used solvent has a positive temperature coefficient at working conditions.

Temperature T_1 is set in a region where the charge dilutes and lower temperature T_2 is set in a region of the crystal growth, the growth chamber placing under the dilution chamber (Fig. 5.45). As a result, the solution in the hot chamber with temperature T_1 begins to float upwards and arrives into the colder upper chamber. As quartz solubility at T_1 is greater then at T_2 , the solution is found to be supersaturated at T_2 and may feed the growing quartz seed. Then the liquid with T_2 moves downward and ascending and descending flows form together under the action of buoyancy force a common closed loop of free convection. Convective mass transport is very important for the process realization because it provides continuous entry of the supersaturated solution from the hotter charge to the colder seed. In a rare instance of retrograde solubility, location of the chambers for dilution and growth should be inversed.

A liquid growing medium has to assure a sufficiently large absolute value of solubility for the crystal growth. Weakly concentrated soda and alkaline water solutions are usually used for quartz growth because of higher in comparison with pure water quartz solubility; fluoride, acid and some other solutions are also used for special purposes. For the major part of manufacturing technologies, a sufficient level of quartz solubility is reached at temperatures above 300°C. Diluted water solutions may exist at these temperatures only under high pressure; the last also stimulates the crystallization process and permits to produce crystals of higher quality. In practice, pressures of 70-200 MPa are commonly used. The choice of a particular level of pressure for a given technology depends on specifics of growth and desired quality of the crystals.

For practical realization of hydrothermal synthesis, it is important that the relation between the necessary levels of temperature and pressure allows one going without external source of pressure and performing the process in isochoric conditions. In this case, the necessary pressure at the given temperature may be created only due to temperature expansion of the working medium (the water solution) and depends on the relative value of the working space infill. The infill factor is the main pressure governor for hydrothermal synthesis; the necessary value of it may be found from the p-v-T diagram of the working solutions, the latter being constructing from independent investigations.

From the above considerations it appears that hydrothermal synthesis of quartz should be realized in upright autoclaves (autoclave is a high-pressure vessel without an external source of pressure) with controlled systems for heating and heat shield. Specially oriented quartz seeds are placed in the growth chamber at metal frames, the quartz charge is placed into the dilution chamber in metal containers. As a rule, natural crystalline materials in size from 20 to 40 mm are used as a charge. Surface area of the charge should be fully five times larger than the total surface area of the seeds; in this case charge dilution does not restrict the seeds growth.

The volume of the autoclaves may vary in wide limits, from a few cubic centimeters for laboratory bombs till a few cubic meters for an industrial equipment. It was shown that the overall growth rate is higher in smaller reactors than in larger, all other parameters are being equal (temperature and the temperature



Figure 5.45: The scheme of crystal growth by the method of temperature drop. Here $T_1 > T_2$; 1) the pressure vessel with water solution; 2) the growing quartz seed; 3) the perforated diaphragm; 4) the container with diluting quartz charge. Arrows show convectional circulation of the solution.

drop). Small-size vessels with an internal diameter less then 300 mm are in considerable use because they are not heavy and are convenient in manufacturing and sealing during following exploitation. However, the autoclaves of chief commercial importance have an internal diameter of above 600 mm. Large autoclaves provide a possibility to grow larger and more perfect crystals because keeping of stable growth parameters is aided by large mass and thermal inertia of the vessel. They are also more economical in exploitation because they need less maintenance staff, working area and so on.

The geometrical shape of the working space plays a great role for the successful synthesis. Ratio of the height of the working space to its diameter has to be in limits of 8 - 15 because some instabilities of the thermal regime arise in too much elongated reactors. Nevertheless, autoclaves with elongation factor of 20 - 30 are producing and successfully working in Japan. An additional constructional feature, which helped to solve the problem of stable and controlled mass transfer providing, is a perforated diaphragm that divides the reactor into two parts: a hotter chamber for quartz charge dilution in the bottom of the reactor and a colder chamber for crystallization above it. Structure of the diaphragm often undergoes various modifications to improve and optimize the mass transfer in the vessel. However, the structure complication leads to reliability degradation and does not compensate a probable improvement of the solution circulation. For this reason, relatively simple perforated diaphragms are usually used in practice, but the choice of a flow section value is one of the fine problems of synthesis.

At once before the process beginning, the working space is partially filled with a working solution according to the chosen infill factor. Pressure starts to grow on heating but this growth is not uniform (Fig. 5.46). In an early stage of heating the working medium is in two-phase state, the working solution and its saturated vapor being in the vessel. At this stage, pressure depends only on temperature and not depends on the infill factor. Pressure growth is relatively slow at this stage, 0.01-0.05 MPa/degree. If heating proceeds, the system reaches the critical point at p_c , T_c and converts into a single-phase state. Temperature

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Figure 5.46: Schematic temperature dependence of pressure for the working solution inside the heated autoclave.

growth of pressure in homogeneous stage becomes approximately linear (1–2 MPa/degree) and uniquely depends on the infill factor.

Processes of charge dilution and crystal growth are energy-reciprocal, so a moderate energy is necessary to keep the mass transfer at a given temperature to the condition of appropriate thermal protection of the autoclave. Duration of quartz growth by hydrothermal method can reach about 300-400 days, and accuracy of temperature and pressure maintenance has to be in limits of 0.5-2 °C and 0.5-1 MPa correspondingly. Autoclaves must be safe and reliable; at the same time they should be serviceable for assembling and dismantling because of recurrence or the growth process and necessity to clean internal parts of the vessel from spontaneous crystals at the top and heavy fluid at the bottom.

5.5.3 The Main Problems of Hydrothermal Synthesis of Quartz

Phase Equilibria in the System SiO₂-H₂O

Hydrothermal synthesis is a recrystallization process under relatively high temperature and pressure conditions. This process is realized by means of continuous mass transfer from a dissolving charge to a growing seed, the driving force of the process being the supersaturation. To create the supersaturation, which is necessary for the crystal growth in a preset dissolvent with a given rate, it is necessary to know the phase diagram of the system that is the temperature and pressure dependence of the matter solubility. A region with appropriate value of temperature solubility coefficient may be then chosen at this dependence to provide the mass transfer, but some additional kinetic requirements should be taken into account to provide the desired high quality of the grown crystals.

The first qualitative information on solubility of different forms of silica was obtained in the middle of the thirties of the last century. Two kinds of scientists applied their efforts to the problem solving; those who were interested in artificial crystal production and geologists. The latter ones faced with consequences of wide occurring hydrothermal synthesis in nature, in particular with abundance of crystalline quartz. Clarification of the mechanism and conditions of formation of quartz single crystals was for geologists the way to comprehend the Earth's crust formation. This is why so much information on the theme we find in the geological literature.

The most comprehensive study of phase equilibrium in the system quartz-water over a wide range of temperature and pressure was performed in 1950 by G. C. Kennedy [115]. He investigated in details the



Figure 5.47: Temperature dependence of quartz solubility in water in hydrothermal conditions according to [115].

temperature region in the range from 160 to 610 $^{\circ}$ C and pressures up to 170 MPa that is just that hydrothermal conditions which are typical for quartz formation in nature. Quartz solubility was studied in isothermal conditions by the quenching method but not quartz samples but the overall autoclaves were quenched. Quartz solubility was determined from mass loss of the sample stated at regular intervals. The attainment of a steady state was found from stopping in mass loss changes, the non-change behavior examining over a long period. The results of this great laborious work are presented at Fig. 5.47.

Three different regions may be singled out for the system from the presented phase diagram: a threephase region for heterogeneous equilibrium "quartz + water solution + vapor" and two regions for twophase equilibriums, "quartz + water solution" and "quartz + vapor". A dividing line between two-phase regions is conventional and may be considered as corresponding to the critical temperature for water, i.e. approximately 374 °C. Water solubility of quartz increases with temperature in the three-phase region as far as nearly 332°C and reaches here its maximal value 0.075 %. On further heating to the critical temperature (very close to 374.11 °C for pure water) the solubility begins to reduce to 0.023 %.

Solubility of quartz in the saturated vapor in equilibrium with liquid water and quartz (that is along the low boundary of the three-phase region) is extremely small up to T=360 °C and $p \cong 21$ MPa. At moderate temperature and pressure, a percentage distribution of diluted silica between liquid and vapor phases is proportional to a ratio of densities for these phases; therefore, it is rather small. However, it begins to increase rapidly over 360 - 374 °C interval and reaches 0.023 % in the critical point. In the point A_{cr} (Fig. 5.47) at critical temperature and pressure, the liquid and its vapor become indistinguishable and form a so-called fluid phase or supercritical liquid. Since water solubility of quartz is rather low, the point A_{cr} is very close to the critical point of pure water. Above this point, the system is in two-phase state: "quartz + fluid phase". The point A_{cr} is the lower critical point of the system SiO₂-H₂O as distinct from the upper critical point of the three-phase region "quartz + water solution + vapor" concerning to a region of the melts. In the region of homogeneous state of the solvent, i.e. above the curve of the three-phase equilibrium (Fig. 5.47), a retrograde water solubility of quartz takes place under pressures below 70 MPa, the solubility



Figure 5.48: Solubility of quartz in supercritical water according to [116].

being temperature independent at 70 MPa and sharply increasing at pressures above this value.

Kennedy's data were later supplemented by investigations of other researchers which studied water solubility of quartz up to 900 °C and 1.0 GPa [116] (Fig. 5.48). As it follows from the experimental data, the main factor, which is responsible for solubility of quartz in near-critical and supercritical water, is a state of the fluid, and first of all - its density. If the density is kept constant, the solubility of quartz grows with temperature. Thermodynamic analysis of the experimental data showed that solubility of quartz against temperature and density of water phase in temperature range 200 - 600 °C and pressures below 200 MPa may be described by the following equation [117]:

$$c = D^2 \exp\left(\frac{Q}{RT+h}\right) \;,$$

where c is the molar fraction of dissolved silica; D is the density of the water solution; Q is the differential heat of solution which is equal on average to 39.6 Joule/mol; h = 0.362 is the constant of integration.

Another approximation for Kennedy's data was suggested by F. G. Smith [118] but the extrapolation of the found equation to the region of high p-T values gave a significant deviation from the experimental data of the work [116]. A similar extrapolation of the equation of the work [117] gives only a little better result. Because different forms of silica have a different solubility, the $\alpha - \beta$ transformation of quartz on heating and the further transformation into tridymite can be the possible reason of these failures. It is also possible that the deviations are related to particular features of structure and properties of supercritical water under high temperature-pressure conditions, especially, its degree of dissociation.

The presence of two critical points at a phase diagram is typical for binary systems if one of the components has a very high volatility like H₂O and the other component has low solubility like SiO₂. Already the first schematic phase diagram for the SiO₂-H₂O system [119] predicted two critical points and was in many respects true. The fist quantitative experimental study of the upper critical point of the system was performed in [120] for $T = 1000 - 1300^{\circ}$ C and p = 120 - 200 MPa but the final phase diagram was constructed again by G. C. Kennedy together with coauthors [121]. They stated the position of the invariant curve up to 1080 °C and 970 MPa and constructed the full diagram involving the previous results (Fig. 5.49).



Figure 5.49: The melting curve of silica in equilibrium with water [121].

Presence of water reduces the melting temperature of silica even at a moderate pressure of steam. The cristobalite melting temperature decreases with the steam presence as the pressure rises up to 40 MPa. At the higher pressures, cristobalite becomes metastable but tridymite is stable up to 150 MPa. Quartz is stable at still larger pressures and similar to other forms of silica it gives the melt with significant water content. Hence, there are two quadric points in the system SiO₂–H₂O according to the presented diagram: the first point ($T = 1160^{\circ}$ C, p = 150 MPa) corresponds to equilibrium between quartz, tridymite and two fluid phases (the melt and the vapor); the second point that corresponds to equilibrium between tridymite, cristobalite, melt and vapor, is located at $T = 1470^{\circ}$ C and p = 40 MPa. It was also shown [122] that quartz can retain stable at temperatures considerably above its quadric points if the pressure is sufficiently large. Neither cristobalite nor tridymite can keep their stability under elevated pressure.

One can see from the diagram (Fig. 5.49), that the melting temperature of silica is sharply diminished with pressure in the fields of cristobalite and tridymite stability but remains much the same in the field of quartz. Thus, change in pressure from 200 MPa to the critical value of 970 MPa reduces the melting temperature of quartz by 50°C only. By comparison, in waterless conditions the melting temperature of quartz grows with pressure from 1870 °C in vacuum to 2150 °C at 700 MPa and 2300 °C at 1200 MPa [123].

Compositions of two fluid phases coexisting along the upper three-phase boundary were also established in [121] (Fig. 5.50). The left branch of the cupola relates to the water-rich vapor, which is being in equilibrium with the silica-rich melt and the solid phase. The right branch relates to the melt, which is being in equilibrium with the solid and the vapor. The solubility of quartz in water-rich fluid (vapor) changes with pressure from 5.7 % at 200 MPa to nearly 75 % at 970 MPa in the vicinity of the critical point. On the contrary, water content in the silica-rich melt rises slowly from 4.4 % at 200 MPa to nearly 6 % at 600 MPa. At further elevation of pressure water content in the melt rises steeply up to 25 % at the critical pressure.



Figure 5.50: Compositions of the fluid phases along the upper three-phase boundary for the system SiO_2-H_2O .



Figure 5.51: Water solubility of quartz (1), chalcedony (2), cristobalite (3) and amorphous silica (4) according to [2].

Comparison of Figs. 5.49 and 5.50 shows the difference of the upper and lower three-phase regions in the system SiO₂-H₂O. Compositions of the both fluids vary over wide limits in the upper three-phase region and change moderately in the lower region, reaching the maximal value for silica solubility in water of 0.075 %. Hydrothermal synthesis is usually performed in p - T conditions close to the lower critical point.

The effect of water on silica melting is in accordance with the thermodynamic treatment [121]. However a theoretical melting curve calculated with regard to thermodynamic data is distinguished appreciably from

the experimental data for pressures 200–900 MPa, i.e. when the melting temperature of quartz change very slowly but water solubility in the melt and silica solubility in the vapor rise regularly. The simulated curve is S-shaped but the experimental curve is nearly straight. This appears to be related to specifics of water solution in the melts and changes in steam state with pressure [2].

Silica Dissolution in Water Solutions of Salts and Liquid Phase Separation at Hydrothermal Conditions

For the purpose of hydrothermal synthesis, it is important to increase the solubility of the charge. It was established that different phases of silica has different solubility in water (Fig. 5.51), and the highest solubility is shown by amorphous silica. Unfortunately, as it was mentioned above, crystallization ability of amorphous silica is very high, too, and spontaneous crystallization stops soon the dilution process. Additions of salts to water can significantly elevate water solubility of quartz and therefore were much investigated; some of the typical results are presented at Figs. 5.52 and 5.53 (citation according to [112]). At the same time, as it is often the case in hydrothermal synthesis, the phenomenon appears to be much more complicated and its application is rather limited.



Figure 5.52: Temperature dependence of solubility of quartz in water solutions of Na₂CO₃ for different content of soda. The infill factor is 70 %. Citation is according to [112].

Already one of the first systematic works on quartz solubility in the system H₂O-Na₂O-SiO₂ [124] revealed the main problems of this method although the later studies of the same and many others researchers significantly refined and supplemented the obtained information. The authors of [124] performed their hydrothermal experiments with NaOH solutions at 250, 300 and 350 °C (temperatures of 400 and 500 °C were studied later), content of sodium hydroxide changing from 1.5 to 38.8 wt. %. Autoclaves of minor capacity did not permit to measure pressure, but temperature only. This is the reason why the constructed phase diagrams were specified as polybaric; one of the diagrams is presented at Fig. 5.54. The area investigated is divided into two principal regions by the complicated curve H₂O-A-B-C-D-E-F. All compositions



Figure 5.53: Temperature dependence of solubility of quartz in water solutions of NaH_4F for different content of the solute. Citation is according to [112].

to the left of the curve are unsaturated at 250 $^{\circ}$ C, and all the mixtures to the right of the curve consist of two liquids or of one liquid and one or more crystalline phases. Let us consider this ternary diagram from the point of view of hydrothermal synthesis.



Figure 5.54: Polybaric saturation relations at 250 °C in the system H₂O-Na₂O-SiO₂ [124].

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The lower axis of concentration triangles corresponds to the binary system H_2O -SiO₂. As it was discussed above, water solubility of silica is quite low but addition of alkali increases it; that is the solubility increases when a figurative point presenting the system composition moves upwards from the side H₂O- SiO_2 . After the first alkali oxide additions the point gets into the narrow two-phase region where silica is in equilibrium with the liquid which has a composition between H_2O and A. The further addition of alkali leads to the further motion of the figurative point upwards and it comes into the spacious triangle A-C-SiO₂. This region is of great importance for the purpose of hydrothermal synthesis because it includes working compositions. Quartz coexists here with two liquids. One of them is a "thin" water-rich liquid A, and another one is "a clear water-soluble glass" with composition represented by point C [124]. In the Tuttle and Friedman experiments, the glass always occupied the lowest point in the bomb and therefore was named as a heavy phase. As the temperature increases, the point C shifts to the right, towards the Na₂O-SiO₂ system and the heavy phase enriches silica. If after heat treatment at 250 °C this quenched glass has a hardness of about 2.5 and is readily soluble in water, after treatment at 300°C it is noticeably less soluble, and the 350 °C glass is very brittle, has a hardness of approximately 5 and is slowly soluble in water. At the temperatures of experiment, the glass was shown to be a liquid, and was quenched during the bomb cooling.

Liquid phase separation of the working solution is a damaging factor for crystal growth by hydrothermal synthesis. In this case, the water-rich liquid plays the role of the working medium. The heavy phase localizes at the bottom of the autoclave and partially covers the batch preventing its dilution in the working medium. In addition, small drops of the heavy phase are carried away with convection upstream, incorporate into the growing crystal as a non-structural admixture and thereby worsen its quality. Decrease in the temperature drop will cause the convection rate to diminution and prevent the heavy phase admixture incorporation into the crystal, but at the same time, it decreases its growth rate.

The further increase in alkali content leads the figurative point moving into regions where sodium silicates have to be crystallized. Silicates formation is also detrimental for hydrothermal synthesis because the crystals precipitate on walls of the working chamber, cover the batch and stop its further dilution. As a result, it becomes necessary to clean the autoclave periodically. Increase in temperature aggravates the situation because it leads to a broadening of silicates crystallization fields. From the above it appears that attempts to increase quartz solubility in water by increasing its alkali content may start some detrimental processes. Hence, the right choice of the synthesis parameters including the nature and content of additions is a delicate question, the successful solution depending in many respects on the operator's experience.

The phase diagrams constructed in [124] give the principal understanding of the problems but unfortunately they are quantitatively incorrect. Weight losses of quartz in the presence of two liquids do not define its solubility at the given temperature (as it correctly took place in the Kennedy's experiments and as it was incorrectly assumed in Fig. 5.54) because silica diluted is divided in some proportion between the two liquids. The knowledge of the true quartz solubility in a "thin" water-rich phase is necessary for hydrothermal synthesis because it is precisely this phase which is a convective medium of the synthesis. The later investigations significantly refined the quantitative data [124] on quartz solubility. At Fig. 5.52 the curve for 2 % Na_2CO_3 belongs to the solution without phase separation, but the curves for 5 and 11 % correspond to phase separated liquids.

Seeds

A specific feature of quartz growing on a seed consists of using plate seeds instead of usual point ones. In any physicochemical conditions of the synthesis, quartz crystals are essentially not building upon *m*-faces of the hexagonal prism. As a result, a crystal in the form of a needle extended along L_3 axis grows from the point seed. The shape, size and crystallographic orientation of the seeds determine appreciably the shape and size of growing quartz crystals. To produce a large crystal of quartz it is necessary to set its size in the section perpendicular to the *c*-axis by a lengthy seed. Besides the plates with (0001) *c* orientation, (11 $\overline{2}0$) ($\pm x$), (10 $\overline{1}1$) *R* and (01 $\overline{1}1$) *r* orientations are often used, the two latter are employed for jewelry quartz production. Other orientations including irrational ones may be also used for special purposes.



Figure 5.55: The cellular relief on the faces of the c-crystal of quartz grown on a seed with (0001) c orientation.

Capture of structural and non-structural impurities depends on the crystallographic orientation of the seed to a considerable degree. Impurity distribution over growth pyramids and zones leads to formation of sectorial and zonal structures together with parasitic growth pyramids (a secondary sectoriality) and twins in the growing individual crystals. As a result, real faces of crystals produced by hydrothermal method are not ideal planes but always have some specific for the given crystal face relief. The mechanism of some types of the crystal face reliefs like cellular structure on Fig. 5.55 (named also a cobblestone road) is comprehended in a general way [113].

If the crystal grows not from its melt but from a solution, concentration gradients evolve near the growing faces. In some conditions it leads to so called concentration supercooling in the close vicinity of the crystallization front (Fig. 5.56). If in the growing crystal the equilibrium concentration of the admixture is lower then in the feeding solution, the admixture is rejected by the crystal and accumulated in the nearboundary layer (Fig. 5.56a). It is well known that commonly an admixture reduces the melting temperature. At Fig. 5.56b melting temperature of the crystal, T_m , decreases to T_{m-s} ; if in the close vicinity of the boundary T_{m-s} is lower than the medium temperature, the crystal growth stops. Furthermore, if there is a sufficiently small temperature gradient near the growth surface, temperature of the solution may occur lower than T_{m-s} (the region of concentration supercooling) in the near-boundary layer of the solution and crystal growth is possible here. It means that any bump on the smooth crystal surface has a tendency to move in solution until it reaches the point D where the temperature is equal to the melting temperature. Diffusion along sidewall of bumps makes this process easier. Size and form of the cells on the crystal face depend on several factors such as temperature gradient, concentration and diffusion rate of the admixture, surface free energy on the crystal-solution boundary for the different crystallographic planes. The morphology of the crystallization front changes with temperature gradient and cellular growth changes into dendritic one under very high supercooling. Frost flowers (patterns) on window glasses are the most prominent example of this case. Natural quartz crystals never have cellular relief [21] because an extreme slowness of the growth processes in nature results in concentration equalization in the solution. For industrial production of high-quality piezoelectric quartz, it is necessary to create and regularly supplement a bank of seeding material produced from defect-free single crystals of natural quartz.

The main factors, which act on the growth rate in the temperature drop method, are:

- The value of the temperature drop, ΔT , between the dilution and growth chambers;
- Surface area of the seed plate;

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Figure 5.56: Cellular growth caused by concentration supercooling: *a*) concentration of admixture in the crystal (c_{cr}) and solution (c_s); *b*) temperature gradient near the growth surface (dashed line) and melting temperature of the crystal in dependence on the admixture content (T_m and T_{m-s}); *c*) a form of the growth surface in the region of concentration supercooling.

- Area of the active surface of the diluting charge;
- Intensity of the solution circulation (mass flow) between the chambers of dilution and growth;
- Thickness of the diffusion layer around the growing crystal faces;
- Diluting surface of the quartz charge.

The growth rate of the crystal faces is a linear function of ΔT , but there is an upper limit for legitimate value of ΔT , above which a spontaneous crystallization begins on the inner walls of the autoclave. The limit is equal approximately 15-17 °C for soda solutions, but has a higher value in NaOH solutions and permits to reach in them higher crystallization rates (up to 4 mm/day for short-term experiments). In long-term

experiments, spontaneous crystallization appears even at the growth rate of 3.5 mm/day. Because of the low temperature coefficient of quartz solubility in NaOH solutions, the specific growth rate is lower as compared with soda solutions. The latter phenomenon is of great practical importance since for NaOH solutions there is no need in so fine temperature control as for soda solutions. If all other crystallization conditions are fixed, increase in pressure leads to the increase in the crystal growth rate because of increasing in solubility of quartz and sodium silicates, the latter may form simultaneously with quartz and disturb the process.

5.6 Concluding Remarks

Quartz is usual sand under our feet but it is a very unusual substance. A large number of researches is devoted to studying of its properties, but they often put more questions than give answers. I tried to tell about its important, but poorly known properties, as physical as well mysterious. I also tried to present an explanation of these properties, at least, of the physical ones. This explanation is connected with the electronic structure of the silicon atom and its interaction with oxygen. The same reason - presence of empty *d*-orbitals in silicon - leads to very different consequences: to the great variety of structural forms of silicas and silicates; to unusually high chemical reactivity that permits to form heat-resistant crystals at low temperatures; to thermal contraction of the SiO_4 -tetrahedrons. May be, it explains also the mysterious properties of quartz? Who knows?!

5.7 Appendix: The Crystal Skulls

A recent film about Indiana Jones adventures in search of the mysterious crystal skull seems to be a fully made-up story. However this is not the case because crystal skulls do exist in reality. Here, I do not mean present-day objects made of semiprecious stones and priced from tens of dollars to tens of thousands dollars. These crystal skulls of all shapes and sizes are being usually done by carvers in Brazil and China. But there are others: enigmatical artifacts that can be found on display in such famous museums as the British Museum, Musée de l'Homme (Trocadéro Museum) in Paris or the National Museum of the American Indians in New York. The presented here discussion on this topic is based on press and internet sources.



Figure 5.57: The large skulls from opaque quartz minerals. The Rose Quartz Skull was found in Mexico and called Rosie (a). The Amethyst Skull made from unbroken pieces of Amethyst; it was discovered in the early 1900s, in Guatemala, and now is kept in Japan (b). The Mayan Crystal Skull was discovered, in the early 1900s, in Mexico (c).

There are two kinds of ancient crystal skulls. Wikipedia attributes smaller bead-sized skulls as actual Mesoamerican beads or as rosary beads of Mexican Catholics that have been carved not so long ago (the first specimens appeared in the mid-19th century). However, there is evidence that smaller crystal skulls were

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rather widespread in the XV and XVI centuries, in Italy and South America. Larger skulls are practically life-sized; some of them are quite primitive and carved from opaque quartz minerals (Fig. 5.57), while others are transparent, as the skull from the British Museum, and also have an amazing degree of perfection, as the famous Mitchell-Hedges Skull (Fig. 5.58). All of the photos were taken from [125]. Some other high quality photos can be found in [126].





Figure 5.58: The large transparent skulls produced from unbroken pieces of quartz: *a*) The British Museum skull. It had been brought from Mexico by a Spanish officer before the French occupation (in 1863) and was sold to an English collector. The details can be found at the web site of the British Museum [127]. *b*) The Mitchell-Hedges Crystal Skull. The most famous and most studied skull. It was found in 1924 by F. A. Mitchell-Hedges in Lubaantun, Belize. A history of the skull and its famous owners can be found in [128].

Independent experts investigated these skulls, carefully and repeatedly, in attempt to establish the period of their making but the results obtained were contradictory. Let us briefly consider the main problems that exist in connection with large skulls. There is no foolproof and independent method for determining the age of quartz handicrafts. Quite effective geological methods allow one to determine the age of quartz to be determined with an accuracy of millions years. But when were the skulls carved from it? Contrary to a popular belief, no satisfactory scientific technique is available for an accurate determination of the period when a stone object was carved. There are two ways to answer the question: either to find a place of given artifacts in a known culture of some nation or to investigate the manufacturing technique and to relate it to history of technology.

All large crystal skulls were found in more or less modern time, and none of the skulls in museum collections came from documented excavations. All of them were cut from unitary blocks of quartz materials, and the transparent skulls were made from quartz single crystals. A detachable jaw of the Mitchell-Hedges Crystal Skull was produced from the same crystal of quartz as the cranium. The majority of the large skulls were investigated by scientists who faced an unusual problem: it was impossible to carve the skull using modern methods.

Crystalline quartz is a substance with the hardness of 7, which is lower than that of diamond, whose hardness rates 10. It requires either other quartz crystals or special diamond tools to attempt to carve a crystal skull. The hardest parts to duplicate in carving a crystal skull are the various angles and shapes of the bone, which comprise the skull and the jaw. Even utilizing the most sophisticated lasers of today, it would be an incredible challenge to precisely cut a crystal skull to exactly match our own human skull [129]. Art restorer Frank Dorland, who studied the Mitchell-Hedges skull for six years, set up the hypothesis for making the skull, according to which, it was roughly hewn out with cutting by diamond tools, this procedure being followed by a thorough finishing treatment with the use of a mild mixture of silicon sand and water. The exhausting job – assuming it could, possibly, be done in this way – would have required man-hours adding up to 300 years to complete [130].

Several ancient crystal skulls have been brought to Hewlett-Packard (HP) Laboratories, located near the San Francisco area in California. HP has long been known as a manufacturer of computer printers and systems, in addition to having one of the most extensive scientific and crystal research laboratories in the world. The Mitchell-Hedges skull was there lowered into a vat of benzyl alcohol, where it became nearly invisible. This proved that the skull was actually quartz crystal (alcohol and quartz have the same refraction index). The HP researchers also determined that the skull was carved from a single piece of quartz [131]. It was reported that "the lab found that the skull had been carved against the natural axis of the crystal. Modern crystal sculptors always take into account the axis, or orientation of the crystal's molecular symmetry, because if they carve "against the grain", the piece is bound to shatter – even with the use of lasers and other high-tech cutting methods". The other strangeness consists in that Hewlett-Packard lab could find no microscopic scratches on the crystal which would indicate it had been carved with metal instruments [130].

As well as the Mitchell-Hedges skull, other skulls presented in Fig. 5.57 were studied at HP, and they were also found to be inexplicably cut against the axis of the crystals. The later investigations of some skulls (the British Museum skull and the Smithsonian Institution skull) undertaken by the British museum using high-powered microscopy has shown some traces of rotary lapidary tools on the surface of the skulls. The tool marks on the skulls are very different to those on ancient Mexican rock crystal objects, which were carved by hand. Pre-Columbian MesoAmerican lapidary techniques never included rotary wheels, thus the skulls could not be carved in ancient time. More detailed and critical description of the skulls investigations with citation of original scientific papers, including SEM images of the skull surfaces, is presented in [132].

According to [125], the enigma of the skulls, however, does not end with just their making. The zygomatic arches of the Mitchell-Hedges skull (the bone arch extending along the sides and front of the cranium) are accurately separated from the skull piece, and act as light pipes, using principles similar to modern optics, to channel light from the base of the skull to the eye sockets. The eye sockets, in turn, are miniature concave lenses that also transfer light from a source below, into the upper cranium. Finally, in the interior of the skull, there is a ribbon prism and tiny light tunnels, by which objects held beneath the skull, are magnified and brightened. It seems the skull was designed to be placed over an upward shining beam. The result, with the various light transfers and prismatic effects, would illuminate the entire skull and cause the sockets to become glowing eyes.

Certainly, some unusual phenomena have occurred around the Crystal Skulls. Observers of the Mitchell-Hedges skull have reported that it appears to influence all five human feelings. It changes color and light, it emits odours, it creates sound, it gives off sensations of heat and cold to those who touch it, even though the crystal has always remained at a physical temperature of 70 degrees. Observers have seen strange scenes reflected in the eye sockets, buildings and other objects, even though the skull is resting against a black background [125, 129, 133].

A considerable amount of information on crystal skulls is available in internet, books and documentary films. Returning to Indiana Jones, it is necessary to say that some espionage interest was indeed involved and theft took place, in connection with ancient skulls, but not from the direction of KGB. The secret mystical organization of Nazis, Ahnenerbe, tried to purloin from museums the crystal skulls of 'the Goddess of Death'. A few agents of Ahnenerbe were detained in 1943, in Brazil, and gave evidence that they had fulfilled the Abwehr task to get hold of the Brazilian skulls. It is possible that some of non-caught agents succeeded in their mission. Some of the larger crystal skulls were purloined, in reality. The so-called Rose quartz (a skull compared, in its perfection, with the Mitchell-Hedges skull) has enigmatically disappeared in Honduras.

The enigma of the large crystal skulls is not something unique. For example, a large quartz dish in form of three-leafed flower is kept in the Historical museum of Cairo. Similar to the skulls, the dish is carved from a quartz single crystal against its natural axes. In St. Petersburg, two large Egyptian sphinxes look, for many years, towards each other on an embankment of the river Neva, opposite to the St. Isaac's Cathedral. The surface of the sphinxes is performed with surprising quality and radically differs from machined surface of great columns of the St. Isaac's Cathedral. At present, riddles of ancient technologies are not understood to the full, and time for their solution has not come yet.

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6 Structure, Thermodynamic Properties, Solubility and Synthesis of the Different Modifications of Silica

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Writing a book is an adventure. To begin with it is a toy and amusement. Then it becomes a mistress, then it becomes a master, then it becomes a tyrant. The last phase is that just as you are about to be reconciled to your servitude, you kill the monster and fling him out to the public.

Winston Churchill

Abstract

An analysis is given of the main physical properties of the crystalline and amorphous modifications of silica, the main emphasis being directed to their thermodynamic characterization, determining both their position in the phase diagram, and their synthesis and possible applications. An approximative method is developed allowing one to estimate the standard entropy and enthalpy of all the modifications of silica, based on the knowledge of their respective density data, only. In this way the thermodynamic properties even of those silica modifications can be computed with sufficient accuracy, for which at present the corresponding measurements are lacking or have given controversial results. Particular attention is also devoted to the possibilities to determine the solubility of the modifications of silica in water and in aqueous solutions at hydrothermal conditions: thus new possible variants of hydrothermal synthesis are anticipated. In addition, various possible methods of synthesis of one of the crystalline forms of silica - of cristobalite - are analyzed in detail because of the interesting properties both its modifications have: the negative value of the Poisson coefficient of its α -modification and the high temperature resistivity of its β -form. A detailed analysis of pre-activated sinter-crystallization, of sol/gel methods of its formation is given together with estimates of the utility of classical hydrothermal synthesis routes of this modification. The problems of silica deposits, their mining and the possible extraction of SiO₂ from industrial or natural waste products, even of plant origin, are also discussed at the end of the present review.

6.1 Introduction

At present, in the international scientific literature claims are pronounced on the existence of more than 40 different modifications (or better said: *structural varieties*) of silicon dioxide, SiO₂, traditionally called *silica*. More or less well defined and internationally scientifically recognized modifications of SiO₂ at normal pressure are, however, only the four well known crystalline modifications: quartz, tridymite, cristobalite and quartz glass.

Quartz and cristobalite have both a low temperature α - and a high temperature β -modification. Moreover, for tridymite several, usually three modifications (α , β , and γ) are in discussion. However, in present day literature the opinion prevails that tridymite has not to be considered as a "full constituent of the SiO₂family" and of the crystalline silica modifications: its existence and stability is due to the influence of different chemical stabilizers, in most cases alkaline oxides. This is why in the present contribution relatively little place is given to this SiO₂ modification (or better structural variety) of silica. Nevertheless, tridymite has enormous significance in several industrial applications, mainly connected with the production of refractory materials for glass industry and metallurgy (the so-called "tridymitization" of DINAS – refractories).

In the mineralogical literature there is also widely discussed the structure and the properties of a great variety of SiO₂ forms: both crystalline and amorphous or semi-crystalline. Some of these varieties are of significance as gemstones (mostly different vitro-crystalline variants of quartz-like silica, sometimes with a relatively high aqueous content): like chalcedony, opals etc. or as the SiO₂-constituent of magmatic rocks. In the present review, we consider, however, mainly (or even only) these SiO₂-modifications (crystalline or amorphous) to which more or less distinct positions can be attributed as pure SiO₂-forms in the thermodynamically more or less precisely founded phase diagrams at both normal and especially at increased pressure, p.

In this respect of particular significance from an academic point of view are the two high pressure, high density crystalline modifications of SiO_2 , called coesite and stishovite. They possess a well defined structure, significantly differing from that of the other modifications of SiO_2 and thus they display also specific thermodynamic properties. This applies especially to stishovite, to which many investigations have been devoted in the last twenty years. To the third high pressure modification, keatite, also artificially synthesized at the end of the 60s of the 20th century, relatively little attention is given in the present review: It is assumed in literature, that it (similarly to tridymite) exists in the presence of stabilizing dopants, only. Its chemically stabilized structure is intermediate between that of quartz and coesite.

Of particular geophysical and even cosmological significance are the newly described, the so-called post-stishovite silica modifications. They are at present only artificially synthesized at colossal pressure values (80 - 100 GPa). Most probably, they are of importance for the structure of the Earth's mantle and especially for the propagation of earthquakes etc. It is assumed in geology that stishovite is synthesized in nature in the depths of the Earth at 300 km below the surface of our planet. The structure of these new high pressure phases of SiO_2 and especially of stishovite can be compared with that of some of the structural forms of elemental carbon – with diamond, in particular. In some respects only carbon has so numerous structural varieties as shown by SiO₂: graphite, diamond, fullerenes, nanotubes, vitreous carbon, and the still experimentally not realized hypothetical structure of liquid carbon. The newly synthesized post-stishovite modifications of SiO₂ are (as well as stishovite itself) the hardest known oxides, matching in hardness with diamond and with cubic boron nitride (BN), only. In eliminating the mentioned mineralogical varieties of quartz and the amorphous modifications of SiO₂ as well as structures like tridymite and keatite (existing only in the presence of stabilizing dopants), the crystalline modifications of SiO₂ are reduced to nine properly defined modifications, only. In geophysics and in Earth's geology, they play it seems a role, similar to the role of carbon and its organic compounds in life structures. In discussing the structure of SiO_2 modifications, usually their analogy with the structures of water and ice and of the known seven or eight crystalline modification of the latter is underlined.

Water, similarly to SiO_2 and carbon, plays an essential role in geophysics, cosmophysics and life. In this sense, it is also interesting to mention here the great number of investigations connecting the structure

6.1 Introduction

of the crystalline modifications of SiO_2 with those of water. The interplay between SiO_2 and H_2O is of great significance for both the synthesis of the different modifications of SiO_2 and for the existence of life on our planet. Particular interest in Earth science literature is also given in the last years to the mechanism of penetration of water through the most densely structured SiO_2 modifications: stishovite and post-stishovites. The particular significance of stishovite and of its higher pressure analogues is the circumstance, that in them the highest possible density of structural packing of oxygen is achieved.

The present review is organized in the following way: First an analysis is given of the way we made our literature research, then the general phase diagrams of SiO_2 are discussed, followed by the analysis of existing or possible methods for the synthesis of all the modifications of pure SiO₂, beginning with those stable at normal pressure: quartz, cristobalite and of silica glass. Then the particular thermodynamic properties of both the "normal" and high pressure modifications of SiO₂ are discussed. Special attention is attributed in this analysis to those thermodynamic properties, which are of importance either for the synthesis or for the industrial applications of the existing SiO₂-modification. As far as all the crystal forms of SiO₂ can be synthesized hydrothermally, particular emphasis is given to the thermodynamics of the SiO_2 aqueous solutions. In one of the following sections also consideration is given to the possibilities of cristobalite synthesis and of the stabilization of its high-temperature β -modification. Both modifications of cristobalite display exceptional properties and in this respect both "ceramic" and sol/gel methods of its synthesis, known from other fields of silicate technology, have been of particular interest. Traditionally the methods of quartz synthesis are usually discussed in more details in reports, connected with the different modifications of silica. Knowing the high importance of quartz single crystals in present day optics and instrument-building, we have also attempted a small historical survey on the hydrothermal synthesis of quartz.

Hydrothermal synthesis in its different variants gives the possibility to synthesize practically all nine above mentioned crystalline modifications of silica. A thorough knowledge of the thermodynamic properties of all the crystalline and amorphous modifications of silica is necessary in any possible way of their synthesis. However, the analysis and description of thermodynamics of silica in general and of any of its modifications in particular is a difficult task: high temperatures and extreme pressures are required. Even more difficult turn out to be the solubility determinations of the silica modifications at hydrothermal conditions, involving high temperatures (around and above 1000° C) and pressures in the GPa-region (as in the case of stishovite synthesis). This is why we developed, in the framework of the present analysis, a particular semi-empirical method to calculate the solubility of all the crystalline and amorphous modifications of SiO₂, using only one structurally significant property – their density, ρ . This method, based on the generic application of the thermodynamics of known SiO₂ modifications is developed in details in Section 6.6. It is performed in order to calculate the solubility and to predict a way for the hydrothermal synthesis even of the less investigated modifications, for which only their density, ρ , is known with sufficient accuracy.

Particular attention in this generalized analysis of the hydrothermal synthesis of the crystalline silica modifications is given to the solubility of silica glass and to the possible synthesis of quartz, cristobalite, keatite, coesite from aqueous solutions of silica glass. Also the possibilities are discussed for production of stishovite (and maybe even post-stishovite) in an industrial scale via the hydrothermal way. Such a production could be eventually of practical importance, considering the extraordinary interesting mechanical properties of substances like the low-temperature α -cristobalite or of stishovite and post-stishovite.

The main source of silica are the geochemically well investigated quartz deposits of both hydrothermal and magmatic origin, in industrial quantities known to exist in Brazil or in the Ural mountains. On these deposits mainly depends the world's industrial production of pure silica in its ten or eleven modifications. In the last sections of the present review also some information is summarized on another possibility to obtain silica in industrial scales: out of natural plant products, containing a relatively high percentage of SiO₂ and of natural waste products, like rice husk, as possible raw materials for high purity silica production.

As far as the chemical nature of silicon (Si-Si) and silica (Si-O) bonding and of the structural and chemical similarities of carbon compounds and of silicates are given in greater details in the review of Dr. Irina G. Polyakova (Chapter 5 in the present monograph), we abstain here from a discussion of these problems.

6.2 Literature Sources and Ways of Literature Search in the Field of Silica Modifications

The present review is based on a thorough literature harvesting in which we used three different possibilities to obtain information about the properties, the synthesis, the thermodynamics and the general physicochemical properties of the various modifications of SiO_2 . First a search was made through the classical reference literature, connected with SiO_2 and silicates.

6.2.1 Classical SiO₂ Literature

The physical chemistry of the SiO_2 modifications, of silicates and of glasses, of natural and synthetic silicates are referred in Eitel's book, "The Physical Chemistry of Silicates", in its two editions: from 1954 and from 1976 [1, 2]. Further on comes the book of Iler [3] on the chemistry of silica and Toropov's reference books on the phase diagrams of silicate systems [4, 5]. Also was taken into account Levy's well known classical reference book on the phase diagrams of silicates.

The data on the thermodynamic properties of SiO_2 modifications were mainly taken from Landolt-Boernstein [6, 7] and from the Russian series of reference books on the thermodynamics of inorganic substances, published under the editorship of Glushko [8] and compared with Barin and Knacke's thermodynamic reference data book [9]. Also of significance were several of the classical books on the properties of silica [10, 11], published in Russian literature, summarizing the results obtained in the Leningrad (St. Petersburg) Institute of the Chemistry of the Silicates. Of general use were also the two volumes of Hinz's book [12], "Silikate". The books "The Thermodynamics of Silicates" by Babushkin, Matveev and Mchedlov – Petrosyan [13], the book of Gutzow and Schmelzer on the properties and the thermodynamics of vitreous state [14] and Morey's "Properties of Glass" [15] were also of significance in generalizing the necessary thermodynamic data.

In structural problems, "The Structural Inorganic Chemistry" of Wells [16] and "The Structural Chemistry" of Evans [17] were mainly taken into account. Also were consulted several of the well known German encyclopedic reference book series and especially the newest editions of "Roempp's Chemistry Lexikon" [18] and "Ullmann's Encyclopedia of Industrial Chemistry" [19]. The mineralogical side of the SiO₂modifications was compared with several reference books out of which we would like to cite here the optical mineralogy of Winchell [20], Betechtin's course of mineralogy [21] and the "Crystal Habits of Minerals" by Kostov and Kostov [22]. Also of significance for the present review were two books on the properties of silicate glasses written by Vogel [23] and by Scholze [24].

6.2.2 Literature Connected with the Different Silica Modifications

Particular emphasis was directed to the original literature on the synthesis, the properties, the thermodynamics and the transformations between different phases of SiO_2 as it is given mostly in the mineralogical, geochemical and cosmo-chemical publications. The respective literature is cited in the following text in details. Here we would like to mention only several general review articles which are of significance in analyzing the thermodynamics and the phase status of the silica modifications (Swami and Saxena et al. [25], Holm et al. [26], Dorogokupets et al. [27] and Richet, Botinga et al. [28]). We also consulted several papers in which an attempt is given for a calculation of the thermodynamic properties of SiO_2 out of first principles: by using more or less known molecular-statistics models. A typical example in this respect is the paper of Keskar et al. [29]. However, it turns out that this and similar papers are based mainly on Lennard - Jones potentials and the mentioned first principle calculations are far from giving useful information for the task of the present review.

6.2.3 Internet Search Engines

Of general informative significance was also a search through the Internet literature, we performed in a fanlike manner in which we browsed the database for keywords in the abstracts in the time scale starting 1999 up to present days publications. This resulted in approximately 950 resumes from international scientific literature, connected with the general properties of SiO_2 and its main modifications (quartz, tridymite, cristobalite, keatite, coesite and stishovite were our key words).



Figure 6.1: Fenner's phase diagram of SiO_2 in the representation given by Eitel [1]. Bold lines give the expected course of the vapor pressure of the phases, stable in the respective temperature range. Their broken extrapolations denote metastable states. With open points equilibrium temperatures indicated at the abscissa are given. The nearly vertical dashed lines present anticipated change of the equilibrium temperatures with increasing pressure.

Also were employed standard search engines in Internet to obtain an additional update mainly on products of technical use. This gave us also an output of about 50 literature sources, mainly connected with natural plant products containing SiO₂.

6.3 Phase Diagrams of SiO₂

There are several variants of phase diagrams of SiO_2 . Some of them are only of historic interest and mostly illustrative, in many details even misleading, but from most of the present day phase diagrams really distinct conclusions can be made.

6.3.1 Fenner's Classical Diagram

The study and the discussion of the different crystalline and amorphous modifications of SiO_2 begin usually with the classical phase diagram of Fenner from 1913 (see Fig. 6.1). However, this diagram gives only a qualitative picture of the relative stability of the SiO_2 modifications using as an illustrative criterion of phase stability the virtually constructed temperature dependence of the vapor pressure of the considered amorphous and crystalline forms of SiO₂. These vapor pressures of the silica modifications are in fact extremely low, they can not be measured experimentally and they can be only calculated from the respective thermodynamic potential differences, which were not known in Fenner's times. Thus, Fenner's diagram is only a qualitative illustration of the thermodynamic potential diagram, which could be constructed only from the present-day knowledge of the thermodynamics of SiO₂. Moreover, this diagram is criticized for the inclusion of tridymite as an independent stable phase of SiO₂. More recent investigations have shown, however, as mentioned above, that the three modifications of tridymite can be formed and exist only in the presence of a measurable amount of dopants, mostly alkali oxides and especially K_2O . In Fenner's diagram, the high pressure crystalline modifications of SiO₂, synthesized many years after Fenner had published his phase diagram, are not to be seen: neither coesite, nor keatite and stishovite appear on this picture.

6.3.2 Flörke's Diagram

Another diagram often referred to in literature has been established supplementary to Fenner's diagram by Flörke [30] in 1956 (see Fig. 6.2). Here, the stability regions of the three modifications (quartz, cristobalite and liquid SiO₂ known at the time when this diagram was constructed) are again schematically indicated, however without tridymite. Flörke was in fact the first author to prove that tridymite is not formed in the absence of alkali oxides.



Figure 6.2: Flörke's phase diagram [4, 30] of SiO_2 . The vertical bold lines give the stability ranges of the respective modifications at normal pressure. Shaded regions indicate the corresponding metastable states.

Also schematic in the description of the low-pressure phases is the diagram (see Fig. 6.3), usually given up to the end of the 1970-ies in one of the best known reference books of Russian silicate literature [4], where, however, (already) coesite was introduced. The most interesting point in this diagram is that here the coexistence curve quartz-coesite was constructed using thermodynamic measurements, supported by evidence on the transition kinetics among the different phases. Here again, tridymite is schematically considered as a natural member of the silica family, while stishovite, just synthesized at this time, is still not present on the diagram. The synthesis of stishovite was carried out under pressures exceeding 80 kbar. Further on, coesite was also synthesized and exists in the field of pressures exceeding 10 kbar and at temperatures higher than 1400°C, as seen from Fig. 6.3.

6.3.3 Contemporary p - T-Diagrams of the Phases of SiO₂

Quantitative phase diagrams of SiO2 were constructed only according to the thermodynamic properties of the SiO_2 modifications, investigated and experimentally determined. However, calorimetry of the SiO_2 modifications even at normal pressure is a very difficult task: the specific heats have to be measured up to 2000 K and the melting enthalpy has to be determined at approximately 2000 K. The transformation heats between the stable SiO_2 phases at normal pressure are traditionally determined by solution experiments in hydrofluoric acid, performed in platinum calorimeters. However measurements of the specific heats in the indicated temperature limits are a tedious task and such investigations were performed only in several cases (see [26, 27, 28]). There is a lack of direct determinations of the melting enthalpy of cristobalite: here in reference literature usually only the difference between the dissolution heats of SiO_2 glass (not as necessary: of the melt) and of stabilized (i.e chemically doped) high temperature β -cristobalite is given. Moreover, in such measurements (necessarily performed at room temperatures) often even low temperature α -cristobalite is employed and considered as β -cristobalite (and vice versa). In this way only estimates of the melting enthalpy ΔH_m of cristobalite are given in fact in literature. The transformation enthalpies between the high pressure modifications (coesite, stishovite) are also usually determined only at normal pressure and extrapolated using Hess'es law. Nevertheless in this way quantitative data of eight of the crystalline modifications of SiO_2 are to be found in the reference literature [8, 9].



Figure 6.3: The thermodynamically calculated (p, T)-phase diagram of SiO₂ in its preliminary form (still without stishovite). The (p, T)-lines of the "normal" phases are more or less qualitatively drawn, the quartz - cristobalite - coesite line is thermodynamically calculated accounting for the respective volume changes. The open squares are kinetic experimental results confirming the general thermodynamic expectation (according to [4]).

In our present calculations of the solubility of quartz, cristobalite, coesite and stishovite we use as an

estimate for ΔH_m the following dependence

$$\Delta H_m \cong 2\Delta H_a^{298}(T) \; ,$$

where $\Delta H_g^{298}(T) = (H_{SiO_2-glass}^{298} - H_{\alpha-quartz}^{298})$ is the difference between the enthalpies of quartz glass and of α -quartz at room temperature. This estimate followed from an empirical dependence, first mentioned 60 years ago by G. Tammann and widely discussed in [14] (see also literature cited there). It is employed here in the series of calculations, summarized in Section 6.7. At present the validity of this approximation is confirmed for more than 100 substances (various silicate, borate, phosphate and organic glasses) for which it is known that in fact $\Delta H_g \sim (1/2)\Delta H_m$ [14]. That is why we preferred to use this estimate in our calculations in Section 6.7 as a better, empirically founded approximation, instead to take the difference between the enthalpies of glass and the respective stable crystal modifications as a measure for ΔH_m .



Figure 6.4: Thermodynamically constructed phase diagram of SiO_2 with kinetic data from different authors summarized by Swami, Saxena et al. [25]. This in fact is the continuation of Fig. 6.3 and a next stage in the development of the construction of the SiO_2 diagram. Generalization made by Swami, Saxena et al. [25].

Stishov went a significant step further as compared to the evidence given on Fig. 6.3: he proposed, using thermodynamic data and the respective p(T)-dependencies, the following approximation (see [4])

$$p = (97500 \pm 5000) + 20.33T$$

for the line dividing the T(p)-fields of coesite (given on Fig. 6.3) and stishovite. This border line (not introduced on Fig. 6.3) is very essential for the whole physics and structure of SiO₂ in its different modifications. It divides the regions of the two main structural fields in the crystalochemistry of this substance: quartz or coesite-like from stishovite-like structures. In some respect it is similar in its significance to the Simon-Leipunskii-line in the physics of carbon, dividing graphite-like from diamond-like structures (see [31]).

The further developments of the thermodynamics of the SiO_2 modifications were due mainly to the particular importance of the high temperature modifications of SiO_2 in Earth science and in tectonics. It was assumed, and thermodynamic calculus verified this hypothesis, that in the depth of the Earth's mantilla

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6.4 The Modifications of SiO₂ and Their Synthesis

the predominant modifications of SiO_2 are coesite and stishovite: latter being stable at depths below 300 km. Later on coesite and stishovite were found in meteoritic impact craters on the Earths surface (the most significant example being the Arizona crater) and the thermodynamics of stishovite and coesite became of significance in cosmology and cosmogony.



Figure 6.5: The enlarged SiO_2 -diagram generalized by Swami, Saxena et al. [25] in its full pressure and temperature ranges. Note that Fig. 6.4 is only a part of Fig. 6.5.

From a series of measurements performed from the end of the 1960s to the end of the 1980s mainly in geological laboratories the specific heats and enthalpies of transitions of quartz, cristobalite and SiO₂ glass, coesite and stishovite are known at least for their stable modifications [25–29]. Using the expected and calculated change of the thermodynamic properties with pressure (i.e. at the quartz/coesite and the coesite/stishovite p(T)-lines) the real phase diagrams of SiO₂ (including stishovite) were constructed as they are presented on Figs. 6.4, 6.5 and 6.6. On Figs. 6.4 and 6.5 the experimentally determined kinetic transition points are seen, on which these diagrams are additionally based. Fig. 6.6 is given in the more convenient representation: pressure, p vs. temperature, T. A comparison of these three phase diagrams shows the way the final, usually employed diagram on Fig. 6.6 is constructed. It is seen that Figs. 6.4, 6.5 and 6.6 are comparable in a qualitative way: the differences between them are due mainly to the lack of exact experimental thermodynamic data on the molten SiO₂-modifications. Nevertheless the most significant features of the SiO₂ phase diagram are clearly seen on these figures. They illustrate the stability regions of the high temperature phases (stishovite and coesite) and their relation with the phases of silica, stable at normal pressure (quartz and cristobalite).

6.4 The Modifications of SiO₂ and Their Synthesis

6.4.1 SiO₂-Modifications and their Mineralogical Characteristics

At present the following crystalline and amorphous SiO₂ modifications are considered in literature and are discussed here: α - and β -quartz, α - and β -cristobalite, keatite, coesite, stishovite, SiO₂ – glass, amorphous precipitates (or disperse amorphous), and molten SiO₂. Their space groups and temperature stability ranges



Figure 6.6: A present day representation of the SiO_2 phase diagram as it is recommended in the reference literature [18] and used throughout the present review. The densities of the corresponding phases are given in brackets. It is based on diagrams like those given on Figs. 6.4 and 6.5. Note, however, that here the more comfortable presentation with temperature as an abscissa is used.

are given in Table 6.1, while the main structural types of SiO_2 are seen on Fig. 6.7. Besides, Table 6.1 also contains data for several "non-systematic" modifications.

6.4.2 Synthesis of Quartz

The formation of quartz in Nature follows both a hydrothermal way [1, 2] and via crystallization of magmatic rocks. The first artificial synthesis of quartz was performed hydrothermally using the different solubility of crystalline quartz and of quartz glass [32, 33, 34].

Isothermal Methods: Wooster and Nacken

As discussed in more details further on, the increased thermodynamic potential of quartz glass as a frozenin system determines its higher solubility as this was expected by both Wooster [33, 35] and Nacken [34] in England and Germany respectively during the years of World War II. In both cases, the relatively high supersaturations at the temperatures and pressures reached in the autoclaves (see Section 6.6 and our calculations there) brought about very poor results: no growth of greater quartz crystals (which was the task of both authors) could be realized with these isothermal methods. The details of the isothermal synthesis in which the route SiO₂ (glass) \rightarrow SiO₂ (quartz) was exploited are given critically and in great details in Smakula's book [32] and may be followed in both Wooster's two publications [33, 35] and in Nacken's report [34] (see also [36]). In the already mentioned survey of Dr. Polyakova in the present volume some additional details of this way of synthesis may be also found.



Figure 6.7: The SiO₄/2 tetrahedron and the SiO₆/3 octahedron (top) together with the corresponding distances. Bottom row gives the cis-trans arrangement of tetrahedra in quartz; right-hand scheme: the possible rotations of the two tetrahedra (from [19]).



Figure 6.8: Impurity distribution in quartz single crystals (from Ullmann's Encyclopedia, 1993 [19]): types of fluid inclusions. V - vapor, L - liquid in the system $H_2O - CO_2 - SiO_2$. Squares, rectangles and triangles represent schematically different crystals.

Gradient Methods

The failure of the isothermal SiO₂glass $\rightarrow \alpha$ -quartz route is the reason why soon different temperature gradient methods were developed for single crystal quartz synthesis (see [32, 36] and Barrer [37]). In this way of synthesis, silicate glasses, quartz glass, quartz crystals were suspended in autoclaves, in which supercritical aqueous solutions of NaOH and of Na₂SiO₃ were formed and an externally applied temperature gradient determined a relatively low supersaturation between the SiO₂-precursor and the growing crystal. Thus, large quartz single crystals were grown, which could be directly used in the piezo-technique. In both World War I and II the hydrophones used in the anti-submarine warfare were constructed exploiting the singular piezo-electric properties of quartz single crystals.

Isothermal Synthesis of Quartz from Cristobalite

The isothermal synthesis of quartz and especially of fine grained quartz was also attempted using as a precursor in the autoclaves α - or β -cristobalite. These two SiO₂-modifications being metastable at the temperatures used in hydrothermal synthesis have an elevated thermodynamic potential and thus higher solubility than quartz. On this subject there are several literature data (see [38] and references cited there). In Section 6.6 a thorough discussion on this subject is given in terms of the solubility curves, we constructed there.

Name	Crystal system	Space group	Stability range	
Low quartz (α)	trigonal	$C3_12$ and $C3_22$	Up to 573°C	
High quartz (β)	hexagonal	$C6_22$ and $C6_43$	573 – 870°C	
Low tridymite (α)	orthorhombic	-		
Middle tridymite	hexagonal	-	870 – 1470°C	
$(\beta 1 \text{ or } \beta)$	(trigonal)			
High tridymite $(\beta 2 \text{ or } \gamma)$	hexagonal	$C\frac{6}{m}mc$		
Low cristobalite (α)	tetragonal (trigonal)	$P4_{1}2_{1}$	280°C	
High cristobalite	isometric	$P2_{1}3$	1470 – 1713°C	
(β)	(cubic)			
Keatite (silica K)	tetragonal	$P4_12_1$ and $P4_32_1$	-	
Coesite (silica C)	monoclinic	$C\frac{2}{c}$ or Cc	1300°C	
Stishovite	tetragonal (rutile type)	-	800°C	
Post-stishovite 1	Tetragonal (CaCl ₂ type)	-	?	
Post-stishovite 2	tetragonal $(\alpha$ -PbO ₂ type)	-	?	
Lechatelierite	amorphous	-	1100°C	
(silica glass)				
Amorphous silica	amorphous	-	-	
Chalcedone	trigonal	-	-	

 Table 6.1: Silica polymorphs.

Inclusion of Impurity Droplets into Quartz

Usually the synthesis of quartz is discussed in literature having in mind the formation and growth of nearly perfect large quartz single crystals. For the synthesis of ultra pure glass out of quartz is also of interest the synthesis of fine grained quartz where the crystals are so small, that the inclusion of bubbles containing residual alkaline traces, filled with the precursor aqueous solutions is minimal (see Fig. 6.8). This problem was discussed in more details in the technological literature [19].

Of particular significance in performing hydrothermal synthesis of quartz and of other modifications of SiO_2 are the solubility diagrams of SiO_2 as given on Fig. 6.9 (as an amorphous SiO_2 -phase in pure H_2O). The pressure resulting in an autoclave with a given degree of initial filling with an aqueous solution is seen on Fig. 6.10. In [19, 32] detailed information is given on the construction and the maintenance of different autoclave models both for industrial and laboratory applications and for scientific investigations.

6.4.3 Synthesis and Stabilization of β -Cristobalite

Cristobalite is one of the most interesting and promising modifications of SiO₂. Its low temperature or α modification possesses a negative (auxetic) Poisson ratio, i.e. it becomes wider when stretched and thinner
when compressed [40, 41]. The high temperature, β -form of cristobalite is stable up to the melting point
of SiO₂ (1725°C) and it is characterized by a very low coefficient of thermal expansion (almost tending to



Figure 6.9: Solubility diagram of amorphous SiO_2 in pure water at approximately 80 MPa. Mineralizers (NaOH, Na₂CO₃) additionally increase the indicated SiO_2 solubility (according to [19]).



Figure 6.10: The (p - T)-diagram of H₂O: Isochores for various percentages of autoclave filling (given as a parameter to each line). With C the critical point of water (22.04 MPa, 574.4 K) is indicated (after [19]).

zero) [42-46]. However, there is a general disadvantage in using β -cristobalite as a refractory material. At about 250°C cubic β -cristobalite transforms, by what is usually described, as a first order displacive phase transition into its low temperature polymorph - into α -cristobalite possessing a tetragonal structure. This transition is connected with a considerable volume dilatation (of about 5%) resulting in crack formation or even in the destruction of pure β -cristobalite samples in their down-cooling to room temperatures. That





Figure 6.11: The content X_{β} of the β_x -cristobalite-like phase in glass-ceramic samples obtained by the activated reactive sinter-crystallization method. (a) Dependence of X_{β} on of the dopant concentrations C_{dop} . All samples in Fig. 6.11a are heat-treated employing two stage heat-treatment regime: 1 h at 1350°C and 18 h at 1500°C. Here "O", "1" and "2" denote the pure cristobalite sample and samples containing 6.5 and 13.5 mol% dopants (CaO and Al₂O₃ in equimolar ratios), respectively. (b) Kinetics of formation of X_{β} -cristobalite-like phase in glass-ceramics samples containing 13.5 mol% dopants at 1450°C. The values of X_{β} are also given for three other temperatures: 1350°C (hollow square), 1400°C (hollow circle) and 1500°C (hollow triangle) after 6 h exposure.

One way to inhibit the $\beta \rightarrow \alpha$ transformation of cristobalite is by the so-called "stuffing" mechanism analogous to that used for the stabilization e.g. of the high temperature modifications of quartz or of zirconia (ZrO₂) [59-61]. The suppression of the $\beta \rightarrow \alpha$ transition by this mechanism is due, as first stated by Buerger, to the incorporation of appropriate (alkaline or alkaline-earth) "stuffing" cations into the large voids of the cristobalite structure built up by six-membered rings of SiO_{4/2} tetrahedra [48]. The charge of the dopant "stuffing" cations is compensated by replacing a part of the Si⁴⁺ ions in the SiO₂ network by Al³⁺ or by other three valence cations. This way of stabilization is also known as chemical stabilization as it is connected with a change of chemical composition, determined by the dopants introduced.

Li [50] was as it seems the first who synthesized alkali-free glass-ceramic materials containing as the main crystalline phase stabilized β -cristobalite-like solid solutions. For this purpose Li used a conventional glass-ceramic technology: glasses with the desired dopant concentration (up to several molar percent, typically 3-6% Ca0, 3-6% Al₂O₃) were synthesized just above the melting point T_m of silica and then sintercrystallized at lower temperatures. A serious disadvantage of this technology is, however, the extremely high temperatures (nearly 1800°C) and the prolonged melting times (of about 100 h) needed to produce the initial silica reach precursor glasses with a homogenous dopant distribution. The uniform dopant distribution as shown by a number of investigations is an obligatory prerequisite to prepare glass-ceramics with a high content of stabilized β -cristobalite (or more correctly a β -cristobalite-like solid solution). Very long heat-treatment times (also up to 100 h) are also necessary for the second stage of the synthesis: for the formation of the stabilized β -cristobalite phase by sinter-crystallization of the powders, obtained after milling of the pre-melted glasses.

Another possible route for the synthesis of stabilized β -cristobalite is connected with the application of different sol/gel techniques [52-58]. Their most important advantage are the relative low temperatures needed to achieve homogeneous distribution of stabilizing cations of the above mentioned concentration in the SiO₂ network of the precursor glass. Shortcomings of this way of synthesis are, however, the high prices of the reagents usually employed in the SiO₂-sol preparation and the complex and time consuming sol/gel transition procedures. That is why alternative intermediate approaches, also involving sol-gel routes, are of particular interest, e.g. the so called "incipient-wetness" techniques [62]. Other methods for the synthesis



Figure 6.12: Influence of the dopant content on the thermal (a), structural (b) and dilatational (c) behavior of the stabilized β -cristobalite glass-ceramics investigated. Here "T" denotes the sol/gel derived sample doped with 3.25 mol% CaO and 3.25 mol% Al₂O₃ and synthesized according to Sections 6.3.1 and 6.3.3. Samples "1" and "2" have the same dopant percentage as the respective samples in Fig. 6.11a. Sample "T" is heat-treated 4 h at 1350°C, two stage heat-treatment regime is employed to sample "O", "1" and "2": 1 h at 1350°C and 18 h at 1450°C. Sample "2a" possesses the same composition as sample "2", however, with respect to sample "2a" a longer second heat-treatment stage of 30 h instead of 18 h is employed. (a) The heat flow curves proportional to the specific heat $C_p(T)$ -dependencies of the samples. (b) The relative change $\gamma(T) = (V - V_o)/V_o$ in the volume V of the elementary cell of the pure cristobalite phase crystallized in the reference sample "O" and of the cristobalite-like solid solutions formed in samples "1", "2" and "T". (c) The relative elongation $\Delta L(T)/L_o$ of the samples as a function of temperature. Here, $\Delta L(T) = L(T) - L_o$ where L(T) and L_o are the lengths of the samples at temperature T and at room temperature, respectively. Note the shift of peak positions in the heat flow curves and of the 'inflection" points in the $\gamma(T)$ - and $\Delta L(T)/L_o$ -curves to lower temperatures with the increase of the dopant concentration from sample "O" to sample "2". Note also the absence of a thermal effect and of a stepwise change in the $\gamma(T)$ - dependence of sample "O" to sample "0" to sample "O" to sample "2".

of β -cristobalite glass ceramic materials were also developed by the authors of the present review. One of them, we called the activated reaction sinter-crystallization approach [63], and modified sol/gel techniques [64] are described in two of the next sections.

Activated Reaction Sinter-Crystallization Approach in β -Cristobalite Glass Ceramics Synthesis

The main advantage of such an approach in the synthesis of stabilized β -cristobalite glass-ceramics, which could be also useful in other cases, is that the high temperature glass pre-melting stage typical for the conventional glass-ceramic technology is avoided. It is based on an activated reaction sinter-crystallization

process of precursor mixtures containing all necessary components in a chemically, mechanically or thermally pre-activated state. The stuffing Ca²⁺ cations are introduced as freshly de-carbonated highly reactive calcium oxide (CaO), instead of CaCO₃ conventionally used. Finely milled alumina (Al₂O₃) and quartz glass (both with particle sizes smaller than 40 μ m) are employed as pre-activated sources of the Al³⁺ cations and of the SiO₂ itself. In this way, it becomes possible glass-ceramic materials with a high percentage of stabilized β -cristobalite-like phase to be *directly* synthesized in the course of a single chemically activated sinter-crystallization process at relatively low temperatures (not higher than 1450°C) and short heat-treatment times (of about 20 h), omitting the usually employed high-temperature pre-melting procedure.

Two main problems are to be considered and resolved in applying this technique for the synthesis of stabilized β -cristobalite glass-ceramics:

- 1. the influence of the dopant concentration and the sinter-crystallization heat-treatment regime on the stability and on the content of β -cristobalite-like phase formed;
- 2. the influence of concentration of the stabilizing dopants on the nature of $\alpha \rightarrow \beta$ cristobalite transition.

Figs. 6.11a and b illustrate how the concentration of the stabilizing additives and the sinter-crystallization heat-treatment regime influence the content of β -cristobalite-like phase.

The nature of the $\alpha \rightarrow \beta$ cristobalite change was studied in details in [63]. The main results of these investigations are shown in Figs. 6.12a-c. As seen in these figures the increase of the dopant concentration C_{dop} lowers the thermal effect and diminishes the step-like first-order type of volume changes. Moreover, the temperature of this transition is shifted to lower temperatures with the increase of C_{dop} . Such a lowering of the $\alpha \rightarrow \beta$ -transition point was observed with respect to the α -and β -modifications of quartz [65].

The analysis of Figs. 6.12a and b and the results of the high temperature X-ray investigations shown in Fig. 6.12c indicate that increasing the dopant concentration the conventionally assumed as a first order displacive transition can be transformed into a second order change between the α - and β -polymorphs of cristobalite. The shift to lower temperatures of the $\alpha \rightarrow \beta$ transition point immobilizes the building units of the system (both in cristobalite and in quartz) and converts the modification change from its originally displacive mechanism to a more or less pronounced process of tilting of the SiO_{4/2} tetrahedra. In increasing the dopant percentage the formation of α - and β -cristobalite-like solid solutions with nearly equal lattice parameters becomes possible. Thus, the volume change at the $\alpha \rightarrow \beta$ -transition is minimized or even nullified as in the case of the sol/gel derived sample "T" (see Figs. 6.12a and b). This conversion of the first order displacive $\alpha \rightarrow \beta$ transition into a second-order phase change caused by the incorporation of an appropriate concentration of stabilizing cations into the cristobalite structure is most probably of significant technological importance.

Hydrothermal Synthesis of Cristobalite

On the hydrothermal synthesis of cristobalite there are several publications up to now in which mainly the production of micro- or even nano-sized cristobalite powders is described out of alkaline aqueous solutions at hydrothermal conditions: both in small experimental apparatus, but also in relatively large autoclaves [66, 67]. In this way of cristobalite synthesis, only alkaline solutions were employed up to now, which makes it difficult or even excludes the use of hydrothermally prepared cristobalite as a constituent of materials, which have to be alkaline-free. Here, the possibility of introducing Ca²⁺- and Al³⁺-ions into the aqueous solution should be investigated at conditions, described in more details in Section 6.6.4. It is interesting to note that according to [66, 67] hydrothermally synthesized high-temperature β -cristobalite is relatively stable at room temperature because of the high content of alkaline dopants included into it from the host solution. However, the thermal stability of β -cristobalite and the mechanism of $\alpha \rightarrow \beta$ transition between hydrothermally grown α - and β -cristobalite modifications are according to our experience not sufficiently cleared up to now. Usually, the low-temperature α -cristobalite is obtained at lower autoclave temperatures. Its use as an auxetic material (i.e. as crystals or micro-crystals with a negative Poisson ratio) is discussed also in Section 6.6.4 and at the end of the present review article.

Sol-Gel Methods of Synthesis

Three different sol-gel techniques were developed for reproducible synthesis of glass-ceramic materials with a high content of the stabilized β -cristobalite like phase. The first one is analogous to those used in previous publications of one of the present authors for the preparation of optical materials, especially of silica doped with Ho³⁺ or Tb³⁺ ions [68, 69]. The second and the third methods are derivatives of the so called "wet impregnation methods" also used in the preparation of optical materials, in which the precursor oxide powders are impregnated with a doping solution containing a soluble nitrate or chloride dopant. Bellow, these three methods for stabilization of cristobalite are discussed in details.

A) "Pure sol/gel method"

As a first step in this way of synthesis a homogenous, transparent sol with a composition $n_{\rm TEOS}$: $n_{\rm EtOH}$: $n_{\rm H2O} = 1$: 1: 4 is prepared at room temperature by mixing of the necessary amounts of tetraetoxysilane (TEOS) used as a SiO₂ source, ethyl alcohol (EtOH) and 0.55M aqueous solutions of Ca(NO)₂ and Al(NO)₃ for the introduction of the stabilizing cations. After that it is followed by acid hydrolysis at pH=2 (2 h under stirring), catalyzed by HCl and the successive gelation of the sol (48 h at 50°C in closed boxes). Typical starting amounts of TEOS are 5 ml. As a result transparent gels were obtained, indicating with their transparency that a molecular distribution of the dopand in the gel has taken place.

It is well known from sol-gel chemistry, that gelation times can be decreased by increasing the pHvalue of the gelation temperature. In such sol-gel procedures, the possibility always exists for an unwanted phase separation of the doping oxides. The next steps were druying (120 h at 50°C), grinding, second drying (1h at 90°C) and sintering (4h at 700°C). The amorphous powders thus obtained were milled again and pressed using as a binder aqueous solution of polyvinyl alcohol (PVA). The compact pellets were heat-treated at different temperatures in the range from 1350 up to 1500°C. It turned out that the highest content of the stabilized β -cristobalite like phase (of about 95-98 vol%) was achieved for the sol-gel synthesized samples containing 3.25 mol% CaO and 3.25 mol% Al₂O₃ and heated 4 h at 1350°C in air.

The disadvantage of this sol gel technique is the relatively high amount of the residual water (about 25%) in the samples which makes difficult their sintering. To overcome this problem two ways were tested. The first one was to modify the described sol-gel technique by increasing the drying time (from 1 to 4 h) and the temperature and the duration of the sintering (from 4h at 700°C to 5h at 800°C). Further enhancement of sample sintering was achieved by replacing 2% of SiO₂ by TiO₂. The X-ray diffractogram of a sample prepared by this second improved sol-gel method is given in Fig. 6.13. The samples synthesized in this way are characterized by a full suppression of the α/β cristobalite transition and are used as reference samples in the investigation of the glass-ceramics obtained by the activated reaction sinter-crystallization approach (see Figs. 6.13). Typically, sintered powders prepared using a "pure" sol-gel method do not contain mullite traces, they contain only cristobalite.

B) "Mixed sol/gel method"

Another significant aim of the present investigations was to find cheaper substitutes for the expensive sol-gel reagents (e.g. TEOS) usually used as a SiO₂-source in the sol-gel techniques. For this purpose a "mixed" sol/gel method was developed in which the main part of silica (up to 90 wt%) is introduced using a micrometer grained quartz glass powder suspension under stirring, containing 0.174 mol Si/l. The rest (10 wt%) of SiO₂ was added in the form of an acid silica sol with a SiO₂ concentration of about 2.75 mol 1⁻¹. The idea of this preparation way was to check the use of commercial sol products like LEVASIL[®] (BAYER AG, Leverkusen) for the preparation of larger amounts of β -cristobalite.

The stabilizing dopants were introduced using 0.55 M aqueous solutions of $Ca(NO_3)_2$ and $Al(NO_3)_3$. The as prepared suspension was stirred (24 h at room temperature) and thus was followed by solvent evaporation at heating and drying of the obtained powders. After grinding the samples were sintered for 4h / 700°C and than sintered for 4 h at 1350 °C to obtain β-cristobalite.



Figure 6.13: X-ray diffraction patterns of the sol/gel derived reference sample "T" (see Figs. 6.12a and 6.12b). The sample is doped with 3.25 mol% CaO and 3.25 mol% Al₂O₃ and heat-treated 4 h at 1350°C. In the insert the X-ray diffractogram of a pure cristobalite sample obtained by sinter-crystallization of quartz glass powder is also shown. Note that in the X-ray diffractogram of the reference sample "T" the two characteristic peaks of α -cristobalite (denoted by arrows in the insert) are missing which indicates for the full suppression of α/β -cristobalite in this sample.

C) "Wet impregnation method"

In addition, a third preparation method, close to the above described procedure, but without using of a colloidal silica sol was also employed in the framework of the described sol/gel techniques in order to obtain β-cristobalite. This method can be characterized as a "wet impregnation method". As a silica source, only a micrometer grained quartz glass powder suspension under stirring containing 0.174 mol Si/l is used. The impregnation, stirring, evaporation, drying and heating conditions are the same as described in the "mixed sol-gel method".

The sol-gel techniques proposed and more especially the "wet impregnation method" could be used for the relatively low cost production of small cristobalite articles (e.g. for details with a high electric resistance at elevated temperatures, e.g. for application in the electronic industry). Employing this "wet impregnation method" glass-ceramics samples were obtained containing up to 60-70 vol% stabilized β -cristobalite phase. It seems, that the β -cristobalite content is not substantially affected (only about a 10% increase) by the use of colloidal silica suspensions. On the other hand, a content of 70% stabilized β -cristobalite phase can be obtained by improving the homogenization conditions of the "wet" impregnation method.

It is important to note, that powders obtained by the "wet impregnation method" and by the "mixed sol/gel method" contain mullite as a second phase after heating 4 h at 1350 °C. The "pure sol/gel method", however, leads to a high content of β -cristobalite (about 95%) and α -cristobalite traces only.

Another important feature of the sol/gel synthesis of cristobalite and cristobalite–reach materials is, that a high percentage of the stabilized β -cristobalite phase is achieved at temperatures about 100°C lower and at heat-treatment regimes times substantially shorter than those, needed in the production of the glass-ceramic materials, synthesized by the reaction sinter-crystallization approach. This effect in the sol/gel approach is again due to the formation of chemically very active nano-sized dopants: here of silica nano-particles, facilitating the low temperature homogeneous distribution of the stabilizing dopants and their incorporation into the SiO₂-matrix. However, up to now both the analysis of international literature and

evidence from experimental work, obtained in the framework of the work on the present review, indicate that it is impossible to form via the sol/gel route articles of dimensions and with the technological properties, obtained via direct ceramic technologies indicated above.

In comparison with the also discussed hydrothermal methods of synthesis of cristobalite the sol/gel route also offers some advantages: the expensive (and requiring very particular attention, e.g. anti-explosion measures and provision) hydrothermal autoclave equipment is not necessary. On the other side present-day sol/gel equipment cannot secure production and yields in industrial scales, possible for both hydrothermal methods and in the also discussed sinter-crystallization glass-ceramic ways of production of cristobalite or any other of the silica modifications. Maybe the also mentioned small scale production of particularly important cristobalite wares or of cristobalite in sand-pile state could be the perimeter for both hydrothermal and sol/gel technical synthesis.

6.4.4 Synthesis of Keatite: Classical Aspects

The SiO₂ modification called after its initial synthesizer P. P. Keat is the first artificially synthesized SiO₂ modification, obtained under hydrothermal conditions in 1954. The conditions employed are described in great details by Keat himself in the respective publication in the journal Science [70]. He determined the density of keatite and drew attention to the fact that the refractive indexes of SiO₂ modifications changed linearly from vitreous silica via tridymite, cristobalite, keatite and quartz (from 1.460 to 1.540) with their densities (increasing from 2.20 for vitreous silica to 2.60 for α -quartz).



Figure 6.14: Dependence of the coefficient of optical refraction, n, on density, ρ [in g/cm³] for the different phases of silica and of water (according to Iler [3]).

Later on, it turned out that keatite could exist in the form of solid solution only and that it possesses a structure intermediate between those of quartz and coesite. Nevertheless, the success of P. P. Keat brought about the search for other possible high pressure crystalline modifications of silica. They were soon found by Loring Coes, Jr. and S. M. Stishov and S. V. Popova [18, 19] with the two modifications bearing the names of two of the mentioned scientists, who first synthesized them. These two modifications obtained

under considerably increased pressure showed the same linear dependence of the refractive index, n, on density, ρ , as seen on Fig. 6.14. An important result of this development was that stishovite had a structure differing from all other up to now known crystalline silica modifications: its structural units are not the classical SiO_{4/2}-tetrahedra, but SiO_{6/2} octahedra (see Fig. 6.7).

6.4.5 Synthesis of Coesite

The structure of coesite is constituted (as that of cristobalite and quartz) of $SiO_{4/2}$ tetrahedra, however, in a particular, denser arrangement, than in quartz and cristobalite.

Coesite is usually synthesized at $500 - 800^{\circ}$ C at 35 kbar and is characterized by a relatively high density ($\rho = 2.93$). In nature it is found in meteorite impact craters on sandstone soils and in the kimberlite tubes. In both cases these locations are rocks with a prehistory of enormous pressures and high temperatures (the South African kimberlites are a well known deposit of natural diamonds). According to our estimate of the solubility of coesite (we have made using thermodynamic data, calculated via density relations (see Section 6.6)), this silica modification could be also synthesized hydrothermally. At normal pressure coesite decomposes at 1300°C giving quartz. Up to now no technological process is developed for its industrial production: only microscopic crystals are obtained of this SiO₂ polymorph.

6.4.6 Stishovite: Synthesis and Thermal Stability

For the synthesis of stishovite two general methods have been employed up to now: hydrothermal nucleation and growth at high temperatures and pressures greater than 80 kbar [71] in Belt, and anvil and hammer cameras similar to those employed for the synthesis of diamond. However, up to now only stishovite microcrystals have been synthesized and their price is even higher than that of diamond micro-crystals of good quality. The initial synthesis of stishovite was performed by Stishov under pressures of approximately 100 kbar. In the last ten years in the literatures are published several investigations in which the synthesis of the so-called post-stishovite modifications of SiO_2 is described: these are crystalline silica modifications obtained and stable as it seems at even higher pressures than stishovite (up to 800 kbar!).



Figure 6.15: The small ultra-high pressure autoclave cell of Lityagina, Dyuzheva et al. [71] used to synthesize stishovite crystals at 9.5 GPa and 1170-1770 K: 1) current feed-through; 2) metal disk; 3) graphite heater; 4) inner autoclave ampoule; 5) outer part of autoclave.

6.4 The Modifications of SiO₂ and Their Synthesis

The interest in stishovite comes from the circumstance that both experimental findings and theoretical predictions [72, 73] indicate that stishovite and post-stishovite structures are most probably the hardest oxides ever known and ever synthesized. It is claimed in [72, 73] that their mechanical properties are surpassed only by diamond and by cubic boron nitride (BN). However, the thermal stability of stishovite is even less than that of coesite: it decomposes at normal pressures even below 800°C into SiO₂-glass and than – into cristobalite and at the end of the process – into quartz (see Fig. 6.15). Stishovite has been also found (like coesite) in the meteorite impact crater of Arizona.

Hydrothermal Methods, Anvil and Hammer, and Belt Cameras. Direct High Pressure Synthesis

In a recent paper of Litiyagina et al. [71] the hydrothermal synthesis and growth of stishovite is described in great details. The synthesis is performed in the system H_2O/SiO_2 in a high pressure cell (in fact a little autoclave with a high filling percentage) at pressures from 90 to 95 kbar (see Fig. 6.15). This pressure is developed by heating the autoclave to 1200 K. In this way, stishovite crystals up to 1 mm large have been obtained and thoroughly investigated [71]. This investigation, performed in the Institute of High Pressure Physics of the Russian Academy of Sciences in Troitzk, indicates the technical developments which could be used in order to grow even larger stishovite crystals. A schematic picture of the cell employed in [71] is given on Fig. 6.15. The habit of the stishovite crystals thus grown is illustrated on Fig. 6.16.



Figure 6.16: Stishovite crystal synthesized by the authors of [71]: a) real crystal and b) face symbols.

Post-Stishovite Modifications of SiO₂ with CaCl₂ Structure and PbO Structure

The hammer and anvil and Belt high pressure cameras for direct synthesis of stishovite are described by Dubrovinskaya and Dubrovinsky [72, 73] in their papers, in which the synthesis of stishovite-like structures with α -PbO and CaCl₂ structure is given. As mentioned, stishovite has been observed in meteorite impact material on the Earth. Typical in this respect are results described in several publications [74, 75].

Amorphization of Stishovite under Normal Pressure and at Elevated Temperatures

It was pointed out above, that stishovite, when heated up to $600 - 1000^{\circ}$ C disintegrates into amorphous silica; the product thus obtained has a structure analogous to the structure of the usual silica-glass obtained e.g. by the melting of quartz. This process has been thoroughly investigated in [75, 76, 77], mostly by employing DSC and DTA techniques. Further heating of the amorphous SiO₂ thus obtained leads to the

formation of quartz crystals (see Fig. 6.17). Here, it is to be especially mentioned that this is the interesting phenomenon of the phase transition of a crystal (stishovite) stable only under very high pressures to another crystal (cristobalite, quartz) through the intermediate structure of an amorphous solid: the silica-glass. It seems that the direct transformation of crystalline stishovite into crystalline coesite is impossible or very difficult to be realized because of the enormous structural change connected with this process. The change of stishovite to amorphous SiO₂ was investigated from its thermodynamic point of view in the already cited literature [25, 28].



Figure 6.17: Change of coesite (a) and stishovite (b) and (c) during heat-treatment at normal pressure. The heat released during the process is indicated as a parameter to the respective curve: (a, b) heating runs obtained at 5 K/min and (c) at 20 K/min. The first peak on (b, c) represents the transition of stishovite to amorphous SiO_2 (glass); the second peak the subsequent crystallization of cristobalite (according to [38]).

From a technical point of view the disintegration of stishovite into amorphous SiO₂ and quartz strongly limits its possible application at normal pressures as an extra hard oxide to temperatures only below 600 or 700°C. The mentioned stishovite transition is, however, very significant from a geochemical point of view, because it is a process taking place in the Earth's mantle. It is also of interest for all the possible changes stishovite \rightarrow quartz taking place in volcanic eruptions and in catastrophic meteorite impacts on the Earth's surface. These problems are analyzed in many publications in the geological literature.

6.4.7 Synthesis of the Amorphous Modifications of Silica

The synthesis of SiO_2 -glass via the direct melting of quartz is a well known process and needs no particular description here. Of greater technical significance are at present chemical methods of synthesis of superpure SiO_2 via the following gaseous reaction:

$$SiCl_4(g) + H_2O(g) \rightarrow SiO_2(s) + 4HCl(g)$$
.

It leads to a condensate called Suprasil and to similar products, which are obtained according to the above reaction in a voluminous cotton-like form. These products are, however, relatively expensive and their

technical application is restricted only to special cases.

The production of microsized SiO₂-glass spheres (ballotines) is also well-known: this is a process in which SiO₂-glass powder of the desired fraction is heated up above the melting point of silica on carbon soot powders. The synthesis of SiO₂ in amorphous form via sol-gel reaction is clear from Section 6.4.2, where the sol-gel synthesis of cristobalite is described. In this way super-clean SiO₂-glass can be obtained: however, again at a very high cost.

The Problem of Stishovite Glasses

It is not clear as yet, whether stishovite, melted e.g. at 80 kbar, could produce a 6-fold coordinated stishovite glass. In some respects this possibility is analogous to the attempts to synthesize beside "normal" graphite–like sp^2 structured vitreous carbons, also carbon glasses with a diamond-like sp^3 - structure.

The usual amorphous SiO₂-modifications synthesized and existing in stable form at normal pressure are built (as quartz, cristobalite, and coesite) of four coordinated SiO₂, i.e. out of SiO_{4/2}-tetrahedra. There have been suggestions in literature that similarly to water and liquid carbon a "poly-amorphism" of vitreous silica could be also expected if melting of this substance should proceed at extremely high pressures (in the stability region of stishovite (see Fig. 6.6)). In this sense, stishovite and maybe coesite-like liquids and glasses could be expected in the development of further synthesis of the amorphous modifications of SiO₂ (coesite glass: with a denser stochastic arrangement than the "normal" quartz glass). Up to now, no direct synthesis of these possible structural polymorphs of amorphous SiO₂ has been performed or reported in literature.

6.5 Thermodynamic Properties and the Structure of the SiO₂-Modifications

As mentioned in the introduction, SiO_2 is the major constituent of rock forming minerals in Earth's magmatic and metamorphic rocks. It is also an important component of sediments and soils. Bound in the form of silicates, SiO_2 accounts for approximately 75 wt% of the Earth's crust [19]. Free silica predominantly occurs in nature as quartz, which makes 12-14 wt% of the lithosphere. Quartz is the thermodynamically stable modification of silica at ambient pressure (see Figs. 6.1-6.6), occurring as one of the main products of slowly cooled silica rich magmas, granites, granodiorites and related rocks. Despite of its chemical simplicity SiO_2 displays as seen from above evidence a remarkable diversity of crystal structures. Apart from the ultra-high pressure modification, stishovite with ocathedrally coordinated silicon (see Fig. 6.7) and some artificial silica products where chains of edge sharing tetrahedral occur, all other crystal structures of silica are made from a three dimensional framework of corner sharing tetrahedra (see Fig. 6.7 and [16, 17]).

The non-crystalline silica phases existing and stable at normal pressure also consist of continuous random three-dimensional networks of corner sharing tetrahedra [14]. The Si-O-Si bond has a mixed character: about 50% ionic and 50% covalent. The bonding results in inter-tetrahedral Si-O-Si bonds which are bent in the range from 120 to 180° with a mean value of about 147° (see again Fig. 6.7). The strong bonds and the three dimensional connectivity of the SiO₄/₂ tetrahedrons are the reason for the following properties: high hardness of SiO₂-modifications (quartz has a Mohs hardness of 7, stishovite, however, approaches 10), the lack of good cleavage, for the high elasticity, the high melting point (approximately 2000 K of cristobalite), the high activation temperature of the quartz/cristobalite transformation (ca. 1300 K), and for the high glass transition temperature, T_g , of silica glass (1300 K). In contrast to these properties, the resistivity of silica to irradiation damage is relatively low.

Silica in all its forms is an insulator, a property that is utilized in the fabrication of silicon based microelectronic devices and in the semiconductor technique. The SiO_2 tetrahedra of the crystal modifications, stable at normal conditions can be considered as rigid structural units which remain almost unchanged upon thermal expansion or compression by high pressures. They can only rotate or tilt instead. The variability



Figure 6.18: Volume changes at the phase transitions of the SiO_2 modifications upon heating at normal pressure: (a) cristobalite, tridymite, coesite after [25]; (b) cristobalite, and c) quartz after Ullmann [19].

of the inter-tetrahedra Si-O-Si angles and the unrestricted torsion angle of connected tetrahedra account for the topological diversity of crystal structure of silica and of its high tendency for glass formation.

Quartz is, as already pointed out, the stable SiO₂-form under ambient conditions. Thermal expansion of α -quartz is relatively high $\alpha_{11} = 13.3 \cdot 10^{-6} \text{ K}^{-1}$, $\alpha_{33} = 7.1 \cdot 10^{-6} \text{ K}^{-1}$ and drops to even slightly negative values at the displacive phase transition to the high temperature β -quartz modification at 573°C (Fig. 6.18). The respective volume change ($\Delta V/V$) is seen on Fig. 6.18.

<u>**Cristobalite**</u> is the low pressure high temperature modification of silica. It persists as a metastable phase (α -cristobalite) at low temperatures. A displacive phase transition from the tetragonal low temperature α -cristobalite form to the cubic high temperature form (β -cristobalite) takes place at nearly 540 K. This transition is usually accepted to be of the first order (as witnessed by the ΔV change in Fig. 6.18a and b)

with a hysteresis of more than 20 K (at heating! – which is quite unusual) and a volume discontinuity of approximately 5%. However, there are also opinions expressed in literature that this α/β transition is of mixed first and second order. Our own experimental results, given here in some details in Section 6.4.3, are strongly supporting this second assumption. The crystal structure of β -cristobalite is a derivative structure of the diamond structural type, in which carbon is replaced by silicon and oxygen is located midway between neighboring Si-atoms. This network can be described as a stacking of parallel layers of six membered rings of tetrahedra, alternately pointing upwards and downwards.

Phase	Density, g cm ⁻³	Molar volume, cm ³ mol ⁻¹
Low quartz (α)	2.65	22.69
High quartz (β)	2.60	22.86
Low tridymite (α)	2.30	26.53
Middle tridymite (β 1)	2.30	-
High tridymite ($\beta 2$)	2.27	27.51
Low cristobalite (α)	2.32	25.74
High cristobalite (β)	2.21	27.40 *
Glass	2.20	27.31
Keatite	2.50	24.04
Coesite	3.01	20.64
Stishovite	4.35	14.01
Amorphous	-	30.04
Liquid **	?	27.20 (?)

Table 6.2: Volumetric properties of the SiO₂-phases (* at 623 K; ** at 1673 K, however, in fact as a glass).

A very particular property of α -cristobalite is that the low temperature form of SiO₂ exhibits a negative Poisson coefficient, i.e. at elongation the crystal is not thinned, but swelled. The high volume discontinuity at the transition of α/β -cristobalite leads to the generation of micro-cracks. Up to now the displacive cubic to tetragonal $\beta \rightarrow \alpha$ transition could not be suppressed by quenching, however, the structure of β cristobalite can be stabilized in the way of chemical stuffing and toughening as this was already discussed in the previous sections. Other compounds with α -cristobalite type of structure are the high temperature forms of AlPO₄ and GaPO₄ [57]. This is also used as an idea for possible toughening of the structure of α -cristobalite with the help of these compounds. At high temperatures β -cristobalite has a nearly zero value coefficient of thermal expansion. For more details in this direction we refer to both the mentioned paragraphs in the present review, as well as to the papers [44, 45] entirely devoted to face this problem.

Tridymite is formed in the range 1200 – 1800 K at ambient pressure, however, only in the presence of foreign ions (K⁺ or Na⁺), as already pointed out. Its crystal structure is a derivative of the hexagonal wurtzite type. With respect to the structural bonding requirements tridymite is much less balanced than cristobalite. As a consequence tridymite undergoes a cascade of displacive phase transitions (α , β , γ , see Fig. 6.1). In the present analysis, as far as we are interested only in modifications of pure SiO₂, no further discussion of tridymite and of these modifications is given.

<u>Coesite</u> is the high pressure modification of silica with the densest framework of $SiO_{4/2}$ -tetrahedra. It is composed out of four membered rings of tetrahedra which are linked in the form of chains of rings. Coesite exists as a metastable crystalline silica polymorph at normal ambient pressure and at temperatures up to 1300 K, then it is transformed to quartz (see Figs. 6.3 and 6.6).

<u>Stishovite</u> crystallizes in the rutile structural type with silicon atoms in the mentioned six fold oxygen coordination. The SiO_{6/3}-octahedra form chains by sharing opposite edges. The arrangements result in a very close packing of oxygen even though the Si-O-bonds are longer than in SiO₄ tetrahedra (see Fig. 6.7). Stishovite is about 43% denser than coesite. In the mentioned post-stishovite modifications with CaCl₂ or α -PbO₂ structure the highest density of packing of oxygen atoms, theoretically possible, seems to be



achieved. The change to the even denser $CaCl_2$ structure type is expected to involve a peculiar tilting of the octahedra.

Figure 6.19: Difference ΔG [in cal/mol] in the thermodynamic potential between the SiO₂-phases existing in stable or metastable equilibrium at normal pressure. This difference is expressed with respect to G_{298} of β -cristobalite (given as a zero ordinate). The numbers above or below the arrows indicate the temperatures for transition to or from β -cristobalite (data [13]).

Moreover, in mineralogical crystallographic literature several additional modifications of SiO_2 are discussed which are essential for the structure of chalcedones, chalcites and opals. Accounting for the purpose of the present analysis, we are not going into detail with respect to such varieties of crystalline and amorphous SiO_2 as moganite, melanophlogopite etc.

<u>Keatite</u> has a tetragonal framework of corner sharing $SiO_{4/2}$ -tetrahedra similar to the structure of β -spodumene (LiAlSi₂O₆). Another variety of SiO₂ is also known which is formed above 1500 K according to the reaction

$$H_2 + SiO_2 \rightarrow SiO + H_2O$$
.

This is in fact a silicon monoxide (SiO) rich modification.

In the mineralogical literature, glassy silica of natural occurrence is called lechatelierite. It originates from molten silica formed by lightning strikes (forming the so called fulgurites) or by meteoritic impacts on quartz sand or silica rocks. The volumetric properties of the SiO₂-modifications are summarized in Table 6.2. The thermodynamic properties of the SiO₂-modifications, as they are given in the literature [8, 9, 25, 26, 27] are reproduced here in Tables 6.3, 6.4 and 6.5. The heats and entropies of transition between the different phases, stable or metastable at normal pressure, are best illustrated according to [13] on Fig. 6.19, where the respective Gibbs free energies of transition are given with respect to cristobalite.

6.6 Solubility of the Different Modifications of SiO₂

6.6.1 General Thermodynamic Dependencies

The solubility of the different modifications of SiO_2 is considered and calculated in the present section, using available thermodynamic data, results of our previous investigations summarized in [14] and a classical

Phase Literature source	Enthalpy of formation J mol ⁻¹ [25]	$\begin{tabular}{c} Entropy & of \\ formation \\ J mol^{-1} K^{-1} \\ [25] \end{tabular}$	Enthalpy of formation J mol ⁻¹ [8]	Entropy of formation J mol ⁻¹ K ⁻¹ [8]	Enthalpy of formation J mol ⁻¹ [103]	$\begin{tabular}{c} Entropy & of \\ formation \\ J mol^{-1} K^{-1} \\ [103] \end{tabular}$
Low quartz (α)	-910.70	41.46	-910.57	41.80	-870.70	42.22
High quartz (β)	-910.50	41.70	-	-	-	-
Low tridymite (α)	-906.91	45.12	-	-	-	-
$\begin{array}{c} \text{Middle} \\ \text{tridymite} \\ (\beta 1) \end{array}$			-	-	-	-
High tridymite $(\beta 2)$	-		-	-	-	-
Low cristo- balite (α)	-906.03	46.06	-904.55	43.47	-859.41	43.26
High cristo- balite (β)			-907.39	42.64	-	-
Glass	-	-	-900.70	46.80 [13]	-	46.82
Keatite	-	-	-	-	-	-
Coesite	-906.90	40.50	-905.00	40.34	-	-
Stishovite	-864.00	29.50	-860.70	27.76	-	-
Liquid	-901.00 [25]	49.00	-	-	-	-
Amorphous (disperse)	-	-	-895.98	-	-	-

Table 6.3: Thermodynamic properties of the silica phases at 298 K and normal pressure. Note that the authors of [25] indicate in fact as liquid the SiO₂-glass.

approach, introduced by I. F. Schroeder into the physical chemistry of solutions many years ago – at the end of the 19-th century (see [78] and literature cited there).

In calculating the solubility of the different modifications of silica we assume, that the solubility of SiO_2 under hydrothermal conditions at temperature T can be described with sufficient accuracy according to the dependence

$$\log C_x \simeq -\frac{\Delta H_x^{298}}{2.3RT} + \frac{\Delta S_x^{298}}{2.3R} \,. \tag{6.1}$$

Here ΔH_x^{298} and ΔS_x^{298} indicate the molar enthalpy and the molar entropy of dissolution of the respective x-modification in the hydrothermal solution, respectively, and R is the universal gas constant. As known, hydrothermal SiO₂-solutions are much diluted: in pure water C_x corresponds to concentrations in the order of several ppm at temperatures of 300 – 500 K. In this case, the classical dissolution model of Schroeder can be employed according to which in Eq. (6.1)

$$\Delta H_x^{298} \cong \Delta H_{mx}^{298} \tag{6.2}$$

and

$$\Delta S_x^{298} \approx \Delta S_{mx}^{298} \tag{6.3}$$

Phase	Specific heats,	Specific heats,
Literature sources	$J \text{ mol}^{-1} \text{ K}^{-1}$ [25]	$J \text{ mol}^{-1} \text{ K}^{-1} [8]$
Low quartz (α)	44.59	44.39
High quartz (β)	44.59	-
Low tridymite (α)		-
Middle tridymite (β_1)	44.25	-
High tridymite (β_2)		-
Low cristobalite (α)	44.20	44.14
High cristobalite (β)	44.30	44.56
Glass	-	-
Keatite	-	-
Coesite	42.79	45.35
Stishovite	42.16	42.93
Liquid	44.22	-
Amorphous (disperse)	-	43.47
Low quartz (α)	-	-

Table 6.4: Specific heats of the SiO₂-phases at 298 K and normal pressure.

Table 6.5: Molar enthalpies and entropies of transition between the different phases of SiO_2 .

Transition	<i>T</i> , [8]	$\Delta H, [8]$	$\Delta S, [8]$	ΔH , [26]	ΔS, [26]	ΔH , [103]	Δ <i>S</i> , [103]
	К	J mol ⁻¹	$\begin{vmatrix} \mathbf{J} & \mathbf{mol}^{-1} \\ \mathbf{K}^{-1} \end{vmatrix}$	$J mol^{-1}$		$\mathbf{J} \mathbf{mol}^{-1}$	$\begin{array}{c c} \mathbf{J} \mathbf{mol}^{-1} \\ \mathbf{K}^{-1} \end{array}$
$\begin{array}{c} \alpha \text{-quartz} \rightarrow \\ \beta \text{-quartz} \end{array}$	846	0.63	0.75	-	-	0.75	-
$\begin{array}{c} \beta \text{-quartz} \rightarrow \\ \text{tridymite} \end{array}$	1140	0.50	0.46	-	-	-	-
$\begin{array}{c} \alpha \text{-quartz} \rightarrow \\ \text{melt} \end{array}$	1883	8.53	4.51	-	-	14.21	-
$\begin{array}{c} \alpha \text{-cristob.} \rightarrow \\ \beta \text{-cristobalite} \end{array}$	515	1.30	2.51	-	-	-	-
β -cristob. \rightarrow melt	2001	7.70	3.85	-	-	8.78	-
α -quartz \rightarrow cristobalite	-	-	-	2.68	-	-	-
α -quartz \rightarrow coesite	-	-	-	5.06	-	-	-
α -quartz \rightarrow silica glass	-	-	-	8.99	-	12.54	-
quartz \rightarrow stishovite	-	-	-	49.32	-	-	-
cristobalite → silica glass	-	-	-	6.31	-	-	-

6.6 Solubility of the Different Modifications of SiO₂

have to be substituted. Here ΔH_{mx} and ΔS_{mx} denote the molar enthalpy and entropy of melting of the considered SiO₂ modification, respectively. Thus, in correspondence with Schroeder's model of dissolution of very slightly soluble crystals [78], we assume that $\Delta H_m^{mix} \sim 0$ and $\Delta S_m^{mix} \sim 0$, where ΔH_m^{mix} and ΔS_m^{mix} are the molar enthalpy and the molar entropy of mixing corresponding to the dissolved quantity of the respective substance – in our case the considered silica polymorph. Because of the low solubility of SiO₂ both quantities (ΔH_m^{mix} and ΔS_m^{mix}) can be neglected, as indicated here. Accounting for the mentioned low concentrations of the SiO₂ modifications at hydrothermal conditions (in molar terms: $C = 10^{-4}$ to 10^{-6} mol 1^{-1}) this is a quite acceptable approximation.



Figure 6.20: Experimental data on the solubility C_x of simple inorganic glass-forming systems in coordinates $\log C_x$ vs. (1/T) according to Eq. (6.1). As a measure of the solubility the respective molar fraction C is used. Solubility of SiO₂ in water (from hydrothermal autoclave experiments); Solubility of Se in liquid CS₂; Solubility of As₂O₃ in water. In all cases with 1 is indicated the respective crystalline phase (quartz for SiO₂, monoclinic Se and cubic As₂O₃) and with 2 - the respective vitreous phase (from [14]).

From a more general kinetic and thermodynamic point of view, Eq. (6.1) with constant ΔH - and ΔS - values is a typical case of the so-called first approximation of Ulich [70] which is widely accepted as a most direct way in thermodynamical calculus of chemical reaction kinetics and solubility. This second approximation (the assumption of $\Delta H_m = \Delta H(T) = \text{const.}$ and $\Delta S_m = \Delta S(T) = \text{const.}$) is quite satisfactorily in our case at temperatures $T \ll T_m(\text{SiO}_2)$. It is shown experimentally that for temperatures lower than the critical temperature of H₂O, the log C vs. 1/T dependencies give in fact straight lines corresponding to Ulich's approximation. This is seen from the three cases of solutions of glass-forming systems, illustrated on Fig. 6.20. Schroeder's model of dissolution of crystals assumes that the process determining the dissolution of a slightly soluble crystal is the melting of its crystalline structure in order to reach the liquid state of the considered solution.

In order to determine the enthalpy and the entropy of melting indicated with Eqs. (6.1)-(6.3) we could use in the framework of Ulich's approximation the following estimate

$$\Delta H_{mx}^{298} \cong H_x^{298}(liquid) - H_x^{298}(solid)$$
,

i.e. we can assume that $\Delta H_{mx}(T_m) \sim \Delta H_x^{298}$. Under "solid" in above approximations we could include also the enthalpy of dissolution of the respective vitreous modifications of SiO₂ or of any other solute. However, as a rule we do not know the respective melting enthalpies and entropies of the SiO₂ modifications. This is so, because of the extremely high temperatures of melting of cristobalite (approaching 2000 K and even the calculated temperature of melting of quartz is ~ 1880 K). Usually are known only the differences between the enthalpies ΔH_g and the entropies ΔS_g between the SiO₂ glass and the respective crystal modification because these quantities can be easily determined in any dissolution calorimeter operating with hydrofluoric acid as a solvent. This is why we decided to use two empirical dependencies known in glass science [14] according to which

$$\Delta H_g \cong \frac{1}{2} \Delta H_m , \qquad (6.4)$$

$$\Delta S_g \cong \frac{1}{3} \Delta S_m . \tag{6.5}$$

These two dependencies, proposed years ago by Tammann (1932) and by Gutzow (1971), are satisfactory fulfilled for more than 100 cases of glass-forming systems. This is why we decided to use them in a reverse way in order to estimate from the known values of ΔH_g and ΔS_g which can be found in reference literature [8, 9, 13] the values of ΔH_m and ΔS_m . However, in the case of SiO₂ even the standard values of ΔH_m and ΔS_m (i.e. the values extrapolated to 298 K) are not known for all modifications.



Figure 6.21: Molar entropy of formation S^{298} at 298 K of the SiO₂ modification in dependence of their density, ρ . Only the data for those cases are presented (as black points) for which in the reference literature [8, 9] the thermodynamic data are given (c.f. Tables 6.2 and 6.3). The dotted line presents the value of the entropy S^{298} of the melt according to Eq. (6.5). The straight line corresponds to Eq. (6.6) with the constants given there.

This is why we decided to find an easier way to predict the solubility of the different modifications of SiO₂ via Eqs. (6.1)-(6.5) by exploiting the simple fact that many properties of the SiO₂-modifications can be related to their density, ρ . From a more general standpoint such a dependence of ΔH_m and ΔS_m could be expected as far as both thermodynamic quantities are essentially configurational in their nature: they have to depend on the relative free volume of the respective crystal, determining its configurational properties. Especially in the case of melting entropy it could be expected (see [14]) that $\Delta S_m \sim R \ln(\Delta V_o)$ where



Figure 6.22: Molar enthalpy of formation H^{298} of the modifications of SiO₂ for which data are given in [8, 9] in dependence of the respective density, ρ . With a solid line the quadratic dependence (Eq. (6.8)) is drawn with the values of the constants given there. The horizontal dotted line presents the enthalpy H^{298} of the SiO₂ melt, using Eq. (6.4) with $\Delta H^{298} = H^{298}_{glass} - H^{298}_{cryst}$ in accordance with points 2 and 5 (presented by bold squares).

 ΔV_o is the difference in the relative free volumes V_o of the melt and of the respective crystal. Expanding the logarithm in above simple approximative dependence at $V_o < 1$, we could even expect that

$$\Delta S_x^{298} = a_o + b\rho \,, \tag{6.6}$$

where a_o and b_o are constants. As seen from Fig. 6.21, such a dependence between the known ΔS_x^{298} – values and ρ gives an acceptable straight line for all the modifications, with $a_o = 61.9$ and $b_o = -7.2$, when ΔS is expressed in J mol⁻¹ K⁻¹. It is seen that this dependence in some respects corresponds to the already cited linear relation (see Fig. 6.14) between the refractive index, n, of the crystalline and of the amorphous modifications of SiO₂ and their density, ρ .

The enthalpy difference ΔH should be in general a more complicated function of the density: in fact the enthalpy according even to very simple mean field models described in [14] is a quadratic function of the free volume (e.g. $\Delta H \sim \text{const.}(1 - \rho)\rho$ as indicated in [14]). In fact as seen from Fig. 6.22

$$\Delta H_{mx}^{298} \simeq c_o + g\rho + h\rho^2 \tag{6.7}$$

with the values of the constants being equal to $c_o = -746$, g = -119.3, h = 21.6, when ΔH is expressed in kJ mol⁻¹ and ρ is given in g cm⁻³. Thus, we can write Eq. (6.1) in the form

$$\log C_x = -\frac{\Delta H_{mx}^{298}}{2.3RT} + \frac{\Delta S_{mx}^{298}}{2.3R}$$

$$= \frac{1}{2.3R} \left[-\left(\frac{H^{298}(liquid) - H^{298}(cryst)}{T}\right) + \left(S^{298}(liquid) - S^{298}(cryst)\right) \right].$$
(6.8)

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The respective enthalpy and entropy values can be taken, where known, from reference literature. In our case using Eqs. (6.6) and (6.7), we obtain from Eq. (6.8)

$$\log C_x = \frac{1}{2.3R} \left[-(A_0 - g\rho - h\rho^2) \frac{1}{T} + B_0 - b\rho \right] \,. \tag{6.9}$$

Here A_0 and B_0 are constants depending on the units in which C_x is expressed.

When we know the solubility and the respective $\log C$ vs. (1/T) line of one of the modifications (e.g. for x = 1), the solubility ratio with another substance (x = 2) can be expressed via the following dependence

$$\log\left(\frac{C_1}{C_2}\right) = \frac{1}{2.3R} \left[-\frac{g\left(\rho_1 - \rho_2\right) + \left(\rho_1 - \rho_2\right)^2 h}{T} + b\left(\rho_1 - \rho_2\right) \right] .$$
(6.10)

In a more condensed form the above expression can be written as

$$\log\left(\frac{C_1}{C_2}\right) = -\frac{(\rho_1 - \rho_2)}{2.3R} \left[\frac{g + (\rho_1 - \rho_2)h}{T} - b\right] .$$
(6.11)

In this way by knowing the solubility curve of one of the modifications of SiO₂ we can calculate using above described simple formalism the solubility curve of any other of the SiO₂-modifications with a known density, ρ .

In the respective calculations performed in the next paragraph we construct the solubility curves of all the SiO_2 modifications using the van Lier dependence (see Iler's book [3]). According to this relation from room temperature to the critical point of water the solubility of quartz is expressed via

$$\log C_{quartz} = 0.51 - \frac{1162}{T} . \tag{6.12}$$

In this way using Eq. (6.12) for C_{quartz} we constructed Fig. 6.23 presented in the next section for all other modifications of SiO₂. By accepting Eq. (6.12) as a sufficiently good approximation for the solubility data of quartz at hydrothermal conditions, we change in fact the value of the right-hand side additive member in Eqs. (6.1), (6.8) and (6.11) to $\left[\left(\Delta S_x^{298}/2.3R\right) + \text{const.}\right]$. Here the value of the constant depends on the dimensions used in expressing C_x .

6.6.2 Solubility Diagram of SiO₂. Ostwald's Rule of Stages

We constructed the solubility diagram of SiO₂ shown on Fig. 6.23 using Figs. 6.21 and 6.22, which represent the S^{298} vs. ρ and the H^{298} vs. ρ dependencies. In doing so we first introduced into both Figs. 6.21 and 6.22 the values of S^{298} (liquid) and H^{298} (liquid) as

$$S^{298}(liquid) = S^{298}(quartz) + 3\Delta S_q^{298}$$
(6.13)

and

$$H^{298}(liquid) = H^{298}(quartz) + 2\Delta H_q$$
 (6.14)

according to Eqs. (6.4) and (6.5). In this way taking

$$S^{298}(quartz) = 56.8 \,\mathrm{Jmol}^{-1} \mathrm{K}^{-1} \;, \qquad H^{298}(liquid) = -891 \,\mathrm{Jmol}^{-1}$$

and

$$\Delta S_g = 5 \operatorname{Jmol}^{-1} \mathrm{K}^{-1} , \qquad \Delta H_g = 9.87 \operatorname{Jmol}^{-1}$$

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Figure 6.23: The calculated solubility of all SiO₂ modifications (including tridymite) in water using the data from Figs. 6.21 and 6.22 and Eqs. (6.8) and (6.10) with the constants given there. In order to make possible qualitative comparison with the experimental data in Fig. 6.24, the solubility of quartz is calculated according to van Lier's dependence (Eq. (6.12)) and introduced as $C_1(1/T)$ into Eq. (6.10). Note that Eqs. (6.8) and (6.10) refer only to aqueous solutions below the critical point of water. In the insert the solubility of stishovite is presented calculated under the assumption that it is not transformed into SiO₂ glass at the hydrothermal experiment. Note the positive slope of the log C vs. (1/T) dependence for stishovite.

(c.f. Table 6.6), we obtain

$$H^{298}(liquid) = -895 \,\mathrm{Jmol}^{-1}$$
, $S^{298}(liquid) = 56.8 \,\mathrm{Jmol}^{-1} \mathrm{K}^{-1}$.

In order to compare our thus calculated diagram with existing experimental data we used further on (as already pointed out) for the solubility of quartz the equation of van Lier, Eq. (6.12) in which the solubility C is expressed in ppm. On Fig. 6.24 is given the known data for the solubility of several different modifications of SiO₂, stable at normal pressure, as they are summarized in the book of Iler [3]. In this figure are shown results not only for temperatures below the critical point of water (647 K) but also such corresponding to solubility above the critical point (see the solubility data on the figure below the left-hand maximum). As seen our schematic construction on Fig. 6.23 is in satisfactory agreement with existing experimental data given on Fig. 6.24 as compiled by Iler [3] for the solubility of quartz, cristobalite and vitreous SiO₂. For each of the SiO₂ modifications we constructed the respective log C vs. 1/T straight line in order to determine the values of $\Delta H_x^{298} = H^{298}(\text{liquid}) - H_x^{298}$ and $\Delta S_x^{298} = S^{298}(\text{liquid}) - S_x^{208}$ in Eq. (6.1). It is seen that from vitreous SiO₂ to coesite the log C vs. 1/T solid lines follow the expected course, using the H and S values given in Figs. 6.21 and 6.22.

With respect to its solubility, stishovite takes a very particular position. If this SiO₂-modification could

Table 6.6: Peer values of the thermodynamic properties at 298 K and normal pressure of the phases of silica used in the calculation of the solubility at hydrothermal conditions: ^a Data according to Glushko et al. [8] compared and corrected employing the data of Swami and Saxena [25]; ^b H₂₉₈ (liquid) calculated as H₂₉₈ (quartz) + ΔH_m^{298} (quartz) and S_{298} (liquid) calculated as S_{298} (quartz) + ΔS_m^{298} (quartz); ^c ΔH_m and ΔS_m were calculated according to known empirical dependencies like $\Delta H_g = (1/2)\Delta H_m$ and $\Delta S_g = (1/3)\Delta S_m$; ^{d,e}) estimates given by Glushko et al. [8].

Phases and	Enthalpy of formation ^(a) ,	Entropy of formation ^(a) ,
phase transitions	H, J mol $^{-1}$	S, J mol $^{-1}$ K $^{-1}$
Liquid ^b	-890.83	56.80
Amorphous (disperse)	-896.00	22.74
Glass	-900.70	46.80
High cristobalite (β)	-907.39	42.64
Low cristobalite (α)	-904.55	43.47
Low quartz (α)	-910.57	41.80
High quartz (β)	-	-
Coesite	-905.00	40.34
Stishovite	-860.70	27.76
Phase transition	Enthalpy of change ^(d) ,	Entropy of change ^(e) ,
	Δ H, J mol ⁻¹	Δ S, J mol ⁻¹ K ⁻¹
Melting of low quartz (α) ^(c)	19.74	15.00
Glass transition \rightarrow	9.87	5.00
low quartz (α)		
Melting of high cristobalite (β)	(7.69)	(3.85)
Glass transition \rightarrow	-	-
high cristobalite (β)		

exist at pressures of the order of 300 - 400 bars and temperatures up to 800 K at hydrothermal conditions, its solubility would be many times higher than that of glassy SiO₂. Accounting for the particular six fold symmetry SiO_{6/3} structure of stishovite and the extremely low values of its entropy and high value of its enthalpy at 298 K, the solubility of stishovite in the coordinates of Fig. 6.23 would be represented by a straight line as it is given in the insert of this figure. However, as already mentioned stishovite decomposes rapidly at elevated temperatures and low pressures (i.e. outside its field of stable existence): it forms SiO₂ glass (see [75, 76, 77] and Fig. 6.17). In this way it seems impossible to measure at "normal" pressures the real solubility of stishovite obtained at hydrothermal synthesis in "normal" autoclaves (i.e. not at ultra-high pressures).

A similar situation although not so drastic is also to be expected with respect to coesite. The latter also decomposes outside its stability region (see the phase diagram on Fig. 6.6). At the conditions of "normal" autoclave synthesis it could be expected that coesite should grow in the presence of amorphous or glassy SiO_2 as all other modifications. However, in considering further applications of coesite it should be remembered that it decomposes rapidly at normal pressure when heated above 1300 K.

The SiO₂ diagram we constructed and show on Fig. 6.23 illustrates that glassy or any other amorphous form of SiO₂ could be used as a precursor phase in the isothermal hydrothermal synthesis of all other modifications of SiO₂ except stishovite. Accounting for the already cited results on the synthesis of poststishovite modifications of SiO₂ (of the α -PbO₂ and CaCl₂ type) they should have even higher values of H^{298} and lower S^{298} -values when compared with the respective thermodynamic properties of stishovite. Hence, it could be expected that log C vs. 1/T-curves for these modifications should lie higher than that of stishovite and should also have a positive slope (see the insert on Fig. 6.23). Above summarized findings can be of distinct significance for the industrial production of any SiO₂ crystal modification for which relatively cheap amorphous (i. e. glassy) SiO₂ is obtained as a technological residual product with sufficient purity.


Figure 6.24: Hydrothermal solubility of the SiO₂ modifications according to data compiled by Iler [3]. Above the critical point of water (574.4 K) the log C vs. (1/T) dependence changes its slope. With different letters are indicated Quartz: A, Van Lier equation (dashed line); B, Morey; C, Morey - 1000 bars; D, Willey - in sea water; E, Mackenzie and Gees; F, Morey, Fournier and Rowe. Cristobalite: G, Fournier and Rowe. Amorphous: H, Stöber; I, Elmer and Nordberg; J, Lagerström, in 0.5 M NaClO₄; K, Willey; L, Jones and Pytkowicz; M, Goto; N, Okkerse; O, Jorgensen, in 1.0 M NaClO₄.

In considering the solubility and the relative stability of the different modifications of SiO_2 it is of interest to compare them with another system with many modifications – the carbon system. In making this comparison it is of interest to note that the metastable form of carbon – diamond which is thermodynamically stable only at high pressures (exceeding 50 kbar) begins to graphitize at normal pressures at temperatures exceeding 1600 K. In this way diamond can grow either under metastable conditions (i.e. at elevated temperatures and at normal pressure) or in solution (e.g. in metallic solutions like Ni-alloys). However, at temperatures lower than 1600 K sufficiently high attachment rate for diamond growth is to be expected. The same can be anticipated as it is experimentally verified in [31] at temperatures from 1000 to 1300 K also at gaseous exchange reactions in which diamond grows using vitreous carbon as a precursor of C-saturation (see evidence and literature, given in [31]).

The low stability of stishovite at normal pressures and elevated temperatures gives no possibility, so it seems, to grow or synthesize this SiO_2 – modification at metastable conditions (i.e. at normal pressure) either hydrothermally or using gaseous exchange reactions, as done with diamond. The foregoing results in

international literature and our experience summarized in Fig. 6.23 shows, however, that all other "normal" or high pressure modifications of SiO₂ could be hydrothermally synthesized or grown in a way analogous to the growth of diamond either by gaseous reactions or from solution using vitreous SiO₂ as precursor. The diagram on Fig. 6.23 gives also a direct possibility to determine the thermodynamic driving force $\Delta \mu_{1,2}$ and the relative supersaturation $\gamma_{1,2}$ for the synthesis of any of the SiO₂-modifications from any other crystal form of SiO₂ employing the well known formalism of the theory of crystal nucleation and growth [14, 79, 80, 81].

According to this formalism, in our case we have

$$\Delta \mu_{1,2} = RT \ln \left(\frac{C_1}{C_2}\right) \,, \tag{6.15}$$

where R is again the universal gas constant, T is the considered temperature at which the phase 1 with solubility C_1 is the precursor for the growth of the phase 2 with solubility C_2 . The relative supersaturation playing a cardinal role in determining nucleation and growth conditions is given as

$$\gamma_{1,2} = \frac{\Delta \mu_{1,2}}{RT} \,. \tag{6.16}$$

Thus, in our case we have

$$\gamma_{1,2} = \ln\left(\frac{C_1}{C_2}\right) = 2.3 \log\left(\frac{C_1}{C_2}\right) \approx 2.3 \left[\frac{C_1 - C_2}{C_2}\right]$$
 (6.17)

Now we can see that in the already cited experiments of Wooster [33] and Nacken [34] the relative supersaturation for quartz growing with a precursor substance amorphous SiO₂, relative supersaturations $(\gamma_{1,2} > 1)$ are obtained leading to nucleation. On the other hand, if we imagine a process of quartz synthesis at hydrothermal conditions and using cristobalite and not directly SiO₂-glass as a precursor substance the value of $\gamma_{1,2}$ is considerably lower guaranteeing at $\gamma_{1,2} < 1$ the smooth growth of quartz. On contrary, the synthesis of high dispersity quartz should require relative supersaturations $\gamma_{1,2} > 1$ approaching even $\gamma_{1,2} = 2 - 4$.

In this way, the synthesis of ideal single quartz crystals should be realized under other conditions when compared with the also interesting case of formation of micro- or even nano-sized quartz populations e.g. in using pre-crystallization in order to purify SiO₂ [38]. The same applies also for the crystallization of cristobalite. The sequence of straight lines plotted on Fig. 6.23 gives in fact the sequence of supersaturation or relative supersaturations using Eqs. (6.15), (6.17) and the respective $\ln(C_1/C_2)$ data for chosen T. However, the real sequence of formation of the different SiO₂-modifications should be governed not directly by the thermodynamics of nucleation (i.e. by the $\gamma_{1,2}$ values) but by the kinetics of these processes, i.e. by kinetic restrictions and recommendations following from Ostwald's Rule of Stages [14, 81, 82, 83, 84]. According to this rule at a given supersaturation $\gamma_{1,2}$, not the formation of the thermodynamically most stable phase is to be expected as the first precipitate as indicated by Fig. 6.23 but in another sequence, as it is given by the contemporary formulation of Ostwald's Rule of Stages. It says in these formulations, that nucleation is being determined from the phase which formation is kinetically most favorable. Thus, in most cases of condensation from vapor phase the initially formed phase is not the most stable one but an intermediate metastable liquid phase, which afterwards transforms into the thermodynamically more stable crystalline condensate.

The kinetic interpretation of Ostwald's Rule of Stages was initially proposed by Stranski and Totomanov [83] and was then further developed in a series of publications by Gutzow and Avramov [84] and Gutzow, Schmelzer and Möller [14, 84, 85, 86]. Remaining in the framework of classical theory of nucleation, it can be derived as done in [14, 84] that the fulfillment of Ostwald's Rule of Stages, i.e. the formation of the metastable phase f from an initial supersaturated phase i will then take place instead of the formation of the stable phase c from i, when the inequality

$$\left(\frac{\phi_{i,c}}{\phi_{i,f}}\right) \left(\frac{\sigma_{i,c}}{\sigma_{i,f}}\right)^3 \left(\frac{V_c}{V_f}\right)^2 > \left(\frac{\Delta\mu_{(i\to c)}}{\Delta\mu_{(i\to f)}}\right)^2 > 1$$
(6.18)

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is fulfilled. Here $\mu_{(i \to c)}$ and $\mu_{(i \to f)}$ indicate the thermodynamic driving forces, the supersaturations, determining the change from the initial phase *i* into either the metastable phase *f* or into the stable phase *c*. With σ_{if} , $\sigma_{i,c}$ and σ_{if} are denoted the interfacial energies at the i-phase/c-phase and i-phase/f-phase interfaces, respectively. With the symbols $\phi_{i,c}$ and $\phi_{i,f}$ are indicated the nucleation activities of eventually introduced active nucleation cores favoring the formation either of the metastable phase *f* or of the stable phase *c*.

The inequality Eq. (6.18) is easily derived taking into account that according to the classical theory of nucleation, the rate, J, of nucleation of a given phase is determined via

$$J = \text{const}_1 N_i Z_i \cdot \exp\left[-\frac{\Delta G_{i \to x}}{RT}\right] , \qquad (6.19)$$

where Z_i is the impingement rate of ambient phase molecules to the growing critical clusters of the newly formed phase x, $\Delta G_{i \to x}$ is the nucleation barrier in the formation of this critical cluster and N_i is the number of molecules i per cubic centimeter of the ambient phase. The thermodynamic barrier $\Delta G_{i\to x}$ is called in the theory of nucleation the nucleation work and it is written in a spherical shape approximation for the critical cluster as

$$\Delta G = \frac{4\pi \sigma_{i,x}^3 V_x^2}{3\Delta \mu_{i,x}} \Phi_{i,x} .$$
(6.20)

In all above given formulas V_x (or V_f , and V_c) indicates the molar volume of the respective phases.

Now, in following the ideas of Stranski and Totomanov in giving a kinetic explanation for Ostwald's Rule of Stages we have to compare at a logarithmic scale the rates $J_{i,f}$ and $J_{i,c}$ assuming an equal impingement rate Z_i in both cases. From Eqs. (6.19), (6.20) we thus arrive directly at Eq. (6.18). In considering the applicability of Eq. (6.18) we have to know σ_{ix} for both phases. This is not so easy to be done and here in developments given by Gutzow and Schmelzer [14] the formula of Stefan, Skapski, Turnbull is used, according to which the specific interfacial energy at the *ix* interface can be estimated via

$$\sigma_{i,x} = \alpha_0 \frac{\Delta H_{i,x}}{N_A^{1/3} V_x^{2/3}} , \qquad (6.21)$$

where ΔH_{ix} is the respective change of enthalpy when going from the *i* to the *x* phase, N_A is Avogadro's number and V_x is the already introduced value of the molar volume of the newly formed phase.

Thus into Eq. (6.18) can be introduced instead of the interfacial energy, the respective values of the molar enthalpy of change $\Delta H_{i,x}$ upon the corresponding phase formation or the respective entropies $\Delta S_{i,x}$ ($\Delta H_{i,x} = \Delta S_{i,x}T_x$). In this way, the inequality Eq. (6.18) can be transformed (as done by Gutzow, Dobreva and Schmelzer [85]) into dependencies, stating that under given conditions, usually out of the initial phase *i* this phase will be formed from two or more possible phases which having the nearest structural resemblance with the initial phase. Using such a line of ideas and possible computations, Fig. 6.23 can be transformed from a thermodynamic picture into a kinetic scheme giving the way, the probability and the paths in which from one phase *i* the desired phase *f* or *c* or any other one can be predominantly formed.

We have also to mention here that according to the investigations performed in [87] the formation of cristobalite is observed in the presence of Cu or Au nucleating cores of micrometric dimensions. In this sense, Eq. (6.18) gives also possibilities to induce the formation of different phases by introducing nucleation active cores favoring the formation either of the c or of the f-phase. The nucleation activity of different substances and especially of noble metals is analyzed in details in [88].

6.6.3 Size Effects in the Solubility of SiO₂

According to a well known formula of the classical thermodynamic theory of nucleation, the formula of Thomson-Gibbs, the radius r of the critical cluster can be expressed as

$$r = \frac{2\sigma_{i,x}V_m}{\Delta\mu} . \tag{6.22}$$

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Thus, the solubility C_r of a phase x of radius, r, when compared with its solubility C_{∞} of sufficiently large crystallites can be given by $\Delta \mu_r$, where

$$\Delta \mu_r = RT \ln \left(\frac{C_r}{C_\infty}\right) \,. \tag{6.23}$$

Thus from Eq. (6.22) it follows that at T = const. the solubility C changes with r, as

$$\ln C_r = \frac{2\sigma_{i,x}V_x}{RT} \frac{1}{r} + \ln C_{\infty} .$$
(6.24)

By adopting again the equation of Stefan-Skapski-Turnbull, Eq. (6.21) and accounting for the simple relation

$$\left(\frac{V_x}{N_A}\right)^{1/3} \cong d_{o,x} , \qquad (6.25)$$

where d_{ox} is the mean intermolecular distance in the phase x, we can write

$$\ln\left(\frac{C}{C_0}\right) \cong 2\alpha_0 \frac{\Delta S_{m,x}}{R} \frac{T_{m,x}}{T} d_{ox} \frac{1}{r} .$$
(6.26)

Thus, from known values of the entropy $\Delta S_{m,x}$ of dissolution, of the melting point $T_{m,x}$ and of the intermolecular distance $d_{o,x}$ of the phase x, we can determine α_0 from latter relation or directly via Eq. (6.21).



Figure 6.25: Solubility of amorphous nano-grained SiO₂ at 25°C in dependence on mean particle diameter.

In Iler's book [3] is given the size dependence of the solubility of amorphous (or glassy) SiO₂ in hydrothermal solutions at 25°C at pH-values ~ 8. In coordinates $\log C_r$ vs. reciprocal particle diameter the experimental data give a straight line with a slope of $1.5 \cdot 10^{-7}$ cm⁻¹ (see Figs. 6.25 and 6.26). This gives with Eq. (6.26) at $\alpha_0 = 0.5$ for $\Delta S_g/R$ a value of 0.4. This is a satisfactory value when compared with the value of ΔS_g for quartz glass given in Table 6.6, according to which $\Delta S_g/R = 0.6$. It is evident that a change of α_0 by 20% would give the expected value of $(\Delta S_g/R)$ obtained experimentally. Expressing ΔS_m through the well known dependence $\Delta H_m = \Delta S_m T_m$ we can introduce in Eq. (6.26) $\Delta H_{m,x}$ when this quantity is known from direct experimental observations. From the slope of the log C vs. 1/r dependence in Fig. 6.26 a value of $155 \cdot 10^{-3}$ J m⁻¹ is obtained for the specific surface energy $\sigma_{i,x}$ at the

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Figure 6.26: Experimental data on the solubility of amorphous SiO_2 vs. the reciprocal particle diameter according to Eq. (6.26). Data in Figs. 6.25 and 6.26 are taken from Iler [3].

 SiO_2 glass/aqueous solution interface. Comparing this value with the data from solubility experiments with various substances it can be claimed that the classical theory of nucleation as in many other cases gives nearly satisfactory results when the processes of nucleation are treated in the framework of its capillary approximation.

In this way, the results on the size dependence of the solubility of amorphous quartz indicate that the treatment of the precipitation kinetics in terms of Ostwald's Rule of Stages, introduced in the framework of the classical theory of nucleation, could also give satisfactory results – at least appropriate for initial technical use.

6.6.4 Possibilities of SiO₂-Nucleation and Growth at Hydrothermal Conditions and Their Technological Aspects

In the foregoing Section 6.6.3 we discussed the possibilities to synthesize by a process of nucleation and growth different modifications of SiO₂ using quartz glass as a precursor phase in the autoclave. More convenient could be the use of cristobalite as a precursor, e.g. in the growth of quartz crystals. According to the general conclusions of the classical nucleation theory, growth could be expected in the cases when the relative supersaturation $\gamma_{1,2}$ is limited in the range from 1.5 or even down to 0.1 - 0.2. Under such conditions, especially at $\gamma_{1,2} < 1$, smooth growth of single crystals could be expected. Our solubility diagram (Fig. 6.23) shows that such a possibility exists firstly for the growth of α -cristobalite single crystals out of SiO₂ glass. Even more interesting could be the possibility of growing directly β -cristobalite by using SiO₂ glass as a precursor. According to Fig. 6.23 it is obvious that the growth of introduced β -cristobalite micro-crystals could be performed smoothly at relatively low temperatures. There are indications in literature [38] that in fact by changing the temperature the hydrothermal synthesis of the different modifications of cristobalite is possible. Our diagram gives the possibilities to discuss and initiate experiments in which at relatively low temperatures hydrothermal growth of large cubic β -cristobalite crystals could be realized if in the solution appropriate cations stabilizing the high temperature form of cristobalite are added. There are in the literature proposals to stabilize hydrothermally grown β -cristobalite by introducing sodium and aluminum cations into the hydrothermal solution. It is interesting to investigate the possibility of cristobalite hydrothermal synthesis by using instead of NaOH-solutions, Ca(OH)₂-solutions when the presence of alkali cations has to be excluded. This would require a particular study of the solubility and of the precipitation of $Ca(OH)_2$ under hydrothermal conditions. It could give a new way of toughening of β -cristobalite with Ca^{2+} and Al^{3+} in hydrothermal solutions. Another interesting possibility following from our results summarized on Fig. 6.23 is the possibility to nucleate at high temperatures and grow large coesite crystals at hydrothermal conditions.



Figure 6.27: Solubility of phenolphtaleine in water as a crystal (1) and as a glass (2) according to measurements of Grantscharova and Gutzow [14, 89]. With T_m is indicated the melting point of phenolphtaleine and with T_g , its glass transition temperature.



Figure 6.28: Dissolution curves of phenolphtaleine in water at two temperatures: at $22^{\circ}C$ (the upper two curves) and at $13^{\circ}C$ (the bottom two curves) for crystalline (1) and for vitreous (2) phenolphtaleine.

In foregoing model experiments by Grantscharova and Gutzow [89, 90] growth experiments from aqueous solutions of a model glass-forming system, phenolphthalein, were performed. On Fig. 6.27 the solubility of phenolphthalein is given as a glass and as a crystal in the temperature range from 10 to approximately 100°C. The respective solubilities were determined by analyzing the kinetics of dissolution of both crystalline and glassy phenolphthalein as shown on Fig. 6.28. Such experiments carried out with the different

6.6 Solubility of the Different Modifications of SiO₂

modifications of SiO₂ could give more precise solubility values than those calculated or given in literature and leading to pictures like Figs. 6.20 or 6.24. Usually, in existing measurements the solubility is determined under static conditions and not by kinetic experiments as done on Fig. 6.28. With the phenolphthalein/water system we performed (see [89, 90]) growth experiments under isothermal conditions, demonstrating the smooth growth of phenolphthalein single crystals using phenolphthalein glass as a precursor. In the experiments of Wooster and Nacken [33, 34] quartz glass was also used as a precursor. However, as seen on Fig. 6.23 relatively high supersaturations $\gamma_{1,2}$ are to be expected in the temperature interval (300-400 K) used by these authors and they resulted as already mentioned in the nucleation of many small quartz crystallites and not in the smooth growth of large quartz single crystals.



Figure 6.29: Two possibilities to use glass as a precursor for crystal growth at isothermal conditions: a) ampoule growth of diamond (2) from vitreous carbon (1) using gas transport reaction at 1050° C (here: $C + S_2 \rightarrow CS_2$; see Gutzow et al. [31]). b) The growth of crystalline phenolphtaleine (2) from glassy phenolphtaleine (1) in aqueous solution (Grantscharova and Gutzow, [14, 63]).

The hydrothermal growth of β - and α -cristobalite crystals to relatively large dimensions could be of particular scientific and technological interest. In a number of present day investigations [91, 92] it is demonstrated, that α -cristobalite exhibits the unusual property of becoming wider when stretched and thinner when compressed: thus it is a material with negative Poisson ratio. Such auxetic properties of larger crystals could be of exceptional significance in instrument making industry. From Fig. 6.23 is also evident the possibility of growth of coesite at hydrothermal conditions using β -cristobalite as a precursor, guaranteeing very low supersaturations and smooth growth even at high temperatures.

In our foregoing experimental investigations on the solubility of vitreous phenolphthalein and of the crystalline modification of the same substance we also constructed a simple apparatus shown on Fig. 6.29b. On Fig. 6.29a is also seen the principal scheme of the growth of diamond single crystals at isothermal conditions using vitreous carbon as a precursor and the gaseous reactions as the carrier agent. In both cases (phenolphthalein and diamond) glass was used as a precursor for the growth of single crystals either in solution or at chemical transport reaction. In the case of diamond, these transport reactions involved CCl_4 , CS_2 or CH_4 and the respective chemical equilibria [31].

The hydrothermal growth of SiO_2 in closed volumes supplies us with an exceptional possibility to regulate the pressure resulting in the autoclave by the relative filling of its volume. On Fig. 6.10 is given the pressure obtained in an autoclave by its filling to different degrees and heating the system to different temperatures. On Fig. 6.9 this dependence is enlarged to include the known solubilities of SiO_2 beginning from room temperatures and ending at temperatures higher than the critical point of water. In this sense hydrothermal synthesis gives extraordinary possibilities of regulating temperature, pressure and solubility in the autoclave in a simple way within wide limits.

In a recent publication, the construction of a simple camera autoclave (Fig. 6.15) with relatively small volume was reported in which the growth of stishovite crystals up to dimensions of several millimeters was

realized (see Fig. 6.16). The same device could be also used for coesite growth. Stishovite according to a number of literature sources is one of the hardest materials ever known and the hardest oxide ever synthesized. In this respect the synthesis of stishovite single crystals could bring materials with exceptional properties, however, at prices nearly equal or even surpassing the price of diamond and cubic BN. In comparing the properties of stishovite and coesite as single crystals and the possibilities for their metastable growth (i.e. at pressures outside the stability pressure region of both crystals) it should be remembered that stishovite and coesite decompose to SiO₂ glass at temperatures approaching $600 - 800^{\circ}$ C and 1300° C, respectively.

6.7 Mineral and Natural Resources of the Silica Modifications

Silicon dioxide is the major constituent of rock forming minerals and an important component of sediments and soils. In the form of silicates it accounts for 75 wt% of the Earth's crust. It is also a constituent of many plants in a measurable quantity.

6.7.1 The Mineral Resources of Quartz

Quartz in its low temperature α -modification forms 12 wt% of the Earth's lithosphere and is after feldspars the most widely spread mineral on the Earth. At hydrothermal conditions in the Earth crust single crystals are formed, reaching up to 1.5 and 2 m in size. The SiO₂- tetrahedra in quartz are arranged along its trigonal *c*-axis. Two types can be distinguished in this arrangement: left- and right-handed and this property results in the optical activity of quartz with a considerable polarization power for visible light. The right- and lefthanded crystals are mirror images of each other. The two-fold symmetry axis perpendicular to the screw axis is polar and mechanical stress along the axis produces a direct piezo-electric effect. The reverse effect is utilized in oscillatory devices. Mainly due to this property, high quantities of quartz crystals are produced most often hydrothermally. The thermal expansion of α -quartz is high (13.3.10⁻⁶ K⁻¹) and drops to even slightly negative values after the displacive transition into its high temperature modification, into β -quartz.

Many special, trade and trivial names exist for silica rocks often with various meanings and imprecise definitions. Different classifications are accordingly given in literature. Silica rocks typically contain up to more than 90 wt% SiO₂. Ordinary sandstones contain only about 65 wt% silica, mainly as quartz grains. The rest is matrix and cement (feldspars, CaCO₃, mica, clay, etc.). Different transformation processes occur in silica rocks with increasing the burial depths in the Earth's crust which results in a reduction of porosity and water content. Thus, quartz can be solidified to quartz sandstone and grades by crystallization into quartzites under pressure at elevated temperatures. Similarly, non-crystalline biogenic silica remnants of diatoms, radiolarian etc. are transformed under compression into porcelanite and finally to chert. When the biogenic origin is known these rocks are designated as diatomite, radiolarite or spiculite. Lidite is a rock formed from the remnants of radiolarites from the Paleozoic era. A great number of different semicrystalline or quasi-amorphous minerals are known and described in mineralogy and geology.

Of technical importance for all silicate industries, and in particular for the glass, ceramic and porcelain industries are high quality (especially: free of iron oxides) quartz-sand deposits like the quartz-sand fields in Hoehenbocka or Weferlingen in Germany. Of global significance for the production of high-purity quartz single crystals are the huge quartz deposits on Madagascar, in Brazil and in the Ural Mountains: in most cases they are the result of processes of growth under natural hydrothermal conditions. In several places (also in Europe) venous quartz formations of magmatic origin are also in technical utilization.

6.7.2 The Plant Resources of Silica

Of great significance in future developments may be also the SiO_2 content in organic residuals and especially in rice husks, bamboo, cocoa shells, oats, etc. There are several different methods to obtain and use the so called white ash of rice husk (i.e. the amorphous SiO_2 resulting from the oxidation heat treatment of rice husk). Micro- and nano-cristobalite crystalline phases are easily obtained at relatively low temperatures (of 850 - 950 °C) upon oxidation heat-treatment or directed pyrolysis. Taking into account that rice is a basic food of millions of people in the Asiatic regions of our world, rice husk can be considered as a possible natural source of SiO₂ of industrial importance.

Two points are of significance in this respect: First, the circumstance that a relatively great percentage of alkali oxides (either Na₂O or K₂O) are usually present in rice husks and any other natural product. Such impurities which some times form three or five percent of the mentioned white ash can be, however, easily washed out with mineral acids. Secondly, it is of importance that in plant silica heavy metals are to be found only in relatively low concentrations: the plants themselves decline to absorb oxides, toxic for their growth. The third essential point in possible plant silica production and purification is the circumstance that SiO₂ is contained in the plants structure in an amorphous nano- or micro-sized form and is obtained in the "white ashes" both as amorphous silica, or (in dependence of heat-treatment history and of dopants present) as α - or β -cristobalite. Plant silica is thus chemically very active and can be easily dissolved by mineral acids and can in this way be subjected to various purification procedures.

The present day status of the both scientifically, ecologically and technically very important problems of the state of SiO_2 in the plants, the processes of plant pyrolysis [93, 94, 95, 96], the possibility of formation and of directed synthesis of silicon carbides, of silica and of active carbons (all of them with possible industrial applications!) is treated in great details in international literature, an extract of which is given here with the mentioned papers and especially with [94]. It is also to be noted that the results obtained by one of the present authors with plant silica [97] and with the analysis of the respective processes of pyrolysis [98, 99] and of active silica crystallization initiated some of the developments, connected with the polymorphous transitions of cristobalite and amorphous SiO_2 , with quartz etc., described in more or less detail in the present review. It is also to be noted, that biological activities of the animal world (of worm populations [100]) and of enzymes [101] have been proposed as possible methods of degradation of rice husk waste products and their following transformation into more or less useful forms of silica and silicon compounds .

6.7.3 Industrial Waste Sources of Silica

Fly ashes from the chemical and metallurgical industry can also supply SiO₂ in a highly active form. However, here, contamination with toxic oxides and heavy metals can be a severe problem. It has only to be mentioned that the active amorphous phase formed out of plant SiO₂ is directly transformed into high temperature β -quartz, which, however, at low temperatures gives again α -cristobalite.

6.7.4 Coesite and Stishovite as Impactite Remnants

Coesite and stishovite which initially were artificially synthesized are not only found in impactite minerals at meteoritic craters like the great Arizona meteorite crater. Of greater significance is the experimentally verified geological fact, that in the depths of the Earth's crust quartz minerals are transformed into coesite and stishovite and thus these minerals are of exceptional significance in following, predicting and analyzing earthquakes and other processes in the Earth's crust.

6.8 Several Particularly Interesting Properties of the Silica Modifications

We would like to emphasize here finally several aspects on the properties of silica both in the form of its crystalline and amorphous modifications. Usually one thinks only about the properties of quartz and quartz sand and some of the already mentioned unusual properties of some of the modifications of SiO₂ are disregarded. They can be, however, of significance not only in technology and instrument production but

could be also of commercial interest. This is why we repeat here several of the properties we did already mention in the previous sections.

In order to reconsider the possible significance of SiO_2 materials in a new light, beginning with the most dense and most unusual modifications of SiO_2 , it should be repeated that stishovite and the two post-stishovite modifications are the hardest synthesized oxides up to now. Their hardness is surpassed only by cubic BN and by diamond. In comparing stishovite and post-stishovites with BN and diamond it should be, however, encountered that stishovite has a lower thermal stability than diamond under normal pressure: diamond can be used up to $1100 - 1200^{\circ}C$ while stishovite transforms into SiO_2 glass at temperatures beginning from $650 - 700^{\circ}C$. Nevertheless, it could be a very useful material for the production tools when only silicon and oxygen should be in contact with the material which has to be treated. The already mentioned hydrothermal synthesis at super-high pressures of stishovite could be maybe developed to an industrial scale.

Cristobalite in its high temperature β -form is the SiO₂ crystalline phase with the highest refractoriness: it could be used at temperatures above 1500°C. Moreover, β -cristobalite has a coefficient of thermal expansion at high temperatures which approaches zero and this gives additional perspectives to the employment of β -cristobalite as a major constituent in both glass-ceramic materials and – in the form of little appropriately preformed substrates etc. – in the high temperature electronic technique. Of particular significance is on the other side the circumstance that α -cristobalite has a negative Poisson ratio. This is a property α -cristobalite shares with only four or five inorganic substances. Materials, possessing such a property are extraordinary resistant against the impact of projectiles entering its structure even with a very high speed (e.g. bullets in a modern chain-plated armor). Many other applications of such auxetic materials are discussed in present day literature, partially mentioned above (see [91, 92]). It is interesting to note also, that only the low temperature α -modification of cristobalite possesses this property: in the α/β transition the high temperature β -cristobalite emerges without the auxetic properties of the α -modification. On the other side it is also to be noted that with quartz the reverse case is observed: here as already noted the high temperature β -quartz is slightly auxetic, while the low-temperature α -modification has a normal (positive) Poisson ratio.

Also into account has to be taken the chemical resistivity of cristobalite which makes this material a promising and competitive substance for the construction of high temperature refractory chemical resistant building material for chemical applications. The same applies also to β -cristobalite chemically stabilized in the already described way with CaO and Al₂O₃.

Silica in its amorphous form as a glass has exceptional applications because of its chemical inertness, temperature resistance (however only to $1000 - 1050^{\circ}$ C! Then, crystallization begins) and its extraordinary low coefficient of thermal expansion ($0.3 \cdot 10^{-6}$ K⁻¹). The properties of amorphous SiO₂ in disperse form, as it results e.g. from the oxidation heat treatment of natural plant products, are also well known and used in applications connected with absorption, etc.

6.9 General Discussion in Terms of Technical Perspectives

The foregoing sections give the possibility for several conclusions:

- 1. The most promising material (with exception of quartz glass) out of all possible modifications and forms of existence of SiO₂ is stabilized β -cristobalite. Its particular properties concerning the coefficient of thermal expansion, thermal stability, chemical stability makes this modification a very promising material with many applications. The results described in literature concerning its synthesis show that it can be synthesized in several quite different ways, any of them applicable for different purposes:
 - (a) The activated reaction sinter-crystallization approach of synthesis with the introduction of chemical stabilizers (CaO + Al₂O₃) developed recently by the authors of the present review shows that this method could lead (eventually combined with hot pressing) to the production of different technical parts.

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- (b) Results obtained with a combined sol-gel ceramic way of synthesis (the so-called "wet impregnation" method) could also be a promising method of developing objects even on a larger scale. This method could give additional perspectives because it requires lower temperatures of sintercrystallization.
- (c) As a method of direct formation of small dimension objects useful in high temperature electronics could be the direct sol-gel method of synthesis of chemically stabilized β -cristobalite described in one of the previous sections.
- (d) Cristobalite can be also synthesized by hydrothermal methods as this is demonstrated in literature and it could be produced in such a way as to give micro- or even nano-sized powders of β -cristobalite, stabilized, however, with alkaline oxides.
- 2. The hydrothermal method of synthesis can be used to produce in commercial quantity and in different forms and sizes not only quartz (as known for more than 50 years) but also cristobalite and coesite using either SiO_2 glass (in the synthesis of cristobalite, coesite and quartz) but also cristobalite for the synthesis of quartz. However, it has to be accounted for that in most applications the autoclave hydrothermal method works efficiently only in alkaline solutions: in this way only crystals with a measurable content of alkaline pollutants can be formed.
- 3. It should be of interest to develop methods of hydrothermal synthesis based either on pure aqueous solutions of SiO₂ (without any alkalizing additives) or on the development of hydrothermal methods of synthesis in which solutions with high pH-values could be formed by exploiting the basic character of CaO or other alkaline-earth oxides. Here, however, up to now no experimental evidence or theoretical considerations are known to the authors of this review.
- 4. Hydrothermal synthesis could be also considered as a method of purification of both quartz crystals and quartz micro- and nano-crystals, e.g. in synthesizing micro-quartz crystallites from either glassy SiO₂ or cristobalite as a precursor. Due to the small sizes of the micro-crystals, the number of included bubbles, containing initial solvent could be brought to a minimum. However, the alkaline solutions, with pH \sim 8-9, employed in present day hydrothermal synthesis could bring additional problems. Vitreous or any other form of amorphous SiO₂ can be more easily purified.
- 5. The synthesis of cristobalite as micro-disperse powders could give other possibilities for the method of production of quartz glass macro-tubes employing the plasma technique. Here, a role could play its density, which for β -cristobalite is nearly equal to this of quartz glass. This, however, should require chemically stabilized β -cristobalite to be used. This would bring CaO and Al₂O₃ into the quartz glass.
- 6. SiO₂ is a substance which, like carbon, exists in a great variety of modifications. Up to now only two of these forms quartz glass and quartz macro-crystals are implemented in industry. We hope that the theoretical predictions made for the water solubility of SiO₂ modifications reveal new perspectives for the synthesis and the future applications not only of the "common" ambient pressure forms of SiO₂ but also of the their "exotic" high pressure forms. The method of activated reaction sinter-crystallization synthesis of stabilized β -cristobalite glass-ceramics developed by the authors of this review opens the possibility for their economically profitable industrial production and many fields for their application.

In the last time, attempts have been made to use different "unusual" sources of SiO₂ for the synthesis of stabilized β -cristobalite glass-ceramics e.g. purified diatomite [102]. Here, the most important problem is to find effective, simple and affordable methods for the purification of similar biogenic resources of SiO₂. Lately, new possibilities were realized in this respect, namely in the purification of rice husk ashes considered as mentioned as a promising plant source of active silica. Since in these ashes SiO₂ is in amorphous nano- and micro-sized form it can be expected that the preparation of stabilized β -cristobalite glass-ceramics as well as of other SiO₂-containing materials could be realized at substantially lower temperatures and shorter heat-treatment times.

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7 Solid-State Transformations and the Thermal Conductivity of Solid Ethanol

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> Manche Männer bemühen sich lebenslang, das Wesen einer Frau zu verstehen. Andere befassen sich mit weniger schwierigen Dingen z.B. der Relativitätstheorie.

Albert Einstein

Abstract

New results of experimental low temperature investigations of the thermal conductivity of solid ethanol in various phases have been obtained at $T \ge 2$ K. The effect of annealing in the thermal conductivity of solid ethanol in the orientationally – ordered phase has been observed in a wide range of temperatures. This phase was obtained as a result of a first – order phase transition from an orientationally – disordered crystal of cubic structure. The temperature behavior of the thermal conductivity of the sample obtained at $T_{anneal} = 109$ K is similar to the dependence typical of an imperfect fine grained crystal of 1-butanol in the so-called "glacial" state. The thermal conductivity was observed to increase as the monoclinic lattice changed from a less stable phase to a more stable one. The growth may be due to the improved quality of the completely orientationally – ordered crystal.

7.1 Introduction

Pure ethanol is without doubt the most interesting object among molecular substances for investigations of thermal properties of one-component molecular solids with disordering. Solid ethanol at some conditions can have three metastable long-living states with molecular disorder in addition to the thermodynamically stable fully orientationally-ordered crystalline phase (FOC, monoclinic, Z=4, Pc): a structural glass (SG), an orientational glass (OG, bcc) and a crystal with orientational dynamic disorder (e.g. [1-6]). Hydrogen bonds afford a diversity of metastable states in the alcohols. In the condensed phases of alcohol the H-bond determines the behavior of all the molecules forcing them to fit into the linear chains. The chains are bonded by the van der Waals forces. The H-bonded chains play an important role in the local structure of any phase of condensed alcohol. The glass-formation process in alcohols is dependent on the force of the molecular dispersion interaction and the structural difference between the liquid and crystalline phases.

On fast cooling the normal liquid ethanol becomes supercooled and transforms into a structural glass below the glass transition temperature, T_g . Structural glass is an amorphous solid that can be obtained by cooling a liquid below the glass transition temperature, T_g , at a rate allowing no crystallization. At T_g the motion of molecules is frozen, and the formed molecular glass has neither translational nor orientational molecular ordering. Molecular glasses have been attracting special interest because some of them enable one recognizing the importance of orientational degrees of freedom in the dynamics of glasses [3-11].

The phase of orientational glass (OG) in solid ethanol is formed in molecular crystals at freezing of orientational disorder in cubic crystal structure (orientational glass-like transition). In [2-4, 12] was shown

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that the OG phase of ethanol is formed by cooling a metastable state of plastic crystal (i.e., crystal with rotational disorder, RPC). In ethanol the temperature of freezing is about the glass transition temperature T_g of supercooled liquid. Since these temperature regions coincide for the SG and OG states of ethanol, it is easy to compare the temperature dependencies of the thermal conductivity of these states within one temperature interval and see how the orientational degrees of freedom of molecules influence the heat transfer in a glassy state of alcohol.

At low temperatures the properties of structural glasses are essentially different from those of the corresponding completely ordered crystals. For example, the heat capacity is always higher and the thermal conductivity is always lower in glasses than in corresponding crystals. The thermal conductivity, $\kappa(T)$, of a glass exhibits a universal behavior and is weakly dependent on the structure or the chemical composition of a substance [13]. The temperature dependence of the thermal conductivity of a glass has three distinct regions: a low temperature region in which $\kappa(T)$ grows with temperature as $\kappa(T) \sim T^2$, a plateau in the interval T = 5 - 30 K and a region above $T_{plateau}$ in which $\kappa(T)$ continues to increase by a quasi-linear law.

According to recent data [10], ethanol glass is a special case in the mentioned series of glasses. It belongs to type II glasses which form an orientationally – disordered plastic phase. The investigations by the methods of calorimetry, Brillouin light scattering and X-ray diffraction have shown [12] that the phase diagram of solid ethyl alcohol under equilibrium vapor pressure is more complex than it was thought before. At least four types of different monoclinic structures (denoted as α , β , γ , and δ structure), which appear at different preparation conditions, can be separated in the orientationally – ordered phase having a monoclinic lattice with orientational long-range order. The metastable monoclinic state (α structure) is formed at solid-state transformations of cubic structure (RPC) to monoclinic structure.

In this study the thermal conductivities of the structural and orientational glasses of ethanol as well as the orientationally – ordered crystalline phase in the course of changing its monoclinic structure on approaching the thermodynamic equilibrium have been analyzed and compared.

7.2 Experimental Details

The thermal conductivity was measured under equilibrium vapor pressure by the steady-state potentiometric method using setup [14] (see Fig. 7.1). The sample container (1) is a stainless steel 40 mm long tube 22 mm in diameter with the wall thickness 0.3 mm, with a copper bottom (6) and cap (4). The container bottom was fixed in the cooled zone of the cryostat connected to a helium bath (10). Two copper wires 1 mm in diameter were passed through the container perpendicular to its axis, which permitted measurement of the average temperature along the isothermal plane running across the sample. At the outer surface of the container copper sockets were soldered to the wires to cartridge two temperature sensors (2, 3). The upper sensor (2) is a Cernox – SD resistance thermometer (Lake Shore Cryotronics, Inc.) measuring the temperature difference; the lower sensor (3) is a TSU2 resistance thermometer (VNIIFTRI) used to stabilize and control the temperature. Thermometer was used to measure the temperature along the sample with the heat flow on and off. The liquid ethanol sample was put in the container (1) of the measuring cell under He₄ gas flow. The helium gas was used to improve the heat exchange between the sample and the container. The container with the sample was vacuum-tight covered with the copper cap (4) and an indium ring. A heater was fixed on the container cap to generate a downward heat flow in the sample.

A vacuum jacket with a removable bottom part (cup) (15) separates the measuring cell from the outer helium bath (10). The upper part of the vacuum jacket is connected to the cup with an In-seeled flange (16). In the course of measurements of thermal conductivity the vacuum in the jacket was maintained at 10^{-5} - 10^{-4} Pa. Sample preparation and thermal conductivity measurements were completely automated including recording the thermal history parameters such as the temperatures registered by the upper and lower thermometers, the power of the sample heater, the current time, etc.

Liquid ethanol C_2H_5OH 96% (SWW 2442-90) produced by Polskie Odczynniki Chemiczne S. A. was purified up to 99,9% (according to chromatogram method) directly before the thermal conductivity mea-

7.2 Experimental Details



Figure 7.1: The scheme of low-part setup for measuring of the thermal conductivity samples: (1) is a sample container; (2) is a Cernox – SD resistance thermometer; (3) is a TSU-2 resistance thermometer; (4) is a copper cap with heater; (5) is an upper unit; (6) is a copper bottom (a cold zone, a thermal link); (7) is the thermal shield; (8) is the helium volume; (9) is the heat exchanger; (10) is a helium bath; (11) is a tube; (12) is the low-temperature faucet; (13) is the throttle with filter; (14) is the line of helium pump; (15) is a removable bottom part (cup) of a vacuum jacket; (16) is an In-seeled flange.

surement.

The different phases were prepared within the container using different cooling – heating cycles for the same sample and taking into account the thermal history. The processes of preparing different states of ethanol are explained in Fig. 7.2 [2, 5, 12]. The structural glass (route 1) was prepared by very fast cooling (above 50 K min⁻¹) of the room-temperature liquids through their glass transition regions to the boiling temperature of liquid N₂. Since the glass transition temperature T_g of C₂H₅OH is higher than the boiling point of nitrogen, the glass sample was prepared by immersing the container with the sample directly into liquid nitrogen. The measurements of thermal conductivity of structural glass were performed at gradually decreasing temperature. After reaching the lowest point of the experiment the measurement was continued at increasing temperature. Above T_g the glass sample transforms into a supercooled liquid (SCL). By further heating the SCL, a first-order phase transition into the plastic crystal (route 2, Fig. 7.2) irreversibly occurs around 105–110 K. The orientational glass (OG) phase was obtained on cooling a plastic crystal below the temperature of its transition to an orientationally-disordered phase. The thermal conductivity $\kappa(T)$ of the OG phase was measured first at a successively lowering temperature (down to 2 K) and then at an increasing temperature.

The moments of the liquid - plastic crystal and plastic crystal – orientational glass transitions show up as features in thermogram curves of sample preparation. The features of some heating and cooling curves are shown in Fig. 7.3. The phase transitions in ethanol entail a heat release/absorption [2], which was



Figure 7.2: Schematic state diagram of ethanol [2, 5, 12] and thermal routes (arrows 1-4) followed in the experiments. T_g is the glass transition temperature; T_m is the melting temperature; SCL is the supercooled liquid; SG is the structural glass; OG is the orientational glass; FOC, α is the fully orientationally ordered crystal, structure α ; FOC, β is the fully orientationally ordered crystal, structure β .



Figure 7.3: The typical features of the curves of heating/cooling solid ethanol in the course of the phase transformations: a) heating: structural glass – supercooled liquid transition; b) cooling: a first-order irreversible phase transition from a supercooled liquid to a plastic crystal (RPC); c) heating: transition from an orientational glass to a plastic crystal; d) heating: a first-order irreversible phase transition from a plastic crystal to a monoclinic FOC.

clearly registered with two thermometers (see the heating/cooling curves). Near the temperature of glass formation the heating rate decreases and the structural glass (SG) changes into a supercooled liquid (SCL)

(see Fig. 7.3a). On cooling the SCL transforms into a plastic crystal (RPC) (Fig. 7.3b). This transition occurs with a heat release below $T \approx 125$ K, which suppresses significantly the rate of the sample cooling. The change in the heating rate during the OG \rightarrow RPC transition is illustrated in Fig. 7.3c. The sharpest feature in the sample heating thermogram (Fig. 7.3d) is caused by the heat release during the irreversible first-order phase transition from the metastable plastic crystalline phase to the monoclinic phase of a fully orientationally-ordered crystal (FOC). The sample heating curve has no sharp features in the orientationally – ordered crystal in the interval from 2 K to $T_m = 159$ K (T_m is the melting temperature).

7.3 Structural Transformations in Solid Ethanol

As mentioned above, among the simple alcohols, ethanol is noted for its rich polymorphism. Each of its states – structural glass, orientational glass, a fully orientationally-ordered crystal – has distinctive features that are clearly evident in the temperature behavior of the thermal conductivity. The effect of thermal conductivity relaxation caused by annealing the sample was first observed on ethanol in the completely – ordered phase (FOC) formed due to the OG \rightarrow RPC \rightarrow FOC transition.



Figure 7.4: Thermal conductivity relaxation during SG \rightarrow SCL \rightarrow RPC (\Box), and RPC \rightarrow FOC phase transitions at T = 109 K (\blacktriangle); subsequent annealing of FOC at the average T = 124 K (\circ) and T = 156 K (*). Lines are calculated dependencies $\kappa(t) = \kappa(\infty) - \Delta \kappa \exp(-t/\tau)$, where τ is the characteristic relaxation time, $\Delta \kappa$ is the change in the thermal conductivity, $\kappa(\infty)$ is the thermal conductivity of saturation.

The RPC \rightarrow FOC transition (see Fig. 7.2, route 3) was carried out at the average temperature T = 109 K. In the course of the transition, the thermal conductivity increased slowly and exponentially with time $\kappa(t) = \kappa(\infty) - \Delta\kappa \exp(-t/\tau)$ ($\tau = 58.5$ h is the characteristic relaxation time, $\Delta\kappa = 0.095$ Wm⁻¹K⁻¹ is the change in the thermal conductivity) for 200 hours (see Fig. 7.4). When $\kappa(t)$ stopped growing and reached its saturation value, $\kappa(\infty) = 0.214$ Wm⁻¹K⁻¹, the thermal conductivity, $\kappa(T)$, was measured as a function of temperature in the interval T = 109 - 2 K. The dependence $\kappa(T)$ corresponding to the structure α_1 of FOC (see Fig. 7.5, curve α_1) was noticeably different from $\kappa(T)$ of an orientational glass.

Further relaxation of the thermal conductivity $\kappa(t)$ was observed for 70 hours at T = 124 K with the characteristic relaxation time $\tau = 24$ h and $\Delta \kappa = 0.013$ Wm⁻¹K⁻¹ (see Fig. 7.4). The dependence $\kappa(T)$



Figure 7.5: The temperature dependence of the thermal conductivity of solid ethanol sample in various structural states: OG (\Box) [11], after annealing FOC at T = 109 K (structure α_1 (\blacktriangle)), 124 K (structure α_2 (\circ)) and 156 K (structure β (\ast)). Lines – fitting the experimental data with the theoretical curves calculated within the Debye-Peierls model [13]. Straight lines – the dependencies $\kappa(T) \sim T^2$ and $\kappa(T) \sim T^{1.35}$.

taken after the relaxation at T = 124 K is shown in Fig. 7.5 (curve α_2). This dependence corresponds to the new relaxed monoclinic structure α_2 of FOC whose thermal conductivity is considerably higher than that of FOC α_1 .

The annealing of the FOC α_2 structure in the pre-melting region at 156 K (Fig. 7.2, route 4), where the monoclinic structure FOC- β is formed, led to a fast sharp increase in $\kappa(T)$ of FOC- β (Fig. 7.5). The dependencies $\kappa(t)$, taken at different temperatures (109 K, 124 K and 156 K), are shown in Fig. 7.4. The dependencies $\kappa(T)$ for different FOC structures are illustrated in Fig. 7.5. It is seen (see Fig. 7.5) how the curve $\kappa(T)$ of OG phase transforms into the curve $\kappa(t)$ of the thermodynamically - equilibrium phase of a FOC with low contents of defects (structure β) passing in turn through various structural states (monoclinic structures α_1 and α_2) at increasing of annealing temperature. The curves describing the thermal conductivity of completely orientationally – ordered crystals FOC ($\alpha_1, \alpha_2, \beta$) are similar to the curves $\kappa(T)$ with a phonon maximum that are typical for dielectric crystals. The sample obtained through the solid phase transformation at T = 109 K (structure α_1) has an anomalously low thermal conductivity. The thermal conductivity of the crystal with structure α_1 of the ethanol sample is slopping smoothly. At low temperatures the thermal conductivity is considerably lower than $\kappa(T)$ of the OG crystal. $\kappa(T)$ grows with increasing temperature and at $T \approx 8$ K becomes equal to the thermal conductivity of the OG crystal. The fact that at low temperatures the thermal conductivity of the FOC crystal with the structure α_1 is even lower than the thermal conductivity of OG suggests that the α_1 -phase of FOC is most likely an intermediate state with a large number of defects. Below 8 K the thermal conductivity of crystal with structure α_1 is proportional to $T^{1.35}$, which suggests intensive phonon scattering by point and linear defects. As the temperature rises, the thermal conductivity increases and reaches its maximum, $\kappa_{max} \approx 0.25 \text{ Wm}^{-1} \text{K}^{-1}$, which is only 20% higher than κ_{max} of the OG crystal. The smeared maximum in the thermal conductivity of crystal with structure α_1 appears at a temperature identical with that of the κ_{max} of the OG crystal (T = 51 K).

After annealing at T = 124 K, the crystal with structure α_1 transforms into a crystal with structure

7.3 Structural Transformations in Solid Ethanol

 α_2 . Its maximum thermal conductivity ($\kappa_{max} \approx 0.36 \text{Wm}^{-1} \text{K}^{-1}$) exceeds κ_{max} of the structure α_1 and the temperature of the maximum shifts towards low temperatures ($T_{max} = 25.3 \text{ K}$). The κ -curves of α_2 and OG structures intersect at $T \approx 5.5 \text{ K}$; below this temperature the thermal conductivity of the crystal with structure α_2 is lower than $\kappa(T)$ of the OG but higher than $\kappa(T)$ of the crystal with structure α_1 . In the low temperature region the thermal conductivity of crystal with structure α_2 rises more steeply than in the crystal with structure α_1 and is proportional to $T^{1.7}$. This indicates that the structure α_2 is superior to the structure α_1 in quality and has fewer defects. The crystal with structure β obtained by annealing the crystal with structure α_2 at $T \approx 156 \text{ K}$ has the highest thermal conductivity which is about an order of magnitude higher than $\kappa(T)$ of the crystal with structure α_1 at low temperatures. In this series the crystal with structure β is noted for the highest quality and the lowest content of defects. It has a distinct maximum of thermal conductivity ($\kappa_{max} = 2.32 \text{ Wm}^{-1} \text{K}^{-1}$) which is almost an order of magnitude higher than κ_{max} of the crystal with structure α_1 . It occurs at $T_{max} = 11.2 \text{ K}$. Below T_{max} , the thermal conductivity of the crystal with structure β is proportional to the quadratic temperature dependence, which corresponds to the scattering of phonons by linear defects (dislocations).



Figure 7.6: Temperature dependence of the thermal conductivity of 1-butanol in three states – SG (Δ), "glacial" (∇) and stable crystal (\circ). Data of [15] and [16]. Straight line is the dependence $\kappa(T) \sim T^{1.35}$.

Fig. 7.5 shows the temperature dependencies $\kappa(T) \sim T^2$ and $\kappa(T) \sim T^{1.35}$ (straight lines) along with the fitting of the experimental results for FOC ($\alpha_1, \alpha_2, \beta$) to the theoretical curves calculated within the Debye-Peierls model [13] allowing for the resistive U – processes of phonon scattering and the phonon scattering by point and linear defects. It is seen that the model describes quite accurately the experimental data for the three completely orientationally – ordered crystals. The difference in the thermal conductivities of the FOC- α_1 structure and FOC- β structure may be connected with improving quality of the crystals in the course of annealing.

It is interesting that the κ -values in the curve of the structure α_1 with the highest content of defects are very low (see Fig. 7.5). This is a basically new result obtained for the first time on an ethanol sample. A very similar behavior of the thermal conductivity was observed previously on a sample of 1-butanol in its exotic metastable so-called "glacial" state [15, 16] (see Fig. 7.6). The state (its nature has been discussed much in literature [17-19]) was obtained from a supercooled liquid at $T \approx 122$ K. At low temperatures the

thermal conductivity of "glacial" 1-butanol is dependent on temperature as $T^{1.35}$ [16]. The highest $\kappa(T)$ of the "glacial" 1-butanol state occurs at T = 51 K which is T_{max} of 1-butanol structural glass (Fig. 7.6). Besides, κ_{max} of the "glacial" state is about 25% higher than κ_{max} of 1-butanol structural glass. The similarity of the thermal conductivities of "glacial" state of 1-butanol and ethanol obtained through the solid-state RPC-FOC phase transition (Fig. 7.5, curve α_1) suggests a common origin of both. It is likely [15, 16] that the so-called "glacial" state is a mixture of two coexisting phases – nano-crystalline grains of a stable crystal in a disordered phase.

7.4 Conclusions

The effect of annealing in the thermal conductivity of solid ethanol in the orientationally – ordered phase has been observed in a wide range of temperatures. This phase was obtained as a result of a first – order phase transition from an orientationally – disordered crystal of cubic structure. The temperature behavior of the thermal conductivity of the sample obtained at $T_{anneal}=109$ K is similar to the dependence typical of an imperfect fine grained crystal of 1-butanol in the so-called "glacial" state, which suggests their identical origin. The thermal conductivity was observed to increase as the monoclinic lattice changed from a less stable phase to a more stable one. The growth may be due to the improved quality of the completely orientationally – ordered crystal.

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8 Thermally Driven Capillary Fluctuations of Large Argon-like Clusters

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> We are usually convinced more easily by reasons we have found ourselves than by those which have occurred to others.

Blaise Pascal

Abstract

Spectra of the cluster surface equilibrium fluctuations are treated by decomposition into the bulk and net capillary ones. The bulk fluctuations without capillary ones are simulated by the surface of a cluster truncated by a sphere. The bulk fluctuations spectrum is shown to be generated primarily by the discontinuity in spatial distribution of cluster internal particles. The net capillary fluctuations slice spectrum is obtained in molecular dynamics simulation by subtraction of the bulk fluctuations spectrum from the total one. This net spectrum is in the best agreement with a theoretical estimation if we assume the bare surface tension to be independent of the wave number. The wave number cutoff is brought in balance with the bare surface tension and excess surface area induced by the capillary fluctuations. It is shown that the ratio of the ordinary surface tension to bare one can be considered as a universal constant independent of the temperature and cluster size. Data obtained by molecular dynamics simulation are used to find the effective surface tension for the capillary fluctuations, which characterizes the deviation of Fourier spectrum obtained in simulation from the spectrum of macroscopic capillary waves. The variational method was used to recover this quantity from simulation data. It is revealed that the effective surface tension is almost constant within a rather wide wavelength range.

8.1 Introduction

The capillary wave model [1, 2] (CWM) is now considered as a promising way of doing interface investigation, which can remove discrepancies between theory, experiment, and numerical simulation. Among widely discussed items are, e.g., the problem of interface thickness divergence and the form of density dependence on the coordinate normal to the interface. CWM considers an imaginary fluctuation surface assigned to any instant configuration of molecules at the interface. Fluctuations of this surface are treated in a macroscopic way using the classical capillary wave Hamiltonian. Unification of CWM, microscopic definition of the fluctuation surface, and density functional theory is now in progress [3, 4].

In recent studies, attention was focused on the microscopic structure of the interfaces between liquid and vapor or two immiscible liquids. Such studies assume numerical simulation by Monte Carlo [5] and molecular dynamics (MD) methods [6, 7]. Microscopically defined fluctuation surface was treated by Tarazona and Chacón [5] and Chacón et al. [8] for the liquid–vapor interface, and by Chowdhary and Ladanyi [6, 7] for the liquid–liquid interface. These simulations revealed strong oscillations of the density defined relative to the fluctuation surface. The same effect for water was displayed in Ref. [8]. The wave number spectrum of capillary fluctuations showed relatively fast decay, and the effective bare surface tension seemed to in-

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crease substantially with the wave number [5]. Models for the interacting surfaces of immiscible liquids and their wave number spectra led to the conclusion about the importance of both the bulk fluctuations, which dominate in the short-wavelength spectral region, and a correct wave number cutoff criterion [7]. The importance of a correct identification of capillary and bulk fluctuations was discussed by Stillinger [9], who proposed to introduce a subset of inherent structures and to define an intrinsic density profile free of the capillary fluctuations.

Study of clusters is an independent field of research, which can represent a complementary method for the investigation of liquid–vapor interface. The surface of a sufficiently large cluster is a good approximation to the flat interface; at the same time, variation of cluster radius allows investigation of the curvature effect. The wave number and frequency Fourier spectra were calculated in MD simulation of the Lennard-Jones clusters in Ref. [10], where the surface particles that mark the fluctuation surface were defined as the most external cluster particles, which form percolating umbrellas over the internal particles [11]. The main conclusion of this study, which we will refer to as the previous study, is a considerable discrepancy between the calculated spectrum and predictions of the early version of CWM applied to liquid clusters [12] both in the wave number and temperature spectral dependencies. However, theoretical analysis in the previous study was restricted to an order of magnitude estimate of the spectral density. To our knowledge, no analysis of the liquid cluster surface fluctuations was undertaken in the literature.

The objective of this paper is to give a detailed analysis and theoretical interpretation of the results obtained in the previous study. The spectral densities calculated in this MD simulation are treated as a sum of two components, the net capillary and bulk fluctuations. The latter are estimated using the procedure for a free cluster surface applied for the clusters truncated by a sphere, which removes the surface and some adjacent particles. Truncation is assumed to prepare a particle configuration with the surface particles most closely approaching an ideal sphere undisturbed by the capillary fluctuations. Thus, we can associate such configuration with the absence of capillary fluctuations and calculate the bulk fluctuations wave number spectrum. This spectrum estimated using MD data can be reproduced to a good accuracy in a simple model assuming random uniform spatial distribution of the internal (bulk) particles. Therefore, discontinuity of cluster bulk rather than instantaneous density nonuniformity proves to be a reason for the bulk fluctuations. Net capillary fluctuations spectrum is then obtained as a difference between the total and bulk spectrum. The net spectrum associated with CWM is restricted by a short-wavelength cutoff that confines the curvature of capillary fluctuation surface. Such cutoff turns out to be of the order of several interparticle distances and is therefore larger than the cutoff of common occurrence.

To compare the CWM with modified cutoff and MD simulation results directly, a recalculation of theoretical 2D spherical spectra to one-dimensional slice spectra was performed. Here, net slice spectra were calculated for individual spherical harmonics. The sum of all spectral amplitudes was found to be in a reasonable agreement with net slice spectra obtained in MD simulation, which corroborates a theoretical approach developed in this paper.

We introduce the effective surface tension that allows for a finite-width region of spectral amplitude vanishing as a alternative to their cutoff. It appears that, at $l > \Lambda$, the contribution of spherical harmonics to the slice spectra drops abruptly. A direct restoration of $\gamma_{\text{eff}}^{-1}(l)$ from the cross section spectra is a typical example of an ill-posed mathematical problem. To solve this problem, different trial functions for the $\gamma_{\text{eff}}^{-1}(l)$ dependence, the values of which were best fitted using the data of molecular dynamics simulation, were used. Results of calculations testify to the fact that, irrespective of the form of trial function, resultant spectra qualitatively comply with the assumption of an abrupt vanishing of spectrum.

The paper is organized as follows. In Sec. 8.2, the bulk fluctuations are defined and determined from MD data and theoretical considerations, in Sec. 8.3, the bare surface tension and short-wavelength cutoff dependent on the excess surface area are discussed, and in Sec. 8.4, theoretical estimates for one-dimensional slice spectra are obtained and compared with the spectra calculated using MD simulation. A smooth dependence of the bare surface tension on the wavelength is treated in Sec. 8.5. The results are summarized in Sec. 8.6.

8.2 Bulk Fluctuations

8.2 Bulk Fluctuations

In the present section, a method of capillary and bulk fluctuations decomposition is developed. In Sections 8.2–8.4, the presentation follows Ref. [13]. The system under consideration consists of an isolated cluster in the state of unstable equilibrium with surrounding vapor of monomers (clusters in the vapor are ignored). The system is characterized by the constant temperature T and vapor number density n_v . Such system was simulated in the previous study using the (P, T)-ensemble method, in which the cluster under investigation is situated close to the center of a spherical cell; the cell surface performs the function of vapor particles generation and removal. The Lennard-Jones interaction potential between two particles has the form

$$u(r) = \begin{cases} v(r) - v(r_c) , & r \le r_c , \\ 0, & r > r_c , \end{cases}$$

$$v(r) = 4\varepsilon \left(\frac{a^{12}}{r^{12}} - \frac{a^6}{r^6}\right) , \qquad (8.1)$$

where r is the interparticle distance; $r_c = 2.5a$ is the cutoff radius; ε is the well depth; and a is the length scale. In this paper, we use the MD units: $\tau_0 = a\sqrt{M/24\varepsilon}$ for the time (M is the particle mass); a for the distance; a^{-3} for the particle density; ε for the energy and temperature, and ε/a^2 for the surface tension.

Calculation of the wave number spectra was performed in the previous study for the surface particles confined within two parallel planes at the distance $h/2 = 1/2\sqrt{3}n_{\ell}^{1/3}$ from cluster center-of-mass each. Here, n_{ℓ} is the number density of internal cluster particles, i.e., the bulk number density. We will call such one-dimensional spectra the slice spectra. The definition of surface particles is given by Eq. (2) of Ref. [10]. It is based on widely discussed assumption concerning the spatial homogeneity of a cluster (or liquid slab in the simulation with a flat interface) and abrupt drop of particle number density at cluster surface (see Refs. [10] and [11] and references therein). This implies existence of a single monolayer of the surface particles that have a reduced number of nearest neighbors as compared to the internal particles. The above-mentioned definition of these particle types postulates that for each internal particle of a sufficiently large cluster, there exists at least one outermost surface particle, whose "umbrella" of the radius h covers this particle. Note that such definition of the outermost layer of particles and resulting identification of the fluctuation surface is qualitatively similar to that proposed by Stillinger [14]. The value $h = 1/\sqrt{3}n_{\ell}^{1/3}$ was selected to ensure the best fit of surface and internal particle distributions over the number of bonds to respective Gaussian exponents in the expansion of total distribution in the pair of exponents. In the slice snapshots like Fig. 4.3 in Ref. [15], the surface particles really seem to form a monolayer over the internal particles. One can verify that small variations of h would not change this situation. However, a substantial change leads to obvious surface layer distortions. Thus, the decrease in h depletes the monolayer (internal particles take the place of surface ones); the increase of h results in the intrusions of surface particles in the bulk of a cluster. In both cases, the distributions over number of bonds for both particle types deviate from the Gaussian type. Therefore, an appropriate choice of the surface particles allows using them as pivots for the fluctuation surface and its cross sections analyzed in the previous study.

To decompose the surface and bulk fluctuations, we will focus our attention on the latter and formulate the procedure that makes it possible to estimate the bulk fluctuation spectrum. At the first step, we will define a configuration with zero capillary fluctuation. It is natural to assume that for such configuration, any thermodynamic potential quantity (in treated case, the Gibbs free energy) includes no term corresponding to the fluctuations other than the ones that occur in the bulk. Therefore, we must construct such configuration solely of internal particles. If all surface particles would lie on a spherical surface, the capillary fluctuations were equal to zero identically. However, the probability to find such configuration is equal to zero. It is then necessary to select a set of configurations in the vicinity of such improbable one (this conforms to the idea of Ref. [9]). To make this selection usable for numerical simulation, we define a configuration with no capillary fluctuation as the cluster truncated by a sphere with the radius \bar{R} smaller than the minimum

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distance between a surface particle and the cluster center-of-mass. In other words, all the surface and some internal particles at the distances larger than \bar{R} are removed.

The slice spectra were calculated for truncated clusters following the method discussed in detail in the previous study. We used also the cluster configurations obtained therein, which have been stored for the runs at T = 0.75 and the clusters including initially g = 30000 particles. Truncation at $\overline{R} = 18.4$ guaranteed that only the internal particles were retained; the cluster size was decreased down to 20000. Then, the surface particles were identified and isolated for *truncated* clusters in the same way it was done for the free surface (for truncated clusters, the result is naturally insensitive to the removal of virtual chains). A slice was formed by the particles falling between two planes at the distance h = 0.6, with the cluster center-of-mass at the half-distance.



Figure 8.1: The slice snapshots of surface particles for the free surface (left) and truncated cluster (right) at g = 20000 and T = 0.75.

Figure 8.1 presents snapshots of the surface particles for the free surface and the surface of a truncated cluster. Long-wavelength fluctuations are recognizable on the free surface, and the amplitude of bulk fluctuations with predominantly short wavelengths on the truncated surface is noticeably high.

The slice surface particles with polar coordinates (r_i, φ_i) were considered as pivots for a continuous periodical function $\tilde{P}(\varphi)$, whose values are known at random points, $\tilde{P}(\varphi_i) = r_i$. $\tilde{P}(\varphi)$ was resampled to the analytical grid and then Fourier analyzed for different slices corresponding to cluster rotation relative to the slice plane. Its squared spectral amplitude was averaged over the rotation angles and cluster configurations to calculate the spectrum of bulk fluctuations R_k as a function of the mode number k. Note that for R_k , the convergence of averaging is much faster than that for the free surface. Variation in \bar{R} in relatively wide limits reveals scaling property of kR_k , which is much more accurate than for the total spectrum (see Fig. 4.8b of Ref. [15]). Given the temperature, kR_k is a universal function of k/\bar{g}_{cs} , where \bar{g}_{cs} is the average number of surface particles in a slice. After scaling, respective dots almost coincide. The bulk fluctuation spectrum scaled to the initial cluster size is shown in Fig. 8.2. At small k, R_k varies slowly; at large k, R_k vanishes due to finiteness of \bar{g}_{cs} .

It will be shown below that R_k can be calculated within a simple model. We will assume a random uniform spatial distribution for all cluster particles and ignore correlations of their positions. Then φ is uniformly distributed on the interval $0 \le \varphi < 2\pi$, and the value of function $\tilde{P}(\varphi)$, on $\bar{R} - \Delta < \tilde{P}(\varphi) < \bar{R}$, where Δ is the distribution width. Hence, the probability to find a particle at the distance between r and r + dr from the origin of the coordinate system, which is assumed to coincide with the cluster center-ofmass, is

$$p_r(r) dr = \begin{cases} \frac{dr}{\Delta} , & \bar{R} - \Delta < r < \bar{R} ,\\ 0 , & r \le \bar{R} - \Delta \quad \text{or} \quad r \ge \bar{R} , \end{cases}$$

$$(8.2)$$



Figure 8.2: Bulk fluctuations spectra scaled to the cluster size g = 30000 at T = 0.75 calculated from MD simulation data (truncated clusters, dots) and by Eqs. (8.2) and (8.3) (line).

and the distribution for φ has similar form. The probability to find a surface particle in a given slice is $p_{cs} \simeq h/2\bar{R} \ll 1$. If g_s is the total number of surface particles, $\bar{g}_{cs} = p_{cs}g_s$ coincides with the variance of the number of surface particles in a slice g_{cs} . Hence, the probability distribution to find g_{cs} surface particles in a slice has the Gauss form

$$p_g(g_{cs}) = \frac{1}{\sqrt{2\pi\bar{g}_{cs}}} \exp\left[-\frac{(g_{cs} - \bar{g}_{cs})^2}{2\bar{g}_{cs}}\right] .$$
(8.3)

An independent numerical simulation of the bulk fluctuations was performed as follows. First, the number g_{cs} was generated at random with probability distribution Eq. (8.3), where $\bar{g}_{cs} = 76$ was calculated from MD data. Then g_{cs} pairs of polar coordinates were generated with distribution Eq. (8.2). The function $\tilde{P}(\varphi)$ obtained in such a way was resampled to an analytical grid and Fourier analyzed. Averaging over 10^6 realizations of this procedure yields a model bulk fluctuations spectrum shown in Fig. 8.2. In this simulation, Δ was adjusted to fit the distribution obtained from the MD data; the best fit value proved to be of the order of the distance between surface particles, $\Delta \simeq 2\pi \bar{R}/\bar{g}_{cs}$. A good correlation between independent estimations of R_k seen in Fig. 8.2 is evidence of the fact that the basic reason of the bulk fluctuations treated in this paper is the discontinuity of cluster bulk.

For a crude estimation of R_k , we can assume that $\tilde{P}(\varphi)$ has the uniform distribution, and distribution Eq. (8.3) has a zero width, i.e., $g_{cs} \equiv \bar{g}_{cs}$. Then the bulk fluctuations are white noise, and R_k is constant in the interval of mode numbers from 1 to \bar{g}_{cs} , which in this simplified case is the highest mode number. The contribution of bulk fluctuations to the total fluctuation variance defining the interface width is then

$$\sigma_b^2 = \frac{1}{2} \sum_{k=1}^{g_{cs}} R_k = \frac{\bar{g}_{cs} R_1}{2} = \frac{\Delta^2}{12} .$$
(8.4)

Estimation Eq. (8.4) is indicative of the fact that σ_b^2 does not diverge both at small and large g. The scaling law is obvious from Eq. (8.4):

$$kR_k = kR_1 = \frac{k\Delta^2}{6\bar{g}_{cs}} , \qquad (8.5)$$

i.e., kR_k depends solely on k/\bar{g}_{cs} . Since $\bar{g}_{cs} \propto \bar{R}$, kR_k is also scaled with k/\bar{R} .

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As is seen in Fig. 8.2, the bulk fluctuations spectrum deviates from the white noise one. This is caused by converting the random values of φ to analytical grid. To conserve the variance of original pivots, their number must be less than that of points on the analytical grid (see the discussion in Sec. 8.4), whence it follows that some values of $\tilde{P}(\varphi)$ at neighboring grid points are equal. This implies a buildup of R_k for small k. If we did not ignore particle correlations, less number of $\tilde{P}(\varphi)$ values would coincide, and R_k would be less different from white noise in the long-wavelength region. This clarifies the less pronounced buildup in this region for R_k calculated from MD data.

In spite of the deviation of MD R_k from the white noise distribution, its variance can be to high precision approximated as follows [see Eq. (8.4)]:

$$\sigma_b^2 = \sum_{k=1}^{k_{\text{max}}} R_k \simeq \frac{\Delta^2}{12} + \delta g^{-1/3} , \qquad (8.6)$$

where for T = 0.75, $\Delta = 2.0$ and $\delta = -0.8$; summation extends up to $k = k_{\text{max}}$, at which R_k vanishes; this approximation is valid at g > 400. Equation (8.6) defines the contribution from bulk fluctuations to the total interface variance. As regards the spectral density of net capillary fluctuations Q_k , one can write it in the form

$$Q_k = S_k - R_k av{8.7}$$

where S_k is the total spectral density.

8.3 Capillary Fluctuations

Consider the CWM for an isotropic cluster. We will use the formalism proposed first by Rayleigh [16] for treatment of liquid drop oscillations. Since any real configuration includes the bulk fluctuations, a net capillary fluctuation does not exist, and, therefore, it is impossible to formulate an appropriate microscopic definition. We will treat the fluctuations not included in the set of bulk ones, which give rise to some *mesoscopic* excess surface area, and call them the capillary fluctuations. According to CWM we write the additional Gibbs free energy of their formation in the form

$$\Phi = \gamma_0 \Delta A = \frac{\gamma_0}{2} \int_{\Omega} \left| \nabla \xi(\mathbf{r}) \right|^2 dS , \qquad (8.8)$$

where γ_0 is the bare surface tension; ΔA is the excess surface area induced by a fluctuation. The integral Eq. (8.8) is taken over the entire cluster equimolar surface Ω with the radius R, and $\xi(\mathbf{r})$ is the position of fluctuation surface relative to Ω , so that

$$\int_{\Omega} dS = 4\pi R^2 , \qquad \int_{\Omega} \xi(\mathbf{r}) \, dS = 0 .$$

It is assumed that in the spherical coordinates (r, ϑ, φ) , the fluctuation surface is defined by the equation $r = R + \xi(\vartheta, \varphi)$. Note that Eq. (8.8) implies that γ_0 is independent of the wave vector (see Sec. 8.4) and the fluctuation amplitude is small so that $|\nabla \xi(\vartheta, \varphi)| \ll 1$. In contrast to the previous study, we use γ_0 instead of the ordinary surface tension γ .

We expand $\xi(\vartheta, \varphi)$ in spherical harmonics $Y_{lm}(\vartheta, \varphi)$,

$$\xi(\vartheta,\,\varphi) = R \sum_{l,m} a_{lm} Y_{lm}(\vartheta,\,\varphi) \,, \tag{8.9}$$

where $-l \leq m \leq l$, to derive

$$\Phi = \frac{\gamma_0 R^2}{2} \int_{\Omega} |\nabla \xi(\vartheta, \varphi)|^2 \sin \vartheta \, d\vartheta d\varphi = \frac{\gamma_0 R^2}{2} \sum_{l,m} |a_{lm}|^2 \, (l-1)(l+2) \,. \tag{8.10}$$

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8.3 Capillary Fluctuations

Note that if $|a_{lm}| \ll 1$, expansion Eq. (8.9) conserves the cluster volume,

$$\int\limits_{V} d^3 \mathbf{r} = (4\pi/3)R^3$$

where V is the volume bounded by the fluctuation surface $r = r(\vartheta, \varphi)$; the momentum conservation dictates that $l \ge 2$.

The expression for average squared expansion amplitude follows from the equipartition theorem

$$\left\langle |a_{lm}|^2 \right\rangle = \frac{T}{\gamma_0 R^2 (l-1)(l+2)} \,.$$
(8.11)

This means that $\langle |a_{lm}|^2 \rangle$ is independent of m, and Eq. (8.11) is actually the approximation of linear independent modes. The latter is a consequence of the assumptions that $|a_{lm}| \ll 1$ and γ_0 is independent of l, m.

We average Eq. (8.10) to deduce the excess surface area

$$\left\langle \Delta A \right\rangle = \frac{\left\langle \Phi \right\rangle}{\gamma_0} = \frac{R^2}{2} \sum_{l,m} \left\langle \left| a_{lm} \right|^2 \right\rangle (l-1)(l+2) \,. \tag{8.12}$$

Substitution of Eq. (8.11) into Eq. (8.12) yields

$$\langle \Delta A \rangle = (T/2\gamma_0) \sum_l (2l+1) ,$$

which diverges at large l. We introduce the largest (cutoff) number $l = \Lambda$ to make $\langle \Delta A \rangle$ finite:

$$\langle \Delta A \rangle = \frac{T}{2\gamma_0} \sum_{l=2}^{\Lambda} (2l+1) \simeq \frac{T\Lambda^2}{2\gamma_0} , \qquad (8.13)$$

if $\Lambda \gg 1$. Since the cluster is isotropic, averaging Eq. (8.8) yields one more relation for $\langle \Delta A \rangle$:

$$\left\langle \Delta A \right\rangle = \frac{1}{2} \int_{\Omega} \left\langle \left| \nabla \xi(\vartheta, \varphi) \right|^2 \right\rangle \, dS = 2\pi R^2 \kappa^2 \,, \tag{8.14}$$

where

$$\kappa = \sqrt{\left< \left| \nabla \xi(\vartheta, \, \varphi) \right|^2 \right>}$$

is the root-mean-square gradient of the capillary fluctuation surface. According to the previous study if we exclude virtual chains of particles (overhangs), for which $|\nabla \xi(\vartheta, \varphi)| \gtrsim 1$, the remaining surface satisfies the condition $|\nabla \xi(\vartheta, \varphi)| \lesssim 1$. Hence, one could expect that κ was some constant of the order of unity and that the ratio $\langle \Delta A \rangle / 4\pi R^2 = \kappa^2 / 2$ was independent of the temperature and cluster size. We compare Eqs. (8.13) and (8.14) to deduce the cutoff number

$$\Lambda = 2R\kappa \sqrt{\frac{\pi\gamma_0}{T}} . \tag{8.15}$$

It follows from the definition of the ordinary surface tension γ , $4\pi R^2 \gamma = 4\pi R^2 \gamma_0 + \langle \Delta A \rangle \gamma_0$, and Eq. (8.14) that γ_0 is related to γ as

$$\frac{\gamma}{\gamma_0} = 1 + \frac{\kappa^2}{2} . \tag{8.16}$$

Thus, the ratio γ/γ_0 is a constant greater than unity ($\kappa^2 > 0$). We substitute γ_0 from Eq. (8.16) into Eq. (8.15) to eventually derive

$$\Lambda(\kappa) = R\kappa \left[\frac{8\pi\gamma}{(2+\kappa^2)T}\right]^{1/2}.$$
(8.17)

The maximum wave number corresponding to cutoff Eq. (8.17)

$$q_{\max} = \frac{\Lambda}{R} = \kappa \left[\frac{8\pi\gamma}{(2+\kappa^2)T} \right]^{1/2}$$
(8.18)

is for treated conditions several times smaller than that corresponding to the interparticle distance.

The contribution from the capillary fluctuations to the total interface variance is [see Ref. [12] and Eq. (8.31)]

$$\sigma_c^2 = \frac{R^2}{4\pi} \sum_{l=2}^{\Lambda} \left(2l+1\right) \left\langle \left|a_{lm}\right|^2 \right\rangle \simeq \frac{(2+\kappa^2)T}{8\pi\gamma} \ln\frac{(2\Lambda-1)(2\Lambda+5)}{7} \,. \tag{8.19}$$

Since $\Lambda \propto R \propto g^{1/3}$, σ_c^2 [Eq. (8.19)] diverges as $\ln g$, which is similar to the variance divergence of a flat interface in the absence of gravity as the surface area is increased [2].

8.4 CWM Slice Spectra

An objective of this section is to calculate the slice spectra of net capillary fluctuations Q_k given its 2D spectrum [Eqs. (8.11) and (8.17)] and to compare the result with the slice spectra obtained in MD simulation. A single adjustable parameter in this calculation will be κ . The simplest way to do this is to create configurations with the net capillary fluctuations in the form of individual spherical harmonics. As in the foregoing, fluctuation modes are assumed to be independent. Therefore, each spherical harmonic with the numbers l, m must contribute additively to the squared spectral amplitude of the slice mode with the number k and can be treated separately.

We take an arbitrary configuration of particles stored during MD simulation corresponding to desired cluster size and isolate the surface particles. Within the accuracy of our calculations, the result proved to be fully insensitive to the choice of a concrete configuration because for each surface particle with the spherical coordinates $(r_i, \vartheta_i, \varphi_i)$, we substitute r_i for the coordinate of a capillary fluctuation in a special form. We use the relation $Y_{lm}(\vartheta, \varphi) \propto P_l^m(\cos \vartheta) e^{im\varphi}$, where $P_l^m(\cos \vartheta)$ is the Legendre function, to pass from the complex Fourier series Eq. (8.9) to real one and to write the new coordinate r_i as

$$r_i = R + A_{lm} \sqrt{\frac{T}{\gamma(l-1)(l+2)}} P_l^m(\cos\vartheta_i) \cos m\varphi_i .$$
(8.20)

Here, the normalization constant is

$$A_{lm} = \begin{cases} \left\{ 2\pi \int_{0}^{\pi} [P_l^m(\cos\vartheta)]^2 \sin\vartheta \,d\vartheta \right\}^{-1/2}, \quad m = 0, \\ \left\{ \frac{\pi}{2} \int_{0}^{\pi} [P_l^m(\cos\vartheta)]^2 \sin\vartheta \,d\vartheta \right\}^{-1/2}, \quad m > 0, \end{cases}$$
(8.21)

and we use the exact expressions for $P_l^m(\cos \vartheta)$ at $l \le 5$ or $l = m [P_l^l(\cos \vartheta) \propto \sin^l \vartheta]$, and the asymptotic representation

$$P_l^m(\cos\vartheta) \simeq \sin^{-1/2}(\vartheta) \cos\left[\left(l+\frac{1}{2}\right)\vartheta - \frac{\pi}{4} + \frac{\pi m}{2}\right] , \qquad (8.22)$$

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8.4 CWM Slice Spectra

for l > 5 and $l \neq m$. Note that mode Eq. (8.20) corresponds to the average squared amplitude

$$\left\langle \left|a_{lm}\right|^{2}\right\rangle = T/\gamma R^{2}(l-1)(l+2)$$

which includes γ rather than γ_0 [see Eq. (8.11)] because the latter depends on yet unknown κ . However, the problem linearity allows to correct this factor later.

For each surface particle configuration formed in such a way, we perform the slice Fourier analysis; i.e., we define a periodic function $\tilde{P}^{(l,m)}(\varphi_i) = r_i$ and expand it in the Fourier series (for a detailed discussion, see the previous study)

$$\tilde{P}^{(l,m)}(\varphi) = \frac{\alpha_0^{(l,m)}}{2} + \sum_{k=1}^{k_{\max}} \alpha_k^{(l,m)} \cos k\varphi + \sum_{k=1}^{k_{\max}} \beta_k^{(l,m)} \sin k\varphi , \qquad (8.23)$$

where k_{max} is the maximum mode number, at which Q_k is assumed to vanish. Then the cluster is rotated around the Euler angles ψ_1 and ψ_2 , and the contribution from all l th spherical harmonics corresponding to the case $\gamma_0 = \gamma$ to the slice spectrum mode with the number k is calculated by averaging over slice amplitudes and summing over m:

$$\tilde{S}_{k}(l) = \sum_{m=0}^{l} \frac{\left\langle g_{cs} \left[\left(\alpha_{k}^{(l,m)} \right)^{2} + \left(\beta_{k}^{(l,m)} \right)^{2} \right] \right\rangle_{\psi_{1},\psi_{2}}}{\langle g_{cs} \rangle_{\psi_{1},\psi_{2}}} .$$
(8.24)

The rotation starts from random values of ψ_1 and ψ_2 generated for each spherical harmonic to eliminate the interference with zeros of spherical harmonics (result was found to be insensitive to these values). Hence, in the approximation of modes linearity and independence, we arrive at the capillary fluctuations slice spectrum

$$Q_k = \left(1 + \frac{\kappa^2}{2}\right) \sum_{l=2}^{\Lambda(\kappa)} \tilde{S}_k(l) , \qquad (8.25)$$

where the factor in parenthesis corrects the replacement of γ_0 by γ in Eq. (8.11), and the cutoff number $\Lambda(\kappa)$ is defined by Eq. (8.17).

We adjusted κ to fit Q_k [Eq. (8.25)] to the net spectrum of capillary fluctuations obtained in MD simulation. Calculations were performed for two temperatures (Fig. 8.3) at $\kappa = 0.548$, which provided the best fit. The slice widths h = 0.60 and 0.59 corresponded to the bulk liquid number densities $n_{\ell} = 0.76$ and 0.80 at T = 0.75 and 0.69, respectively. Figure 8.3 shows a fast decay of Q_k as k is increased. The spectral density of bulk fluctuations exceeds Q_k at $k > k_0$, where the threshold value k_0 is noticeably smaller than k_{max} . It is noteworthy that for both temperatures at $k < k_0$, Q_k [Eq. (8.25)] was found to be almost independent of the slice thickness as it was varied within 15%.

One can estimate Q_k roughly assuming that the contribution from spherical harmonics with certain l is evenly distributed between slice modes with $k \leq l$ (then the cutoff for k is Λ , same as for l). In addition, the harmonics with even l contribute solely to l/2 even slice modes (even k), and the harmonics with odd l contribute to l/2 odd slice modes (odd k). If a fluctuation was formed by the harmonics with a certain $l \gg 1$, the surface variance would be

$$\frac{l}{2}\frac{\tilde{S}_k(l)}{2} = \frac{R^2}{4\pi} \sum_{m=-l}^l \frac{T}{\gamma R^2(l-1)(l+2)} \simeq \frac{T}{2\pi\gamma l} \,. \tag{8.26}$$

Then it follows from Eqs. (8.25) and (8.26) that

$$Q_k \simeq \left(1 + \frac{\kappa^2}{2}\right) \frac{2T}{\pi\gamma} \frac{1}{2} \sum_{l=k}^{\Lambda} \frac{1}{l^2} \simeq \left(1 + \frac{\kappa^2}{2}\right) \frac{T}{\pi\gamma} \left(\frac{1}{k} - \frac{1}{\Lambda}\right) , \qquad (8.27)$$



Figure 8.3: Net slice spectra of the cluster capillary fluctuations for (a) g = 30000 and T = 0.75 and (b) g = 19300 and T = 0.69. Calculation by Eqs. (8.25) and (8.17) (solid line), rough estimation of Eq. (8.27) (dashed line), and estimation from MD simulation data (solid circles). The bulk fluctuation spectra (open circles) are shown for reference.

where the factor 1/2 accounts for the summation over even or odd l.

As is seen in Fig. 8.3, estimation Eq. (8.27) is in reasonable agreement with the numerical calculation of Q_k [Eq. (8.25)] at $k < \Lambda$. Vanishing of Eq. (8.27) at $k = \Lambda$ arises from the neglect of the spherical harmonics contribution to the slice modes with k > l. This contribution is unavoidable under the conditions that the ratio of spectral amplitudes at $l \sim 1$ and the maximum l is about 10^3 . The low tail of capillary fluctuations spectrum at $k > \Lambda$ indicates the level of accuracy of the calculations including resampling procedure and numerical Fourier analysis rather than any physical reality: though cutoff Eq. (8.17) excludes capillary fluctuations at $l > \Lambda$, it is hard to eliminate the effect of harmonics with $l < \Lambda$ on the modes with $k > \Lambda$ in slice spectra.

8.4 CWM Slice Spectra

The scaling law follows from Eq. (8.27):

$$kQ_k = \frac{T}{\pi\gamma_0} \left(1 - C\frac{k}{\bar{g}_{cs}} \right) , \qquad (8.28)$$

where $C = \bar{g}_{cs}/\Lambda = (\Gamma h/4r_{\ell}^2\kappa)(T/\pi\gamma_0)^{1/2}$, $\Gamma = g_s g^{-2/3} \approx \text{const}$, and $r_{\ell} = (3/4\pi n_{\ell})^{1/3}$. At fixed temperature, kQ_k is a function of a single quantity k/\bar{g}_{cs} . It follows from scaling law Eq. (8.5) and Eq. (8.7) that the total slice spectral density $kS_k = kQ_k + kR_k$ is also scaled, as revealed in the previous study. For $1 \ll k \ll \Lambda$, $kQ_k \simeq T/\pi\gamma_0$, which, accurate to the substitution of γ_0 for γ , coincides with the spectral density of capillary fluctuations of a flat liquid interface at zero gravity [2]. Hence, in this limit, the difference between the cluster surface and a flat interface vanishes.

One can estimate the boundary $k = k_0$ between the small wave number region of capillary fluctuations and the large wave number region of bulk fluctuations by the relation $Q_{k_0} = R_{k_0}$. We derive the following from Eqs. (8.5) and (8.27)

$$k_0 = \left(\frac{\pi\gamma_0\Delta^2}{6\bar{g}_{cs}T} + \frac{1}{\Lambda}\right)^{-1}.$$
(8.29)

For Figs. 8.3(a) and 8.3(b) $\bar{g}_{cs} = 76$ and 66, respectively, and $\bar{g}_{cs} = \Gamma h g^{1/3} / 2r_{\ell} \propto g^{1/3}$ if $h \propto r_{\ell}$; corresponding k_0 [Eq. (8.29)] are equal to 21 and 19. This agrees with the results of numerical calculations of Q_k and R_k : $k_0 = 25$ and 21, respectively (Fig. 8.3). It is worth mentioning that, unlike Λ [Eq. (8.17)], k_0 increases with the increase in temperature. However, these quantities are still not much different, $\Lambda = 29$ for both temperatures.

Since the cluster relaxation time is defined by the harmonics with l = 2 and it is relatively long, corresponding slice spectral densities S_k may be in error for the smallest k. To inspect this possibility, MD simulation of cluster evolution was performed once more for the same T = 0.75 and initial cluster size g = 30000 as in the previous study but for the vapor number density $n_v = 0.01402$, which was adjusted so that the cluster was very close to equilibrium (simulation cell radius was increased up to 42). Consequently, the cluster size did not change noticeably, and a single run was recorded in this simulation with the total time of cluster evolution of 36000 that was considerably longer than in the previous simulation (\sim 7000). Cluster configurations from run start to the time of 8500 were ignored as nonequilibrium ones. It was found that during the averaging procedure, S_2 converged to the value of 0.7804 at h = 0.6, so that previous simulation underestimated this quantity by nearly 10 percent. A new run was performed for the lower temperature T = 0.69. For the cluster sizes, which varied from q = 20000 to 18700 during cluster evolution, this temperature was somewhat higher than the melting one. At this temperature and cluster size, the cluster is close to equilibrium with surrounding vapor if $n_v = 0.00771$. After the equilibration time of 10000, cluster configurations during the evolution time of 17500 were used to estimate the quantities S_k , R_k , and Q_k with h = 0.59. For both temperatures, when the slice thickness was varied, S_k and R_k changed but their difference Q_k was almost independent of the thickness.

Figures 8.3(a) and 8.3(b) demonstrate a good correlation between the estimation from MD simulation and calculation by Eqs. (8.17) and (8.25). The oscillations of Q_k [Eq. (8.25)] at k > 5 are caused by the transfer from exact Legendre functions to their approximation [Eq. (8.22)]; insignificant discrepancies at $k > \Lambda$ are of no interest because of a minor role of the capillary fluctuations in this region. Similar calculations were performed using the cluster configurations from the previous simulation for g = 3000and T = 0.75 and 0.67. The same $\kappa = 0.548$ provides the best fit to Q_k in these cases as well, whence it follows that this value is independent of the cluster size (if the cluster is sufficiently large to isolate its surface particles) and can be applied to a flat liquid–vapor interface. Moreover, the constancy of κ is also indicative of a nontrivial fact that the ratio γ/γ_0 is temperature independent.

Based on the results of previous and recent MD simulations discussed above, the total variance of the cluster surface σ^2 defining the interface width was calculated (Fig. 8.4). This quantity can be evaluated by

8 Thermally Driven Capillary Fluctuations of Large Argon-like Clusters

a direct calculation of the surface particles radial unweighted variance

$$\sigma^{2} = \left\langle \frac{1}{g_{s}} \sum_{i=1}^{g_{s}} r_{i}^{2} - \left(\frac{1}{g_{s}} \sum_{i=1}^{g_{s}} r_{i} \right)^{2} \right\rangle , \qquad (8.30)$$

where g_s is the total number of cluster surface particles; averaging is performed over cluster configurations. The second estimation comes from the relation $\sigma^2 = (1/2) \sum_{k=1}^{k_{\text{max}}} S_k$. It can be seen that both estimates are close. The direct estimate is insignificantly higher than spectral one, probably, due to overestimated unweighted large deviations and somewhat depressed short-wavelength region of slice spectra.



Figure 8.4: Surface variance as a function of cluster size: direct calculation of the surface particles radial variance (triangles), estimation by the slice spectral amplitudes (circles); theoretical estimations with [solid line, Eqs. (8.6) and (8.19)] and without the account of bulk fluctuations and bare surface tension [dashed line, Eq. (8.31)].

The surface variance can be analytically estimated using Eqs. (8.6) and (8.19): $\sigma^2 = \sigma_b^2 + \sigma_c^2$. Figure 8.4 demonstrates a good agreement with the results arising from MD simulation both in the slope of a curve and its height. The slope is noticeably improved as compared to the early version of CWM [12], where

$$\sigma^2 = \frac{T}{4\pi\gamma} \ln \frac{(2\Lambda_0 - 1)(2\Lambda_0 + 5)}{7} , \qquad \Lambda_0 = 2.2g^{1/3} , \qquad (8.31)$$

due to the difference between γ and γ_0 not taken into account in Eq. (8.31). The neglect of bulk fluctuations results in the underestimation of the line height (Fig. 8.4).

It was noted in the foregoing that Q_k is almost independent of simulation parameters, in particular, of the slice width, at least, in the region of capillary fluctuations $k < \Lambda$. However, the form of the spectrum depends on the number of points of the analytical grid. If we adopt a certain definition of the surface particles, a problem of the fluctuation surface determination arises. It has been proposed in Ref. [5] to find a surface that includes the surface particles and has the minimum surface area. We have adopted other definition: the fluctuation surface has the same variance as the surface particles. This definition makes it possible to calculate straightforwardly one of the most important properties of the interface, its width. For the sake of simplicity, consider one-dimensional slice spectra. Since the coordinates (r_i, φ_i) of surface particles form a random grid, the *weighted* variance is

$$\sigma^{2} = \left\langle \frac{1}{2\pi} \sum_{i=1}^{g_{cs}} (\varphi_{i+1} - \varphi_{i}) r_{i}^{2} - \left[\frac{1}{2\pi} \sum_{i=1}^{g_{cs}} (\varphi_{i+1} - \varphi_{i}) r_{i} \right]^{2} \right\rangle , \qquad (8.32)$$

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which includes two integral sums, and the surface particles are numbered counterclockwise. If we pass on to the analytical grid, it is sufficient to select any constant difference between the points satisfying the condition $\Delta \varphi < \min\{\varphi_{i+1} - \varphi_i\}$ to rewrite Eq. (8.32) in the form

$$\sigma^{2} \simeq \left\langle \frac{1}{2k_{\max}} \sum_{j=1}^{2k_{\max}} r_{j}^{2} - \left[\frac{1}{2k_{\max}} \sum_{j=1}^{2k_{\max}} r_{j} \right]^{2} \right\rangle , \qquad (8.33)$$

where $2k_{\text{max}} = 2\pi/\Delta\varphi$ is the number of analytical grid points and $r_j = r_i(\varphi_i)$; φ_i is the random grid point closest to the *j*-th point on the analytical grid. However, if $\Delta\varphi$ is too small the unphysical tail area of the spectral density extends too much. An optimum value used in the previous and this study, which was found to agree on the average with above-mentioned condition, was found to be $k_{\text{max}} = 0.9g_{cs}$. The procedure of the numerical Fourier analysis conserves the variance for each slice,

$$\frac{1}{2k_{\max}} \sum_{j=1}^{2k_{\max}} r_j^2 - \left[\frac{1}{2k_{\max}} \sum_{j=1}^{2k_{\max}} r_j\right]^2 = \frac{1}{2} \sum_{k=1}^{k_{\max}} \left[\left(\alpha_k^{(l,m)}\right)^2 + \left(\beta_k^{(l,m)}\right)^2\right],\tag{8.34}$$

so that the spectral analysis performed in this paper ensures a correct width of the liquid-vapor interface.

8.5 Effective Surface Tension for Thermal Capillary Fluctuations

In previous discussion, the fluctuation spectrum was limited in the short-wavelength region by a cutoff. This implies that the spectrum vanishes abruptly at $l = \Lambda$. In this section, we consider a more realistic situation, in which the bare surface tension vanishes in a finite region, i.e., it is a smooth function of l. This discussion follows Ref. [19].

The objective of this study is to introduce and estimate the effective surface tension that can account for the thermal fluctuation at the liquid-vapor interface. Assume that the average spectral amplitudes $\langle |a_{lm}|^2 \rangle$ are independent of the number m, i.e., $\langle |a_{lm}|^2 \rangle = \langle |a_{l0}|^2 \rangle$. Then we can define the effective surface tension $\gamma_{\text{eff}}(l)$ as a coefficient that relates $\langle |a_{lm}|^2 \rangle$ to the same quantity $\langle |\tilde{a}_{lm}|^2 \rangle$ calculated in the macroscopic capillary wave theory

$$\left\langle \left| \tilde{a}_{lm} \right|^2 \right\rangle = \left\langle \left| \tilde{a}_{l0} \right|^2 \right\rangle = \frac{T}{\gamma R^2 (l-1)(l+2)} , \qquad (8.35)$$

so that

$$\left\langle \left|a_{l0}\right|^{2}\right\rangle = \gamma \gamma_{\text{eff}}^{-1}(l) \left\langle \left|\tilde{a}_{l0}\right|^{2}\right\rangle \,. \tag{8.36}$$

In the molecular dynamics simulation discussed in Sec. 8.4, slice spectra are determined. In the approximation of linear non-interacting modes, the spectral amplitude of k-th mode for the slice spectrum can be written as

$$Q_{k} = \frac{R^{2}}{2\pi} \sum_{l=2}^{\infty} \gamma \gamma_{\text{eff}}^{-1}(l) \left\langle |\tilde{a}_{l0}|^{2} \right\rangle \sum_{m=-l}^{l} s_{k}(l, m) , \qquad (8.37)$$

where $s_k(l, m)$ are geometric coefficients, for which $\sum_{k=1}^{k_{\text{max}}} s_k(l, m) = 1$. Thus, the effective surface tension can be found by solution of the set of linear equations Eq. (8.37) with the coefficients

$$(R^2/2\pi) \left\langle |\tilde{a}_{l0}|^2 \right\rangle \sum_{m=-l}^{l} s_k(l, m) .$$



Figure 8.5: Effective surface tension for the two-parameter (1, 2) and three-parameter trial function (3, 4) at g = 30000, T = 0.75 (1, 3) and g = 19400, T = 0.69 (2, 4).

This system is characterized by the substantial peculiarity.

In a physically significant region $1 \le k \le \Lambda$, the quantity Q_k can be determined with a good accuracy about several percent. However, in the range $\Lambda \le k \le k_{\max}$, capillary fluctuations are dominated by bulk ones and decrease rapidly. Therefore, in this region, the accuracy of Q_k values drops sharply. At $k \sim k_{\max}$, they are determined by computational noise rather than by capillary fluctuations. Due to the same reason, matrix elements of the set of equations Eq. (8.37) are also rapidly diminished and poorly determined at $k > \Lambda$ or $l > \Lambda$. Thus, the solution of this equation set turns out to be an ill-posed mathematical problem. This is exhibited in the irregularity of direct numerical solution of Eq. (8.37): at $l \sim \Lambda$, the accuracy of solution is so low that it is determined only by the order of magnitude, while at $l > \Lambda$, the $\gamma \gamma_{\text{eff}}^{-1}(l)$ values corresponding to consecutive l values become randomly scattered to a great extent differing in both the order of magnitude and sign. Small change in Q_k leads to large change in $\gamma \gamma_{\text{eff}}^{-1}(l)$. All of this makes a direct solution meaningless.

If the pattern of solution is a priori known, e.g. from theoretical considerations, a variational method is often used to solve ill-posed problems. According to this method, the function $\gamma_{\text{eff}}(l)$ can be calculated by minimization of the variance

$$\Delta^{2} = \sum_{k=1}^{\Lambda} k^{2} \left[Q_{k} - \frac{R^{2}}{2\pi} \sum_{l=2}^{k_{\max}} f(l) \left\langle \left| \tilde{a}_{l0} \right|^{2} \right\rangle \sum_{m=-l}^{l} s_{k}(l, m) \right]^{2}, \qquad (8.38)$$

where Q_k is the spectral amplitude of k-th slice mode obtained from molecular dynamics simulation, $f(l) = \gamma \gamma_{\text{eff}}^{-1}(l)$ is the trial function. The summation above is extended to k_{max} rather than to ∞ because we assume that $\langle |a_{lm}|^2 \rangle \to 0$ or $\gamma_{\text{eff}}^{-1}(l) \to 0$ at $l \to \infty$.

Calculations performed with the two-parameter trial function,

$$f(l) = \gamma \gamma_0^{-1} [1 - \theta(l - \Lambda)] , \qquad (8.39)$$

and the three-parameter trial function (here, parameters are γ_0 , Λ , and λ),

$$f(l) = \frac{\gamma}{2\gamma_0} \left[1 - \tanh\left(\frac{l-\Lambda}{\lambda}\right) \right] , \qquad (8.40)$$



Figure 8.6: Cluster capillary fluctuations spectra at g = 19400, T = 0.69 (1) and g = 30000, T = 0.75 (2). Dots represent the simulation; lines, calculation with the three-parameter trial function.

show close results (see Table 8.1 and Fig. 8.5). The value of γ_0 appears to be close to the theoretical value of bare surface tension, which is smaller than the ordinary surface tension γ ; Λ , to the cutoff for the number l. The quantity λ is the width of the region where $\gamma_{\text{eff}}^{-1}(l)$ vanishes. Both trial functions provide a good correspondence between theory and molecular dynamics calculations (Fig. 8.6).

T	g	Number of parameters	γ/γ_0	Λ	λ
0.75	30000	2	1.10	33	-
0.75	30000	3	1.09	37	13
0.69	19400	2	1.08	31	-
0.69	19400	3	1.13	34	20

Table 8.1: Optimum parameter values for different trial functions.

The main conclusion of this study is *the decrease of* λ *with the increase of temperature* (with the decrease of cutoff Λ). Hence, at higher temperatures, *vanishing of spectral amplitudes at large l is abrupt*, as it was assumed in the previous study.

8.6 Conclusions

In this paper, we have evaluated the contributions from capillary and bulk fluctuations to the total equilibrium fluctuations of cluster surface. Since we see no way to expand each individual configuration of the particles at the free cluster surface into the sum of certain bulk and capillary fluctuations, the configurations with zero capillary or bulk fluctuations were created artificially. The case of the bulk fluctuations was shown to be realized for clusters truncated by a spherical surface. The wave number spectrum of bulk fluctuations proved to be generated primarily by the discontinuity of cluster particles spatial distribution, which can be considered as a uniform random one. Since the spectrum of bulk fluctuations depends on the ratio of the wave number to the radius of a truncated cluster, it can be calculated for any cluster size by

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scaling. Subtraction of the bulk fluctuations spectrum from the total equilibrium spectrum of a free surface yields the net spectrum of capillary fluctuations. To evaluate the slice spectra obtained in MD simulation, we constructed the surface particles configurations in the form of individual spherical harmonics with zero bulk fluctuations. The slice spectra obtained for such configurations can be compared with the MD net capillary spectra.

The one-dimensional Fourier analysis of the slice spectra seems to be the only appropriate one, in contrast to a 2D analysis. In fact, the ratio of the average squared amplitude of a capillary fluctuation with $l = \Lambda$, $R^2 \langle |a_{\Lambda m}|^2 \rangle$, to the squared bulk liquid length scale r_{ℓ}^2 is

$$R^2 \left\langle \left| a_{\Lambda m} \right|^2 \right\rangle / r_{\ell}^2 \simeq T / \gamma_0 r_{\ell}^2 \Lambda^2$$

[Eq. (8.11)]. For T = 0.75, g = 30000, $T/\gamma_0 r_\ell^2 \approx 3.91$, and

$$\Lambda = 29, R^2 \left< |a_{\Lambda m}|^2 \right> / r_{\ell}^2 \approx 4.6 \cdot 10^{-3} .$$

Apparently, amplitudes of the shortest-wavelength capillary fluctuations are too small to perform a 2D spectral analysis numerically.

A comparison between the slice spectra of constructed capillary fluctuations and MD net spectra shows that it is sufficient to introduce the bare surface tension γ_0 , which is *independent on the wave number*, in contrast to the effective surface tension introduced for the total spectrum [5]. This property of γ_0 allows one to deduce a balanced relation between the excess surface area induced by the capillary fluctuations (rather than the bulk ones) and their equilibrium spectral amplitudes defined by the constant ratio γ/γ_0 [Eq. (8.16)]. Note that the excess surface area is also defined by the cutoff Λ , which is appreciably smaller than Λ_0 corresponding to the interparticle distance (for g = 30000, $\Lambda_0/\Lambda \approx 2.4$).

It was shown in this paper that the net capillary fluctuations spectrum obtained in MD simulation can be fitted by the theory with a single adjustable parameter $\kappa = 0.548$, which is independent of the cluster size and temperature. Therefore, it can be considered as a universal one and it is suitable for a flat interface as well. Apparently, this universality can be accounted for by formation of virtual chains, which can be treated as the development of an instability of the fluctuation surface with a considerable curvature. Since κ is of the same order of magnitude as the maximum of $|\nabla \xi(\vartheta, \varphi)|$, we can suppose that virtual chains are formed at those surface points, where $|\nabla \xi(\vartheta, \varphi)| \gtrsim 1$. Hence, the curvature radius must be of the same order of magnitude as the interparticle distance, which is much smaller than the cluster radius if $g \gg 1$. This explicates why κ is independent of g. Formation of a virtual chain seems to be weakly dependent on the temperature. The reason for this may be expanded temperature region of a transition between the compact and virtual chain cluster structure [17]. It was noted in Ref. [18] that highly curved regions of the interface detach clusters thus limiting its curvature. In Ref. [18], MD simulation was performed at high temperatures not far from the critical point. Since our simulations correspond to temperatures closer to the melting point, we can assume that in our case the curvature is limited due to formation of the virtual chains, which are in turn the source of evaporating particles.

We have defined the effective surface tension as a function depending on l that relates the fluctuation amplitudes calculated with the ordinary surface tension to real amplitudes and determined this quantity from the variational procedure. It proved to be qualitatively independent of the choice of trial function and the number of variational parameters, and the values of these parameters are close not only for different trial functions but also for different temperatures and cluster sizes. At small l, the relation $\gamma_{\text{eff}}(l) = \gamma_0 < \gamma$ was obtained. Moreover, as in the theory with an abrupt cutoff, the γ/γ_0 ratio is nearly independent of cluster size and temperature (Fig. 8.5). Thus, in this region, the amplitude of fluctuation modes is determined by the quantity γ_0 , whose value is smaller than the ordinary surface tension for a flat surface. At large l, amplitudes decay, which, according to theory, is associated with the formation of virtual chains. In this study, it was discovered that the width of decay region noticeably increases with a decrease in temperature.

The definition of surface particles used in this study, which made it possible to treat the fluctuation surface, is most suitable at the temperatures not too far from the triple point. It is of special interest how

8.6 Conclusions

close to the critical point this definition can be applied. As the temperature is increased from the triple point to critical one, the ratio of liquid and vapor densities decreases, and the average interface width becomes large compared to the molecular diameter. At sufficiently high temperatures, the concentration of small clusters in the vapor phase may be comparable to that of monomers. One can speculate that such clusters may be attached to the liquid–vapor interface rather than virtual chains, which may require a sophisticated definition of the surface particles including the procedure of overhangs elimination. The situation may be complicated by the fact that the contribution from overhangs to the average system density distribution is no longer negligibly small. Strong nonideality of the vapor may force a reconsideration of the liquid phase identification as well. On the other hand, it follows from Ref. [18] that the instantaneous interface density profile is abrupt even at the temperatures compared to the critical one, albeit the surface form fluctuations are great. Since our definition is based on this interface property, one can assume that it may be valid for the most part of the interval between triple and critical temperatures. An investigation of the surface fluctuations at high temperatures including the mechanism of overhangs formation will be addressed in the future work.

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> Man sollte nie soviel zu tun haben, dass man zum Nachdenken keine Zeit mehr hat.

> > Georg Christoph Lichtenberg

Abstract

Charging of a particle located in an ionized gas consisting of an atomic gas with an admixture of electrons and ions is considered under various conditions. The particle charge and a self-consistent particle field depend on the parameters of the charging process.

9.1 Introduction

When a small particle is located in an ionized gas, plasma electrons and ions attach to the particle and later recombine on its surface. Due to attachment processes, the particle becomes charged and creates with a surrounding ionized gas a self-consistent electric field that influences the process of electron and ion attachment. As a result of this process, a small particle becomes a sink for atomic charged particles of the ionized gas. The principal results for this problem were obtained half a century ago and are the basis of the contemporary understanding of this problem. But contemporary studies of new physical objects or other aspects of known objects leads to a new glance on some specific features of the general problem. The goal of this paper is to combine the old principal solutions for charging of a small particle in an ionized gas with simple models and practical algorithms for specific conditions of this process.

Charged particles are some of the components of a dusty plasma [1, 2, 3, 4, 5, 6, 7]. The self-consistent field is created around the particle due to surrounding electrons and ions which interact with the particle. It is significant that electrons and ions attach to the particle surface, and their subsequent recombination proceeds onto the particle surface. Due to absorption of electrons and ions by the particle surface the screening of the particle field by electrons and ions differs from the Debye screening [8, 9]. Our goal is to analyze the self-consistent field near a particle located in an ionized gas that consists of atoms with a small admixture of electrons and ions. Simultaneously this analysis allows one to determine the particle charge and the radius of action of the particle field that follows from the equilibrium of electron and ion currents towards the particle surface. Of course, the character of this equilibrium depends on parameters of the particle and ionized gas, and we consider various conditions for this equilibrium.

9.2 Particle Charging in a Dense Buffer Gas with Rareness Plasma

Modeling a small particle located in an ionized gas as a spherical particle of radius r_o , we use the following criterion for a dense buffer gas

$$r_o \gg \lambda$$
, (9.1)

where λ is the mean free path of buffer gas atoms. In characterizing the drift of electrons in a buffer gas by the diffusion coefficient D_e and the mobility K_e of electrons, we have for the rate $J_e(R)$ of intersection a sphere of a radius R by electrons

$$J_e = 4\pi R^2 \left(-D_e \frac{dN_e}{dR} - w_e N_e \right) , \qquad w_e = EK_e , \qquad (9.2)$$

where $N_e(R)$ is the electron number density at a distance R from the particle center, w_e is the electron drift velocity, and E(R) is the electric field strength on this distance R from the charged particle, that is directed opposite to the electron current. The minus sign in the second term accounts for an opposite direction of the electron flux and electric field strength. Within the framework of the Fuks theory [10] we assume the electric field strength to be relatively small, so that the electron drift velocity is proportional to the electric field strength and ignore a screening of the particle field by an ionized gas, so that the electric field strength is determined by the Coulomb field of the negatively charged particle

$$E = \frac{Ze}{R^2} , \qquad (9.3)$$

where -Z is the particle charge in units of electron charges (Z > 0).

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Since formation and recombination of electrons and ions is absent near the particle, Eq. (9.2) may be considered as the equation for the number density of electrons N_e that has the form (with accounting for Eq. (9.3))

$$J_e = 4\pi D_e \left(\frac{dN_e}{d\frac{1}{R}} - \frac{Ze^2 N_e}{T}\right) , \qquad (9.4)$$

where we used the Einstein relation [11, 12] between the diffusion coefficient and mobility of electrons in a gas

$$K_e = \frac{eD_e}{T} , \qquad (9.5)$$

with the electron temperature T. Solving this equation under the condition $N_e(r_o) = 0$ and introducing the reduced potential energy of an electron in the particle field $u(R) = Ze^2/RT$, we obtain

$$N_e(R) = -\frac{J_e}{4\pi D_e} \int_{r_o}^{R} \frac{dR'}{(R')^2} \exp\left[u(R) - u(R')\right] = \frac{J_e T}{4\pi D_e Z e^2} \left[1 - \exp\left(\frac{Ze^2}{TR} - \frac{Ze^2}{Tr_o}\right)\right] .$$
(9.6)

Using another boundary condition far from the particle $N_e(\infty) = N_o$, we obtain the Fuks formula [10] for the rate of electron attachment to a particle of a negative charge

$$J_e = \frac{4\pi D_e N_o Z e^2}{T \left[\exp\left(\frac{Z e^2}{T r_o}\right) - 1 \right]}$$
(9.7)

From this relation one can find the rate of attachment of positive ions to a particle by replacing $Z \rightarrow -Z$ and the electron parameters by the ion ones. This operation gives

$$J_{+} = \frac{4\pi D_{+} N_{o} Z e^{2}}{T \left[1 - \exp\left(-\frac{Z e^{2}}{T r_{o}}\right)\right]}$$
(9.8)

The equilibrium particle charge follows from the equality of electron and ion current to the particle surface

$$Z = \frac{r_o T}{e^2} \ln \frac{K_e}{K_+} , \qquad (9.9)$$

where we assume the particle to be negatively charged and the electron and ion temperatures to be identical. Since we assume that attachment of an individual electron or ion to the particle surface does not influence the character of electron and ion motion near the particle, the above consideration requires the fulfillment of following criterion

$$Z \gg 1. (9.10)$$

In addition, the used assumption of a weak screening of the particle field by a surrounding plasma holds true under the criterion

$$r_D \gg r_o , \qquad (9.11)$$

where r_D is the Debye-Hückel radius [8, 9] for an ionized gas.



Figure 9.1: From left to right: The reduced number density of electrons $n_e = N_e/N_o$ as a function of u at $u_o = 4$, $u_o = 6$ and the reduced number density of ions $n_+ = N_+/N_o$ at $u_o = 4$, $u_o = 6$.

We give also the limiting cases of the Fuks formulas Eqs. (9.7) and (9.8) for the total flux of atomic charged particles to the surface of a cluster or small macroscopic particle. In the limiting case of a neutral particle $Z \rightarrow 0$ the Fuks formulas Eqs. (9.7) and (9.8) are converted into the Smoluchowski equation [13]

$$J_o = 4\pi D_+ N_o r_o . (9.12)$$

In the case of a large particle charge $Ze^2/(r_oT) \gg 1$ for an attractive interaction potential (a particle and ion have charges of opposite signs) Eq. (9.8) is transformed into the Langevin formula [14]

$$J_{+} = \frac{4\pi Z e^2 N_o D_{+}}{T} = 4\pi Z e K_{+} N_o .$$
(9.13)

Let us analyze, now, some specific aspects of particle charging. For this purpose, we rewrite the space distribution for the number densities of electrons N_e and ions N_i near the particle in terms of the reduced potential energy of an electron in the particle field, u = u(R)

$$N_e(R) = N_o \left[\frac{\exp(u_o) - \exp(u)}{\exp(u_o) - 1} \right] , \qquad N_+(R) = N_o \left[\frac{\exp(u_o - u) - 1}{\exp(u_o) - 1} \right] , \tag{9.14}$$

where $u_o = u(r_o)$. Fig. 9.1 illustrates the dependencies given by Eq. (9.14) at some values of u_o . Note that for a plasma consisting of electrons and ions $u_o \gg 1$ because $K_e \gg K_+$. One can see that at low values of u

$$N_{+} \approx N_{o} , \qquad N_{e} = N_{o}(1-u) .$$
(9.15)

From this condition it follows that only electrons give a contribution to screening of the particle field.

Let us consider the character of particle field screening by a surrounding plasma. Poisson's equation

$$\Delta u(R) \equiv \frac{1}{R} \frac{d^2(Ru)}{dR^2} = \frac{4\pi e^2 [N_+(R) - N_-(R)]}{T}$$
(9.16)

at low \boldsymbol{u} takes the form

$$\frac{d^2(Ru)}{dR^2} = \frac{Ru(R)}{r_D^2} , \qquad (9.17)$$

where the Debye-Hückel radius r_D is determined by electrons and is given by

$$r_D = \sqrt{\frac{T}{4\pi N_o e^2}} \,. \tag{9.18}$$

Correspondingly, the electric potential of the particle $\varphi = uT/e$ has the form

$$\varphi(R) = \frac{Ze}{R} \exp\left(-\frac{R}{r_D}\right) . \tag{9.19}$$

From this relation, one can evaluate the screening charge ΔZ from the plasma around the particle when the criterion Eq. (9.11) holds true

$$\Delta Z = \int_{r_o}^{\infty} 4\pi R^2 dR (N_+ - N_-) = \int_{r_o}^{\infty} 4\pi R^2 dR N_o u = Z , \qquad (9.20)$$

where we use Eq. (9.19) for the particle electric potential and assume that the main contribution to this integral is determined by large distances from the particle $R \sim r_D \gg r_o$. Thus, the shielding charge compensates the particle charge.

Let us define the radius of action l of the particle field in a plasma such that the particle interaction energy with electrons or ions is comparable to their thermal energy, i.e., u(l) = 1. Since $u(R) = Ze^2/RT$ and the particle charge is given by Eq. (9.9), we have

$$l = r_o \ln\left(\frac{K_e}{K_+}\right) \,, \tag{9.21}$$

and l exceeds the particle radius r_o .

The Fuks theory relates to a dense buffer gas Eq. (9.1) under criteria where the particle charge is large Eq. (9.10), the electron T_e and ion T_i temperatures are identical, and the plasma density is small according to the criterion Eq. (9.11). One can generalize the Fuks formula Eq. (9.9) for the particle charge to the case where the Maxwell energy distributions of electrons and ions hold true, but the electron T_e and ion T_i temperatures are different. Because the expressions for electron Eq. (9.7) and ion Eq. (9.8) fluxes on the particle surface are independent, these formulas are conserved for different electron and ion temperatures, and then from their equality we have for the particle charge [15, 16]

$$Z = \frac{r_o T_e}{e^2} \ln \frac{K_-(T_e)}{K_+(T_i)} \,. \tag{9.22}$$

If the energy distribution function differs from the Maxwell one, in accordance with derivation of Eq. (9.7) the value $T_e = eD_e/K_e$ is used as the electron temperature [15, 16]. Note that the Fuks theory is based also on the linear dependence of the electron and ion drift velocities on the electric field strength.

9.3 Particle Charging in Rareness Gas Discharge Plasma

If the particle is located in a gas discharge plasma, simultaneous action of an external electric field of gas discharge and the particle field results in a complex character of attachment of electrons and ions to the particle. In particular, Fig. 9.2 gives the electric potential

$$\varphi = Ex + \frac{Ze}{R} , \qquad (9.23)$$

that is created by a discharge electric field of strength E and by a particle of charge Z. Here the origin is taken at the particle center, and x is the direction along the discharge electric field. As is seen, equipotential curves are closed at distances from the particle below r_1 , where

$$r_1 = \sqrt{\frac{Ze}{E}} . \tag{9.24}$$

One can see that the problem of particle charging in a gas discharge plasma may be reduced to the Fuks theory of particle charging if the criterion $r_o \ll r_1$ holds true. In this case it is necessary to take into account the real dependence $w_e(E)$ for the drift velocity of electrons on the electric field strength in high electric fields.



Figure 9.2: Lines of identical electron potentials in the plane passed through the particle center if an electron is located in the Coulomb center of a charged particle and constant electric field, the length units are such that $r_1 = \sqrt{ze/E} = 4$.

Below for definiteness we consider the case of a helium plasma of a high electric field strength, so that the typical electron energy exceeds significantly the thermal energy of atoms and ions. But this energy is not so high in order to be ignored by ionization processes. Because of small exchange by energy in elastic electron-atomic collisions, the thermal energy of ions is close to the thermal energy of the atoms in a wide range of electric field strengths where a typical electron energy exceeds those significantly [17]. Below we consider this range of electric field strengths and assume the diffusion cross section of electronatom collisions to be independent of the collision energy, as it is found in the helium case. Then the

electron distribution function in a range of electric field strengths under consideration is determined by the Dryvesteyn formula [18, 19], that leads to the following formulas for the electron drift velocity w_e and its diffusion coefficient (for example [20])

$$D_e = 0.29 \left(\frac{M}{m_e}\right)^{1/4} \lambda \sqrt{\frac{eE\lambda}{m_e}} , \qquad w_e = 0.90 \left(\frac{m_e}{M}\right)^{1/4} \sqrt{\frac{eE\lambda}{m_e}} , \qquad eE\lambda \gg T , \qquad (9.25)$$

where $\lambda = 1/(N_a \sigma^*)$ is the mean free path for electrons, so that σ^* is the diffusion cross section of electronatom scattering, m_e and M are the electron and atom masses, T is the atomic temperature. In the helium case ($\sigma^* \approx 6 \text{ Å}^2$, $M/m_e \approx 7700$) these relations have the form

$$D_e = 2.7\lambda \sqrt{\frac{eE\lambda}{m_e}}$$
, $w_e = 0.097\sqrt{\frac{eE\lambda}{m_e}}$, $a = \frac{D_e}{w_e} = 28\lambda$. (9.26)

We have now another dependence on the particle electric field strength for the electron drift velocity and electron diffusion coefficient as compared to those obtained in the Fuks case, and hence we solve once more the transport equation Eq. (9.2) as the balance equation for the electron number density at other dependencies $w_e(E)$ and $D_e(E)$. Taking

$$r_o \ll r_1 = \sqrt{\frac{Ze}{E}} , \qquad (9.27)$$

where E is the electric field strength far from the particle, the rate of electron attachment to the particle surface is given by

$$J_e = -D_e \frac{dN_e}{dR} + w_e N_e . aga{9.28}$$

Considering this relation as an equation for the electron number density, we use the above dependence of the electron diffusion coefficient D_e and the electron drift velocity w_e

$$D_e = D_o \sqrt{1 + \frac{Ze^2}{R^2}} = D_o \sqrt{1 + \frac{r_1^2}{R^2}}, \qquad w_e = w_o \sqrt{1 + \frac{r_1^2}{R^2}}, \qquad (9.29)$$

where D_o and w_o are the electron diffusion coefficient and electron drift velocity of electrons in a buffer gas far from the particle. In the range $R \ll r_1$ the expression for the electron attachment rate has the form

$$J_e = 4\pi R^2 \sqrt{1 + \frac{r_1^2}{R^2}} D_o \left(-\frac{dN_e}{dR} + \frac{N_e}{a} \right) , \qquad (9.30)$$

where $a = D_o/w_o = 28\lambda$. Solution of this equation for the case $r_1 \gg a \gg r_o$ gives

D

$$N_e(R) = -\frac{J_e}{4\pi D_o} \exp\left(\frac{R}{a}\right) \int_{r_o}^{R} \frac{dR'}{R'\sqrt{r_1^2 + (R')^2}} \exp\left(-\frac{R'}{a}\right) \approx -\frac{J_e}{4\pi D_o} \ln(a/r_o) \exp\left(\frac{R}{a}\right) , \quad (9.31)$$

and this solution holds true at $R < r_1$, whereas the minus sign means that the electron flux is directed to the particle. In this case we have

$$J_e = \frac{4\pi D_o r_1 N_o}{\ln(a/r_o)} \exp(-R/a) , \qquad r_1 \gg R \gg a .$$
(9.32)

The particle charge Z follows from equality of rates of electron and ion attachment to the particle, where the latter is given by the Langevin formula Eq. (9.13). It is convenient to use this equality as an equation for $r_1 = \sqrt{Ze/E}$ that has the form

$$\frac{r_1}{a} \exp\left(\frac{r_1}{a}\right) \approx \frac{D_o}{EK_+ a \ln(a/r_o)} , \qquad r_1 \ll a .$$
(9.33)

E/N, Td	$T_{ef}, \text{ eV}$	$\overline{\varepsilon}, eV$	$r_1, \ \mu \mathrm{m}$	$Z, 10^4$
1	0.46	0.61	52	5.1
2	0.92	1.22	48	8.6
4	1.85	2.43	46	16
6	2.78	3.65	41	19

Table 9.1: Parameters of a gas discharge helium plasma and particle charging in it.

Note that the particle charge depends weakly on the particle radius r_o that is located in a range $a \gg r_o \gg \lambda$.

Table 9.1 contains parameters of particle charging under certain conditions, namely, the pressure p = 1 atm that gives for the mean free path $\lambda = 0.6 \mu m$, the particle radius is $r_o = 1 \mu m$, that gives $a = 17 \mu m$. Table 9.1 contains the effective temperature T_{ef} of electrons and the electron average energy $\overline{\varepsilon}$ far from the particle that are given by the formulas

$$T_{ef} = \frac{eD_eE}{w_e} = 0.325 \sqrt{\frac{M}{m_e}} eE\lambda , \qquad \overline{\varepsilon} = 0.427 \sqrt{\frac{M}{m_e}} eE\lambda .$$
(9.34)

The data of Table 9.1 correspond to the criterion

$$r_1 \gg a \gg r_o \gg \lambda . \tag{9.35}$$

Though this sequence of the size parameters holds true, the accuracy of the formulas used is restricted and Eq. (9.33) gives only rough estimates for the particle charge. Note that the particle charge according to Table 9.1 data is approximately by 30 times larger than that according to Eq. (9.9). This shows that the presence of an electric field in an ionized gas can increase significantly the charge of a particle located in this gas. We also note that even in a narrow range of parameters Eq. (9.35) the numerical values of Table 9.1 require the absence of ionization processes near the particle while a large particle charge corresponds also high electric field near the particle, i.e. the above results transfer the tendency in the influence of an external electric field on the value of the particle charge.

9.4 Particle Charging in a Dense Plasma and Double Layer of Gas Discharge

In considering the particle charging in a dense plasma where the criterion Eq. (9.11) does not hold, we assume the criteria

$$r_o \gg r_D , \qquad r_D \gg \lambda$$

$$\tag{9.36}$$

to be fulfilled and use firstly Eqs. (9.14) for the electron and ion number densities as an approximation. Then the relative difference of the number densities of ions and electrons is given by

$$n(u) \equiv \frac{N_{+}(R) - N_{e}(R)}{N_{o}} = \frac{[1 - \exp(u - u_{o})][1 - \exp(-u)]}{1 - \exp(-u_{o})},$$
(9.37)

and Fig. 9.3 gives the dependence n(u) that is symmetric with respect to the transformation $u \to u_o - u$ and has the maximum at $u = u_o/2$, where it is equal to

$$n_{max} = \frac{1 - \exp(-u_o/2)}{1 + \exp(-u_o/2)} \,. \tag{9.38}$$

As is seen, $n(u) \leq 1$, and at low u we have n(u) = u.



Figure 9.3: The reduced difference of the number density of electrons $n(u) = (N_+ - N_e)/N_o$ for $u_o = 2$ (1) and $u_o = 2$ (2).

Let us refuse from the criterion Eq. (9.11) of a low density of charged atomic particles. Approximating the number densities of electrons and ions by Eq. (9.37), we obtain the Poisson equation as earlier in the form

$$\frac{d^2(Ru)}{dR^2} = \frac{Ru(R)}{r_D^2} , \qquad (9.39)$$

and its solution is

$$\varphi(R) = \frac{ze}{R} \exp\left(-\frac{R}{r_D}\right) , \qquad (9.40)$$

where z is an effective particle charge shielded by ions, and $z \leq Z$, while if the criterion Eq. (9.11) holds true, z = Z.

One can apply the above results to the layer near the walls of the gas discharge chamber where the positive column is located. In this case electrons and ions of the gas discharge plasma attach to the walls and transfer them the charge, whereas the plasma far from the walls is quasi-neutral, and the criterion Eq. (9.36) holds true. Using Eqs. (9.37) for the number densities of electrons and ions and assuming $u_o \gg 1$, one can obtain that the relation $N_+ = N_o$ is violated only close to the particle surface. Using this fact in the Poisson equation, we write it in the form

$$\frac{d^2u}{dx^2} = 1 - \frac{N_e}{N_o} , \qquad x = \frac{z}{r_D} , \qquad (9.41)$$

where z is the distance from the walls, and the Debye-Hückel radius is given by Eq. (9.18). In this case the walls are charged negatively, so that this field creates the electric field that prevents attachment of electrons to the walls and equalizes the electron and ion currents toward the walls. The reduced electric potential is given by Eq. (9.21) if the electric potential is zero far from the walls. As a result, we have the following

9.5 Particle Charging in Rareness Ionized Gas with Free Ions

equation for the reduced electric field strength

$$\frac{d^2u}{dx^2} = \frac{\exp(u) - 1}{\exp(u_o) - 1} , \qquad u(\infty) = 0 , \qquad u(0) = u_o = \ln\left[\frac{K_e(T_e)}{K_+(T)}\right] .$$
(9.42)

Let us decrease the order of Eq. (9.41) by multiplication of this equation by du/dx and integration the equation under the boundary $du/dx(x = \infty) = 0$. We obtain

$$\frac{du}{dx} = \sqrt{\frac{2(e^u - u)}{e^{u_o} - 1}} \,. \tag{9.43}$$

From this we have for the electric field strength E_o at the walls

$$E_o = -\frac{T_e}{er_D}\frac{du}{dx} = -\frac{T_e\sqrt{2}}{er_D}\sqrt{1 - \frac{u_o - 1}{e^{u_o} - 1}} = -\frac{T_e\sqrt{2}}{er_D}f(u_o) .$$
(9.44)

Under real conditions $u_o \gg 1$ we have $f(u_o) \approx 1$. Indeed, f(2) = 0.92, f(3) = 0.95, f(4) = 0.97. Therefore in reality we have for the electric field strength E_o at the walls

$$E_o = -\frac{T_e \sqrt{2}}{e r_D} \,. \tag{9.45}$$

9.5 Particle Charging in Rareness Ionized Gas with Free Ions

Particle charging in a rareness ionized gas corresponds to the criterion

$$\lambda \gg l \,, \tag{9.46}$$

where l is a radius of action of the particle field, and this criterion is opposite with respect to the criterion Eq. (9.1). Let us assume that positive ions screen the negative particle charge. Defining by U(R) the potential energy of a self-consistent field that is established in the course of ion flight in the particle field, we below determine this potential that acts on positive ions. In determination of this self-consistent field, we go over from dynamics of ion motion in the particle field to statistical mechanics on the basis of the ergodic theorem [21, 22] that gives the space distribution function [9, 23] of free ions in the particle field. In this transfer we assume the probability dP_i of ion location in a given space region to be proportional to a time range dt during which a given ion is located in this space region. Correspondingly, the ion number density is proportional to the above probability $N_i(R) \sim dP_i$. In turn, a time range dt for ion location in a space region of distance between R and R + dR from the particle follows from the equation of motion [24]

$$dt = \frac{dR}{v_R} = \frac{dR}{v\sqrt{1 - \rho^2/R^2 - U(R)/\varepsilon}} ,$$
(9.47)

where $v_R(R)$ is the normal velocity component of an ion at a distance R from the particle, v is the ion velocity far from the particle, $\varepsilon = m_i v^2/2$ is the ion kinetic energy far from the particle, so that m_i is the ion mass, and ρ is the impact parameter of collision.

On the other hand, we have the ion number density $N_i(R)$ at a distance R from the particle as

$$N_i \sim \frac{\int \rho d\rho dP_i}{4\pi R^2 dR} \,. \tag{9.48}$$

Normalizing this relation such that in the absence of interaction the ion number density is equal to the ion number density N_o far from the particle, we have

$$N_i(R) = N_o \int_0^{\rho(R)} \frac{\rho d\rho}{\sqrt{1 - \frac{\rho^2}{R^2} - \frac{U(R)}{\varepsilon}}},$$
(9.49)

where for free ion motion U(R) = 0 the impact parameter of ion-particle collision is $\rho(R) = R$ if R is the distance of closest approach.

Let us divide the ion trajectories into two groups, so that the first group includes the trajectories with ion capture by the particle $\rho \leq \rho_c$, where ρ_c is the impact parameter of collision above which the ion-particle contact is impossible. This impact parameter of ion capture in the self-consistent field with the particle radius r_o as the distance of closest approach is given by [24]

$$\rho_c^2 = r_o^2 \left[1 - \frac{U(r_o)}{\varepsilon} \right] \,. \tag{9.50}$$

If an ion moves along a trajectory of the second group, it goes to infinity after approach to the particle. Summarizing both types of trajectories in the ion number density, we obtain Eq. (9.49) in the form [25]

$$N_i(R) = \frac{N_o}{2} \left[\sqrt{1 - \frac{U(R)}{\varepsilon}} + \sqrt{1 - \frac{\rho_c^2}{R^2} - \frac{U(R)}{\varepsilon}} \right] .$$
(9.51)

Averaging on the Maxwell distribution function of ions

$$f(\varepsilon) = N_o \frac{2\varepsilon^{1/2}}{\sqrt{\pi}T_i^{3/2}} \exp\left(-\frac{\varepsilon}{T_i}\right) , \qquad (9.52)$$

we obtain for the ion number density in the range of strong ion-particle interaction [25]

$$N_i(R) = N_o \left[\sqrt{\frac{|U(R)|}{\pi T_i}} + \sqrt{\frac{|U(R)| - |U(r_o)| r_o^2 / R^2}{\pi T_i}} \right] , \qquad |U(R)| \gg T_i .$$
(9.53)

We are guided in this formula by ion-particle attraction.

We now determine the potential energy U(R) for a self-consistent field that is created by the particle charge and is screened by free ions. The particle has a negative charge Z such that $|Z|e^2/r_o \gg T_i$. Therefore the ion number density in the region of strong ion attraction is $N_i \gg N_o$, and because the electron number density in this region, N_e , electrons do not take part in screening the particle field, and hence we below neglect the presence of electrons in a region of strong ion-particle interaction and assume that the radius of action of a self-consistent field l exceeds the particle radius $(l \gg r_o)$.

Let us introduce a current charge z(R) inside the sphere of a radius R that is the sum of the particle charge and a charge of ions located inside this sphere. According to the Gauss theorem [26, 27] we have

$$\frac{dz}{dR} = -4\pi R^2 \cdot N_i(R) = -4\pi R^2 \cdot N_o \sqrt{\frac{4|U(R)|}{\pi T_i}},$$
(9.54)

where $z(r_o) = |Z|$ and we restricted by a region $R \gg r_o$ in Eq. (9.53). The potential energy U(R) of the self-consistent field is

$$U(R) = \int_{R}^{\infty} E(R)dR \approx \frac{z(R)e^2}{R} , \qquad (9.55)$$

and the used simplification leads to an error ΔU in the potential energy that may be determined in the following order of the perturbation theory.

We give in Fig. 9.4 the ratio of the accurate value in the right hand side of the equation for z(R) to its approximated value depending on a distance R from the particle and will use below its approximated value. Then the equation for a current charge z(R) is

$$\frac{dz}{dR} = -4\pi R^2 \cdot N_o \sqrt{\frac{4ze^2}{\pi T_i R}} , \qquad (9.56)$$

and has the following solution

$$z = |Z| \left[1 - \left(\frac{R}{l}\right)^{5/2} \right]^2 , \qquad l = \frac{0.66}{N_o^{2/5}} \left(\frac{|Z|T_i}{e^2}\right)^{1/5} = \frac{0.66|Z|^{2/5}}{N_o^{2/5} R_o^{1/5}} , \tag{9.57}$$

where $R_o = |Z|e^2/T_i$, and $R_o \gg r_o$. Note that according to the derivation of this formula, it holds true until $|U(R)| \gg T_i$ and if this criterion violates, we use the above formulas as an approximation.



Figure 9.4: The correction to the simplified potential energy $U(R) = z(R)e^2/R$ of self-consistent field leads to a replacement of this potential energy by the value $U(R) - \Delta U = \int_{R}^{\infty} ze^2 dR/R^2$. Dark triangles relate to shielding by free ions, whereas open triangles correspond to screening of the particle charge by trapped ions.

In determination the particle charge Z, we assume that each contact of an ion or electron with the particle surface leads to charge transfer and take into account that electron and ion currents to the particle surface are originated in a region with a weak particle field. Then we have for the rate of ion J_i and electron J_e attachment to the particle surface [24]

$$J_i = N_o \sqrt{\frac{8T_i}{\pi m_i}} \left(1 + \frac{|Z|e^2}{r_o T_i} \right) \cdot \pi r_o^2 , \qquad J_e = N_o \sqrt{\frac{8T_e}{\pi m_e}} \cdot \pi r_o^2 \exp\left(-\frac{|Z|e^2}{r_o T_e}\right) , \tag{9.58}$$

where N_o is the number density of electrons and ions far from the particle, T_i , T_e are the ion and electron temperatures correspondingly, m_e , m_i are the electron and ion masses. Equalizing the rates of ion and electron attachment to the particle surface and introducing the parameter $x = |Z|e^2/(r_oT_e)$, we obtain

$$x = \frac{1}{2} \ln \frac{T_e m_i}{T_i m_e} - \ln \left(1 + x \frac{T_e}{T_i} \right) .$$
(9.59)

Taking $xT_e \gg T_i$, we have the following equation for x [28]

$$x = \frac{1}{2} \ln \frac{T_i m_i}{x^2 T_e m_e} \,. \tag{9.60}$$

In particular, for an example of a gas discharge argon plasma with the parameters $T_e = 1$ eV and $T_i = 400$ K Eq. (9.60) gives x = 2.86 or $|Z|/r_o = 2.0$ nm⁻¹. Note that we are guided by a large particle

charge $|Z| \gg 1$, so that attachment of one electron or ion does not influence on the subsequent process of attachment of electrons and ions. For the above example this corresponds to $r_o \gg 0.5$ nm. We note also that Eqs. (9.59) and (9.60) require that the potential energy of an electron on the particle surface is $|Z|e^2/r_o$. This holds true if the radius of action of the particle field, l, exceeds the particle radius r_o .

The above consideration is based on the criterion Eq. (9.46) that has the form

$$N_a l \sigma^* \ll 1 , \tag{9.61}$$

where σ^* is diffusion ion-atom cross section of scattering that is assumed to be independent of the collision velocity. If an atomic ion is located in a parent gas, the diffusion cross section of ion-atom scattering is expressed through the cross section σ_{res} of ion-atom resonant charge exchange as $\sigma^* = 2\sigma_{res}$ [29], and the criterion Eq. (9.46) takes the form

$$2N_a l \sigma_{res} \ll 1 . \tag{9.62}$$

In particular, the cross section of resonant charge exchange at the collision energy in the laboratory frame of reference 0.01 eV is equal to $\sigma_{res} = 83\text{\AA}^2$ [30], and the regime under consideration is realized at the pressure $p \ll 0.1$ Torr, if the particle radius is $r_o = 1\mu\text{m}$ and the ion temperature is comparable to the room one.

One can see that criteria Eqs. (9.1) and (9.46) relates to two opposite regimes of particle screening in an ionized gas. Note that in reality $l \gg r_o$ and, in particular, for the above example of the argon plasma with parameters $T_e = 1 \text{ eV}$, $T_i = 400 \text{ K}$, $r_o = 1 \ \mu\text{m}$ and |Z| = 2000 we have $l = 90\ \mu\text{m}$ and $l = 36\ \mu\text{m}$ for $N_o = 10^9 \text{ cm}^{-3}$ and $N_o = 10^{10} \text{ cm}^{-3}$ correspondingly. In addition, the cross section of electron-atom scattering at low energies is small compared to the ion-atom cross section of scattering. For example, in the helium case the electron-atom diffusion cross section lies in the range of $5 - 7 \text{ Å}^2$, while the cross section of resonant charge exchange at the ion energy of 0.01 eV is $43 \ \text{Å}^2$. From this it follows that there is a large range of particle sizes between the cases given by Eqs. (9.1) and (9.46).

9.6 Particle Charging in Rareness Ionized Gas with Trapped Ions

Along with free ions, trapped ions, i.e. captured in a closed orbit, may be responsible for particle screening [31]. These ions are formed as a result of the charge exchange process in the particle field, where a formed atom transfers its energy to a formed ion, and the latter occupies a closed orbit. Though the probability of resonant charge exchange is small for an ion propagated through a region of particle field action, this small probability is compensated by a large lifetime of a trapped ion captured in a closed orbit. The trajectories of trapped ions are different for the Coulomb particle field and a screening Coulomb field [24, 32], as it is demonstrated in Fig. 9.5.

The role of the captured ions in screening of the particle charge was studied widely, in particular, in [1, 33, 34, 35, 36, 37, 38, 39, 40, 41]. We below represent a simple and practical version [25] with using that the cross section σ_{res} of resonant charge exchange is independent of the collision energy and exceeds significantly that for elastic ion-atom scattering; as a result, colliding particles in the resonant charge exchange process are moving along straightforward trajectories [42, 43] (the relay-race character of charge transfer). Accounting for these facts allows us to restrict a number of parameters that determine the ion capture in a closed orbit as it is given in Fig. 9.6. We below determine formation of trapped ions in appropriate range of parameters and spread the results as a model in the other parameter range.

We use the criterion

$$R_o = \frac{|Z|e^2}{T_i} \gg r_o , \qquad (9.63)$$

and take into account that a captured ion may become free if it is located near the boundary of particle field action, i.e. if $R \approx l$, whereas ions captured at distances $R > \sqrt{r_o R_o}$ are moving along stable closed



Figure 9.5: The trajectories of the trapped ions captured on the closed orbit in the Coulomb center (left) and the screened Coulomb center (right). 1 is the particle, 2 is the trajectory origin, 3 is the end point of the trajectory part.

trajectories. Hence, trapped ions influence the screening of the particle field at the criterion

$$l > \sqrt{r_o R_o} . \tag{9.64}$$

In this case a subsequent charge exchange process transfers the ion in closed orbits that are nearby to the particle. If a distance from the particle is less than $\sqrt{r_o R_o}$, a subsequent charge exchange event leads to ion capture by the particle. Thus, under the criterion Eq. (9.64), the kinetics of a trapped ion consists of a series of ion transitions in nearby closed orbits of this ion, and in the end the ion attaches to the particle surface. Because of many acts of subsequent events of charge exchange, the number density of trapped ions may be high enough and can exceed the number density of free ions in the particle field for a rareness plasma. Therefore in this limit trapped ions determine the screening of the particle field.

Because the cross section of resonant charge exchange exceeds significantly that for elastic ion-atom collisions, colliding ion and atom in this process are moving along straightforward trajectories, and the formed ion acquires the energy ε and the direction of motion of the former atom [42, 44]. Assuming that the ion trajectory does not touch a particle surface (the distance of closest approach r_{min} exceeds the particle radius r_o), we have from the orbital momentum conservation [24] for ion transition into a stable close orbit [25]

$$\frac{R^2}{r_o^2} \le 1 + \frac{U(R) - U(r_o)}{\varepsilon} , \qquad (9.65)$$

where U(R) is the particle potential energy for an ion at a capture distance R. For simplicity we consider the range of parameters

$$|U(r_o)| \gg |U(R)| \gg \varepsilon , \tag{9.66}$$

at which a trapped ion cannot go to infinity and is captured into a closed orbit. If an ion is formed with an energy ε at a distance R from the particle, the probability $P_{tr}(R, \varepsilon)$ of capture of a free ion in a closed orbit or the probability $p_{tr}(R, \varepsilon)$ of transition of a trapped ion in another closed orbit are given by

$$P_{tr}(R,\varepsilon) = p_{tr}(R,\varepsilon) = \int_{0}^{\cos\theta_{o}} d\cos\theta = \cos\theta_{o} = \sqrt{1 - \frac{r_{o}R_{o}}{R^{2}}}, \qquad R \ge \sqrt{r_{o}R_{o}}.$$
(9.67)

Spreading this result on a wide range of distances in accordance with the parameters indicated in Fig. 9.6 and accounting for the possibility for an ion to leave a closed orbit at the boundary of the region of action

of the particle field, we represent the probability of ion capture in a closed orbit as

$$P_{tr}(R,\varepsilon) = \sqrt{1 - \frac{r_o R_o}{R^2}} \left(1 - \frac{l}{R}\right), \qquad l > \sqrt{r_o R_o}.$$

$$(9.68)$$

Figure 9.6: Used ion parameters of a trapped ion formed in the resonant charge exchange event that proceeds at a point **R**: r_{min} , r_{max} are the minimum and maximum distances from the particle center for the trajectory of a captured ion, θ is the angle between the direction of ion motion after the resonant charge exchange event and the vector **R**. 1 is the particle, 2 is the point of resonant charge exchange.

In order to find the connection between the number density of free N_i and trapped N_{tr} ions in the region of particle field action, we use the balance equation

$$N_a \sigma_{res} N_i P_{tr} v_i = N_a \sigma_{res} N_{tr} v_{tr} (1 - p_{tr}) , \qquad (9.69)$$

where v_i , v_{tr} are the relative velocities in the charge exchange process for a free or trapped ion and atom, P_{tr} , p_{tr} are the probabilities of ion transition in a closed orbit for a free and trapped ion correspondingly. For ion distances R from the particle under consideration we have $|U(R)| \gg \varepsilon$, and the velocity of a free ion is $v_i = \sqrt{2|U(R)|/m_i}$. The kinetic energy of a trapped ion is in the average |U(R)|/2 according to the virial theorem [45] if the ion is located in the Coulomb particle field. This gives for the velocity of a trapped ion $v_{tr} = \sqrt{|U(R)|/m_i}$, and $v_i/v_{tr} = \sqrt{2}$. Since $P_{tr} = p_{tr}$, we obtain from the balance equation Eq. (9.69)

$$N_{tr}(R) = N_i(R) \frac{R^2 \sqrt{2}}{r_o R_o} \sqrt{1 - \frac{r_o R_o}{R^2}} \left(1 + \sqrt{1 - \frac{r_o R_o}{R^2}} \right) \left(1 - \frac{l}{R} \right) , \qquad l \gg R \ge \sqrt{R_o r_o} , \quad (9.70)$$

and the last term takes into account existence of closed orbits for a trapped ion only at R < l. Though our derivation corresponds to middle ion distances from the particle and is spread to the particle field boundary, the results may give reliable evaluations. From this it follows that at a low number density N_o of a surrounding plasma trapped ions dominate in screening the particle field, whereas at a high plasma density trapped ions are absent and free ions determine the screening of the particle field.

9.7 Particle Charging and Screening in Rareness Ionized Gas

Simultaneous participation of free and trapped ions in screening the particle field complicates the calculation of screening parameters. We use below a simple algorithm taking into account only free or trapped ions and at parameters when the contributions of free and trapped ions in the particle field screening are comparable,

9.7 Particle Charging and Screening in Rareness Ionized Gas

we use both these versions. A proximity of the results of these limiting versions justifies this algorithm. We below represent this algorithm.

As in the case of a dense buffer gas, we introduce a current charge z(R) for a total charge in a sphere of a radius R and use a simplified expression for the potential energy U(R) of a self-consistent field,

$$U(R) = \frac{z(R)e^2}{R} ,$$
 (9.71)

and in Fig. 9.6 is indicated the accuracy of this simplification. In the case where free ions dominate in screening of the particle field, the number densities of free N_i and trapped N_{tr} are determined by Eqs. (9.53), (9.57) and (9.70)

$$N_i(R) = N_o \sqrt{1 + \frac{4R_o}{\pi R} \left[1 - \left(\frac{R}{l}\right)^{5/2}\right]^2}, \qquad N_{tr}(R) = N_i(R) \cdot \frac{2R^2 \sqrt{2}}{r_o R_o} \Phi(R) \left(1 - \frac{R}{l}\right),$$
(9.72)

and the function $\Phi(R)$ is given by

$$\Phi(R) = \frac{1}{2}\sqrt{1 - \frac{r_o R_o}{R^2}} \left(1 + \sqrt{1 - \frac{r_o R_o}{R^2}}\right) .$$
(9.73)

In the other limiting case when trapped ions dominate we are based on the equation for a current charge z(R)

$$\frac{dz}{dR} = -4\pi R^2 \cdot N_i(R) , \qquad (9.74)$$

with the boundary condition $z(r_o) = |Z|$, and use the number density of trapped ions N_{tr} in this equation instead of $N_i(R)$. The accuracy of this approximation is given in Fig. 9.4 by open triangles for trapped ions. Solution of this equation gives

$$z = |Z| \left[1 - \left(\frac{R}{l}\right)^{9/2} \right]^2, \qquad l = 1.05 \left(\frac{|Z|r_o \sqrt{R_o}}{N_o \Phi(9l/11)}\right)^{2/9}.$$
(9.75)

From this we have for the number density of free and trapped ions for the second version when trapped ions dominate

$$N_i(R) = N_o \sqrt{1 + \frac{4R_o}{\pi R} \left[1 - \left(\frac{R}{l}\right)^{9/2}\right]^2}, \qquad N_{tr}(R) = N_i(R) \cdot \frac{2R^2 \sqrt{2}}{r_o R_o} \Phi(R) \left(1 - \frac{R}{l}\right), \quad (9.76)$$

and the particle charge Z given by Eqs. (9.59) and (9.60) is independent of the version because electron and ion currents Eq. (9.58) are started outside the particle field.

On the basis of the above expressions for the number densities of free and trapped ions we find the screening charge due to free Q_i and trapped Q_{tr} ions for each version according to formulas

$$Q_{i} = \int_{r_{o}}^{l} 4\pi N_{i}(R)R^{2}dR , \qquad Q_{tr} = \int_{\sqrt{r_{o}R_{o}}}^{l} 4\pi N_{i}(R)R^{2}dR , \qquad (9.77)$$

and according to definition of the action size l of the particle field action we have

$$Q = Q_i + Q_{tr} = |Z| . (9.78)$$



Figure 9.7: The part of the screening charge due to trapped ions Eq. (9.78) for an argon plasma with the electron $T_e = 1 \text{eV}$ and ion $T_i = 400 \text{K}$ temperatures. Open circles correspond to version when free ions dominate in screening of the particle field, and closed circles describe the version when trapped ions dominate.

From this we find the part of the screening charge ξ that is determined by trapped ions

$$\xi = \frac{Q_{tr}}{Q_i + Q_{tr}} \,. \tag{9.79}$$

Fig. 9.7 gives the dependence of the part of screening charge ξ due to trapped ions Eq. (9.79) on the reduced number density of a surrounding argon plasma far from the particle for the electron $T_e = 1 \text{ eV}$ and ion $T_i = 400 \text{ K}$ temperatures. As is seen, two versions where the number density of ions is determined by Eqs. (9.72) and (9.76) give nearby results. In particular, at the reduced number density $N_o r_o^2 = 100 \text{ cm}^{-1}$ of the plasma the contribution of trapped ions into the charge screening is $\xi = 0.53$ and $\xi = 0.50$ for the first and second version correspondingly.

In accordance with two versions under consideration, where the number densities of ions are given by Eqs. (9.76) and (9.77), we have on the basis of Eqs. (9.57) and (9.75) for the reduced radius of action of the particle field l_{free} when free ions dominate and for the radius action l_{trap} if trapped ions dominate in the particle screening. We then have

$$\frac{l_{free}}{r_o} = \frac{A}{(N_o r_o^2)^{2/5}} , \qquad \frac{l_{trap}}{r_o} = \frac{B}{(N_o r_o^2)^{2/9}} , \qquad (9.80)$$

$$A = 0.66 \frac{(|Z|/r_o)^{2/5}}{(R_o/r_o)^{1/5}}, \qquad B = \frac{1.05}{\Phi} (|Z|/r_o)^{2/9} (R_o/r_o)^{1/9}.$$
(9.81)

Fig. 9.8 gives the reduced radius of action of the particle field in accordance with Eq. (9.81) as a function of the reduced number density of a surrounding plasma for an argon plasma with the electron $T_e = 1 \text{eV}$ and ion $T_i = 400\text{K}$ temperatures. In particular, for $N_o r_o^2 = 100 \text{cm}^{-1}$ Eqs. (9.81) give for the reduced radius of particle field action l/r_o correspondingly 28 and 29 for the first and second versions.

Note that from the above analysis it follows that parameters of particle field screening depend on the number density of a surrounding plasma N_o and particle radius r_o through the combination $N_o r_o^2$. The same



Figure 9.8: The reduced radius of action of the particle field in accordance with Eq. (9.81) as a function of the reduced number density of a surrounding plasma for an argon plasma with the electron $T_e = 1 \text{ eV}$ and ion $T_i = 400 \text{ K}$ temperatures. Open circles relate to the first version if free ions dominate in particle field screening and the ion number densities are given by formulas Eq. (9.76), where as the dark circles correspond to the second version with the number densities of ions according to formula Eq. (9.77).



Figure 9.9: The number densities of free (squares) and trapped (circles) ions in a surrounding argon plasma with the electron $T_e = 1 \text{eV}$ and ion $T_i = 400 \text{K}$ temperatures as a function of the reduced distance from the particle. Dark signs correspond to Eqs. (9.57), while Eqs. (9.75) relate to open signs.

contribution of free and trapped ions for the above example of an argon plasma takes place roughly at the reduced plasma density $N_o r_o^2 = 100 \text{cm}^{-1}$, whereas trapped ions disappear at the reduced plasma number density $N_o r_o^2 = 10^3 \text{cm}^{-1}$ in the example example of an argon plasma. In addition, Fig. 9.9 gives the space distribution for the number density of free and trapped ions at an indicated reduced number density $N_o r_o^2 = 100 \text{cm}^{-1}$ of a surrounding plasma.

From the above analysis we conclude that in a rareness buffer gas in accordance with the criterion Eq. (9.46) the particle charge Z depends weakly on the character of shielding of the particle charge by a surrounding plasma because the electron and ion currents to the particle surface are created in a region where ion-particle interaction is absent, and Eq. (9.60) allows one to determine the particle charge on the basis of a simple algorithm with using the two versions where the free or trapped ions give the main contribution to the particle screening. In addition, parameters of the particle screening are expressed through the parameter combination $N_o r_o^2$.

Let us consider the limiting case of a low plasma density if this plasma does not screen the particle field and $l = R_o$. Trapped ions dominate in this case, and their number density according to Eq. (9.70) is given by

$$N_{tr}(R) = \frac{4\sqrt{2}}{\sqrt{\pi}} \frac{N_o R^{3/2}}{r_o \sqrt{R_o}} \left(1 - \frac{R}{R_o}\right) , \qquad R_o \ge R \gg \sqrt{R_o r_o} .$$
(9.82)

From this formula it follows that the maximum number density of ions is found at the distance $R_{max} = 0.6R_o$ from the particle and is equal to

$$N_{tr}(R) = 0.59 N_o \frac{R_o}{r_o} . (9.83)$$

This number density exceeds significantly the number density N_o of electrons and ions far from the particle. We have from Eq. (9.82) for the charge of ions inside a sphere of a radius R_o

$$Q_{tr}(R_o) = \frac{4\pi\sqrt{2}R_o^4 N_o e}{r_o} \approx 0.86 \frac{N_o R_o^4}{r_o} .$$
(9.84)

This leads to the following criterion for a smallness of the particle charge $Q_{tr} \ll |Z|e$, that is

$$N_o R_o^3 \ll \frac{T_i r_o}{e^2}$$
 (9.85)

In particular, for the above example of an argon plasma with $T_e = 1 \text{eV}$, $T_i = 400 \text{K}$ and a particle radius $r_o = 1 \mu \text{m}$ we have $R_o \approx 210 \text{nm}$, and the criterion Eq. (9.85) gives $N_o \ll 3 \cdot 10^5 \text{cm}^{-3}$, so that under laboratory conditions the particle field screening is of importance.

Note that the above consideration is better for a non-equilibrium plasma $T_e \gg T_i$. Indeed, we have two boundaries for trapped ions, so that ions are captured in closed orbits at $R \ge \sqrt{r_o R_o}$, and the other boundary of existence of trapped ions corresponds to R < l ($l < R_o$). The above formulas for the number density of trapped ions are better, the stronger is the difference between these two boundaries. In particular, for the above example of an argon plasma at $T_e = T_i$ we have for the ratio of distances for these boundaries $\sqrt{R_o/r_o} \approx \sqrt{\ln(m_i/m_e)} \approx 3.3$, while in the case of a non-equilibrium plasma $T_e = 1$ eV, $T_i = 400$ K we have

$$\sqrt{R_o/r_o} = \sqrt{|Z|e^2/(T_i r_o)} \approx \sqrt{T_e/T_i \cdot \ln(m_i/m_e)} = 18$$
(9.86)

in the limit of a low number density of this plasma.

9.8 Conclusion

In analyzing screening and charging of particles in an ionized gas, we restrict ourselves only to the part of these problems related to a large particle charge. In this case fluctuations of the particle charge are

9.8 Conclusion

relatively small, and the particle charge is grouped around its average charge that is considered as the particle charge. Next, we assume the rate of ionization in a plasma surrounding the particles is large compared to the recombination rate due to attachment of electrons and ions to particles. This condition is fulfilled in a laboratory plasma, but is violated in an astrophysical plasma. In addition, the basic concepts under consideration have been worked out more than fifty years ago, and now reliable simple models and realistic simplified formulas are of interest for the analysis of these problems, that was the goal of this paper.

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10 Soliton-like Dynamical Clusters in Atomic Layers

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Am Anfang gehören alle Gedanken der Liebe. Später gehört dann alle Liebe den Gedanken.

Albert Einstein

Abstract

We discuss here the excitation of soliton-like intrinsic localized excitations in two-dimensional atomic systems at the nano-scale level. First we study the excitation, the propagation and the speed of solitons created using appropriate initial conditions near to the lattice boundary hence by sudden addition of momentum, which simulate hard knocks or shocks. Then we investigate the spontaneous generation of solitonic structures in thermal systems at moderately high temperature. We show that due to polarization effects at the nano-size, electrical structures are induced which may influence the transport properties.

10.1 Introduction

It is known that some non-linear discrete one-dimensional systems can support localized excitations as solitons [1-4] and discrete breathers [5]. These excitations of one-dimensional (1d) nonlinear lattices are well explored, starting with the Fermi-Pasta-Ulam models [1] and several analytical solvable other models like the Toda lattice [2]. Continuing Davydov's and Scott's works [6, 7] making use of the Morse potential we have discussed how electron trapping by solitons leads to a new form of electric conduction on anharmonic 1d-lattices [8-16]. These excitations bring a new form of "dressed" electrons formed as compound of two superposed nonlinearities: (electro-soliton)-lattice soliton dynamic bound states. In the 1d-case these bound states have been called, in short, "solectrons" to mark the difference with Davydov's original electro-solitons. Indeed, the investigation of nonlinear excitations in 1d- or quasi-1d discrete structures was stimulated in part by studies of biomolecules.

We shall consider here the excitations of lattice solitons in two-dimensional or quasi-twodimensional lattices. This work was stimulated by recent studies of nonlinear excitations in the layers of cuprate-like lattices and related materials [29, 30, 31]. The mentioned work was concentrated on the observation of moving breathers. Here our main attention is devoted to soliton-like excitations. As lattice solitons we denote strong, localized compression-expansion waves (we shall focus on the compression) able to travel practically undeformed with sound velocity or even, supersonic velocity. In two-dimensional (2d) systems, solitonic effects are expected to play also a similar role as in 1d-systems [14, 15, 16]. We are, however,

aware that solitons in 2*d*-systems are difficult to rigorously define. However as in 1*d*-systems we still may find compression waves or, in other words, intrinsic localized modes running approximately with sound or supersonic velocity. In the field of hydrodynamics, the existence of 2*d*-solitonic excitations moving along surfaces and in falling films is known both in theory and experiment [17-20]. For optical lattices, the existence of soliton-like excitations in 2*d*-systems was also shown theoretically [21] and found experimentally [22, 23].

Further, several authors [24-28, 32] have shown the existence of soliton-like excitations in 2*d*-molecular square and hexagonal lattices with in-plane displacements. Eilbeck, Marin, and Russell found in a 2*d*-hexagonal lattice model propagating breathers, and reported about nonlinear excitations, they called *quodons* [29, 30, 31]. These authors aimed to study the nonlinear excitations in the layers in cuprate-like lattices and postulate a connection to phenomena of high-temperature superconductance. We are using here a similar model neglecting so far however onsite interactions. Further we mention interesting experimental studies of strongly localized dynamical structures in Uranium and other materials [33, 34]. In this context we mention also several hotly contested claims about dynamical stripe structures observed in the copper oxide materials notoriously used as high-temperature superconductors [35, 36, 37].

The present work is on a more abstract level. We study here strongly nonlinear local phenomena in 2d-lattices of molecules with Morse interactions excited either by hand through appropriate initial conditions or by thermal effects. We investigate here transient nonlinear structures at the nano-scale including not more as 10 - 100 molecules and lasting not longer than several pico - seconds (ps). Such local phenomena we consider as "dynamical clusters" which bear some analogy to the standard clusters of molecular physics. In [15] we presented a first study of soliton-like excitations in 2d-lattices at zero temperature. Here we continue to study the properties of 2d-excitations, in particular their velocity and the interaction of the soliton-like excitations. These soliton-like excitations under the influence of temperature, demonstrating this way the spontaneous onset of 2d-excitations in such *heated* lattices.

10.2 The Dynamic Model of Atomic Layers

Let us specify now the model which will be studied in the following. The classical lattice Hamiltonian models a 2d-set of atoms arranged in a plane

$$H_a = \frac{m}{2} \sum_n v_n^2 + \frac{1}{2} \sum_{i,j} V(r_i, r_j) .$$
(10.1)

The subscripts locate atoms sitting near to lattice sites and the summations run from 1 to N. The characteristic distance determining the repulsion between the particles in the lattice is σ . We shall assume that the lattice particles repel each other with exponentially repulsive forces and attract each other with weak dispersion forces. We limit ourselves to a potential depending on the relative distance $r = |r_n - r_k|$ and use a modified Morse potential (see Fig. 10.1) with a smooth cut-off at 1.5σ

$$V(r) = 2D \left\{ \exp\left[-2b(r-\sigma)\right] - 2\exp\left[-b(r-\sigma)\right] \right\} \left\{ 1 + \exp\left[(r-d)/2\nu\right] \right\}^{-1} .$$
(10.2)

In Fig. 10.1 the original Morse potential is shown by a dotted line and the modified one Eq. (10.2) with parameter value d = 1.35 by a full curve. Beyond the cut-off radius the potential is set equal to zero.

To study, at varying temperature, the nonlinear excitations of the lattice and the possible electron transport in a lattice in the simplest approximation it is sufficient to know the lattice (point) particles coordinates at each time and the potential interaction of lattice deformations with electrons. Coordinates of particles are obtained by solving the equations of motion of each particle under the influence of all possible forces. The latter include forces between particles which are supposed to be of the Morse kind and the friction and random forces accounting for a Langevin model bath in the heated lattice. For convenience in the 2*d*-lattice dynamics we use complex coordinates Z = x + iy, where x and y are Cartesian coordinates. Then the



Figure 10.1: Interaction between the atoms: Comparison of the original Morse potential (dotted line) and the "truncated" (modified) Morse potential (solid line) used for our computer simulations (parameter values $b\sigma = 4$, $d = 1.35\sigma$, $\nu = 0.02\sigma$).

Langevin model brings the equation for the lattice units

$$\frac{d^2 Z_n}{dt^2} = \sum_k F_{nk}(|Z_{nk}|) z_{nk} + \left[-\gamma_0 \frac{Z_n}{dt} + \sqrt{2D_v} \left(\xi_{nx} + i\xi_{ny}\right)\right] , \qquad (10.3)$$

where the index *n* identifies a particle among all N particles of the ensemble, γ_0 is a friction coefficient, D_v defines the intensity of stochastic forces, $\xi_{nx,y}$ denotes statistically independent generators of the Gaussian noise, $Z_{nk} = Z_n - Z_k$. Further $z_{nk} = (Z_n - Z_k)/|Z_n - Z_k|$ is a unit vector defining the direction of the interaction force F_{nk} , corresponding to the Morse potential, between the *n*-th and the *k*-th particles.

To have dimensionless variables we consider the spatial coordinates normalized to the length σ used in the Morse potential Eq. (10.2). Time is scaled with the inverse frequency of linear oscillations near the minimum of the Morse potential well, ω_M^{-1} . As earlier noted, the energy is scaled with 2D, where D is the depth of the Morse potential well. Further the parameter b defines the strength of the repulsion between particles. In view of the above only those lattice units with coordinates Z_k , satisfying the condition $|Z_n - Z_k| < 1.5$, are taken into account in the sum in Eq. (10.3). In computer simulations the interaction of particles is considered to take place inside a rectangular cell $L_x \cdot L_y$ with periodic boundary conditions and $L_{x,y}$, depending on the symmetry of an initial distribution of units and their number N. For illustration we consider a distribution corresponding to the minimum of potential energy for an equilibrium state of a triangular lattice $10\sigma \cdot 10\sqrt{3\sigma/2}$ for N = 100 or $20\sigma \cdot 20\sqrt{3\sigma/2}$ for N = 400.

We introduce now two methods for the visualization of nonlinear lattice excitations. Since the excitations we want to study are on the nanoscale and comprise just some 10 - 100 atoms, we need appropriate methods to see and to identify the dynamic structures we are searching for. Let us first discuss a method of visualization tracking the atomic electron densities. The lattice units, molecules or atoms, may be modeled as points on a plane which are surrounded by little spheres formed by the "atomic" electrons. We will assume that these atomic electrons may be represented by a Gaussian distribution centered on each lattice site

$$\rho(Z,t) = \sum_{|Z-Z_i(t)|<1.5} \exp\left[-\frac{|Z-Z_i(t)|^2}{2\lambda^2}\right] \,. \tag{10.4}$$

Beside the method of visualization based on atomic electron densities we developed also a second one based on the polarization fields which an injected charge say an electron moving between the atoms would feel. As known since Debye and Fröhlich the atoms interact with charges by an induced polarization potential. Let us assume that the charge (the electron) is located at the (complex) position Z and the atoms are located at the (complex) positions Z_i . Let h be a characteristic distance and U_e the maximal polarization energy. For the potential generated by the atoms with number i at the (complex) position of the charge Z generated by the atomic positions $Z_i(t)$ at time t we assume

$$U(Z,t) = -U_e \sum_{|Z-Z_i(t)|<1.5\sigma} \left[\frac{h^4}{(|Z-Z_i(t)|^2 + h^2)^2} \right] .$$
(10.5)

In accordance with our model potential we also here truncate the polarization potential at the cut-off distance $r = 1.5\sigma$. This generates some distribution of the potential acting on test charges (electrons) due to the interaction with the lattice units. Looking at Eq. (10.5) we see that any cluster of atoms generates a potential hole in which the electron density might be concentrated. Further any displacement of the atoms changes the polarization energy. The electron will try to follow up these changes what in a zeroth approximation may be described by a Boltzmann distribution [16]. This is the basic effect leading to the solectron formation which we considered in other work [16]. Looking at Eq. (10.5) we see that any cluster of atoms generates a potential hole in which the electron density will be concentrated.



Figure 10.2: Propagation of soliton-like excitation in a triangular lattice. Left we visualized the density of the atomic cores of N = 400 particles. In the center we represent the polarization potentials and at the right we show a cumulated representation. In order to study the evolution of perturbations we changed the initial positions of the atoms at t = 0 in a small region. The parameters values are: N = 400, $b\sigma = 4$, $\lambda = 0.3$, T = 0.01.

There is one special feature of the polarization potential wells in 2d-systems: The potential wells are like moving valleys with a small extension in the direction of the moving and a larger extension perpendicular to the direction of the soliton speed. In spherical valleys the resulting repulsion energy is too large, the formation of bisolectrons in spherical potential wells is practically impossible. However in longer valleys the situation changes. We note that for some parameter values, namely if the polarization energies are larger than the Morse energies, self-trapping effects may give the determining effects as shown by Davydov, Scott and others [6, 7]. Here we remain by purpose in a region where the mechanical effects are strong and the electrical self-trapping gives only small corrections. We checked that in the considered parameter range the deformations are mainly determined by the mechanical forces. However the influence of the deformations on the forces acting on the electron are rather strong. Since the energy landscape, which the injected charge will feel, depends strongly on the local configurations of the atoms in the neighborhood we can use the polarization field as a detector for deformations. The local electric potential is a quite sensitive measure of the local excitations. We are using this measure as an alternative method for the visualization of the dynamics of the nonlinear excitations. We want to underline that the electrical structures we study here are restricted to nano-scales since at macroscopical scales the screening effects make such structures impossible.

10.3 Excitation of Soliton-like Modes by Externally Given Initial Conditions at the Border

Let us assume a triangular lattice with all atoms at rest. Now we give some initial conditions of the atoms near to the boundary with a sudden addition of momentum, this might simulate an initial knocking or a sudden shock arriving at the boundary. Already in several preliminary studies [15, 16] we demonstrated that under such conditions the evolution of localized soliton-like excitations is possible.



Figure 10.3: Speed of the solitons in dependence on the width of the profile. The density of atomic electrons of N = 400 particles in a triangular lattice: In order to study the evolution of perturbations we changed the initial density at t = 0 in a small region (N = 400, $b\sigma = 3$, $\lambda = 0.3$, T = 0.01).

The parameters values are: N = 400, $b\sigma = 4$, we used a modified Morse potential with a cut-off 1.5σ . The excitations we have found move clearly with supersonic velocity. In order to check this in more detail we have shown in Fig. 10.2 the dependence of the velocity on the soliton width parameter κ of the initial excitations. We observe a wide range of supersonic excitations. In order to check for solitonic properties we investigated also the interaction of oppositely moving excitations. The density distribution (the left column), the "electric" potential landscape (the right column) are presented for three time moments. We observe a transformation of the initial piece of a plane wave to the soliton-like horseshoe-shaped supersonic excitation (it is shown best of all in the representations for the polarization potential). With respect to the velocity we see that the excitation overcomes the distance of about 16 units in the time t = 8, that is velocity is 16/8 = 2 in units of the sound velocity in a 1*d*-lattice. We remind that $v_{sound} = 1$ in our variables for 1*d*-lattices. Further we mention that in a triangular 2*d*-lattice the sound velocity is slightly larger than the sound velocity in a 1*d*-lattice.

In a subsequent set of simulations we studied two solitons excited initially, the left one propagates to the right, the right one - to the left. The parameters are the same as in the one-solitonic case above. We observed that both wave fronts move against each other and pass through each other without changing their

form. This is one of the characteristic indicators for solitons [1]. This way our simulations prove with some confidence that the localized non-linear waves in triangular lattice may indeed be considered as soliton-like. Of course, they are rather not solitons in a strong mathematical sense because we do not prove that they are stationary waves (and indeed our 2d-excitations are transitory waves) but we demonstrate that they behave like surface solitons at interfaces [17, 18, 20]. They are of course quite different with respect to their size, our phenomena are of nano-size in difference to the hydrodynamic phenomena which occur usually at the cm-scale (or the kilometer scale in the ocean).



Figure 10.4: Interaction of two highly energetic quasi-one-dimensional solitons moving in a triangular lattice in opposite directions during the interval t = 0 - 7 (both with the same parameters N = 400, $b\sigma = 4$, $\lambda = 0.3$, T = 0.01).

We study now the special case of solitons with a very short wave front and correspondingly with rather high energies and velocities up to $2v_{sound}$. What we see in Fig. 10.4 are two solitons with rather high energies and strongly supersonic velocities. Each of them quickly transforms to a horse-shoe wave with decreasing length and size of the wave front. Finally the transverse size of the wave reduces to just one layer excited at a time. The solitons shown in Fig. 10.4 comprise just a few lattice sites and are therefore very much based on the discrete character of the lattice, we cannot expect to find these kind of solitons on continuous 2d-lattices.

By studying this and numerous other examples we came to the conclusion that the quasi-one-dimensional "adapted Toda solitons" with stiffness $b_{eff} \simeq 1.5b$ which are running along chains in the main crystallographic directions are of particular high stability and have a quite long life-time (see Fig. 10.5). For shorthand notation we call these creatures Highly Stable Solitons (HSS). In Fig. 10.6 we show the velocity

distribution of the particles in the direction of the soliton propagation and perpendicular to it. We notice a high peak of the distribution in the direction of soliton motion and a small dispersion in transversal direction corresponding to oscillations perpendicular to the soliton propagation. We underline that only the particular choice $b_{eff} \simeq 1.5b$ and initial directions pointing to the crystallographic axes provide a high stability with respect to perturbations.



Figure 10.5: Filtered density of core electrons near to quasi-one-dimensional solitonic excitations running in a triangular Morse lattice along a crystallographic axis. The initial condition is an "optimized Toda profile". We show 4 subsequent moments of time and demonstrate this way: The "adapted Toda profile" is very stable and runs along a chain for a long time nearly without any visible changes. The last figure is a "bubble-chamber-representation" (including memory). (N = 400, $b\sigma = 4$, $\lambda = 0.3$, T = 0.01).

This way we have found for the highly stable quasi-one-dimensional solitons also a quite good analytical representation (the representation as a Toda soliton with $b_{eff} \simeq 1.5b$. We have shown that this type of excitations is stable also for all other crystallographic axes. We expect that this property holds also for other symmetries, e.g. in the case that rectilinear chains of atoms are realized, as e.g. in NaCl crystals. This remains to be studied in detail.

10.4 Excitation of Soliton-like Modes by Thermal Heating

Finally, in Figs. 10.7 and 10.8, we demonstrate the excitations in thermal systems by simulations for several temperatures. We will show that the highly stable solitons (HSS) demonstrated above are among the most stable and most frequently observed thermal excitations. This means that the fluctuations in a twodimensional excitable thermal system are organized in stripes. We may expect that the electrons essentially will follow this organization.

Our idea for explaining this phenomenon is the following: For a generic Hamiltonian, H, the probability of occurrence of an excitation is proportional to $\exp(-H/k_BT)$. Among the spontaneous excitations we expect to see also the solitonic excitations along with others. Excitations which are "favorable" with respect



Figure 10.6: Filtered density of core electrons near to a highly stable soliton running along a crystallographic axis in a two-dimensional triangular Morse lattice ("bubble chamber representation"). The right picture shows a velocity distribution of the particles. The peak in x-direction corresponds to the propagating soliton, the lateral distribution in y-direction corresponds to oscillations transversal to the direction of the soliton propagation. ($N = 400, b\sigma = 4, \lambda = 0.3, T = 0.01$.

to the Gibbs measure are expected to occur more often, but in principle all possible excitations should occur. As a rule of thumb we may use the observation from thermal physics that one may see a phenomenon already if the mean thermal energy is about 10-20 percent of the needed activation energy. Then in the tail of the Boltzmann distribution there are already enough events to see activation processes. The essential point determining the observability of an excitation is the mean life-time. Since solitonic excitations are conservative phenomena, connected with an invariant of motion, the have a longer life-time as other thermal excitations. This is the idea which we wanted to check by simulations. The evolution of the core density defined by Eq. (10.4) in a heated system is illustrated in Fig. 10.7.

Our methods of visualization tracks excitations in the 2*d*-system of Morse molecules. The initial positions on the triangular lattice at zero temperature ("cold" lattice) are used as initial conditions. Then the lattice is heated by the stochastic source (white noise) to the temperature $T = mD_v/\gamma$. This corresponds to the mean kinetic energy of a particle $\langle T_{kin} \rangle$ reaching the value T. The obtained values of Z_n and $V_n = dZ_n/dt$ are subsequently used as new initial values $Z_n(0)$ and $V_n(0)$ for the lattice at corresponding temperature while setting $D_v = 0$. Notice that by varying $Z_n(0)$ and $V_n(0)$ it is possible to specify a localized excitation in a lattice. Using data about trajectories of particles $Z_n(t)$ and the evolution of velocities $V_n(t)$ we can calculate the mean kinetic and potential energies of the particles, the temperature of the ensemble, and in particular snapshots of the particle distribution $\rho(Z, t)$. The snapshots may tell us about the most frequent excitations. By studying many snapshots of the excitations we may find ones are quite long lasting and of particular high stability, and may expect that they will often be realized in thermal systems.

Let us repeat the general idea: Following the Boltzmann-Gibbs approach we may expect that, when heating the lattice, in principle, all possible static and dynamic excitations may spontaneously appear with some non-vanishing probability. In our case the candidates for highly probable dynamical structures are the highly stable solitons or stable dynamical stripes found above.

In order to check this idea we performed many simulations. The problem which arises is however that the probability may be quite low, to find structures with higher energy and, further, to identify them in the sea of fluctuations. So we need some filtered representation to select salient events. Fig. 10.7 provides a cumulative sequence of the highest excitations in a thermal system which occurred in an interval of 50 time units. The traces shown in Fig. 10.7 may be considered similar as the traces in a bubble chamber. In our case the traces represent the film the time evolution of high energetic events within the observational time interval. We see quite many localized modes which live some 10 - 20 time units, most of them oriented along the three basic crystallographic directions of the triangular lattice. We may conclude that many excitations



Figure 10.7: Thermal excitation of long lasting highly stable solitons. The figure shows a "bubble-chamber picture" of the high-energetic solitons in a thermal triangular Morse lattice. The lattice has N = 400 units, the stiffness is $b\sigma = 4$, $\lambda = 0.25$ and is heated to the temperature T = 5 (in units of 2D) with periodic boundary conditions. We represent the time evolution sequence of highly energetic events leading to local increases of density of the atomic electrons. The picture shows the time evolution of the highest peaks in a cumulative representation of the amplitude-filtered density peaks for a time interval of about 50 time units. In particular the strongest compressions show the features of high-energy solitons, as these compression waves, or intrinsic localized modes, move with supersonic velocity (around $1.2v_{sound}$) and have a life-time of a many time units.

we see in the thermal system have the character of the localized quasi-one-dimensional modes described in the previous section.

The strongly localized excitations of the lattice change the electrical situation in which the electrons are moving. For illustration we have studied the distribution of the polarization potential and the densities in the Boltzmann approximation at several temperatures (see Fig. 10.8).



Figure 10.8: Snapshots for a thermal 2*d*-Morse lattice with N = 100 units. Distribution of the polarization potential at a temperature T = 0.01 (left panel) and at T = 2.0 (right panel). ($b\sigma = 2$).

The left panel in Fig. 10.8 illustrates first the polarization potential for the case of the low temperature T = 0.1. The minima of the polarization potential and the corresponding maxima of the density of free electrons are well separated. The right panel in Fig. 10.8 corresponds to the moderately high temperature T = 2. Note that in this region the specific heat is $C_v \simeq 1.8$, significantly smaller than the Dulong-Petit value and we may expect that many solitons are excited. The snapshots shown in Fig. 10.8 demonstrate that

the electrical potential (and correspondingly the Fermi surface) in a system with strong nonlinear excitations is highly structured. In a dynamical picture including memory effects we would see that stripes have some bias. The electrical structures are expected to follow more or less the dynamical clusters described in this work.

10.5 Conclusions

As well known, in the linear approximation the fluctuations in condensed matter are mainly determined by the spectral distribution of phonons, nonlinear fluctuations are less explored in spite of the fact that there is some theoretical and experimental evidence of strong local fluctuations as the intrinsic localized modes (ILM), quodons and others [5, 29, 30, 31]. We refer also to several experimental studies of strongly localized dynamical phenomena in Uranium and in other materials [27, 33, 34]. The strongly localized structures we investigated here bear some analogy to the standard cluster phenomena. The main difference between standard clusters and the "dynamical clusters" investigated here, is the very short life-time of our strongly localized dynamical structures. Of course nonlinear (strong) fluctuations are interesting not only per se but also for the electronic properties of materials, because of the strong interactions of the state of the atoms with embedded electrons, e.g. by polarization interactions. We are very interested in particular in the implications of strong local deformations for the electronic properties of materials. Some hints to the electrical structures give the snapshots of the polarization potential shown in Fig. 10.8.

In this context we mention also several hotly contested claims about the way electrons behave in the copper oxide materials notoriously used as high-temperature superconductors [35, 36, 37]. Supposedly, they form highly organized patterns called quantum stripes - but only on the picosecond timescale - so the patterns average away over longer periods through the electrons' constant quantum dance. The dispute has lasted so long only because it has proved very hard to nail down such behavior. We suppose here that the formation of stripes in the quantum electron system is supported by the organization of the classical nonlinear fluctuations in stripes as demonstrated here.

In this work we have shown by means of numerical experiments the existence of localized nonlinear excitations, or intrinsic localized modes, at the nano-scale in 2d-systems of Morse atoms at *moderately* high temperatures. They arise as thermal excitations, made visible in an appropriate way that we have specified. Both front profile and front velocity, show these excitations as soliton-like. They propagate in general with slightly supersonic velocity. Therefore these excitations bear similarity to the soliton solutions in Toda's 1d-lattices and the corresponding soliton – like excitations we have observed in cold and in thermal Morse lattices [14]. In some respect the soliton-like excitations at fluid surfaces [17, 18, 20]. However in 2d-systems the nonlinear excitations at the nanoscale show several differences. As we have shown here, the highly stable solitons which we identified as frequently occurring, are quasi-one-dimensional excitations. Further we have shown that these nanoscale excitations induce electrical polarization fields which may influence electron dynamics thus leading to a kind of trapping in stripe structures [16].

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10.5 Conclusions

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11 Self-Similar Regime of Diffusion Growth of a Droplet in a Vapor-Gas Medium with Allowance for Stefan's Flow

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> If you see a formula in the Physical Review that extends over a quarter of a page, forget it. It's wrong. Nature isn't that complicated.

Bernd T. Matthias

Abstract

An analytical self-similar solution of the problem of unsteady diffusion growth of a droplet in a vapor-gas medium has been derived with allowance for the Stefan flow of the medium, for motion of the surface of the growing droplet, and for dependence of the diffusion coefficient of the condensing vapor in the medium on the vapor concentration. The expressions for the diffusion concentration profile of the condensing vapor and the droplet growth rate have been found. It is shown that the combined effects of the Stefan flow of the medium, the motion of the surface of the growing droplet and the dependence of the diffusivity of vapor in the medium on the vapor concentration lead to a renormalization of the droplet growth rate compared with its stationary diffusion growth rate. For small deviations from the regime of stationary growth, non-stationary diffusion and dependence of diffusion coefficient on the composition of the gas-vapor mixture, as well as the Stefan flow, give, generally speaking, corrections of the same order of magnitude.

11.1 Introduction

We are interested in this paper in the description of non-stationary diffusion growth of a condensing droplet in a vapor-gas medium with allowance for the Stefan flow of the medium, for the motion of the surface of the growing droplet, and for the dependence of the diffusion coefficient of the condensing vapor in the medium on the vapor concentration. As it is known [1-3], the Stefan flow compensates for the diffusion outflow of non-condensing gas molecules from the surface of the growing droplet to provide the constancy of total pressure in the vapor-gas medium. This flow can be stationary or non-stationary, depending on the stationary or non-stationary regimes of droplet growth. These regimes of isothermal condensation onto a markedly supercritical droplet (i.e., a droplet over which the saturated vapor pressure can be set approximately equal to the saturated pressure over the flat surface of the liquid) will be analyzed below, first at a constant diffusion coefficient of the vapor in the environment, and then at linear dependence of the diffusion coefficient on the vapor concentration.

We will recall here first the main results of solving the problem of a stationary isothermal diffusion growth of a droplet in the atmosphere of passive gas and vapor with allowance for the Stefan flow and constant coefficient of diffusion, given by Fuchs in Ref. [1]. These results will be needed for further comparison with the solution of the problem of non-stationary diffusion growth.

11 Self-Similar Regime of Diffusion Growth of a Droplet in a Vapor-Gas Medium

Let us set the origin of the spherical reference system into the center of the droplet. We denote the stationary bulk concentrations of the condensing vapor and passive gas at an arbitrary point \vec{r} in the system as n(r) and n'(r), respectively. The temperature of the droplet and the environment in the process of droplet growth remain fixed and is the same everywhere. With taking into account the hydrodynamic flow of the medium with radial velocity $v_r(r)$, the density j(r) of steady flux of vapor molecules can be written as

$$j(r) = -D\frac{\partial n(r)}{\partial r} + v_r(r)n(r) , \qquad (11.1)$$

where D is the constant diffusion coefficient of vapor molecules in the vapor-gas mixture. Similarly, the density j'(r) of the steady flux of passive gas can be written as

$$j'(r) = -D\frac{\partial n'(r)}{\partial r} + v_r(r)n'(r) , \qquad (11.2)$$

where the diffusion coefficient is the same as in Eq. (11.1). It follows at constant total pressure of the vapor-gas medium in the approximation of the ideal gas that

$$\frac{\partial n(r)}{\partial r} = -\frac{\partial n'(r)}{\partial r} \,. \tag{11.3}$$

We denote the radius of the droplet as R. Note that when calculating the vapor flow in the approximation of stationary diffusion, the radius R is assumed to be fixed. Consider the concentric with the droplet sphere of radius r > R. Under spherical symmetry of the problem and steady vapor flux at any value $r \ge R$, we have

$$j(r)r^2 = j(R)R^2 . (11.4)$$

In view of the impermeability of the droplet surface for the passive gas molecules, the steady flux density of the passive gas molecules equals j'(r) = 0. As a consequence, in view of Eqs. (11.1) - (11.4) we find

$$j(r)r^2 = \tilde{n}v_r(r)r^2 = j(R)R^2 , \qquad (11.5)$$

where $\tilde{n} \equiv n(r) + n'(r) = \text{constant}$ is the total local concentration of molecules in the vapor-gas medium. Substituting the expression

$$v_r(r) = j(R)\frac{R^2}{\tilde{n}r^2} \tag{11.6}$$

for the radial velocity of the Stefan flow (which follows from Eq. (11.5)) into Eq. (11.1) and taking into account Eq. (11.4), we obtain finally

$$\frac{\partial n(r)}{\partial r} - \frac{j(R)R^2}{\tilde{n}Dr^2}n(r) = -j(R)\frac{R^2}{Dr^2}.$$
(11.7)

Integration of Eq. (11.7) with the boundary conditions $n(r)|_{r=R} = n_{\infty}$ (n_{∞} is the concentration of vapor saturated over a flat surface of the condensate) and $n(r)|_{r\to\infty} = n_0$ (it is required $n_0 > n_{\infty}$ for the growth of the droplet) gives [1] for vapor concentration n(r) and density j(R) of the vapor flux the following expressions

$$n(r) = \tilde{n} + (n_0 - \tilde{n}) \exp\left(-\frac{j(R)}{D\tilde{n}}\frac{R^2}{r}\right) , \qquad (11.8)$$

$$j(R) = -\frac{D}{R}\tilde{n}\ln\frac{\tilde{n} - n_{\infty}}{\tilde{n} - n_0} .$$

$$(11.9)$$

In the approximation of small vapor content in the gas-vapor medium, i.e. at $n_0 \ll \tilde{n}$ and $n_\infty \ll \tilde{n}$, Eq. (11.9) for the vapor flux density transforms into

$$j(R) = j_s(R) \left[1 + \frac{1}{2} \frac{n_0 + n_\infty}{\tilde{n}} \right] , \qquad (11.10)$$

where

$$j_s(R) \equiv -\frac{D}{R} \left(n_0 - n_\infty \right) \tag{11.11}$$

is the density of the steady vapor flux in the absence of Stefan's flow (the Maxwell formula [1-3]). As follows from Eq. (11.10), the corrections to the density of the steady vapor flux due to the Stefan flow are of the first order of smallness in the parameter $n_0/\tilde{n} \ll 1$.

We did not find in the literature a solution of the problem of non-stationary diffusion with allowance for the Stefan flow which would be in any way analogous to the previous consideration. There are known, however, self-similar solutions of the problem of non-stationary droplet diffusion growth in absence of the Stefan flow [4, 5].

11.2 Equation of Non-Stationary Vapor Diffusion to a Growing Droplet with Allowance for the Motion of the Droplet Surface and the Stefan Flow

We consider now the problem of unsteady growth of a droplet, taking into account the motion of the surface of the droplet and the non-stationary Stefan flow. Let us choose again the origin of coordinates at the center of the droplet. The radius of the growing droplet at time t we denote by R(t). To find the velocity of hydrodynamic flow of the environment, we consider a moving sphere of some radius $R_1(t) > R(t)$ that is concentric with the droplet. If the rate of variation of radius $R_1(t)$ in time coincides with the radial velocity $v_r(r, t)$ of hydrodynamic flow of the gas-vapor mixture at $r = R_1(t)$, so that

$$R_1(t) = v_r(r = R_1(t), t) , \qquad (11.12)$$

then the total number of vapor and passive gas molecules within the sphere of radius $R_1(t)$ does not change in time. In this case, the relation

$$n_l R^3(t) + \tilde{n} \left(R_1^3(t) - R^3(t) \right) = \text{constant}$$
(11.13)

is valid where n_l is the number of molecules per unit volume of the liquid condensate, $\tilde{n} \equiv n(r, t) + n'(r, t)$ is the total concentration of molecules in the vapor-gas medium (\tilde{n} , as in the stationary case, does not depend on the point r and time t).

Differentiating Eq. (11.13) with respect to time at arbitrary $R_1(t) = r$, we find the relation between the radial velocity $v_r(r,t)$ of the hydrodynamic flow of the vapor-gas mixture and the rate $\dot{R}(t)$ of growth of the droplet radius in the following form

$$v_r(r,t) = \dot{R}(t) \frac{R^2(t)}{r^2} \left(1 - \frac{n_l}{\tilde{n}}\right) .$$
(11.14)

Since, as follows from Eq. (11.14), the field of hydrodynamic velocity $v_r(r, t)$ corresponds to the motion of an incompressible medium ($\nabla \vec{v} = 0$), then, to determine the concentration n(r, t) of vapor molecules, we have the following equation

$$\frac{\partial n(r,t)}{\partial t} = D\Delta n(r,t) - v_r(r,t)\frac{\partial n(r,t)}{\partial r}, \qquad (11.15)$$

where D is the constant coefficient of diffusion of vapor molecules in the vapor-gas medium, just the same as in Section 11.1. The boundary conditions for this equation are similar as in the stationary case

$$n(r,t)|_{r=R(t)} = n_{\infty} , \qquad n(r,t)|_{r\to\infty} = n_0 .$$
 (11.16)

Obviously, the droplet can grow only in a supersaturated vapor, so that $n_0 > n_\infty$. Taking into account the spherical symmetry and Eq. (11.14), we rewrite Eq. (11.15) as

$$\frac{\partial n(r,t)}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial n(r,t)}{\partial r} \right) - \dot{R}(t) \frac{R^2(t)}{r^2} \left(1 - \frac{n_l}{\tilde{n}} \right) \frac{\partial n(r,t)}{\partial r} .$$
(11.17)

11.3 Self-Similar Solutions of the Equation of Non-Stationary Diffusion with a Hydrodynamic Flow

To find a self-similar solution of Eq. (11.17), let us pass to a new independent dimensionless variable ρ , defined as [4, 5]

$$\rho \equiv \frac{r}{R(t)} , \qquad n(r,t) \equiv n(\rho(t)) . \tag{11.18}$$

Substituting Eq. (11.18) into Eq. (11.17) transforms it into equation

$$\frac{d^2n}{d\rho^2} + \left[\frac{2}{\rho} + \frac{R\dot{R}}{D}\left(\rho - \frac{\gamma}{\rho^2}\right)\right]\frac{dn}{d\rho} = 0, \qquad (11.19)$$

where a new notation

$$\gamma \equiv 1 - \frac{n_l}{\tilde{n}} \tag{11.20}$$

has been used. The boundary conditions Eq. (11.16) on the vapor concentration can be rewritten in variable ρ as

$$n(\rho)|_{\rho=1} = n_{\infty} ,$$
 (11.21)

$$\left. n(\rho) \right|_{\rho \to \infty} = n_0 \,. \tag{11.22}$$

It is evident that Eq. (11.19) leads to a self-similar solution of the problem only when the dependence of droplet radius on time satisfies the condition

$$R(t)\dot{R}(t) = \text{const.}$$
(11.23)

To elucidate the possibility of the condition Eq. (11.23), we need to consider the balance equation of the condensate molecules at the droplet surface. Conservation of the number of vapor molecules at condensation into droplet leads to the equation

$$n_l \dot{R}(t) = -\left[-D \frac{\partial n(r,t)}{\partial r} + n_\infty \left(v_r(r,t) - \dot{R}(t) \right) \right] \Big|_{r=R(t)} .$$
(11.24)

In view of Eq. (11.14), Eq. (11.24) for the growth rate $\dot{R}(t)$ of the droplet radius can be rewritten as

$$\dot{R}(t) = \frac{D \frac{\partial n(r,t)}{\partial r} \Big|_{r=R(t)}}{n_l \left(1 - \frac{n_\infty}{\tilde{n}}\right)} \,. \tag{11.25}$$

Passing with the help of Eq. (11.18) to the self-similar variable ρ transforms Eq. (11.25) to the form

$$\frac{R\dot{R}}{D} = \frac{\left.\frac{dn(\rho)}{d\rho}\right|_{\rho=1}}{n_l \left(1 - \frac{n_\infty}{\tilde{n}}\right)} \,. \tag{11.26}$$

Thus, as we see from the right-hand side of Eq. (11.26), the condition given by Eq. (11.23) is valid. Therefore, self-similar regime of droplet growth is possible.

Integration of Eq. (11.19) with boundary conditions Eqs. (11.21) and (11.22) yields

$$n(\rho) = n_{\infty} + (n_0 - n_{\infty}) \frac{\int_{-\infty}^{\rho} \frac{dz}{z^2} \exp\left\{-\frac{bz^2}{2} - \frac{\gamma b}{z}\right\}}{\int_{-\infty}^{\infty} \frac{dz}{z^2} \exp\left\{-\frac{bz^2}{2} - \frac{\gamma b}{z}\right\}},$$
(11.27)

where a new dimensionless parameter b has been determined as

$$b \equiv \frac{R\dot{R}}{D} . \tag{11.28}$$

In accordance with Eqs. (11.26) and (11.28) we have

$$b = \frac{\left. \frac{dn(\rho)}{d\rho} \right|_{\rho=1}}{n_l \left(1 - \frac{n_\infty}{\tilde{n}} \right)} \,. \tag{11.29}$$

Substituting Eq. (11.27) into Eq. (11.29), we obtain an equation for the parameter b:

$$b = \frac{a \exp\left\{-b(\gamma + \frac{1}{2})\right\}}{\left(1 - \frac{n_{\infty}}{\tilde{n}}\right) \int_{1}^{\infty} \frac{dz}{z^{2}} \exp\left\{-\frac{bz^{2}}{2} - \frac{\gamma b}{z}\right\}},$$
(11.30)

where an additional dimensionless parameter a has been determined as

$$a \equiv \frac{n_0 - n_\infty}{n_l} \,. \tag{11.31}$$

Eqs. (11.27) and (11.30) together with Eqs. (11.18), (11.28), and (11.31) determine the required self-similar solution of the problem of non-stationary diffusion droplet growth with allowance for the motion of the boundary of the droplet and non-stationary Stefan flow.

11.4 Hydrodynamic Contributions to the Vapor Flux onto a Growing Droplet

The flux I of vapor molecules through the surface of the growing droplet is given by the expression

$$I = -4\pi R^2 \dot{R} n_l , \qquad (11.32)$$

which can be rewritten with the help of Eqs. (11.28) and (11.31) as

$$I = -4\pi R D (n_0 - n_\infty) \frac{b}{a} .$$
(11.33)

Since the steady vapor diffusion flux $I_s \equiv 4\pi R^2 j_s(R)$ in view of Eq. (11.11) equals

$$I_s = -4\pi R D(n_0 - n_\infty) , \qquad (11.34)$$

Eq. (11.33) transforms to

$$I = I_s \frac{b}{a} . \tag{11.35}$$

We see that the effect of non-stationary diffusion droplet growth at an arbitrary degree of deviation from the steady state growth leads to the renormalization of the steady vapor flux by the factor b/a. The difference between fluxes I and I_s expressed by the deviation of the quantity b/a from unity, is caused by the hydrodynamic flow of the vapor-gas medium around a growing droplet. Note that the radial velocity $v_r(r, t)$ of this flow, determined by Eq. (11.14), represents the sum of two contributions corresponding to two different processes:

$$v_r(r,t) = v_r^{(1)}(r,t) + v_r^{(2)}(r,t) .$$
(11.36)

The first of the contributions, namely

$$v_r^{(1)}(r,t) = \dot{R}(t) \frac{R^2(t)}{r^2} , \qquad (11.37)$$

describes the hydrodynamic flow of the environment which would arise around an impermeable for the molecules sphere whose radius is equal to the droplet radius and increases with time like R(t). The second contribution, determined by the expression

$$v_r^{(2)}(r,t) = -\frac{n_l}{\tilde{n}}\dot{R}(t)\frac{R^2(t)}{r^2},$$
(11.38)

takes account of the fact that in reality there is a flux of vapor molecules through the surface of the growing droplet, and in order to provide fulfilment of the condition $\tilde{n} = \text{constant}$ (the constancy of the pressure in the vapor-gas mixture around the droplet), there must be an additional flow of the environment in the opposite direction with respect to the direction of the first flow with velocity $v_r^{(1)}$. In other words, $v_r^{(2)}$ is the velocity of the Stefan flow.

Neglecting the Stefan flow corresponds to $v_r^{(2)}(r,t) = 0$, what is formally achieved by setting $\gamma = 1$ in Eqs. (11.19), (11.27) and (11.30) and, in addition, by replacement of $1 - \frac{n_{\infty}}{\tilde{n}}$ by 1 in Eq. (11.30). A similar result for non-stationary diffusion growth of bubbles was obtained earlier in [6].

11.5 Relations Between the Parameters *b* and *a* in the Problem of Non-Stationary Diffusion

In the general case (for arbitrary values of the parameters a and γ), only a numerical solution of Eq. (11.30) can be found. However, recognizing that growth of droplets in a supersaturated vapor occurs almost always at

$$a \ll |\gamma a| \ll 1 \tag{11.39}$$

(a numerical estimation of this inequality will be given below), we can also find an analytical solution of this equation with a good degree of accuracy.

11.5 Relations Between the Parameters b and a in the Problem of Non-Stationary Diffusion

We begin by considering a limiting case at $n_l \rightarrow \infty$. Using the definitions Eqs. (11.20) and (11.31), we have in this case

$$a \to 0 , \qquad \gamma a \to \frac{n_{\infty} - n_0}{\tilde{n}} .$$
 (11.40)

According to Eqs. (11.30) and (11.40), the parameter b in this limit is proportional to the parameter a, so that $b \rightarrow 0$. Then, in view of Eq. (11.28), $\dot{R} \propto v_r^{(1)} \rightarrow 0$ while the quantity $v_r^{(2)}$ remains finite. Let us emphasize that the non-stationary nature of the diffusion process due to the motion of the surface of the growing drop is in no way taken into account at $\dot{R} = 0$. This situation corresponds exactly to the consideration of the Stefan flow under conditions of stationary diffusion flux of vapor molecules onto the droplet, which was performed in Ref. [1] and in the introduction. Indeed, in view of Eq. (11.40), Eq. (11.30) can be rewritten as

$$\frac{a}{b} = \left(1 - \frac{n_{\infty}}{\tilde{n}}\right) \int_{1}^{\infty} \frac{dz}{z^2} \exp\left\{\left(\frac{b}{a}\right) \left(\frac{n_0 - n_{\infty}}{\tilde{n}}\right) \left(\frac{1}{z} - 1\right)\right\}$$
(11.41)

(we neglected small terms $bz^2/2$ and b/2 in the exponent). Integral on the right side of Eq. (11.41) can be calculated accurately by replacing the variable of integration as $1/z \rightarrow z$, and we find for the quantity b/a at $a \rightarrow 0$:

$$\frac{b}{a} = \frac{\tilde{n}}{n_0 - n_\infty} \ln\left(\frac{\tilde{n} - n_\infty}{\tilde{n} - n_0}\right) \,. \tag{11.42}$$

Substituting Eq. (11.42) into Eq. (11.33) leads to an expression for the flux of vapor molecules in the form

$$I = -4\pi R D \tilde{n} \ln \frac{\tilde{n} - n_{\infty}}{\tilde{n} - n_0} .$$
(11.43)

As follows from equality $I = 4\pi R^2 j(R)$, the flux density given by Eq. (11.9) leads exactly to Eq. (11.43). If the strong inequality $n_0 \ll \tilde{n}$ holds, then Eq. (11.42) is reduced to

$$b = a \left(1 + \frac{n_0 + n_\infty}{2\tilde{n}} \right) , \qquad (11.44)$$

and, correspondingly, Eq. (11.35) transforms as

$$I = I_s \frac{b}{a} = -4\pi RD \left(n_0 - n_\infty \right) \left(1 + \frac{n_0 + n_\infty}{2\tilde{n}} \right) .$$
(11.45)

Thus, the relative difference between parameters b and a provided by the allowance for the Stefan flow is a small quantity of order n_0/\tilde{n} .

Since $R \neq 0$ for a growing droplet (the value of concentration n_l is large, but finite), the use of steadystate diffusion approximation is not obviously self-consistent. To take into account the influence of the motion of the droplet surface on the value of the diffusion flux, we turn again to Eq. (11.30). Note that, in view of the small relative difference between b and a, we can write an equivalent to Eq. (11.39) inequality

$$b \ll |\gamma b| \ll 1 . \tag{11.46}$$

In view of Eq. (11.46), Eq. (11.30) can be with a reasonable accuracy rewritten in the form

$$b = \frac{\tilde{n}}{\tilde{n} - n_{\infty}} \frac{(1 - b\gamma)a}{\int\limits_{1}^{\infty} \frac{dz}{z^2} \left(\exp\left\{-\frac{bz^2}{2}\right\} - \frac{\gamma b}{z} \right)}.$$
(11.47)

Integral in Eq. (11.47) is calculated with using the equality

$$\int_{1}^{\infty} \frac{dz}{z^2} \exp\left\{-\frac{bz^2}{2}\right\} = 1 - \sqrt{\frac{\pi b}{2}} \qquad (b \ll 1)$$
(11.48)

the validity of which is easy to verify. The result is

$$\int_{1}^{\infty} \frac{dz}{z^2} \left(\exp\left\{-\frac{bz^2}{2}\right\} - \frac{\gamma b}{z} \right) = 1 - \frac{\gamma b}{2} - \sqrt{\frac{\pi b}{2}} . \tag{11.49}$$

Substituting Eq. (11.49) into Eq. (11.47), after some manipulations with the use of the definitions Eqs. (11.20) and (11.31), we find for the parameter b the following expression:

$$b = a \left(1 + \frac{n_0 + n_\infty}{2\tilde{n}} + \sqrt{\frac{\pi \left(n_0 - n_\infty\right)}{2n_l}} \right) \,. \tag{11.50}$$

The correction expressed by the last term on the right-hand side of Eq. (11.50) is a result of non-stationarity of the diffusion flux caused by the motion of the droplet surface. Both corrections on the right-hand side of Eq. (11.50) are comparatively small, and the relative role of each of the two correction terms varies depending on the specific conditions of condensation.

As an example, we will give quantitative estimates of parameters a and γ as well as corrections in Eq. (11.50) in two specific cases for the growth of water droplets in air. In both cases, we set $n_0 = 2n_{\infty}$ (vapor supersaturation is equal to unity). In the first case, at a temperature 20°C and normal atmospheric pressure, we have $a = 1.73 \cdot 10^{-5}$, $\gamma = -1.33 \cdot 10^3$, $|\gamma a| = 2.3 \cdot 10^{-2}$. Thus the inequality Eq. (11.39) is well satisfied. The correction caused by the Stefan flow equals $3.42 \cdot 10^{-2}$ in this case, while the correction due to non-stationary diffusion equals $5.21 \cdot 10^{-3}$ and appears to be by an order of magnitude smaller. Thus, neglecting the effect of non-stationary diffusion with simultaneous allowance for the influence of the Stefan flow on the flux of vapor molecules is quite acceptable in this case.

In the second case, we consider the condensation of water vapor at a temperature 60° C and high pressure, which is twenty times greater than the normal atmospheric pressure. In this case, $a = 1.47 \cdot 10^{-4}$, $\gamma = -75.6$, $|\gamma a| = 1.1 \cdot 10^{-2}$, so that inequality Eq. (11.39) still holds. The correction due to the Stefan flow equals now $1.67 \cdot 10^{-2}$, while the correction caused by the non-stationary diffusion turns out to be $1.52 \cdot 10^{-2}$. As is seen, both corrections have similar values in this case. Thus calculation of the flux of vapor molecules with allowance for only one of them, while neglecting the other, becomes unjustified.

11.6 Vapor Diffusivity Dependent on Composition of the Vapor-Gas Mixture

In our calculations in the previous sections, the diffusion coefficient of vapor molecules was assumed to be constant and equal to the limiting value corresponding to zero vapor density in the vapor-gas mixture. At small values of the ratio n/\tilde{n} , the dependence of the coefficient of mutual diffusion of vapor and passive gas on the local composition of vapor-gas mixture can be approximated as

$$D(n(r)) = D\left[1 + \varepsilon \frac{n(r)}{\tilde{n}}\right], \qquad (11.51)$$

where ε is a numerical coefficient of order of unity. Using Eq. (11.51) under conditions of stationary diffusion, we obtain the following equation for the vapor concentration n(r):

$$-D\left(1+\varepsilon\frac{n(r)}{\tilde{n}}\right)\frac{\partial n(r)}{\partial r} = j(R)\frac{R^2}{r^2}\frac{\tilde{n}-n(r)}{\tilde{n}}.$$
(11.52)

11.6 Vapor Diffusivity Dependent on Composition of the Vapor-Gas Mixture

Integration of this equation gives

$$D(1+\varepsilon)\ln(\tilde{n}-n) - D\varepsilon \frac{\tilde{n}-n}{\tilde{n}} = -j(R)\frac{R^2}{\tilde{n}r} + \text{const.}$$
(11.53)

Using the boundary conditions for n(r) leads to the following expression for the flux density j(R)

$$j(R) = -\frac{D}{R} \left(n_0 - n_\infty \right) \left[\left(1 + \varepsilon \right) \frac{\tilde{n}}{n_0 - n_\infty} \ln \left(\frac{\tilde{n} - n_\infty}{\tilde{n} - n_0} \right) - \varepsilon \right] \,. \tag{11.54}$$

It follows from Eq. (11.54) at $n_0, n_\infty \ll \tilde{n}$ that

$$j(R) = -\frac{D}{R} (n_0 - n_\infty) \left[1 + (1 + \varepsilon) \frac{n_0 + n_\infty}{2\tilde{n}} \right] .$$
(11.55)

As is seen from Eq. (11.55), taking into account the dependence of the diffusion coefficient on the local composition of the gas-vapor mixture leads, in general, to a correction of the same order of magnitude in the expression for the density of the vapor flux to the droplet as in the case with allowance for the Stefan flow.

In order to take into account simultaneously also the effect of the moving surface of the growing droplet, let us consider a non-stationary diffusion equation for n(r,t) with the diffusion coefficient determined according to Eq. (11.51). This equation can be written as

$$\frac{\partial n(r,t)}{\partial t} = D\left(1 + \varepsilon \frac{n(r,t)}{\tilde{n}}\right) \Delta n(r,t) + \frac{\varepsilon D}{\tilde{n}} \left(\frac{\partial n(r,t)}{\partial r}\right)^2 - v_r(r,t) \frac{\partial n(r,t)}{\partial r} .$$
(11.56)

With using the self-similar variable ρ determined by Eqs. (11.14) and (11.18) for $v_r(r,t)$, Eq. (11.56) transforms as

$$\frac{d^2n}{d\rho^2} + \left[\frac{2}{\rho} + \frac{R\dot{R}}{D\left(1+\varepsilon\frac{n}{\tilde{n}}\right)}\left(\rho - \frac{\gamma}{\rho^2}\right)\right]\frac{dn}{d\rho} + \left(\frac{\varepsilon}{\tilde{n}}\right)\frac{\left(\frac{dn}{d\rho}\right)^2}{1+\varepsilon\frac{n}{\tilde{n}}} = 0.$$
(11.57)

Boundary conditions for Eq. (11.57) are given by the previous Eqs. (11.21) and (11.22).

As it follows from the balance of the number of vapor molecules at condensation, we have in the case of the diffusion coefficient depending on the composition of the mixture the following equation

$$n_l \dot{R}(t) = -\left[-D\left(1 + \varepsilon \frac{n(r,t)}{\tilde{n}}\right) \frac{\partial n(r,t)}{\partial r} + n_\infty \left(v_r(r,t) - \dot{R}(t)\right) \right] \Big|_{r=R(t)} .$$
(11.58)

This equation is reduced at passing to the self-similar variable ρ to the relation

$$\frac{R\dot{R}}{D} \equiv b = \frac{1 + \varepsilon \frac{n_{\infty}}{\tilde{n}}}{n_l \left(1 - \frac{n_{\infty}}{\tilde{n}}\right)} \left. \frac{dn(\rho)}{d\rho} \right|_{\rho=1} \,.$$
(11.59)

Assuming that condition Eq. (11.46) is fulfilled and taking into account the smallness of the ratio n/\tilde{n} , the Eq. (11.57) can be written in a somewhat simplified form as

$$\frac{d^2n}{d\rho^2} + \left[\frac{2}{\rho} + b\left(\rho - \frac{\gamma}{\rho^2}\right)\right]\frac{dn}{d\rho} = -\frac{\varepsilon}{\tilde{n}}\left(\frac{dn}{d\rho}\right)^2 \,. \tag{11.60}$$

The resulting equation differs from Eq. (11.19) by the presence of a small term on the right-hand side, which can be regarded as a perturbation. This allows us to substitute on the right-hand side of Eq. (11.60) the

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solution Eq. (11.27) of Eq. (11.19). As a result, we have in the adopted approximation the inhomogeneous linear equation for $n(\rho)$:

$$\frac{d^2n}{d\rho^2} + \left[\frac{2}{\rho} + b\left(\rho - \frac{\gamma}{\rho^2}\right)\right]\frac{dn}{d\rho} = -\frac{\varepsilon}{\tilde{n}}\frac{(n_0 - n_\infty)^2}{\rho^4}\exp\left\{-b\rho^2 - \frac{2\gamma b}{\rho}\right\}.$$
(11.61)

Integration of Eq. (11.61) yields

(

$$\frac{dn}{d\rho} = \frac{\exp\left\{-\frac{b\rho^2}{2} - \frac{\gamma b}{\rho}\right\}}{\rho^2} \left[C + \frac{\varepsilon}{\tilde{n}} \frac{\left(n_0 - n_\infty\right)^2}{\rho}\right] \,. \tag{11.62}$$

Constant C is determined after integration of Eq. (11.62) with boundary conditions Eqs. (11.21) and (11.22). As a result, we obtain

$$C = \frac{n_0 - n_\infty}{\int\limits_{1}^{\infty} \frac{dz}{z^2} \exp\left\{-\frac{bz^2}{2} - \frac{\gamma b}{z}\right\}} - \frac{\varepsilon (n_0 - n_\infty)^2}{2\tilde{n}}.$$
 (11.63)

Substituting the expression for $(dn/d\rho)$ into Eq. (11.59), we find the equation for parameter b in the form

$$b = \frac{n_0 - n_\infty}{n_l} \left\{ \left(\frac{1 + \varepsilon \frac{n_\infty}{\tilde{n}}}{1 - \frac{n_\infty}{\tilde{n}}} \right) \frac{e^{-\gamma b}}{\int\limits_{1}^{\infty} \frac{dz}{z^2} \exp\left\{ -\frac{bz^2}{2} - \frac{\gamma b}{z} \right\}} + \frac{\varepsilon \left(n_0 - n_\infty \right)}{2\tilde{n}} \right\} .$$
(11.64)

Note that Eq. (11.64) is written with exceeding the accuracy in the small parameters of the problem, given by conditions $b \ll |\gamma b| \ll 1$ and $n/\tilde{n} \ll 1$. After some transformations with allowance for these conditions, we find for *b*:

$$b = a \left[1 + (1 + \varepsilon) \frac{n_0 + n_\infty}{2\tilde{n}} + \sqrt{\frac{\pi (n_0 - n_\infty)}{2n_l}} \right] .$$
(11.65)

The resulting general expression for b contains as limiting cases the results given by Eqs. (11.50) and (11.55). Thus, the Stefan flow as well as non-stationary diffusion and the dependence of the diffusion coefficient on the composition of the vapor-gas mixture lead, generally speaking, to corrections of the same order of magnitude in the expression for the vapor flux into the growing droplet.

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12 Gas Bubble Growth Dynamics in a Supersaturated Solution: Henry's and Sievert's Solubility Laws

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Small differences in the initial conditions produce very great ones in the final phenomena.

Henri Poincare

Abstract

Theoretical description of diffusion growth of a gas bubble after its nucleation in supersaturated liquid solution is presented. We study the influence of Laplace pressure on the bubble growth. We consider two different solubility laws: Henry's law, which is fulfilled for the systems where no gas molecules dissociation takes place and Sievert's law, which is fulfilled for the systems where gas molecules completely dissociate in the solvent into two parts. We show that the difference between Henry's and Sievert's laws for chemical equilibrium conditions causes the difference in bubble growth dynamics. Assuming that diffusion flux of dissolved gas molecules to the bubble is steady we obtain differential equations on bubble radius for both solubility laws. For the case of homogeneous nucleation of a bubble, which takes place at a significant pressure drop bubble dynamics equations for Henry's and Sievert's laws are solved analytically. For both solubility laws three characteristic stages of bubble growth are marked out. Intervals of bubble size change and time intervals of these stages are found. We also obtain conditions of diffusion flux steadiness corresponding to consecutive stages. The fulfillment of these conditions is discussed for the case of nucleation of water vapor bubbles in magmatic melts. For Sievert's law the analytical treatment of the problem of bubble dissolution in a pure solvent is also presented.¹

12.1 Introduction

This paper presents a theoretical description of diffusion growth of a gas bubble in liquid solution as a result of a considerable pressure drop (in the order of 10^3 times). These conditions of bubble growth process are observed in magmatic melts during volcanic eruptions [1, 2]. After such a significant pressure drop the solution becomes strongly supersaturated; and homogeneous (fluctuational) nucleation of gas bubbles becomes possible. It is the growth dynamics of such bubbles that is the subject of the present paper. It has to be noted that the growth regularities of a solitary bubble are crucial for the description of the whole kinetics of phase transition in supersaturated solution [3, 4, 5].

While describing gas bubble growth in supersaturated solution two rough approximations are traditionally made [3, 6, 7, 4, 5]:

1. The flux of the dissolved gas towards the bubble is assumed to be steady.

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2. The consideration is limited to bubbles with the radius that is large enough to neglect the Laplace pressure in comparison with the external pressure of the solution.

In the present paper, following our preceding works [8, 9], while exploiting the steady approximation, we take into account the Laplace pressure in the bubble considering the bubble from the very moment of its nucleation. Consideration of the time-dependent Laplace pressure in the bubble makes both gas density in the bubble and the equilibrium concentration of the dissolved gas at the surface of the bubble time-dependent as well.

Gas bubble growth in a solution taking into account the Laplace pressure was considered as early as in 1950 in the classical paper by Epstein and Plesset [10], where the authors obtained the equation for the bubble radius as a function of time. In order to relate the equilibrium concentration of the dissolved gas and the solution pressure, [10] presupposed the fulfillment of Henry's law: i. e. the proportional dependence between these two values. Indeed, Henry's law is fulfilled for the solution of CO_2 in magmatic melt [7]; however, it is not valid for the solution of H_2O vapor [3, 6]. In this case, which is crucial for practical reasons, Sievert's law is observed: the equilibrium concentration of the dissolved gas is proportional to the square root of the solution pressure [11]. Sometimes both cases are referred to as "Henry's law", but in the present paper, in order to avoid confusion, we will use the term "Sievert's law" for the case with a square root, following e. g. [12]. Here we analyze the bubble growth dynamics in both cases: for Henry's and Sievert's laws. For Sievert's law we obtain the equation for the bubble radius as a function of time analogous to [10], which has not been obtained previously.

Our analysis shows that, irrespective of the law applied to gas solubility, three characteristic stages can be marked out in the growth dynamics. During the first stage the bubble radius is growing with an increasing rate. On the second stage the growth rate decreases. The third stage, when the growth rate continues to decrease, begins when the Laplace pressure inside the bubble becomes comparable with the external pressure of the solution. We demonstrate that during the first two stages the time dependence of the bubble radius is different for the cases when either Henry's or Sievert's laws are fulfilled, while during the third stage this distinction is no longer observed.

For both Henry's and Sievert's laws we obtain intervals within which the bubble radius changes on each stage, as well as time limits and conditions when the steady approximation is applicable. We show that, as the radius of the bubble increases, the steady condition becomes stricter; and, consequently, as a rule, the steady regime of a multistage bubble growth gradually gives way to the nonsteady one. We obtain analytical expression for the time when Laplace pressure influences on bubble growth vanishes and therefore substantiate the estimation of this time made in [13]. After this time passed the bubble growth reaches a self-similar regime [14]. We also analyze whether the steady approximation is applicable to the case of gas bubbles in magma described by Navon [6] and Chernov et al. [3] for large radius of a bubble (neglecting Laplace pressure). Besides that, we present the analytical description of bubble dissolution in the pure solvent for the Sievert's solubility law, which was not presented before in literature.

12.2 Equilibrium Concentration of the Dissolved Gas

Let us consider a gas dissolved in a liquid. The solution was initially in an equilibrium state at temperature T and pressure P_0 . The concentration of the dissolved gas in the solution under such conditions will be denoted as n_0 . Then we instantly relieve the external pressure to value Π in such way that solution becomes supersaturated. The temperature and volume of the solution remain the same, thus value n_0 still serves for the dissolved gas concentration.

It is more convenient to express the state of the solution in terms of dimensionless variables: supersaturation ζ and gas solubility *s* defined here via

$$\zeta \equiv \frac{n_0 - n_\infty}{n_\infty} , \qquad (12.1)$$

$$s \equiv \frac{k_B T n_{\infty}}{\Pi} , \qquad (12.2)$$

where n_{∞} is the equilibrium concentration of dissolved gas at the external pressure Π , k_B is the Boltzmann constant.

When some time passes after the pressure drop, a gas bubble nucleates and begins to grow regularly. Following [3] we assume that the bubble is in mechanical equilibrium with the solution, and its dynamics is governed only by diffusion process. This assumption will be discussed in Appendix A. The radius of the bubble will be denoted as R. We consider the situation when the solvent is in its stable liquid state; therefore, we assume that the bubble consists of gas only, but not of the solvent vapor. The gas in the bubble is considered to be ideal.

When the bubble is studied after some time t_0 since its nucleation, its radius complies with the strong inequality

$$R \gg 2\sigma/\Pi , \tag{12.3}$$

where σ is the surface tension of the pure solvent (it is true while the solution is considered as diluted). Eq. (12.3) allows us to neglect the influence of Laplace pressure on the bubble growth. Therefore, we can write the following equations for the pressure in the bubble P_R and for the equilibrium solution concentration near the surface of the bubble n_R :

$$P_R = \Pi , \tag{12.4}$$

$$n_R = n_\infty . (12.5)$$

The subscripts ∞ denotes that the equilibrium concentration n_{∞} is related with the equilibrium near the flat surface of phase separation $(R \to \infty)$. From Eq. (12.4) it follows that the gas concentration in the bubble n_g is constant. Using the ideal gas law we have

$$n_g = \frac{\Pi}{k_B T} . \tag{12.6}$$

When Eqs. (12.3), (12.4), and (12.5) are fulfilled and, therefore, Laplace pressure is negligible, the bubble dynamics is evident for the case of steady-state diffusion and can be even described analytically for the non-steady case [13, 14].

From the moment of bubble nucleation and till Eq. (12.3) becomes valid, Laplace pressure influences bubble growth. Thus both quantities P_R and n_R become radius-dependent (and, therefore, time-dependent). For P_R now we have

$$P_R = \Pi + \frac{2\sigma}{R} . \tag{12.7}$$

In order to write the equation for n_R we need to know the solubility law. For the simplest case of Henry's law the equilibrium concentration of dissolved gas is proportional to the corresponding pressure

$$\frac{n_R}{n_\infty} = \frac{P_R}{\Pi} \ . \tag{12.8}$$

However, Henry's law is fulfilled only in such systems where there is no molecules dissociation during gas dissolution. In another important case when the gas molecules completely dissociate in the solvent into two parts the Henry's law is replaced with so-called Sievert's law (see e. g. [15]), and, therefore, Eq. (12.8) is replaced with the following one:

$$\frac{n_R}{n_\infty} = \sqrt{\frac{P_R}{\Pi}} . \tag{12.9}$$

Sievert's law is fulfilled for water vapor dissolved in a silicate melt [11]. Such solutions are important both for glass production [12] and for volcanic systems [3, 6].

The replacement of Eq. (12.8) with Eq. (12.9) means that the boundary condition for the gas diffusion problem will be different for Henry's and Sievert's laws. The change of boundary condition, as we will see further, leads to the change of bubble dynamics.

12.3 Bubble Dynamics Equation

After the nucleation of the bubble, when its growth can be considered regular (i.e. the bubble cannot be dissolved by fluctuations), its growth is governed by the diffusion flux of gas molecules into it. In this paper we will study the case when the diffusion flux can be assumed as steady. The conditions when such approximation is valid will be discussed further.

Taking into account the equality of gas concentration at the bubble surface to the equilibrium concentration n_R and the equality of gas concentration far from the bubble to the initial concentration n_0 , we can write a simple expression for the steady diffusion flux density j_D

$$j_D = D \frac{n_0 - n_R}{R} \,. \tag{12.10}$$

Here D is the diffusion coefficient of gas molecules in the pure solvent (we assume that the solution is diluted).

Now let us write the expression for the number of gas molecules N in the bubble. Exploiting the ideal gas law and using Eq. (12.7) we have

$$N = \frac{4\pi}{3k_B T} R^3 \left[\Pi + \frac{2\sigma}{R} \right] . \tag{12.11}$$

Differentiating Eq. (12.11), using Eq. (12.6), we obtain

$$\frac{dN}{dt} = 4\pi n_g R^2 \frac{dR}{dt} \left[1 + \frac{R_\sigma}{R} \right] , \qquad (12.12)$$

where

$$R_{\sigma} \equiv \frac{4}{3} \frac{\sigma}{\Pi} \tag{12.13}$$

is the characteristic size of the bubble.

Material balance between the dissolved gas and the gas in the growing bubble gives us the following equality

$$\frac{dN}{dt} = 4\pi R^2 j_D \,. \tag{12.14}$$

Substituting expression for diffusion flux density Eq. (12.10) and the rate of change of the number of molecules Eq. (12.12) into material balance equation Eq. (12.14) we have

$$n_g \frac{dR}{dt} \left[1 + \frac{R_\sigma}{R} \right] = D \frac{n_0 - n_R}{R} .$$
(12.15)

Or, exploiting Eqs. (12.2) and (12.6), we equivalently have

$$R\dot{R}\left[1+\frac{R_{\sigma}}{R}\right] = Ds\frac{n_0 - n_R}{n_{\infty}} .$$
(12.16)

Using Eqs. (12.1), (12.7) and, correspondingly, (12.8) and (12.9), the fraction in the r. h. s. of Eq. (12.16) can be expressed as

$$\frac{n_0 - n_R}{n_\infty} = \zeta - \frac{2\sigma}{\Pi R} \tag{12.17}$$

for Henry's law, and

$$\frac{n_0 - n_R}{n_\infty} = \zeta + 1 - \sqrt{1 + \frac{2\sigma}{\Pi R}}$$
(12.18)

12.4 Critical Bubble and Initial Conditions for the Bubble Growth

for Sievert's law. After exploiting in Eqs. (12.17) or (12.18) the definition of R_{σ} (Eq. (12.13)), we have, correspondingly,

$$\frac{n_0 - n_R}{n_\infty} = \zeta - \frac{3}{2} \frac{R_\sigma}{R}$$
(12.19)

and

$$\frac{n_0 - n_R}{n_\infty} = \zeta + 1 - \sqrt{1 + \frac{3}{2} \frac{R_\sigma}{R}} .$$
(12.20)

Eqs. (12.19) and (12.20) allow us to rewrite the equation of bubble dynamics Eq. (12.16) in the final form, namely

$$R\dot{R}\left[1+\frac{R_{\sigma}}{R}\right] = Ds\left[\zeta - \frac{3}{2}\frac{R_{\sigma}}{R}\right]$$
(12.21)

for Henry's solubility law; and

$$R\dot{R}\left[1+\frac{R_{\sigma}}{R}\right] = Ds\left[\zeta+1-\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}\right]$$
(12.22)

for Sievert's solubility law.

While Eq. (12.21) was obtained as early as in 1950 in paper by Epstein and Plesset [10], Eq. (12.22) was not obtained previously. In paper by Cable and Frade it was presented only a special case of Eq. (12.22), when $\zeta = -1$:

$$R\dot{R}\left[1+\frac{R_{\sigma}}{R}\right] = -Ds\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}$$
(12.23)

(Eq. (34) in [12]). Such value of supersaturation corresponds to the dissolution of gas bubble in the pure solvent. And even for this special case of Eq. (12.22) analytical solution was not obtained. We present the analytical solution of Eq. (12.23) in Appendix B.

12.4 Critical Bubble and Initial Conditions for the Bubble Growth

The obtained equations for the bubble growth dynamics Eqs. (12.21) and (12.22) can be applied to the cases of both homogeneous and heterogeneous nucleation. Below we will consider only the homogeneous nucleation case.

Homogeneous nucleation of a gas bubble in a supersaturated solution means fluctuational mechanism of its appearance and needs a significant pressure drop (in the order of 10^3 times). It is these conditions of bubble nucleation that take place in magmatic melts during volcanic eruptions [3]. Since we decided to describe only regular growth of a bubble, we need to exclude the very process of nucleation from our examination and consider a bubble only when it is already supercritical.

Under the notion of critical bubble we understand, as usually [4, 16], such a bubble which radius R_c corresponds to the extremum of work of bubble formation. Critical bubble is in mechanical equilibrium with solution at the initial pressure P_0 and in chemical equilibrium with solution with concentration n_0

$$P_{R_c} = P_0 , (12.24)$$

$$n_{R_c} = n_0 .$$
 (12.25)

These two conditions together with the solubility law unambiguously define the value of R_c . Condition (12.24), using Eq. (12.7), evidently gives us

$$R_c = \frac{2\sigma}{P_0 - \Pi} ,$$
 (12.26)

and condition (12.25) allows us to connect value P_0 with the supersaturation ζ .

Substituting Eqs. (12.24) and (12.25) in Eq. (12.8) (Henry's law) and Eq. (12.9) (Sievert's law) we have correspondingly

$$\frac{n_0}{n_\infty} = \frac{P_0}{\Pi} \tag{12.27}$$

and

$$\frac{n_0}{n_\infty} = \sqrt{\frac{P_0}{\Pi}} . \tag{12.28}$$

For Henry's law we have evidently from Eq. (12.27) using Eq. (12.1)

$$P_0 = \Pi \left(\zeta + 1 \right). \tag{12.29}$$

And, substituting Eq. (12.29) in Eq. (12.26), we have

$$R_c = \frac{2\sigma}{\Pi\zeta} , \qquad (12.30)$$

the well-known expression for the radius of a critical bubble (e. g. [4, 16]).

For Sievert's law, when Eq. (12.27) is replaced by Eq. (12.28), we have

$$P_0 = \Pi \left(\frac{n_0}{n_\infty}\right)^2,\tag{12.31}$$

or, using Eq. (12.1),

$$P_0 = \Pi \left(\zeta + 1\right)^2. \tag{12.32}$$

Finally, substituting Eq. (12.32) in Eq. (12.26) for the critical bubble radius, we have

$$R_c = \frac{2\sigma}{\Pi\left[(\zeta+1)^2 - 1\right]} \,. \tag{12.33}$$

Using Eq. (12.13) and Eq. (12.30) or Eq. (12.33) correspondingly we can write the relations between R_{σ} and R_c for both Henry's and Sievert's laws

$$R_{\sigma} = \frac{2}{3} \zeta R_c , \qquad (12.34)$$

$$R_{\sigma} = \frac{2}{3} \left[(\zeta + 1)^2 - 1 \right] R_c , \qquad (12.35)$$

which will be exploited later.

Here it is important to make a remark regarding the quantity s, the gas solubility. Eqs. (12.1) and (12.2) give us

$$s = \frac{n_0 k_B T}{\Pi} \frac{1}{\zeta + 1} \,. \tag{12.36}$$

12.5 Three Stages of Bubble Growth

If Henry's law is fulfilled, we have $\zeta + 1 = P_0/\Pi$ and, therefore,

$$s = \frac{n_0 k_B T}{P_0}$$
, (12.37)

s is a tabular value defined only by the initial state of the solution (before the pressure drop).

Since we consider Sievert's law, we have (see Eq. (12.32)) $\zeta + 1 = \sqrt{P_0/\Pi}$; thus instead of Eq. (12.37), we obtain

$$s = \frac{n_0 k_B T}{\sqrt{P_0 \Pi}} . \tag{12.38}$$

Here it is convenient to introduce constant K as the coefficient of proportionality in Sievert's law: $K \equiv n_0/\sqrt{P_0}$. It allows us to rewrite Eq. (12.38) in the following form:

$$s = K \frac{k_B T}{\sqrt{\Pi}} . \tag{12.39}$$

Eq. (12.39) shows us that in the case of Sievert's law the solubility value s depends on the final state of the solution. In the current paper a solubility value for Sievert's law is understood as gas solubility at the final pressure Π , i. e. after the pressure drop.

To deal with the dynamic equations (12.21) and (12.22) one needs to provide it with a reasonable initial condition, i. e. to choose the value of constant R_i , initial radius of the bubble, in the following equality

$$R(t)|_{t=0} = R_i . (12.40)$$

In papers [10, 12] there was no special meaning assigned to the value of R_i : the reason of appearance of the bubble was totally excluded from discussion. Here we assume that the bubble nucleated fluctuationally, i. e. crossed the barrier corresponding to radius R_c . It means that R_i has to be not less than R_c , but evidently we cannot use the radius of a critical bubble R_c as the initial value for the radius.

A bubble that nucleates fluctuationally in the solution is capable of regular growth if it passed and, moreover, moved away from the near-critical region where fluctuations are still strong enough. Thus we choose, following [8], $R_i = 2R_c$, i. e.

$$R(t)|_{t=0} = 2R_c . (12.41)$$

Such value guarantees the absence of fluctuations and, as we will see further, provides us with convenient expressions.

The necessary condition for the fluctuational nucleation of a bubble is a high pressure drop $(P_0/\Pi \sim 10^3)$ and, consequently, high supersaturation $\zeta \sim 10^3$ for Henry's law and $\zeta \sim 30 \div 40$ for Sievert's law. Further we will use the following strong inequalities for the supersaturation:

$$\zeta \gg 10 \tag{12.42}$$

for Henry's law, and

 $\zeta \gg 1 \tag{12.43}$

for Sievert's law.

12.5 Three Stages of Bubble Growth

Before we find the explicit solution of Eqs. (12.21) and (12.22), let us qualitatively describe the change of the character of bubble growth process with the increase of its size. This will allow us to mark out the

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representative stages of growth and to determine corresponding characteristic bubble sizes. Duration of the consecutive stages and the character of bubble radius time dependence on each stage will be considered in the next section. It has to be noticed that the stages of our interest do not have anything in common with the stages of evolution of the whole ensemble of bubbles during the decomposition of liquid solution supersaturated with gas.

It will be more convenient to consider both cases of solubility laws separately.

12.5.1 Henry's Law

Let us rewrite Eq. (12.21) in the equivalent form which will be more appropriate for its analysis:

$$\dot{R} = Ds\zeta \left(1 - \frac{R_c}{R}\right) \frac{1}{R} \left(\frac{1}{1 + R_\sigma/R}\right),\tag{12.44}$$

where we took into account Eqs. (12.13) and (12.30).

Each of the three co-factors dependent on R emphasized in the right hand side of Eq. (12.44) describes its physically different contribution to the dynamics of the supercritical bubble growth process. Co-factor $1 - R_c/R$, increasing with R, corresponds to the fast (the scale of change of R is R_c) increase of the driving force of the process (the value $n_0 - n_R$) with the growth of R. Co-factor 1/R, decreasing with the growth of R, describes, as it is seen from Eq. (12.10), the contribution related to the decrease of the gradient of solution concentration near the bubble surface, which decreases the bubble growth rate with the growth of R. Finally, co-factor $1/(1 + R_{\sigma}/R)$, which increases with the growth of R, takes into account the counteraction of Laplace pressure to the bubble growth, i. e. the fact that the bubble growth is facilitated by the reduction of Laplace pressure with the growth of R, while other factors are equal (the scale of its change is R_{σ}). Notwithstanding the mentioned reduction of counteraction, the resulting contribution of the last two factors always leads to the deceleration of growth with the increase of bubble size.

From Eqs. (12.34) and (12.42) it can be seen that $R_{\sigma} \gg R_c$ holds. Using this inequality, Eq. (12.44) and boundary condition (12.41), we have that the growth rate of the bubble radius in its dependence on this radius has to reach the maximum value achieved at certain bubble radius R_m from the interval $2R_c \le R \le R_{\sigma}$. Thus it is natural to consider the growth in the following interval of sizes

$$2R_c \le R \le R_m \tag{12.45}$$

as a first stage of bubble evolution, where the determining factor is the increase of the driving force of the growth. At this stage bubble growth goes with the increasing in time rate, reaching its maximum at R_m .

In order to obtain R_m we will consider the rate of bubble growth as a function of its radius and differentiate both parts of Eq. (12.44) with respect to R:

$$\frac{d\dot{R}}{dR} = Ds\zeta \frac{R_c \left(R_c + R_{\sigma}\right) - \left(R - R_c\right)^2}{R^2 \left(R + R_{\sigma}\right)^2} \,. \tag{12.46}$$

The quantity R_m is defined by the extremal condition

$$\left. \frac{d\dot{R}}{dR} \right|_{R=R_m} = 0 , \qquad (12.47)$$

which using Eq. (12.46) leads to the following result

$$R_m = R_c + \left(R_c^2 + R_c R_\sigma\right)^{1/2} \,. \tag{12.48}$$

Taking into account the strong inequality $R_{\sigma} \gg R_c$, we can simplify the obtained expression for R_m :

$$R_m \simeq \left(R_c R_\sigma\right)^{1/2} \,. \tag{12.49}$$

12.5 Three Stages of Bubble Growth

The second stage of the process will be when the bubble growth occurs within the interval of sizes

$$R_m \le R \le R_\sigma . \tag{12.50}$$

During all this stage, as $R_m \simeq (R_c R_\sigma)^{1/2} \gg R_c$, it is already valid that $R \gg R_c$, thus the driving force $n_0 - n_R$ remains practically constant. As a result, bubble growth decelerates, although, as it was noted above, the counteraction of Laplace pressure to the growth gradually is attenuated. The Laplace contribution $2\sigma/R$ to the pressure inside the bubble decreases during the second stage by $(R_\sigma/R_c)^{1/2}$ times and at the completion of this stage becomes comparable with the external pressure II contribution (from Eq. (12.13) we have strict equality $2\sigma/R_\sigma = 3\Pi/2$). It is this physical condition that defines the completion of the second stage.

On the subsequent, third stage, which corresponds to the interval of sizes

$$R \ge R_{\sigma} , \tag{12.51}$$

monotonic decelerated bubble growth continues. At the same time, the role of Laplace pressure continues to decrease gradually, and the pressure P_R inside the bubble approaches to a constant value equal to the external pressure Π . As it will be shown further, this process is rather protracted, so the concluding phase of the third stage, when the pressure inside the bubble practically does not change and the application of self-similar solution [13, 14] is possible, comes only in the interval of sufficiently large sizes of the bubble, when the condition $R \gg R_{\sigma}$ is satisfied with a certain reserve.

12.5.2 Sievert's Law

Let us investigate behavior of bubble growth rate \hat{R} with the increase of bubble radius for Sievert's solubility law. From Eq. (12.22) evidently stems

$$\dot{R} = \frac{Ds}{R + R_{\sigma}} \left[\zeta + 1 - \sqrt{1 + \frac{3}{2} \frac{R_{\sigma}}{R}} \right] .$$
(12.52)

Eq. (12.52) can be also written in the form similar to Eq. (12.44), to mark out three co-factors. The character of bubble growth rate is presented graphically in Fig. 12.1.

Differentiating Eq. (12.52) by R we obtain

$$\frac{d\dot{R}}{dR} = \frac{Ds}{(R+R_{\sigma})^2} \left[\frac{3}{4} \frac{R_{\sigma}(R+R_{\sigma})}{\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}R^2} - \left(\zeta + 1 - \sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}\right) \right] .$$
(12.53)

It can be easily seen, that, as it is for Henry's law, here bubble radius growth rate as a function of variable R also has the only maximum. Denoting the corresponding radius as R_m , we can obtain its value from Eq. (12.47). Using Eq. (12.53) we rewrite this equation as

$$RR_{\sigma} + R_{\sigma}^2 + \frac{4}{3}R^2\left(1 + \frac{3}{2}\frac{R_{\sigma}}{R}\right) - \frac{4}{3}R^2\sqrt{1 + \frac{3}{2}\frac{R_{\sigma}}{R}}(\zeta + 1) = 0.$$
(12.54)

Assuming that the sought quantity R_m is considerably less than R_σ , we will use for R in Eq. (12.54) the strong inequality $3R_\sigma/2R \gg 1$. Below we will need this inequality to be even more stronger

$$R_{\sigma}/3R \gg 1$$
. (12.55)

It will allow us to omit the second term in the brackets and the second addend in the square root in Eq. (12.54). So this equation can be rewritten as:

$$\sqrt{\frac{8}{3}}\sqrt{R_{\sigma}}(\zeta+1)R^{3/2} - 3RR_{\sigma} - R_{\sigma}^2 = 0.$$
(12.56)



Figure 12.1: Growth rate of bubble radius dR/dt (measured in dimensionless units $Ds\zeta/R_{\sigma}$) as a function of R. Solid curve corresponds to Henry's law, Eq. (12.44). Dashed curve corresponds to Sievert's law, Eq. (12.52). For both solubility laws $P_0/\Pi = 10^3$.

Using Eq. (12.55) we can also omit the second addend in Eq. (12.56) in comparison with the third one. After such a simplification Eq. (12.56) becomes solvable; and for R_m we have:

$$R_m \simeq \frac{\sqrt[3]{3}}{2} \frac{R_\sigma}{(\zeta+1)^{2/3}} \,. \tag{12.57}$$

Substituting Eq. (12.57) in the second addend in Eq. (12.56) we can find a first-order correction to R_m in Eq. (12.57). We have

$$R_m \simeq \frac{\sqrt[3]{3}}{2} \frac{R_\sigma}{(\zeta+1)^{2/3}} \left(1 + \frac{3\sqrt[3]{3}}{2} \frac{1}{(\zeta+1)^{2/3}} \right)^{2/3} .$$
(12.58)

Numerical solution of Eq. (12.54) for $\zeta = 30$ gives for inaccuracy of approximate solution Eq. (12.58) the value less than 2%, and this value evidently decreases with the increase of ζ .

As soon as we explained the behavior of the value R and found the value of R_m we can use the ideas proposed for Henry's law to determine the stages of bubble growth. On each stage the character of bubble growth is different from any other. The three consecutive stages of growth are still defined by Eqs. (12.45), (12.50) and (12.51).

In the next two sections we will obtain the time dependence of bubble radius R for each stage and duration of each stage. Also we will obtain conditions of steadiness of bubble growth for each stage.

12.6 Time Dependence of Bubble Radius

Let us now solve the differential equations (12.21) and (12.22) for the time dependence of the bubble radius with the initial condition Eq. (12.40) of homogeneous nucleation of the bubble. As it was in the previous section it is more convenient here to consider Henry's and Sievert's laws separately.

12.6 Time Dependence of Bubble Radius

12.6.1 Henry's Law

At first we will rewrite Eq. (12.21) in the form which is appropriate for integration:

$$R\dot{R} + (R_{\sigma} + R_c)\dot{R} + (R_{\sigma} + R_c)R_c\frac{\dot{R}/R_c}{R/R_c - 1} = Ds\zeta .$$
(12.59)

Integrating Eq. (12.59), we obtain

$$\frac{R^2}{2} + (R_{\sigma} + R_c)R + (R_{\sigma} + R_c)R_c \ln\left(\frac{R}{R_c} - 1\right) = Ds\zeta (t + \tau) , \qquad (12.60)$$

where τ is the constant which has time dimensionality and which is defined by the initial value of radius at time t = 0. Using initial condition (12.40), from Eq. (12.60) we find

$$\tau = \frac{2R_c(R_\sigma + 2R_c)}{Ds\zeta} . \tag{12.61}$$

Excluding time τ from Eq. (12.60) by means of Eq. (12.61), we obtain

$$\frac{R^2 - 4R_c^2}{2} + (R_\sigma + R_c)(R_\sigma - 2R_c) + (R_\sigma + R_c)R_c \ln\left(\frac{R}{R_c} - 1\right) = Ds\zeta t .$$
(12.62)

Validity of the general relation Eq. (12.62), which strictly takes into account Laplace pressure influence on the bubble growth process, is limited only by the condition of applicability of steady approximation Eq. (12.10) for the diffusion flux. Equation (12.62) does not imply the smallness of quantity R_c/R_{σ} which follows from Eqs. (12.34) and (12.42). Eq. (12.62) complies with the results obtained in papers [10, 12] for the particular case of steady growth of a bubble.

Now let us consider the third stage of bubble growth, when $R \ge R_{\sigma}$. First of all, let us note that at the end of the first stage, when the bubble radius R approaches the value $(R_c R_{\sigma})^{1/2}$, and with even more assurance on the second and the third stages, one can neglect the logarithmic addend in Eq. (12.62). Moreover, since during the third stage the main contribution in the l. h. s. of Eq. (12.62) gradually tends to the first addend, equal to $R^2/2$; and the contribution of the second addend (influence of Laplace pressure) decreases, neglect of logarithmic contribution becomes fairly justified. As a result, Eq. (12.62) conformably to the third stage of bubble growth can be written in the form of

$$\frac{R^2}{2} + R_\sigma R = Ds\zeta t . \tag{12.63}$$

12.6.2 Sievert's Law

Unlike the case of Henry's law (Eq. (12.21)) solution of Eq. (12.22) in general case is too cumbersome and, as we will ensure in the current section, when inequality (12.43) is fulfilled, is even not necessary. Here we present solutions of this equation for two particular cases:

$$R \ll R_{\sigma} \tag{12.64}$$

- the first and the second stages and

$$R \gg R_c \tag{12.65}$$

- the second and the third stages. When strong inequality Eq. (12.43) is fulfilled, these two cases cover the whole range $R \ge 2R_c$ of regular growth of the bubble radius, and that is the reason why general solution of Eq. (12.22) is not necessary for the system under consideration.

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Let us begin with the case when inequality Eq. (12.64) is fulfilled. In this case we can omit 1 in comparison with R_{σ}/R in the l. h. s. of Eq. (12.22) and we can also omit 1 in comparison with the fraction $3R_{\sigma}/2R$ in the r. h. s. of this equation. Thus we have

$$\dot{R} = \frac{Ds}{R_{\sigma}} \left[\zeta + 1 - \sqrt{\frac{3}{2} \frac{R_{\sigma}}{R}} \right] \,. \tag{12.66}$$

Separating variables and exploiting Eq. (12.35) for R_{σ} under the square root, we can rewrite Eq. (12.66) in the form which allows its integration:

$$\frac{dR}{1 - \sqrt{R_c/R}} = \frac{Ds(\zeta + 1)}{R_{\sigma}} dt .$$
(12.67)

Integrating Eq. (12.67) with initial condition (12.40), we finally have

$$R - 2R_c + R_c \ln\left(\frac{R}{R_c} - 1\right) + 2\sqrt{R_c} \left(\sqrt{R} - \sqrt{2R_c}\right) + R_c \ln\left(\frac{\sqrt{2} + 1}{\sqrt{2} - 1}\frac{\sqrt{R} - \sqrt{R_c}}{\sqrt{R} + \sqrt{R_c}}\right) = \frac{Ds}{R_\sigma}(\zeta + 1)t .$$
(12.68)

This formula is different from Eq. (12.62), which means that, when inequality (12.64) is fulfilled, there is a significant difference in the character of growth between Sievert's law and Henry's law.

Now let us proceed with the other case. At first, using Eq. (12.35) we can rewrite Eq. (12.22) equivalently in the form of

$$\frac{\dot{R}[R+R_{\sigma}]}{1-\sqrt{\frac{1}{(\zeta+1)^2}+\frac{R_c}{R}}} = Ds(\zeta+1) .$$
(12.69)

This form makes it obvious that, when strong inequality (12.65) together with inequality (12.43) are fulfilled, the whole square root in the denominator of the l. h. s. of Eq. (12.69) can be omitted in comparison with 1. Therefore, we have

$$R[R+R_{\sigma}] = Ds(\zeta+1) .$$
(12.70)

This expression can be easily integrated. But the use of the initial condition Eq. (12.40) is not just as a result of the fulfillment of strong inequality (12.65). There is arbitrariness in the choice of the initial condition for integration of Eq. (12.70), but the most convenient is to choose a condition at such an "average" radius which simultaneously satisfies Eqs. (12.64) and (12.65), e. g.

$$R(t)|_{t=t_a} = R_a \equiv \sqrt{R_c R_\sigma} . \tag{12.71}$$

Due to $R_a \ll R_{\sigma}$, we can use Eq. (12.68) to obtain the explicit value for time t_a defined in Eq. (12.71). Using inequality $R_a \gg R_c$, Eq. (12.68) gives us

$$t_a \simeq \frac{R_a R_\sigma}{Ds(\zeta + 1)} \,. \tag{12.72}$$

Now, integrating Eq. (12.70) with initial condition (12.71), we have

$$\frac{R^2 - R_a^2}{2} + R_\sigma (R - R_a) = Ds(\zeta + 1)(t - t_a) , \qquad (12.73)$$



Figure 12.2: Growth rate of bubble radius squared dR^2/dt (measured in dimensionless units $2Ds\zeta$) as a function of R. Solid curve corresponds to Henry's law, Eq. (12.44). Dashed curve corresponds to Sievert's law, Eq. (12.52). For both solubility laws $P_0/\Pi = 10^3$.

or, rewriting R_a using Eq. (12.71) and t_a using Eq. (12.72), we have

$$\frac{R^2}{2} + R_\sigma R - \frac{R_\sigma R_c}{2} = Ds(\zeta + 1)t .$$
(12.74)

With the increase of R the contribution of the third addend in the l. h. s. of Eq. (12.74) decreases and at $R \ge R_{\sigma}$ (on the third stage) we can already write

$$\frac{R^2}{2} + R_\sigma R = Ds(\zeta + 1)t .$$
(12.75)

If we also used in Eq. (12.75) strong inequality (12.43), Eq. (12.75) will become identical to Eq. (12.63). It means that, when inequality $R \ge R_{\sigma}$ is fulfilled, any difference in the character of growth between Sievert's law and Henry's law disappears.

When the bubble radius becomes as large as

$$R \gg R_{\sigma} , \qquad (12.76)$$

Eq. (12.63) transforms into the well-known Scriven's [14] self-similar dependence for the steady-state case

$$R^2 = 2Ds\zeta t , \qquad (12.77)$$

when $dR^2/dt = \text{const.}$ This trend of Eq. (12.63) toward Eq. (12.77) was discussed in detail in [8]. This trend is presented graphically in Fig. 12.2.

12.7 Duration of the Consecutive Stages

12.7.1 Henry's Law

Eq. (12.62), giving the explicit dependence of bubble radius on time, allows us, in particular, to find characteristic times corresponding to consecutive stages. According to Eqs. (12.45) and (12.48), at the end

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of the first stage, the bubble radius reaches the value $R_m = (R_c R_\sigma)^{1/2}$. Substituting value $R = R_m$ to Eq. (12.62) and considering that (by virtue of inequalities $R_c \ll R_m \ll R_\sigma$) the main contribution to the l. h. s. of Eq. (12.62) is made by the second addend, we obtain the expression for the first stage duration t_1

$$t_1 = \frac{R_\sigma^2}{Ds\zeta} \left(\frac{R_c}{R_\sigma}\right)^{1/2} . \tag{12.78}$$

Using Eq. (12.34), expression (12.78) can be also presented in the form

$$t_1 = \left(\frac{3}{2}\right)^{1/2} \frac{R_\sigma^2}{Ds\zeta^{3/2}} \,. \tag{12.79}$$

As it follows from Eq. (12.79), with the increase of initial supersaturation of the solution, the first stage duration decreases proportionally to $1/\zeta^{3/2}$.

The second stage of bubble growth starts at the time point t_1 and finishes at the time point t_2 defined by the condition $R|_{t=t_2} = R_{\sigma}$. Substituting value $R = R_{\sigma}$ into Eq. (12.62) and considering that, by virtue of inequality $R_c \ll R_{\sigma}$, the main contribution to the l. h. s. of Eq. (12.62) is made by the first and the second addends, we obtain the expression for t_2

$$t_2 = \frac{3}{2} \frac{R_{\sigma}^2}{Ds\zeta} \,. \tag{12.80}$$

As one can see from this expression, t_2 dependence on initial solution supersaturation is defined by multiplier $1/\zeta$. The duration of the second stage is much longer than the duration of the first stage, as from Eqs. (12.79) and (12.80) it follows that

$$\frac{t_2}{t_1} = \left(\frac{3\zeta}{2}\right)^{1/2} \gg 1 \ . \tag{12.81}$$

Now let us consider the third stage of bubble growth, when $R \ge R_{\sigma}$ and $t \ge t_2$. First of all, let us note that at the end of the first stage, when the bubble radius R approaches the value $(R_c R_{\sigma})^{1/2}$, and with even more assurance on the second and the third stages, one can neglect the logarithmic addend in Eq. (12.62) (it was taken into account earlier, when Eqs. (12.78) and (12.80) were obtained).

Due to Eq. (12.51) the duration of the third stage of bubble growth is infinite. But it is reasonable to estimate the time from the beginning of the third stage and to the moment when bubble radius reaches the value R_0 defined in [13],

$$R_0 \equiv 20 \cdot 2\sigma / \Pi . \tag{12.82}$$

It is assumed *a priori* in [13], that when radius reaches value R_0 the influence of Laplace pressure on the bubble growth is negligible.

As it was found in the previous section, on the third stage of bubble growth the time dependence of bubble radius is given by the simple equation, Eq. (12.63). Let us introduce time t_3 as a duration of bubble growth in the size interval $R_{\sigma} \leq R \leq R_0$. Using Eqs. (12.63) and (12.82) we evidently have

$$t_3 \simeq 480 \frac{R_\sigma^2}{Ds\zeta} . \tag{12.83}$$

The duration of the third stage is much longer than the duration of the second stage (and, moreover, the first stage), as from Eqs. (12.80) and (12.83) it follows that

$$\frac{t_3}{t_2} \simeq 320$$
 . (12.84)

12.8 Steady Flux Conditions

Eq. (12.84) and strong inequality (12.81) allow us to evaluate the whole duration of bubble growth in the interval of sizes $2R_c \leq R \leq R_0$ as t_3 . In [13] the estimation of this duration t_0 was given by the following equation

$$t_0 \simeq \frac{R_0^2}{2Ds\zeta} \,. \tag{12.85}$$

Using Eqs. (12.13) and (12.82) we have $t_0 \simeq 450 \frac{R_{\sigma}^2}{Ds\zeta}$; and therefore

$$\frac{t_3 - t_0}{t_3} \simeq 6\% . \tag{12.86}$$

12.7.2 Sievert's Law

Using Eqs. (12.69) and (12.58) we can obtain expressions for duration of the first two stages t_1 and t_2 for the Sievert's law analogous to Eqs. (12.78) and (12.80). These expression are cumbersome, while qualitatively the time-scale hierarchy for Sievert's law is similar to the one for Henry's law. Therefore we will not present these expressions here.

As long as on the third stage the dynamic equation of bubble growth for Henry's law Eq. (12.63) and for Sievert's law Eq. (12.75) are exactly the same (we need to account $\zeta \gg 1$ also), all the results presented above for the third stage duration are valid for Sievert's law also.

12.8 Steady Flux Conditions

The diffusion flux of molecules toward a growing bubble can be considered steady when the bubble growth is slow enough in comparison with the "diffusion cloud" growth. To be more exact, the radius of the bubble has to be much smaller than the radius of this cloud, the diffusion length. We can express it as

$$R \ll (Dt_R)^{1/2}$$
, (12.87)

where t_R is the characteristic time of the bubble radius change, $t_R \equiv R/R$ the time in which the bubble radius changes significantly. Evidently, Eq. (12.87) can be rewritten as

$$\left(R\dot{R}/D\right)^{1/2} \ll 1$$
. (12.88)

We can make this condition more explicit by means of Eq. (12.21) and Eq. (12.22) that give us correspondingly:

$$\left(s\zeta \frac{R-R_c}{R+R_\sigma}\right)^{1/2} \ll 1 \tag{12.89}$$

for Henry's law, and

$$\left(s\frac{\left(\zeta+1\right)-\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}}{1+\frac{R_{\sigma}}{R}}\right)^{1/2}\ll1$$
(12.90)

for Sievert's law.

Now exploiting Eqs. (12.89) and (12.90) let us obtain the conditions for diffusion flux to be steady on each stage defined above. We will write these conditions as inequalities for the value of solubility, not for supersaturation. The value of supersaturation is already fixed by Eqs. (12.42) and (12.43).



Figure 12.3: Parameter characterizing the steadiness of bubble growth as a function of bubble radius R, l. h. s. of Eq. (12.88) at $P_0/\Pi = 10^3$. Curves are representing (from upper to lower) Sievert's law at s = 1, Henry's law at $s = 10^{-2}$, Sievert's law at $s = 10^{-1}$ and Henry's law at $s = 10^{-3}$.

Obviously the larger the bubble is the more strict condition for steadiness is (see Fig. 12.3). The general condition for bubble growth to be steady at any time is the condition at $R \gg R_{\sigma}$. From both Eqs. (12.89) and (12.90) we have

$$s^{1/2} \ll \left(\frac{1}{\zeta}\right)^{1/2}$$
 (12.91)

This condition is sufficient for steadiness on the third stage for both Henry's and Sievert's laws.

For bubble growth to be steady during the whole second stage it is sufficient to be steady at $R = R_{\sigma}$. This condition, using Eq. (12.42), transforms Eq. (12.89)

$$s^{1/2} \ll \left(\frac{2}{\zeta}\right)^{1/2}$$
 (12.92)

Exactly the same result will be for Sievert's law (see Eq. (12.43) and Eq. (12.90) at $R = R_{\sigma}$).

For bubble growth to be steady during the whole first stage it is sufficient to be steady at $R = R_m$. It is to be reminded that the quantity R_m has different values for Henry's and Sievert's laws (see Eq. (12.49) and Eq. (12.57)). For Henry's law, using Eq. (12.35) this condition leads to

$$s^{1/2} \ll \left(\frac{2}{3\zeta}\right)^{1/4}$$
 (12.93)

And for Sievert's law to

$$s^{1/2} \ll \left(\frac{2}{3\zeta}\right)^{1/6}$$
 (12.94)

Obtaining Eq. (12.94) we used not only Eq. (12.43), but even more strict condition $\zeta^{2/3} \gg 1$. This condition is still fulfilled when $\zeta \sim 30 \div 40$.

12.9 Bubble Growth in Volcanic Systems

Finally, let us also write the condition of steadiness at the very beginning of the regular growth of the bubble, exploiting Eqs. (12.89) and (12.90) with $R = 2R_c$. For Henry's law we have

$$s^{1/2} \ll \left(\frac{2}{3}\right)^{1/2}$$
, (12.95)

and for Sievert's law

$$s^{1/2} \ll \zeta^{1/2}$$
 (12.96)

While deriving Eq. (12.96), the numerical coefficient $(3(1-1/\sqrt{2}))^{1/2}$ in its l. h. s. was replaced with 1 for shortness.

Let us mention the following interesting observation. Since for $R \gg R_{\sigma}$, the bubble dynamics is exactly the same for both Henry's and Sievert's solubility laws, the condition of steady growth for $R \gg R_{\sigma}$ is also the same (see Eq. (12.91) above). For the case of homogeneous nucleation, when the pressure drop $P_0/\Pi \sim 10^3$, the steady condition at $R \gg R_{\sigma}$ as a rule is violated in cases of both Henry's and Sievert's laws. For Henry's law, when $s \sim 10^{-2}$, it is violated due to high supersaturation values $\zeta \sim 10^3$. For Sievert's law, when corresponding supersaturation values are significantly less $\zeta \sim 30 \div 40$, values of gas solubility are significantly higher than for Henry's law (see next section), and that is the reason of the violation of the steady condition. While for Henry's law solubility s is a tabular value (see Eq. (12.37)), for Sievert's law it can be adjusted via settlement of the final pressure II value. It is evident that condition (12.91) can be satisfied at the given solubility value when one decreases the solution supersaturation ζ (the case of heterogeneous nucleation).

In order to satisfy the condition (12.91) of steady growth the value of gas solubility *s* has to be decreased. From Eq. (12.32) for the supersaturation we have

$$\zeta = \sqrt{\frac{P_0}{\Pi}} - 1 .$$
 (12.97)

Than, using Eqs. (12.39), (12.97), let us rewrite product $s\zeta$ in the following form

$$s\zeta = K \frac{k_B T}{\sqrt{\Pi}} \left(\sqrt{\frac{P_0}{\Pi}} - 1 \right) . \tag{12.98}$$

Eq. (12.98) shows us that in order to weaken limitation (12.91) one needs to increase the final pressure Π , leaving the ratio P_0/Π constant.

12.9 Bubble Growth in Volcanic Systems

This section contains the analysis of the steady growth condition obtained in the previous section for bubble nucleation in volcanic systems. Previously, e. g. in papers [3] and [6] the study of such systems exploited steady approximation without the analysis of its applicability.

For our evaluations we will use parameters from [3] for the case of homogeneous nucleation of water vapor bubbles in a magmatic melt. We have

$$P_0 = 100 \text{ MPa} \quad \Pi = 0.1 \text{ MPa}$$

$$T = 1150 \text{ K} \quad w = 3\% \quad \rho_m = 2300 \text{ kg/m}^3.$$
(12.99)

Here w is gas mass fraction of the dissolved gas (water vapor), and ρ_m is magma density.

Let us express the values of s and ζ using data given. From Eq. (12.97), in accordance with Eq. (12.99), we have $\zeta \simeq 31$. Then we need to calculate n_0 and substitute it into Eq. (12.38) to obtain the value of

solubility. As long as we are given mass density of magma and mass fraction of gas, it is convenient to write

$$n_0 = \rho_0 \frac{N_A}{\mu} , \qquad (12.100)$$

where ρ_0 is mass density of the dissolved gas, $N_A = 6 \cdot 10^{23} \text{ mol}^{-1}$ is the Avogadro constant and $\mu = 1.8 \cdot 10^{-3} \text{ kg/mol}$ is the molar mass of the dissolved gas (water). Finally, we need to express the mass density of the dissolved gas. Evidently, we have

$$\rho_0 = w\rho_m , \qquad (12.101)$$

and, therefore,

$$s = w\rho_m \frac{N_A k_B T}{\mu \sqrt{P_0 \Pi}} . \tag{12.102}$$

Using data given by Eq. (12.99) in Eq. (12.102), we have $s \simeq 12$.

Now we can see that for volcanic systems, where the pressure drop is of the order of 10^3 and solubility is more than 1, both conditions (12.91) and (12.92) are violated, and steady approximation is not valid for radii of the order of R_{σ} . Even in the very beginning of bubble regular growth, when $R = 2R_c$, the steady condition (12.96) is fulfilled only at its breaking point: the values of $\zeta^{1/2}$ exceed the value of $s^{1/2}$, but these values are of the same order of magnitude.

12.10 Conclusions

In the presented paper we obtained the equations for the bubble growth dynamics in the gas solution with Henry's and Sievert's solubility laws. We solved these equations analytically for case of bubble growth in strongly supersaturated solution. The equation for the Sievert's law was solved also for the case of bubble dissolution in the pure solvent.

We showed that, irrespective of the to gas solubility law, three characteristic stages could be marked out in the growth dynamics. During the first stage the bubble radius is growing with an increasing rate. On the second stage the growth rate decreases. The third stage, when the growth rate continues to decrease, begins when the Laplace pressure inside the bubble becomes comparable with the external pressure of the solution. We demonstrated that during the first two stages the time dependence of the bubble radius is different for the cases of Henry's and Sievert's laws, while during the third stage this distinction is no longer observed. For both Henry's and Sievert's laws we obtained intervals within which the bubble radius changes on each stage, as well as durations of consecutive stages.

While obtaining the dynamic equations we assumed the diffusion flux to be steady. We obtained conditions when this steady approximation is applicable. We showed that usually, as the radius of the bubble increases, the steady regime of bubble growth gradually gives way to the nonsteady one. Application of the obtained conditions for the volcanic system consisting of water vapor dissolved in the silicate melt showed that the process in such system as a rule cannot be considered as steady.

12.11 Appendices

12.11.1 Appendix A: Effect of Solvent Viscosity on Bubble Growth

In the current paper we neglected the solvent viscosity. Its influence on bubble dynamics can be estimated using Rayleigh-Plesset equation (see e.g. [17]). To take the solvent viscosity into account one needs to replace Eq. (12.7) with the following equality:

$$P_R = \Pi + \frac{2\sigma}{R} + 4\eta \frac{R}{R} , \qquad (12.103)$$

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where η is the dynamic viscosity of the solvent. The inertial terms in Rayleigh-Plesset equation are negligible for any reasonable bubble growth rate.

To neglect the viscous term in Eq. (12.103) (the third addend) in comparison with the surface tension term (the second addend) the following strong inequality has to be fulfilled:

$$\eta \ll \frac{\sigma}{2\dot{R}} . \tag{12.104}$$

This inequality, evidently, is equivalent to inequality $Pe \gg 1$, where Pe is Peclet number.

The higher the bubble growth rate R is, the stronger the inequality (12.104) is. The strongest condition takes place when $R = R_m$. Using Eqs. (12.49) and (12.57) in Eqs. (12.44) and (12.52) correspondingly, for both Henry's and Sievert's laws we have

$$\dot{R} \le \dot{R}\Big|_{R=R_m} \simeq \frac{Ds\zeta}{R_\sigma}$$
 (12.105)

Therefore, using Eq. (12.13), we can rewrite strong inequality (12.104) as

$$\eta \ll \frac{\sigma^2}{Ds\zeta\Pi} , \qquad (12.106)$$

where multiplier 2/3 in the r. h. s. is omitted for shortness.

Let us estimate the value in the r. h. s. of inequality (12.106). Typical values of surface tension both for water and for volcanic systems [6] are $\sigma \sim 10^{-1}$ Nm⁻¹; both for Henry's and Sievert's laws $s\zeta \sim 10$; diffusion coefficient $D \sim 10^{-11}$ m²s⁻¹ [3]; pressure $\Pi \sim 10^5$ Pa. Substituting these values, we have:

$$\eta \ll 10^3 \text{ Pa s}$$
. (12.107)

It should be noted that "common" liquids at normal conditions always satisfy this condition: for water we have $\eta \sim 10^{-3}$ Pa s and even for glycerol $\eta \sim 1$ Pa s [18]. For volcanic systems the values of viscosity that satisfy strong inequality (12.107) are quite typical when SiO₂ content is not too high (basalt, andesite and dactite melts) [1]. However, for rhyolite melts ($\sim 70\%$ SiO₂) viscosity can reach the values of 10^7 Pa s [6]; and, therefore, effect of solvent viscosity has to be taken into account.

We do not discuss here the oscillating settlement of the mechanical equilibrium between the bubble and the solution: as it was shown in [19] this settlement occurs much faster than the settlement of chemical equilibrium, unless the liquid viscosity is extremely low.

12.11.2 Appendix B: Dissolution of the Gas Bubble in a Pure Solvent: Sievert's Solubility Law

Eq. (12.23) allows us to obtain the radius-time relation for the bubble of arbitrary initial size $R|_{t=0} = R_i$ which is put in the pure solvent and also the time of its dissolution t_d , $R|_{t=t_d} = 0$. Separating variables, we can rewrite Eq. (12.23) as

$$\frac{1+\frac{R_{\sigma}}{R}}{\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}}RdR = -Dsdt , \qquad (12.108)$$

or equivalently as

$$\left[\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}} - \frac{1}{2}\frac{\frac{R_{\sigma}}{R}}{\sqrt{1+\frac{3}{2}\frac{R_{\sigma}}{R}}}\right]RdR = -Dsdt.$$
(12.109)

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Using the variable $x \equiv \sqrt{1 + \frac{3}{2} \frac{R_{\sigma}}{R}}$ for integrating in Eq. (12.109) instead of R we have

$$\frac{3}{2}R_{\sigma}^{2}\left[3\frac{x^{2}}{(x^{2}-1)^{3}}-\frac{1}{(x^{2}-1)^{2}}\right]dx = Dsdt.$$
(12.110)

Eq. (12.110) can be easily integrated and therefore we obtain

$$\left[\frac{1}{2}R\sqrt{R^{2} + \frac{3}{2}R_{\sigma}R} - \frac{1}{8}R_{\sigma}\sqrt{R^{2} + \frac{3}{2}R_{\sigma}R} - \frac{1}{8}R_{\sigma}\sqrt{R^{2} + \frac{3}{2}R_{\sigma}R}\right]$$

$$\left. -\frac{3}{32}R_{\sigma}^{2}\ln\left(\frac{4}{3}\frac{R}{R_{\sigma}} - \frac{4}{3}\frac{1}{R_{\sigma}}\sqrt{R^{2} + \frac{3}{2}R_{\sigma}R} + 1\right)\right] \right|_{R}^{R_{i}} = Dst .$$

$$(12.111)$$

Eq. (12.111) gives us an explicit relation between the bubble radius R and time t.

Let us find the time t_d of total dissolution $(R \rightarrow 0)$ from arbitrary initial radius R_i

$$t_{d} = \frac{1}{Ds} \left[\frac{1}{2} R_{i} \sqrt{R_{i}^{2} + \frac{3}{2} R_{\sigma} R_{i}} - \frac{1}{8} R_{\sigma} \sqrt{R_{i}^{2} + \frac{3}{2} R_{\sigma} R_{i}} - \frac{3}{32} R_{\sigma}^{2} \ln \left(\frac{4}{3} \frac{R_{i}}{R_{\sigma}} - \frac{4}{3} \frac{1}{R_{\sigma}} \sqrt{R_{i}^{2} + \frac{3}{2} R_{\sigma} R_{i}} + 1 \right) \right] .$$
(12.112)

The latter expression can be simplified for the two particular cases and short analytical expressions for time t_d can be obtained. The first case is $R_i \gg R_\sigma$:

$$t_d = \frac{R_i^2}{2Ds} \ . \tag{12.113}$$

And the second is $R_i \ll R_\sigma$:

$$t_d = \left(\frac{2}{3}\right)^{3/2} \frac{R_i^{3/2} R_\sigma^{1/2}}{Ds} \,. \tag{12.114}$$

Let us also obtain the expression for dissolution time from $R_i = R_\sigma$

$$t_d = 0.435 \frac{R_{\sigma}^2}{Ds} \,. \tag{12.115}$$

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12.11 Appendices

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13 Interphase Heat Transfer for Different Regimes of Droplet Growth During Bulk Condensation at Flow of Vapor – Gas Mixtures

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> Je gelungener der Schurke, desto besser der Film.

Alfred Hitchcock

Abstract

The solution was obtained for the problem of heat transfer between a single droplet and vapor – gas mixture at different Knudsen numbers of growing droplet. The influence of interphase heat transfer on dynamics of macro-parameters and droplets distribution function was studied with the use of obtained results for process of condensation relaxation after instantaneous creation of supersaturation state in vapor–gas mixture and for bulk condensation at flow of vapor – gas mixture in nozzle. A comparison of results obtained for general formulation and for the case when simplifying assumptions are used about the temperature of droplets was carried out for different regimes of droplets growth.

13.1 Introduction

Heat release during bulk condensation leads to increase of temperatures of both liquid and gaseous phases. As a result the condensation process is slowed down for two reasons. On the one hand the droplet growth rate decreases owing to increase of saturation pressure above a droplet at its heating. On the other hand the nucleation rate decreases owing to reduction of supersaturation ratio at vapor heating. The relationship between these factors slowing down the process of bulk condensation is determined by the temperature difference between droplets and vapor. At high temperature difference the first factor (decrease of growth rate) is the determining one, at low difference the second factor (decrease of nucleation rate) is the determining. In turn, the temperature difference between the phases is determined by the intensity of interphase heat exchange. Thus, in general, the description of the kinetics of bulk condensation should include a description of three simultaneous processes: the formation of new droplets (nucleation), growth of droplets and the interphase heat transfer.

Influence of heat transfer on nucleation was studied in many papers. For example, it was shown in [1] that subcritical clusters have lower temperature than the gaseous phase and supercritical ones have higher temperature. Also definite expression were obtained for the nucleation rate affected by temperature effects. Analytical description of weak and strong thermal effects of condensation of pure vapor in the supercritical droplet was proposed in [2]. Effect of temperature fluctuations on nucleation-growth processes was discussed in [3]. Condensation of binary vapor mixtures was studied in [4] with use of the approaches proposed in [2]. However, only the limiting cases of the Knudsen number of the growing droplet (free-molecular and

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diffusion regimes) were considered due to the use of analytical methods. Also the composition and temperature of the gaseous phase were assumed to be constant. The numerical simulation of interphase heat transfer at bulk condensation used in this paper does not have these limitations. It was shown in [5] that the latent heat and the resulting change in temperature may qualitatively change the scenario of first-order phase transitions in comparison with the case that such effects are neglected. Authors of these studies focused on influence of heat transfer on nucleation, rather than on growth of droplets, our focus is study of heat transfer influence on both of these processes.

Temperature of gaseous phase is minimal value of droplets temperature and saturation temperature at vapor pressure is maximal one. These limiting values are often used in literature as assumptions allowing one the calculation of droplets temperature. Possibility of use of these assumptions is associated with supposition about ratio of two time intervals. First interval is time of equalization of phases temperatures, second one is duration of bulk condensation process. It should be noted that validity of these assumptions can be estimated by comparing the results obtained with their use and in the general formulation. Such comparison is the main objective of this work.

Study of bulk condensation taking into account the heat transfer between phases requires formulas for the calculation of droplet growth rate and interphase heat flux. However there are no such correlations which can be used at arbitrary regime of droplets growth at presence of temperature difference between phases. For example, the known Fuchs formula [6] does not have Knudsen number limits but it was obtained for the same temperatures of droplets and vapor. So we considered the problem of heat transfer between a single droplet and vapor – gas mixture. Results of solution of this problem were used for study of condensational relaxation and bulk condensation during flow in nozzle. An overview on the notations employed in the present analysis is given at the end of the chapter.

13.2 Heat Transfer between a Single Droplet and Vapor – Gas Mixture

We used the method of "dividing sphere" for obtaining formulas for calculation of droplet growth rate and interphase heat flux. The region near the droplet is divided into two parts (see Fig. 13.1), and their boundary lies at a distance Δ from the droplet surface. The value of Δ is close to the mean free path. The temperature of the vapor – gas mixture and the partial pressures of components at this boundary are marked by the subscript " Δ ". In region I (kinetic) processes of condensation and heat transfer are determined by the motion of molecules of vapor and gas without collisions. Diffusion and thermal conductivity are determining factors in region II (continuous matter).

In the kinetic region values of heat and mass fluxes can be found by integrating the velocity distribution functions of vapor and gas molecules. For gas (hereinafter the gas parameters are denoted by subscript "g"), this function is written as a two-sided Maxwell distribution:

$$F_{g} = \begin{cases} \frac{n_{g\Delta}}{(2\pi R_{g}T_{\Delta})} \exp\left(-\frac{\vec{\xi}^{2}}{2R_{g}T_{\Delta}}\right), & \xi_{r} < 0\\ \frac{n_{gd}}{(2\pi R_{g}T_{gd})} \exp\left(-\frac{\vec{\xi}^{2}}{2R_{g}T_{gd}}\right), & \xi_{r} > 0 \end{cases}$$
(13.1)

Here $n_{g\Delta}$ is gas particle number density on the boundary of regions I and II, n_{gd} and T_{gd} are the number densities and temperature of gas molecules reflecting from the droplet surface, R is the gas constant, $\vec{\xi}$ is molecular velocity, and ξ_r is its projection on the *r*-axis. Temperature T_{gd} depends on thermal accommodation coefficient β_q :

$$T_{gd} = T_{\Delta} - \beta_g \left(T_{\Delta} - T_d \right) \,. \tag{13.2}$$


Figure 13.1: Scheme for calculation of droplet growth rate and interphase heat flux.

The value of n_{gd} can be found using the assumption that the surface of the droplet is not penetrable for gas:

$$n_{gd} = n_{g\Delta} \sqrt{T_{\Delta}/T_{gd}} \,. \tag{13.3}$$

Vapor distribution function (hereinafter vapor parameters are denoted by the subscript "v") differs from Eq. (13.1) because there are not only reflecting but evaporating molecules. These groups of molecules can have different temperatures:

$$F_{v} = \begin{cases} \frac{n_{v\Delta}}{(2\pi R_{v}T_{\Delta})} \exp\left(-\frac{\vec{\xi}^{2}}{2R_{v}T_{\Delta}}\right), & \xi_{r} < 0\\ \frac{\alpha n_{s}\left(T_{d}\right)}{(2\pi R_{v}T_{d})} \exp\left(-\frac{\vec{\xi}^{2}}{2R_{v}T_{d}}\right) + \frac{n_{vd}}{(2\pi R_{v}T_{vd})} \exp\left(-\frac{\vec{\xi}^{2}}{2R_{v}T_{vd}}\right), & \xi_{r} > 0 \end{cases}$$
(13.4)

Here α is the condensation coefficient, and $n_s(T_d)$ is the number density of saturated vapor at temperature of droplet. Number density n_{vd} and temperature T_{vd} of reflecting molecules are calculated in the same way as for gas although accommodation coefficients can de different for different components:

$$T_{vd} = T_{\Delta} - \beta_v \left(T_{\Delta} - T_d \right) \,, \tag{13.5}$$

$$n_{vd} = (1 - \alpha) n_{v\Delta} \sqrt{T_{\Delta}/T_{vd}} .$$
(13.6)

It is taken into account in Eq. (13.6) that only a part of vapor molecules moving to surface of droplet are reflecting.

Total heat and mass fluxes are determined as moments of distribution functions [7]:

$$J_I = 4\pi r_d^2 m_v \int_{-\infty}^{+\infty} \xi_r F_v d\vec{\xi} , \qquad (13.7)$$

$$Q_{I} = 4\pi r_{d}^{2} \left(\frac{m_{v}}{2} \int_{-\infty}^{+\infty} (\xi_{r} - u_{v}) \left(\vec{\xi} - \vec{u}_{v}\right)^{2} F_{v} d\vec{\xi} + \frac{m_{g}}{2} \int_{-\infty}^{+\infty} \xi_{r} \vec{\xi}^{2} F_{g} d\vec{\xi} \right) .$$
(13.8)

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Here u_v is vapor velocity projection on the axis r, other projections are equal to zero. This value is calculated as mass flux divided by density [7]:

$$u_v = \int_{-\infty}^{+\infty} \xi_r F_v d\vec{\xi} / \int_{-\infty}^{+\infty} F_v d\vec{\xi} \,. \tag{13.9}$$

Substitution of the distribution functions Eqs. (13.1) and (13.3) into Eqs. (13.4) and (13.5) using the ideal gas equation of state for both components leads to the following expressions:

$$J_I = 4\pi r_d^2 \alpha \left(\frac{p_s(T_d)}{\sqrt{2\pi R_v T_{vd}}} - \frac{p_{v\Delta}}{\sqrt{2\pi R_v T_{\Delta}}} \right) , \qquad (13.10)$$

$$Q_{I} = 4\pi r_{d}^{2} \left(2p_{g\Delta} \sqrt{\frac{R_{g}T_{\Delta}}{2\pi}} \frac{T_{gd} - T_{\Delta}}{T_{\Delta}} + 2\left(\alpha p_{s}\left(T_{d}\right) + (1 - \alpha) p_{v\Delta} \frac{T_{vd}}{\sqrt{T_{\Delta}T_{d}}}\right) \sqrt{\frac{R_{v}T_{d}}{2\pi}} - 2p_{v\Delta} \sqrt{\frac{R_{v}T_{\Delta}}{2\pi}} - \frac{5}{4} \left(\alpha p_{s}\left(T_{d}\right) + (1 - \alpha) \sqrt{\frac{T_{vd}}{T_{\Delta}}} p_{v\Delta} + p_{v\Delta}\right) u_{v} \right) , \qquad (13.11)$$

$$u_v = \frac{J_I R_v / 2\pi r_d^2}{p_{v\Delta} / T_\Delta + \alpha p_s \left(T_d\right) / T_d + (1 - \alpha) p_{v\Delta} / \sqrt{T_\Delta T_{vd}}} .$$
(13.12)

In region of continuous matter mass and heat fluxes are calculated as follows [6]:

$$J_{II} = \frac{4\pi \left(r_d + \Delta\right) D}{R_v T_m} \left(p_{v\Delta} \frac{T_m}{T_\Delta} - p_{vm} \right) , \qquad (13.13)$$

$$Q_{II} = 4\pi \left(r_d + \Delta \right) \lambda \left(T_\Delta - T_m \right) . \tag{13.14}$$

Here D is diffusion coefficient, and λ is thermal conductivity. We calculated them with use of theory of ideal gas [8, 9].

It is obvious that mass and heat fluxes in regions I and II should be equal:

$$J_I = J_{II} , \qquad Q_I = Q_{II} . \tag{13.15}$$

If partial pressures of the mixture components and temperatures of droplets and vapor – gas mixture are known, then this system of two equations has three unknown parameters: the temperature and partial pressures at the boundary of regions T_{Δ} , $p_{v\Delta}$ and $p_{g\Delta}$. The third equation is that gas mass flux in region II is zero, so gas pressure can be found as follows:

$$p_{g\Delta} = p_{gm} T_{\Delta} / T_m . \tag{13.16}$$

Substituting Eqs. (13.10) – (13.14) for mass and heat fluxes into Eq. (13.15) and finding pressure $p_{v\Delta}$ from the first equation of this system

$$p_{v\Delta} = p_{vm} \frac{T_{\Delta}}{T_m} + \frac{p_s \left(T_d\right) - p_{vm} \sqrt{T_{\Delta} T_d} / T_m}{\sqrt{\frac{T_d}{T_{\Delta}}} + \frac{\left(r_d + \Delta\right) D \sqrt{2\pi R_v T_d}}{R_v T_d r_d^2 \alpha}} ,$$
(13.17)

one can reduce Eq. (13.15) to a nonlinear equation for the temperature at the boundary of regions I and II:

$$(r_{d} + \Delta) \lambda (T_{\Delta} - T_{m}) = r_{d}^{2} \left(2p_{gm} \sqrt{\frac{R_{g}T_{\Delta}}{2\pi} \frac{T_{gd} - T_{\Delta}}{T_{m}}} + 2 \left(\alpha p_{s} \left(T_{d} \right) \right) \right)$$

$$+ (1 - \alpha) p_{v\Delta} \frac{T_{vd}}{\sqrt{T_{\Delta}T_{d}}} \sqrt{\frac{R_{v}T_{d}}{2\pi}} - 2p_{v\Delta} \sqrt{\frac{R_{v}T_{\Delta}}{2\pi}} - \frac{5}{4} \left(\alpha p_{s} \left(T_{d} \right) + (1 - \alpha) \sqrt{\frac{T_{vd}}{T_{\Delta}}} p_{v\Delta} + p_{v\Delta} \right) u_{v} \right).$$

$$(13.18)$$

13.3 The Relaxation Problem

Here vapor velocity u_v and pressure $p_{v\Delta}$ are determined by Eqs. (13.12) and (13.17) respectively.

Eqs. (13.10) – (13.12), (13.18) are written for arbitrary values of condensation and accommodation coefficients, further calculations were carried out for $\alpha = \beta_v = \beta_g = 1$. We solved Eq. (13.18) numerically. Obtained values of T_{Δ} , $p_{v\Delta}$ and $p_{g\Delta}$ were substituted into Eqs. (13.10) and (13.11), which were used for calculation of droplet growth rate \dot{r} and density of interphase heat flux q:

$$\dot{r} = -\frac{J_I}{4\pi r_d^2 \rho_l}, \qquad q = \frac{Q_I}{4\pi r_d^2}.$$
(13.19)

Here ρ_l is the density of liquid.

Testing of the model of interphase heat transfer was carried out on two examples:

1. Temperature of droplet is equal to the one of the vapor – gas mixture: In this case use of our model should lead to following results: temperature T_{Δ} is equal to T_m , and droplet growth rate is the same as calculated with use of the Fuchs formula [6]:

$$\dot{r} = \frac{p_{vm} - p_s \left(T_d\right)}{\rho_l \sqrt{2\pi R_v T_m}} \left(1 + \frac{\alpha}{D} \sqrt{\frac{R_v T_m}{2\pi}} \frac{r_d^2}{r_d + \Delta}\right)^{-1} \,. \tag{13.20}$$

This expression was obtained with use of method of "dividing sphere" (see Eq. (13.15)) without considering heat transfer.

2. Free molecular regime of droplet growth: In this case our model should give following results: growth rate and heat flux are equal to the ones calculated with use of Eqs. (13.7) and (13.8) taking into account that parameters on boundary of regions I and II are equal to the ones far from droplet ($T_{\Delta} = T_m$, $p_{v\Delta} = p_{vm}, p_{g\Delta} = p_{gm}$).

In both cases the expected results were obtained. So the proposed model for calculating the growth of droplets and heat transfer works correctly.

13.3 The Relaxation Problem

13.3.1 Formulation

As in our previous papers [10], we considered motionless mixture of vapor and non-condensing gas with given initial supersaturation ratio $s = p_{vm}/p_s(T_m)$. The kinetic equation for droplet size distribution function [11] was used as mathematical description:

$$\frac{\partial f}{\partial t} + \frac{\partial \left(\dot{r}f\right)}{\partial r} = \frac{I}{\rho_{\Sigma}} \delta \left(r - r_{cr}\right) .$$
(13.21)

Here f is the mass distribution function of droplet sizes, r is the droplet radius, \dot{r} is the droplet growth rate, I is the nucleation rate, ρ_{Σ} is the density of the vapor-gas-droplets mixture, δ is the delta function, and r_{cr} is the critical droplet radius.

Decrease of nucleation rate due to heating of droplets was studied in [2] and the following formula was proposed:

$$I = I_0 / (1+k) , (13.22)$$

where I_0 is the nucleation rate without taking into account thermal effects and the parameter k with the nomenclature adopted in this paper is written as follows:

$$k = \frac{\alpha \beta^2 R_v}{C_v \left(1 + \left(\frac{m_g}{m_v}\right)^{1/2} \frac{n_g C_g}{n_v C_v}\right)}$$
(13.23)

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Here $\beta = L/R_v T_m$ is the dimensionless evaporation heat, m_i , n_i and C_i are molecular mass, particle number density and heat capacity of the component *i*. Solution of the relaxation problem was obtained both with taking into account thermal effects (nucleation rate was calculated by Eq. (13.22)) and without it. We used the formula of Frenkel and Zeldovich [12] for calculation of the nucleation rate I_0 . The method of direct numerical solution [10] was used for solving Eq. (13.21).

Additional equations were the following: ideal gas equations of state for vapor and gas, and equations of mass and heat balance. Variation of mass fraction of liquid was calculated with use of distribution function:

$$\begin{cases} \frac{dc_v}{dt} = -\frac{dc_l}{dt} = -\frac{4}{3}\pi\rho_l \frac{d}{dt} \int_{r_{cr}}^{\infty} r^3 f dr \\ c_g = \text{const} \end{cases}$$
(13.24)

Here c_v , c_l and c_g are mass fractions of vapor, liquid and gas, respectively.

Energy equations were used for calculation of temperatures of vapor – gas mixture and droplets. Heat balance equation for a single droplet is written as follows:

$$mC_l dT_d = L dm - qS dt , \qquad (13.25)$$

where m and S are mass and surface of droplet, respectively, C_l is specific heat of liquid, and L is evaporation heat. Taking into account formulas for mass and surface and definition of droplet growth rate $\dot{r} = dr/dt$ one can obtain following equation from Eq. (13.24):

$$\frac{4}{3}\pi\rho_l r^3 C_l \frac{dT_d}{dt} = 4\pi r^2 \left(L\rho_l \dot{r} - q\right) \,. \tag{13.26}$$

Temperature of droplet found from Eq. (13.26) depends on its radius. For simplifying the problem we assumed that all droplets have the same temperature equal to the average one. Equation for average temperature of droplets can be obtained from Eq. (13.26) by multiplying on distribution function and integrating over all droplet radii:

$$\frac{1}{3}\rho_l C_l \frac{dT_d}{dt} \int_{r_{cr}}^{\infty} r^3 f dr = \int_{r_{cr}}^{\infty} \left(L\rho_l \dot{r} - q \right) r^2 f dr .$$
(13.27)

Eq. (13.27) shows that temperature of droplets increases due to heat release during condensation and decreases due to heat transfer to vapor – gas mixture. Equality of temperatures of phases $T_d = T_m$ was used as initial condition for Eq. (13.27). Except the energy equation for droplets, mathematical description includes energy equation for gaseous phase:

$$C_m \frac{dT_m}{dt} = 4\pi \int_{r_{cr}}^{\infty} qr^2 f dr .$$
(13.28)

We also obtained solution of relaxation problem for two limiting cases:

1. Temperature of droplets was equal to one of vapor – gas mixture $(T_d = T_m)$. In this case energy equation is the same for both phases:

$$C_{\Sigma} \frac{dT_m}{dt} = L \frac{dc_l}{dt} \tag{13.29}$$

Here C_{Σ} is specific heat of mixture of vapor, gas and droplets.

2. Temperature of droplets was equal to saturation one at partial pressure of vapor ($T_d = T_s$). In this case we also used Eq. (13.27) because mass fraction of liquid is small and heat supply for changing of droplets temperature can be neglected in comparison with heat release during condensation.

13.3.2 Results for Free-Molecular Regime of Droplet Growth

We considered a mixture of cesium and argon as an example of free molecular regime. Initial parameters were the following: the temperature of mixture was 560 K, the supersaturation ratio was 10, ratio of partial pressures of vapor p_v and gas p_g was variable. Variation of p_v/p_g at constant temperature and supersaturation ratio means that only partial pressure of gas is variable, because $p_v = sp_s(T_m)$ according to the definition of the supersaturation ratio. In all figures with results of calculations, the following notation is used: 1 and $2 - T_d$ is calculated by our model without and with the Kuni modification, respectively, $3 - T_d = T_m$, $4 - T_d = T_s$.



Figure 13.2: Time dependence of the temperature of vapor – gas mixture for cesium and argon at $p_v/p_g = 0.5$ (left) and $p_v/p_g = 0.05$ (right).

Dependencies of the temperature of vapor-gas mixture for different values of p_v / p_g are shown in Figs. 13.2. These dependencies are qualitatively identical for all approaches used for calculation of the droplet temperature; other integral characteristics (supersaturation ratio, numerical density of droplets) also behave similarly. At the beginning of the relaxation process, there is found an induction period during which the formation of droplets and their growth do not lead to appreciable changes in the temperature and supersaturation ratio, and the numerical density of droplets grows linearly because the nucleation rate remains constant. The heat released during condensation is proportional to the growth regime, which is reasonably small at the beginning of the condensation process. When the indicated parameter achieves a certain value, the temperature begins to increase and the supersaturation ratio decreases due to both increase of the saturation pressure and decrease of the partial vapor pressure. Our estimates show that for the considered time interval the coagulation process can be neglected.

With an increase in the droplet temperature, the growth rate decreases. It results in increasing the relaxation time because more time is required for achieving the value of the total droplet surface for which the heat release begins to affect the supersaturation ratio. The lower limit of possible values of the droplet temperature is the temperature of the vapor–gas mixture, and the upper limit is the saturation temperature. Hence, the calculations with use of these approximations give the minimal and maximal relaxation time, respectively.

The intensity of the interphase heat exchange for model of one temperature is higher in comparison with that in the case of equal temperature of droplets and saturation temperature corresponds to the one temperature model. The interphase heat flux grows with increase of the gas pressure. Therefore, it can be assumed that the results obtained taking into account a finite heat exchange rate should come nearer to the data for the one temperature model with increasing the gas pressure and nearer to the data for the droplet temperature, which is equal to the saturation temperature, with decreasing it. The comparison of results



Figure 13.3: Time dependence of relative temperature difference between phases $\delta T = (T_d - T_m)/T_m$ for mixture of cesium and argon at $p_v/p_g = 0.5$ (left) and $p_v/p_g = 0.05$ (right).

presented in Figs. 13.2 confirms this assumption.

The parameter k in Eq. (13.22) shows how heating of droplets affects the nucleation rate. In accordance with Eq. (13.23) it increases with increase of gas concentration, so the nucleation rate becomes closer to the value obtained without heating the droplets. Consequently, influence of droplets heating on the nucleation rate at low gas pressure is much stronger than at low one. Decrease in the nucleation rate leads to decrease of intensity of heat release, so duration of the relaxation increases as compared with the calculation of nucleation rate without the modification proposed in [2].



Figure 13.4: Dependence of distribution function on droplet size for mixture of cesium and argon at $p_v/p_g = 0.5$ and $t = 40\mu$ s (left) and $p_v/p_g = 0.05$ and $t = 40\mu$ (right).

Figs. 13.3 show time dependencies of relative temperature difference between droplets and vapor – gas mixture δT for developed model and temperature of droplets equal to saturation one. It is obvious that for $T_d = T_m$ the value of δT is zero. For our model of heat transfer, temperature of droplets reaches some value between the limiting values T_m and T_s . Total volume of droplets is very small at the beginning of the relaxation process, so a small amount of heat is required for their significant heating. Value of δT remains constant during induction period, because temperatures of phases do not change. With the growth of droplets, their surface area and total heat flux from the droplets to the gas mixture increase, so the temperature difference between the phases reduces. Relaxation time for $T_d = T_s$ is higher than for our model because droplets growth rate decreases with increase of their temperature.

13.3 The Relaxation Problem

The droplet size distribution function is shown in Figs. 13.4 for the ratio of partial pressures of vapor and gas 0.5 and 0.05, respectively. During the induction period the distribution function is stepwise because the nucleation rate is constant, and the growth rate does not depend on droplet radius. Further, the nucleation rate decreases due to decrease of the supersaturation, which causes a decrease in the distribution function for a radius near to the critical one. For the model of one temperature the maximal value of the distribution function is lower than for the temperature of droplets equal to the saturation one, because in the free molecular regime this value is determined by the ratio of nucleation rate to growth rate during the induction period and the growth rate decreases with increasing temperature of droplets. Taking into account the heating effects on the nucleation rate leads to decrease of the distribution function, but the position of the disturbance front remains constant because the growth rate of droplets for curves 1 and 2 in both plots during the induction period is the same.

Distribution function in Fig. 13.4 (left) for the one-temperature model (curve 3) corresponds to the stage where the supersaturation ratio is so low that the nucleation rate is zero. For other models the induction period is still ongoing and the distribution function takes a form similar to the curve for one-temperature model much later. Changing of the distribution function after the end of nucleation in all cases is the movement of profile without deformation to increase the radius of the droplets. As for integral characteristics, qualitative dependence of distribution function on droplet radius and time is the same for all considered cases.

13.3.3 Results for the Transitional Regime of Droplet Growth

Previously we used a mixture of ethane and argon as an example of droplet growth at moderate and small Knudsen numbers (see, for example, [10]). For this mixture kinetic effects play an important role only for droplets of very small size. In continual regime interphase heat flux is calculated as follows:

$$q = \lambda \left(T_d - T_m \right) / r \,. \tag{13.30}$$

Ethane and argon have near values of thermal conductivity ($\lambda_v/\lambda_g = 0.7$), so interphase heat flux depends on partial pressure of gas weakly. Due to this here we considered mixture of ethane and helium, which have significantly different thermal conductivities ($\lambda_v/\lambda_g = 0.12$).



Figure 13.5: Time dependence of the temperature of vapor – gas mixture for ethane and helium at $p_v/p_g = 1.0$ (left) and $p_v/p_g = 0.1$ (right).

Calculations were carried out for following initial parameters: the temperature of mixture was 160 K, the supersaturation ratio was 10, ratio of partial pressures of vapors p_v and gas p_g was variable as for previous mixture. The Knudsen number with average droplet radius as characteristic size changes during



Figure 13.6: Time dependence of relative temperature difference between phases $\delta T = (T_d - T_m)/T_m$ for mixture of ethane and helium at $p_v/p_g = 1.0$ (left) and $p_v/p_g = 0.1$ (right).



Figure 13.7: Dependence of distribution function on droplet size for mixture of ethane and helium at $p_v/p_g = 1.0$ and $t = 4\mu s$ (left) and $p_v/p_g = 0.1$ and $t = 4\mu s$ (right).

relaxation in the range from 10 to 0.01. The performed calculations showed that taking into account finite rate of interphase heat transfer does not lead to qualitative changes in considered process as for considered above free molecular regime.

Time dependencies of temperature of vapor – gas mixture are shown in Figs. 13.5 for $p_v/p_g = 1.0$ and $p_v/p_g = 0.1$, respectively. Figs. 13.6 illustrate the time dependence of relative temperature difference between phases. These results are qualitatively the same as presented above in Figs. 13.2 – 13.3.

Figs. 13.7 show the droplet size distribution function at different moments of time for the ratio of partial pressures of vapor and gas 1.0 and 0.1, respectively. For all the approaches for calculation of droplets temperature the qualitative dependence of the distribution function on radius and time is the same. The distribution function is not stepwise because the growth rate for moderate and small Knudsen numbers decreases with increase of droplet radius.

In the considered case of small and moderate Knudsen numbers the intensity of interphase heat transfer increase with rise of gas partial pressure the same as at large Knudsen numbers. It should be noted that it is correct for continuous matter region only if gas thermal conductivity is higher than vapor one. For low gas concentration (Fig. 13.7 (left)) distribution function obtained with taking into account interphase

heat transfer is near to one for droplets temperature equal to saturation one. If gas concentration is high (Fig. 13.7 (right)), distribution function is near to one for droplets temperature equal to vapor-gas mixture one. Macroscopic parameters of condensational aerosol behave similarly. As in the case of free molecular regime, taking into account the effect of droplets heating on the nucleation rate at low gas pressure leads to more significant changes in macro-parameters and distribution functions, than at high one.

All curves in Figs. 13.7 correspond to the induction period. Exception is curve for one-temperature model in Fig. 13.7 (left). This distribution function is presented for the final stage of relaxation, during which there is no nucleation due to low supersaturation, so distribution function at radius near to critical one is near to zero. For other considered cases the relaxation time is much more than for model of one temperature, so distribution function becomes similar to curve 2 for one-temperature model, much later.

13.4 Bulk Condensation During Flow in a Nozzle

13.4.1 Formulation

We considered a one-dimensional stationary flow of vapor – gas mixture in supersonic part of nozzle. Cross size of the nozzle was much larger than the free path, so methods of continuous matter were used for the description of flow but not for interaction of gas and droplets. Due to the small size of the droplets, velocities of liquid and gaseous phase were assumed to be identical. At the beginning of nozzle, temperature of mixture and partial pressures of vapor and gas were given, vapor was saturated, and velocity was equal to the one of sound. Viscosity of gaseous phase was zero, thermal conductivity was taken into account only in calculation of interphase heat flux at transitional and continual regimes of droplets growth.

The kinetic equation for droplet size distribution function in one-dimensional stationary problem is written as follows:

$$u\frac{\partial f}{\partial x} + \frac{\partial \left(\dot{r}f\right)}{\partial r} = \frac{I}{\rho_{\Sigma}}\delta\left(r - r_{cr}\right) , \qquad (13.31)$$

where u is velocity of flow. We developed a method of direct numerical solution [10] for zero-dimensional non-stationary problems, but it was used for bulk condensation at flow in nozzle with replace of time step by coordinate step divided by velocity.

Equations of gas dynamics were used as the mathematical description of flow:

$$\frac{d}{dx}\left(\rho uS\right) = 0, \qquad (13.32)$$

$$ou\frac{du}{dx} = \frac{dp}{dx}.$$
(13.33)

Here ρ and p are density and pressure of mixture of vapor, gas and liquid, S is cross-section area of nozzle. Equation of mass balance Eq. (13.24) was used for calculation of mass fractions with derivative by coordinate instead of one by time. Energy equations are written in the form similar to Eqs. (13.27) and (13.28) but the kinetic energy should be taken into account:

$$C_{pm}\frac{d}{dx}\left(T_m + \frac{u^2}{2C_{pm}}\right) = Q , \qquad (13.34)$$

$$c_l C_{pl} \frac{d}{dx} \left(T_d + \frac{u^2}{2C_{pl}} \right) = \left(L - C_{pv} \left(T_d - T_m \right) \right) J - Q , \qquad (13.35)$$

where J and Q are mass of condensing vapor and heat transferred from droplets to gaseous phase per mass unit on length unit of nozzle:

$$J = \frac{4\pi\rho_l}{u} \int_{r_{cr}}^{\infty} \dot{r}r^2 f dr , \qquad (13.36)$$

13 Interphase Heat Transfer for Different Regimes of Droplet Growth

$$Q = \frac{4\pi}{u} \int_{r_{cr}}^{\infty} qr^2 f dr .$$
(13.37)

13.4.2 Results and Discussion

Calculations were carried out for mixture of cesium and argon, regime of droplets growth was free molecular. As for the relaxation problem, partial pressure of gas was variable for variation of interphase heat flux.

Results for integral characteristics are presented as their dependencies on time which is defined as coordinate divided by velocity. Dependence of temperature of vapor – gas mixture is presented in Fig. 13.8 for $p_v/p_g = 0.2$. In the relaxation problem, condensation begins at t = 0 because supersaturation at this time is sufficient to start nucleation. For bulk condensation at flow in nozzle the first stage of process is the expansion of vapor – gas mixture without condensation. Pressure of vapor decreases, but temperature and, consequently, saturation pressure decrease also, so the supersaturation ratio increases and reaches some value at which nucleation begins at $x/u \approx 4$ ms. During the second stage of the process condensation does not affect the flow of vapor – gas mixture because mass fraction of liquid is very small. It is analog of the induction period, but for flow in nozzle supersaturation is not constant due to expansion. The end of this stage depends on intensity of heat release, i.e. on the used models for temperature of droplets and nucleation rate. For example, for model of one temperature and saturation pressure. A similar dependence for higher gas pressure ($p_v/p_g = 0.05$) is shown in Fig. 13.8 (right). Qualitatively it is the same as in Fig. 13.8 (left) but results for our model are closer to the model of one temperature because interphase heat flux increases with increase of gas pressure.



Figure 13.8: Temperature of vapor – gas mixture for flow in nozzle at $p_v/p_q = 0.2$ (left) and $p_v/p_q = 0.05$ (right).

The dependence of relative temperature difference between droplets and vapor – gas mixture is presented in Figs. 13.9 for different gas pressures. In contrast to the relaxation problem, the value of δT is variable during the induction period. Expansion leads to increase of δT , but heat transfer leads to its decrease. The first factor is always of importance, the effect of the second one depends on the total surface of droplets S_d , because for free molecular regime the density of interphase heat flux does not depend on droplet size and Eq. (13.37) can be written as follows:

$$Q = qS_d/u . (13.38)$$

Condensation leads to an increase of total heat flux Q. At some time, effect of heat transfer becomes the dominant factor and temperature difference begins to decrease. With increase of gas pressure temperature of droplets becomes closer to temperature of vapor – gas mixture, and the value of δT decreases.



Figure 13.9: Relative temperature difference between phases $\delta T = (T_d - T_m)/T_m$ for flow in nozzle at $p_v/p_g = 0.2$ (left) and $p_v/p_g = 0.05$ (right).

Taking into account the Kuni modification Eq. (13.22) leads to an increase of the second stage of the process (condensation without affecting flow of mixture) due to the decrease of intensity of heat release. As for relaxation problem, at low gas pressure effect of droplets heating is stronger as at high one in accordance with Eqs. (13.22) and (13.23).



Figure 13.10: Dependence of distribution function on droplet size for flow in nozzle at $p_v/p_g = 0.2$ and x/u = 6 ms (left) and $p_v/p_g = 0.05$ and x/u = 6 ms (right).

Dependence of distribution function on droplet radius is shown in Figs. 13.10. At low gas pressure (Fig. 13.10 (left)) all curves except curve 3 (model of one temperature) are for second stage. Though it is analog of the induction period, the distribution function is not stepwise because supersaturation is variable due to expansion. Function at critical radius is determined by the nucleation rate divided by growth rate, so for $T_d = T_s$ (curve 4) it is higher than for our model (curve 1) due to lower growth rate and for results obtained with the Kuni modification (curve 2) it is lower due to lower nucleation rate. For model of one temperature presented results correspond to the third stage (condensation affecting flow of mixture) after end of nucleation, so distribution function at critical size is close to zero. At high gas pressure (Fig. 13.10 (right)) all curves are for the third stage except curve 4 for $T_d = T_s$ which is for the second one. The nucleation rate with the Kuni modification is lower than the one without it if other conditions are the same. Here supersaturation for curve 2 (with the Kuni modification) is higher than for curve 1. As for temperatures of phases

(see Figs. 13.8 – 13.9) distribution function becomes close to one obtained for $T_d = T_m$ at increase of gas pressure and to one obtained for $T_d = T_s$ at its decrease, and effect of the Kuni modification increases with increasing gas pressure.

13.5 Conclusions

For both considered problems taking into account the finite rate of the interphase heat transfer can result in appreciable quantitative changes in the distribution function and integral characteristics in comparison with similar values obtained using the ultimate values of droplet temperature with the qualitative coincidence of the general picture of the process. The calculations showed that the accuracy of the one-temperature model increases with the dilution of the vapor by non-condensing gas. On the contrary, the use of the assumption about the equality of the droplet temperature and the saturation temperature is justified, first of all, for the description of condensation process in pure vapor.

For small and moderate Knudsen numbers interphase heat flux is determined not only by gas concentration, but also by thermal conductivity of mixture components. If gas has higher thermal conductivity, as in the mixture of ethane and helium that is considered here, the increase in the partial pressure of gas leads to increase in the intensity of interphase heat transfer, and the conclusion on the applicability of the limiting cases of droplets temperature made for the free molecular regime remains valid. In the opposite case thermal resistance decreases in kinetic region and increases in the region of continuous matter with increasing gas concentration in the mixture. Change in the intensity of interphase heat transfer is determined by the dominance of one of these factors.

Decrease of nucleation rate due to heat release on surface of droplets has stronger effect on the kinetics of volume condensation at low partial pressure of non-condensing gas, i.e. at low intensity of interphase heat transfer.

Nomenclature

Notations

- c mass fraction, dimensionless
- C_p heat capacity, J/(kg·K)
- D diffusion coefficient, m²/s
- f droplet size distribution function, $1/(kg \cdot m)$
- F velocity distribution function of molecules, s³/m⁶
- I nucleation rate, $1/(m^3 \cdot s)$
- *L* evaporation heat, J/kg
- n number density, $1/m^3$
- p pressure, Pa
- q density of heat flux, W/m²
- Q total heat flux, W
- r droplet radius, m
- \dot{r} droplet growth rate, m/s
- R the universal gas constant, J/(kg·K)
- *s* supersaturation ratio, dimensionless
- t time, s
- T temperature, K
- u velocity, m/s

13.5 Conclusions

Greek symbols

- α condensation coefficient, dimensionless
- β thermal accommodation coefficient, dimensionless
- λ thermal conductivity, W/(m·K)
- ξ molecular velocity, m/s
- ρ density, kg/m³

Subscripts and superscripts

- cr critical radius
- *d* parameter of droplets
- g parameter of gas
- *l* parameter of liquid
- *s* parameter in state of saturation
- v parameter of vapor
- Δ parameter on "dividing sphere"
- Σ parameter of vapor-gas-droplets mixture

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14 Size Effects in Phase Transitions in Aerosol Systems with Nanoscale Particles and Inside Nanoparticles

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Mit dem Wissen wächst der Zweifel.

Johann Wolfgang von Goethe

Abstract

The size effects in phase transitions in aerosol systems with nanoscale particles and in nanoparticles themselves are studied theoretically. The effects related to size dependence of the condensation coefficient in gas-phase homogeneous nucleation and activation energies for diffusion of monomers in nanoparticles and the incorporation of monomers into critical clusters in nucleation in nanoparticles are considered.

14.1 Introduction

It is known that many processes that take place in nanoscale systems are characterized by some specific features [1-3]. In particular, the physicochemical processes occurring in aerosol systems with nanoscale particles and in the aerosol particles themselves can depend on the particle size. The size effects in aerosol systems with nanoscale particles are related to the dependence of the saturated vapor pressure and the condensation coefficient on the particle size and also to the size-dependent processes taking place in nanoparticles. The vacancy concentration in nanoparticles can be higher than in a bulk substance due to the lower cohesive energy in nanoparticles in comparison with bulk matter [4, 5]. A decrease in the cohesive energy with a decrease in the nanoparticle size leads to reduction in the melting temperature of small particles in comparison with bulk matter [5]. It is known that the vacancy concentration affects diffusion of atoms in solid bodies. A change in the mobility of atoms (molecules) in nanoscale particles can affect the processes proceeding in them. Below we consider the influence of the size effects on such processes as condensation of vapor molecules on nanoscale aerosol particles (clusters), homogeneous nucleation in a gas phase and inside nanoparticles.

14.2 Condensation of Vapor Molecules on Small Aerosol Particles (Clusters) and the Problem of Homogeneous Nucleation

The size effect in particle growth by vapor condensation is commonly related to the Kelvin effect, which results in an increase of the density of the flux of molecules evaporated from the particle with a reduction in its size, and to a dependence of the transfer of vapor molecules to the particle surface on the size of the particle. The transfer of vapor molecules to the particle surface depends on the particle size through the Knudsen number Kn that is equal to the ratio of the mean free path of gas molecules to the particle radius. Further we consider for simplicity the free molecular regime when $Kn \gg 1$.

It is worth noting that the sticking (condensation) coefficient can also depend on the particle size [6, 7]. The particle growth rate is proportional to the trapping coefficient β that is defined as the ratio of the density of the resulting flux of vapor molecules into the particle to the density of the flux of vapor molecules incident on the particle surface. The density of the resulting flux of vapor molecules into the particle surface into the particle surface for the density of the resulting flux of the flux of the particle under the assumption of the Maxwellian velocity distribution function for incident vapor molecules in view of [8] can be written as (further we consider for simplicity the isothermal gas-particle system)

$$J = \frac{v}{4} \left[\alpha_c n - \alpha_e n_e \exp\left(\frac{4\sigma_p V_m}{dk_B T}\right) \right] = \beta \frac{nv}{4} , \qquad (14.1)$$

where d is the particle diameter, k_B is the Boltzmann constant, n is the number density of vapor, n_e is the number density of the saturated vapor for a planar surface, v is the mean velocity of vapor molecules, T is the temperature, α_e is the evaporation coefficient, α_c is the sticking (condensation) coefficient which is defined as the probability that an incident molecule does not reflect immediately from the surface, σ_p is the surface tension for the particle, V_m is the volume per molecule in the particle. Taking into account Eq. (14.1), the trapping coefficient of vapor molecules for a small aerosol particle in the free molecular regime is given by

$$\beta = \frac{4J}{nv} = \alpha_c \left[1 - \frac{\alpha_e}{\alpha_c S} \exp\left(\frac{4\sigma_p V_m}{dk_B T}\right) \right] \,, \tag{14.2}$$

where S is the supersaturation ratio.

We assume for simplicity that the condensation coefficient for a planar surface $\alpha_{c\infty}$ is equal to the evaporation coefficient α_e . When the dependence of the condensation coefficient for a small particle α_c on the particle size is taken into account according to [6]

$$\alpha_c = \alpha_{c\infty} \exp\left(-\frac{6\sigma_p V_m}{dk_B T}\right) , \qquad (14.3)$$

the value of β under the above-mentioned assumptions can be written as

$$\beta = \alpha_{c\infty} \exp\left(-\frac{6\sigma_p V_m}{dk_B T}\right) \left[1 - \frac{1}{S} \exp\left(\frac{10\sigma_p V_m}{dk_B T}\right)\right] \,. \tag{14.4}$$

The condition $\beta = 0$ corresponds to the critical diameter of the particle d^* . Equation (14.4) gives the following value for d^* :

$$d^* = \frac{10\sigma_p V_m}{k_B T \ln S} , \qquad (14.5)$$

that is two and half times larger than the value of the critical diameter corresponding to the classical Kelvin equation [8]

$$d^* = \frac{4\sigma_p V_m}{k_B T \ln S} . \tag{14.6}$$

14.3 Critical Size of a Charged Aerosol Particle in the Presence of an Adsorbable Foreign Gas

It is known that in the general case the surface tension depends on the particle size [9, 10, 11, 12]. In particular, an excellent review of the state of affairs related to the thermodynamic analysis of the size dependence of surface tension was given in [10, 11]. In the mentioned papers, a general equation for the size dependence of surface tension was obtained on the basis of the thermodynamic approach and a detailed analysis of this equation was carried out. It was shown that this general equation is consistent with results of other researchers containing their expressions as special cases. It is worth noting as well that in some cases simple approximate equations for describing the size dependence of surface tension - as an approximation to the general solution of the the underlying differential equation - is given

$$\sigma_p = \sigma_\infty \exp\left(-\frac{4\delta}{\delta+d}\right) \,, \tag{14.7}$$

where σ_∞ is the surface tension for a planar surface, δ is the so-called Tolman length.

It is seen from Eq. (14.4) that the value of β decreases with a decrease in the particle size. This is due to both the Kelvin effect and the dependence of the condensation coefficient on the particle size. The size dependence of the condensation coefficient leads to a lower trapping coefficient of vapor molecules in comparison with the case, where the condensation coefficient is assumed to be independent of the particle size. The size dependence of the surface tension leads to an increase in the trapping coefficient in relation to the case of the size-independent surface tension.

The rate of gas-phase homogeneous nucleation J_n is commonly written as [13, 14]

$$J_n = k_Z \omega S^* N^* = k_Z \alpha_c \frac{nv}{4} \pi d^{*2} n \exp\left(-\frac{\Delta G^*}{k_B T}\right) , \qquad (14.8)$$

where $\omega = \alpha_c nv/4$ is the frequency factor for impingement [13], k_Z is the Zeldovich factor, N^* is the number density of the critical clusters, S^* is the surface area of the critical cluster, ΔG^* is the free energy of critical cluster formation.

In classical nucleation theory the value of ΔG^* is equal to $\pi \sigma_p d^{*2}/3$, where d^* is defined by the Kelvin equation that is independent of the condensation coefficient. However, it follows from the above discussion that the size dependence of the condensation coefficient affects the value d^* and accordingly the values of ΔG^* and J_n . It is pertinent to note that, under the above-mentioned definition of α_c , the frequency factor ω in Eq. (14.8) describes the flux density of vapor molecules that stick to the surface of the critical cluster. However, in the general case the frequency factor should be proportional to the probability of incorporation of molecules into the cluster [15].

14.3 Critical Size of a Charged Aerosol Particle in the Presence of an Adsorbable Foreign Gas

In the general case when the condensation coefficient of vapor molecules is not equal to the evaporation coefficient the critical size of the charge particle in the presence of adsorbable foreign gas can be written as [16]

$$\ln S = \frac{V_m}{k_B T} \left[\frac{4\sigma_0}{d^*} - \frac{2q^2}{\pi d^{*4}} \left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_l} \right) \right] + \frac{4V_m n_a}{d^*} \ln \left(\frac{P_L}{P_a + P_L} \right) - \ln \left(\frac{\alpha_c}{\alpha_e} \right) .$$
(14.9)

Here q is the elementary charge, ε_g and ε_l are accordingly dielectric constants of a gas and a liquid, σ_0 is the surface tension of the clean particle surface, n_a is the number of adsorption sites per unit area, P_{α} is the pressure of an adsorbable foreign gas. The value of P_L can be presented in the form

$$P_L = \frac{n_a \left(2\pi m_a k_B T\right)^{\frac{1}{2}} \exp\left(-\frac{Q_a + Q_{a0}}{k_B T}\right)}{\beta \tau_0} , \qquad (14.10)$$

where Q_a is the adsorption energy in the absence of the electric field, Q_{a0} is the component of the adsorption energy related to the influence of the electric field created by the particle charge, τ_0 is the quantity characterizing the oscillation period of the adsorbed molecule in the direction perpendicular to the surface, m_a is the mass of the molecule of the adsorbable gas, β is the sticking coefficient of the foreign gas molecules for the clean part of the surface.

It is seen from Eq. (14.9) that the effect of an adsorbable foreign gas in the case when $\alpha_c/\alpha_e < 1$ can to some extent compensate the effect related to a difference in the condensation and evaporation coefficients. The inequality $\alpha_c/\alpha_e < 1$ can be related to both size dependence of the condensation coefficient and a change in α_c under the influence of external fields (e.g. resonance laser radiation).

14.4 Influence of Resonance Radiation on the Critical Size of the Particle (Cluster)

Let us consider the influence of resonance radiation on the critical size of aerosol particles (clusters). For simplicity here we neglect adsorption of a foreign gas and assume that the condensation coefficient is independent of the particle size and the particle is neutral. The condensation coefficient α_c in the case of the two-level model for transition of molecules from one state to another in the radiation field can be written as

$$\alpha_c = \alpha_1 - \gamma \left(\alpha_1 - \alpha_2 \right) \,. \tag{14.11}$$

Here, α_1 and α_2 are the condensation coefficients of unexcited and excited molecules and γ characterizes a part of excited molecules

$$\gamma = \frac{n'}{n+n'} , \qquad (14.12)$$

where n' and n are accordingly number concentrations of excited and unexcited vapor molecules which are found from equations

$$\frac{dn'}{dt} = \frac{I\sigma_{\nu}}{h\nu} (n - n') - \frac{n'}{\tau_{\nu}} , \qquad (14.13)$$

$$\frac{dn}{dt} = \frac{I\sigma_{\nu}}{h\nu}\left(n'-n\right) + \frac{n'}{\tau_{\nu}}.$$
(14.14)

Here, I is the radiation flux density, t is the time, σ_{ν} is the cross-section for transition of vapor molecules from one state to another, h is the Planck constant, τ_{ν} is the relaxation time for excited molecules, and ν is the radiation frequency. In the stationary case, we have the following equation for γ :

$$\gamma = \frac{\frac{I\sigma_{\nu}\tau_{\nu}}{h\nu}}{1 + \frac{2I\sigma_{\nu}\tau_{\nu}}{h\nu}}.$$
(14.15)

Taking into account above-mentioned considerations, the value of d^* for neutral particles neglecting the adsorption of foreign gas on the particle surface can be written as [17]

$$d^* = \frac{4\sigma V_m}{k_B T \ln\left[\frac{\alpha_1 - \gamma(\alpha_1 - \alpha_2)}{\alpha_e}S\right]}.$$
(14.16)

Equation (14.16) shows that the critical diameter of the aerosol particle depends on the condensation coefficients of unexcited and excited molecules and on the value of γ (and, accordingly, on the value of the

radiation flux density I). For a constant value of S the critical diameter increases with I when $\alpha_1 > \alpha_2$ and decreases when $\alpha_1 < \alpha_2$. It follows from Eq. (14.16) that the critical diameter can be realized in fulfillment of the following inequality:

$$S > \frac{\alpha_e}{\alpha_1 - \gamma \left(\alpha_1 - \alpha_2\right)} \,. \tag{14.17}$$

In the general case the combined influence of heat and resonance effects is realized. For example, with a decrease in the condensation (sticking) coefficient under excitation of vapor molecules heat and resonance effects have the same tendency – they decrease the resultant flux of vapor molecules into the particle. However, when the condensation coefficient of excited molecules is larger than that of unexcited, the heat and resonance effects act in opposite directions, which results in some mutual compensation of them.

14.5 Size Effects in Homogeneous Nucleation Inside Nanoscale Particles

Let us consider the process of homogeneous nucleation in a two-component nanoparticle when the supersaturation of one component in the nanoparticle is realized. The rate of nucleation J_n in the case under consideration can be written as

$$J_n = k_Z k_a n_m N^* = k_Z k_a n_m^2 \exp\left(-\frac{\Delta G^*}{k_B T}\right) , \qquad (14.18)$$

where k_a is the effective rate constant for the attachment of monomers (molecules or atoms) to the critical cluster allowing for both diffusion of monomers to the critical cluster and their incorporation into the cluster, n_m is the number concentration of monomers, N^* is the number concentration of the critical clusters in the nanoparticle, ΔG^* is the free energy of the critical cluster formation in the condensed phase [18].

Let us consider the size dependence of k_a . The value of k_a in the case under consideration by analogy with [19] can be written as

$$k_a = \frac{2\pi d_c D_m}{1 + \frac{2D_m}{k_s d_c}},$$
(14.19)

where d_c is the diameter of the critical cluster, D_m is the diffusion coefficient of monomers in the particle (for simplicity we neglect further diffusion of clusters), k_s is the rate constant of the heterogeneous process related to the incorporation of monomers that are located in the vicinity of the critical cluster into the latter. The value of k_s is given by

$$k_s = k_{s0} \exp\left(-\frac{Q_c}{k_B T}\right) , \qquad (14.20)$$

where Q_c is the activation energy of the incorporation of monomers into the critical cluster, the preexponencial term k_{s0} in Eq. (14.20), which is assumed to be independent of the cluster size, can be estimated as νa , where ν and a are respectively the values characterizing the vibration frequency and the jump length of monomers.

The diffusion coefficient of monomers in the particle D_m can be written as

$$D_m = D_{m0} \exp\left(-\frac{Q_p}{k_B T}\right) , \qquad (14.21)$$

where Q_p is the activation energy for diffusion of monomers in the nanoparticle, the value of D_{m0} is assumed to be independent of the particle size and can be estimated as νa^2 . The value of k_a in view of the aforesaid can be written as

$$k_a = \frac{2\pi d_c \nu a^2 \exp\left(-\frac{Q_p}{k_B T}\right)}{1 + \frac{2a}{d_c} \exp\left(\frac{Q_c - Q_p}{k_B T}\right)}.$$
(14.22)

Taking into account [1, 12], the values of Q_c and Q_p are given by

$$Q_c = Q_{c\infty} \exp\left(-\frac{4}{1+d_{c0}}\right) , \qquad (14.23)$$

$$Q_p = Q_{p\infty} \exp\left(-\frac{4}{1+d_{p0}}\right) , \qquad (14.24)$$

where $d_{c0} = d_c/\delta_c$ and $d_{p0} = d_p/\delta_p$. Here d_p is the nanoparticle diameter, δ_c is the Tolman length for the critical cluster, δ_p is the Tolman length for the nanoparticle, $Q_{c\infty}$ and $Q_{p\infty}$ are the values of Q_c and Q_p without considering the size effect.

It follows from the foregoing that the size dependence of the activation energies Q_c and Q_p can affect the nucleation rate in nanoscale particles. Let us consider the case when the second term in the denominator of Eq. (14.22) is much less than unity (the diffusion controlled regime of nucleation takes place). Under the above-mentioned assumptions we can write for the value of $k_{a0} = k_a/k_{a\infty}$, where $k_{a\infty}$ is the value of k_a without considering the size effect in Q_p ($Q_p = Q_{p\infty}$), the following equation:

$$k_{a0} = \exp\left\{\frac{Q_{p\infty}}{k_BT} \left[1 - \exp\left(-\frac{4}{1+d_{p0}}\right)\right]\right\}$$
(14.25)

It is seen from Eq. (14.25) that k_{a0} increases with a decrease in d_{p0} and decreases with a reduction in the parameter $Q_{p\infty}/k_BT$.

14.6 Conclusions

It was shown that size effects in phase transitions in aerosol systems with nanoparticles and in nanoparticles themselves can be related to a change in the condensation coefficient of vapor molecules, as well as in the activation energies of processes occurring inside nanoparticles, with a reduction in the particle size. The influence of above-mentioned factors on gas-phase nucleation and nucleation in nanoparticles is considered.

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14.6 Conclusions

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15 Cluster Dynamics Study of Defect Evolution in Neutron-Irradiated Dilute and Concentrated Fe-Cr Alloys

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Die Rose ist ohne Warum. Sie blühet, weil sie blühet. Sie achtet nicht ihrer selbst, fragt nicht, ob man sie siehet.

Johann Scheffler alias Angelus Silesius (1624-1677)

Abstract

Cluster dynamics (CD) is used to study the evolution of the size distributions of vacancy clusters (VC), self-interstitial atom (SIA) clusters (SIAC) and Cr precipitates in neutron irradiated Fe-9at%Cr and Fe-12.5at%Cr alloys at T = 573 K with irradiation doses up to 1.5 dpa and a flux of 140 ndpa/s. Transmission electron microscopy (TEM) and small angle neutron scattering (SANS) data on the defect structure of this material irradiated at doses of 0.6 and 1.5 dpa are used to calibrate the model. For both alloys a saturation behavior was found by CD for the free vacancy and free SIA concentrations as well as for the number density of the SIAC above 0.006 dpa. The CD simulations also indicate the presence of VC with radii less than 0.5 nm and a strong SIAC peak with a mean diameter of about 0.5 nm, both invisible in SANS and TEM experiments. CD modeling of Cr precipitates has been performed by taking into account the deviation of this system from the ideal cluster gas. A specific surface tension of about 0.17 J/m² between the α matrix and the Cr-rich α' precipitate and the rate at which Cr monomers are absorbed about 7.94 m⁻¹ were found as best fit values for reproducing the long-term Cr evolution in the irradiated Fe-12.5%Cr alloys observed by SANS.

15.1 Introduction

Ferritic-martensitic chromium steels are candidates of structural materials for future generation of nuclear reactors such as fusion or advanced high temperature reactors (Gen IV) or spallation sources, because of their remarkable resistance to swelling and of their adequate mechanical properties. In operation, these materials will be exposed to high neutron doses (up to about 100 dpa) and high temperatures. However, the formation of irradiation-induced defects and the possible degradation of the mechanical properties under these extreme conditions are not yet well understood. The investigation of neutron-irradiated binary Fe-Cr alloys by TEM (transmission electron microscopy) [1] and SANS (small angle neutron scattering) data [2-4] will significantly contribute to the understanding of the behavior of more complex alloys. For the purpose of predicting irradiation hardening it is necessary to know in detail the size distributions of vacancy clusters (VC), self-interstitial atom clusters (SIAC) and Cr precipitates formed under irradiation at any neutron dose. The latter can be obtained by means of CD (cluster dynamics) simulations. Solubility limit of Cr in Fe-Cr system is about 8.8at% at T = 573 K [2]. Hence, deviation of the Cr precipitates ensemble from the ideal

cluster gas [5] has been taken into account in CD modeling of Fe-9at%Cr alloy and Fe-12.5at%Cr alloy.

15.2 Irradiation Conditions and Experimental Data

The irradiation conditions and experimental results described in [1-4] are summarized below for the purpose of comparison with the CD simulations performed in this study. Both the industrial purity Fe-9at%Cr alloy and Fe-12.5at%Cr alloy (average grain size 1 μ m, pre-existing dislocation density 5.5·10¹³ m⁻²) were neutron-irradiated in the Callisto rig (IPS2) in the Belgian reactor (BR2). An irradiation temperature *T* of 573 K and a neutron flux of about 9·10¹⁷ n/m²s (E > 1 MeV) were maintained. This flux corresponds to a dose rate of about 140 ndpa/s. The neutron exposure covered the range from 0.6 to 1.5 dpa.

TEM investigations of the Fe-12.5at%Cr alloy [1] reveal the presence of dislocation loops of size 6 nm (in diameter) and a total loop density about $1.73 \cdot 10^{21}$ m⁻³ for both irradiation conditions, 0.6 and 1.5 dpa. No voids were observed by TEM under these irradiation conditions. Irradiation-induced features with a diameter of about 2 nm and volume fraction of (4.3 ± 0.4) % for both irradiation conditions and A-ratios (ratio of total and nuclear SANS intensity) of 2.07 ± 0.05 and 2.05 ± 0.05 for a dose of 0.6 and 1.5 dpa, respectively, have been found by SANS. These features were related to pure Cr precipitates in α -Fe as well as to α' particles dispersed in the α -Fe matrix. In [2] a decrease in the scattering cross-section of SANS with decreasing scattering vector, Q, was found, as is typical for the interference effects in concentrated alloys. According to the approach discussed in Ref. [6] the interference factor S(Q) was determined in [7] for this Q-range. Then the mono-disperse hard-sphere model [8], which takes into account the correlation between all hard spheres (depletion zones), was applied to interpret the obtained interference factor. The volume fraction of the hard spheres is found at 14.4% and 13.3% and average distance between them at 2.38 nm and 1.97 nm for the irradiation doses of 0.6 and 1.5 dpa, respectively. The size distribution of the α' particles, reported in [2], was obtained by the indirect transformation method applied to the fitted measured nuclear scattering cross sections. The range of the Q-values was restricted to values larger than 1 nm^{-1} in the fit, where the interference effect can be excluded.

According to TEM study [1] the population of dislocation loops decorated by Cr atoms with diameters of about 7 nm and 13 nm and a total loop density about $1.9 \cdot 10^{21}$ m⁻³ and $1.7 \cdot 10^{21}$ m⁻³ in the Fe-9at%Cr alloy are formed due to irradiation with doses of 0.6 and 1.5 dpa, respectively. SANS experiments [3] indicate for both irradiation conditions the two populations of irradiation-induced features with radius, *R*, in the ranges, R < 2.4 nm and 2.4 nm < R < 7nm, respectively. The A-ratio of these features is higher than those expected for nanovoids and α' - particles, but smaller than those expected for well-developed Cr-carbides. According to SANS the total volume fraction of irradiation-induced features slightly increases with neutron fluency.

15.3 Cluster Dynamics Master Equation

Defect structure of neutron irradiated Fe-Cr alloys containing the free vacancies, SIA, vacancy clusters, pure dislocation loops, dislocation loops decorated by Cr atoms and vacancy – Cr complexes as well as Cr precipitates depends on the irradiation regime [9]. The rigorous CD model has to include description of point defect subsystem and Cr precipitates subsystem with taking into account the link between two these subsystems by means of migration of Cr to the vacancy clusters, transport of Cr atoms to the dislocation loops, the formation and migration of Fe-Cr interstitial, diffusion of Cr atoms, free vacancies and SIA towards to the dislocation net.

The CD model used in our study is close to the CD-P-VIC model from Ref. [10], where the CD simulations are first performed for the free vacancies, SIA and point defect clusters and then for the precipitates taking into account the actual time dependence of the free point defect concentrations obtained in the first step. In addition to Ref. [10] we take into account the Cr-effect on the SIA diffusivity according to the DFT calculations reported in Ref. [11].

15.3 Cluster Dynamics Master Equation

The assumptions used to study the evolution of the Cr precipitates need special attention. Two different mechanisms are discussed in Ref. [9] for the irradiation induced or enhanced formation of α' precipitates in Fe-Cr alloys. The first mechanism suggested for the migration of Cr to the voids is the exchange of chromium atoms with vacancies. This statement is in line with DFT calculations which predict a relatively low barrier for chromium atom exchange with a vacancy in iron [12]. A second mechanism proposed relies on the strong interaction between chromium atoms and SIA leading to a transport of Cr atoms to SIA loops. According to TEM data [1] the first and second mechanism is observed in the irradiated Fe-12.5at%Cr alloy and Fe-9at%Cr alloy, respectively.

Another problem is to take into account the overlapping diffusion field effect and frustration effects in the considered materials that are typical for concentrated alloys [13-15]. Correction of the attachment coefficient of Cr to Cr precipitates caused by relatively high chromium concentration will be accounted for in our study according to the method discussed in Ref. [13]. The frustration effect [14, 15] will be taken into account empirically by the use of the thermodynamic free energy expression from CALPHAD [16] with the correction suggested by Bonny et al. [17].

15.3.1 Matrix Defect System

The public domain library solver LSODA [18] has been used to integrate directly the master equation [19] for the study of the matrix defect subsystem containing free vacancies, spherical VC with sizes up to 1000 vacancies, free SIA and planar SIAC with sizes up to 4000 SIA. The attachment coefficients for the master equation [19] are determined in the diffusion limited regime and following the approach reported in Ref. [20] for spherical VC and planar SIAC, respectively. The emission coefficients in Ref. [19] are fixed using the detailed balance principle for both, VC and SIAC. The values for the pre-existing dislocation density, ρ_0 , and the average grain size, d, are taken from the experiment [1]. Other material parameters are found by fitting to the condition of best reproduction of the experimental data [1] by the results of the CD simulation. The final collection of material parameters used in present study is presented in Table 15.1 in comparison to the data used in Ref. [19]. The only substantial change of material parameters with respect to Ref. [19] is the SIA diffusivity. The values of the pre-factor for SIA diffusion, D_{i0} , amounts to 2.0·10⁻⁸ m²/s (4.8·10⁻⁸ m²/s), and migration energy of the SIA, E_{mi} , amounts to 0.25 eV (0.24 eV) for Fe-9at%Cr (Fe-12.5at%Cr) are taken according to data [11] on SIA diffusivity dependence on the Cr content in Fe-Cr alloys.

15.3.2 Cr Precipitates System

The number density of the Cr-precipitates, C_n , is determined from the Master equation, Eq. (15.1)

$$\frac{\mathrm{d}C_n}{\mathrm{d}t} = \beta_n \left(\left(\frac{n-1}{n}\right)^{1/3} C_{n-1} - \left(1 + \left(\frac{n-1}{n}\right)^{1/3} w_n\right) C_n + w_{n+1} C_{n+1} \right) .$$
(15.1)

Here, *n* is the size of the Cr-precipitate, $2 \le n \le N_{\text{max}}$, and C_n is set equal to zero for $n > N_{max}$, as is the case for all C_n at t = 0. β_n is the absorption rate of an *n*-atomic cluster as obtained to account for the resulting overlapping diffusion field effects similar to the method discussed in Ref. [13]:

$$\beta_n = 4\pi \sqrt[3]{\frac{3\Omega_{Cr}}{4\pi}} D_{Cr}^{irr} \frac{C_{1Cr}}{\Omega_{Fe}} n^{1/3} \frac{1 + kr^{ext}}{1 + k(r^{ext} - r)} , \qquad r \le r^{ext} , \qquad (15.2)$$

$$\beta_n = 4\pi \sqrt[3]{\frac{3\Omega_{Cr}}{4\pi}} D_{Cr}^{irr} \frac{C_{1Cr}}{\Omega_{Fe}} n^{1/3} \left(1 + kr^{ext} \right) , \qquad r \ge r^{ext} , \qquad (15.3)$$

where Ω_{Fe} and Ω_{Cr} are the atomic volume of bcc iron and bcc chromium, and $C_{1\text{Cr}}$ is the concentration of the remaining solute chromium atoms in the matrix, r^{ext} is the mean one half distance between Crprecipitates, it has been taken equal to about 1 nm according to analysis of interference factor S(Q) in [7], k is the rate at which Cr monomers are absorbed.

Table 15.1: Material parameters of matrix defect system.

Material parameters	pure iron [19]	present study		
Vacancy formation energy E_f [eV]	1.60	1.60		
Binding energy of a vacancy dimer E_{b2v} [eV]	0.608	0.608		
Vacancy migration energy E_{mv} [eV]	0.88	0.88		
Vacancy pre-exponential factor D_{vo} [m ² /s]	$2.1 \cdot 10^{-8}$	$2.1 \cdot 10^{-8}$		
Interstitial formation energy E_{fi} [eV]	3.05	3.0		
Binding energy of an interstitial dimer E_{b2i} [eV]	0.8	0.8		
Interstitial migration energy E_{mi} [eV]	0.30	0.25(Fe-9at%Cr)		
Interstitial migration energy E_{mi} [eV]	0.30	0.24(Fe-12.5at%Cr)		
Interstitial pre-exponential factor D_{io} [m ² /s]	$3.6 \cdot 10^{-8}$	2.8·10 ⁻⁸ (Fe-9at%Cr)		
Interstitial pre-exponential factor D_{io} [m ² /s]	$3.6 \cdot 10^{-8}$	4.8·10 ⁻⁸ (Fe-12.5at%Cr)		
Recombination radius, r_{rec} [nm]	0.65	0.65		
Capture efficiency for vacancies by dislocations Z_v	1.0	1.0		
Capture efficiency for interstitial by dislocations Z_i	1.2	1.2		
Burgers vector of the loops assumed to be pris-	0.2	0.2		
matic b [nm]				
Pre-existing dislocation density ρ_0 [m ⁻²]	$7.0 \cdot 10^{13}$	$5.5 \cdot 10^{13}$		
Average grain size <i>d</i> [m]	$2.5 \cdot 10^{-4}$	$1.0 \cdot 10^{-6}$		

The chromium concentration is determined via

$$C_{1\rm Cr} = C_{0\rm Cr} - \sum_{n=2}^{N_{\rm max}} n C_n , \qquad (15.4)$$

with C_{0Cr} being the initial concentration of the chromium atoms. D_{Cr}^{irr} is the irradiation enhanced diffusion coefficient of chromium in iron according to

$$D_{\rm Cr}^{\rm irr} = D_{\rm Cr}^{\rm th} \frac{C_{\rm 1v}^{\rm irr}}{C_{\rm 1v}^{\rm eq}}, \qquad (15.5)$$

where D_{Cr}^{th} is the thermal diffusion coefficient of chromium in iron calculated according to the Arrhenius law with the experimental parameters, $D_0 = 1.29 \cdot 10^{-4} \text{ m}^2/\text{s}$ and $E_m = 2.39 \text{ eV}$ for Fe-12%Cr alloy [21]. C_{1v}^{eq} and C_{1v}^{irr} are the vacancy concentrations for the unirradiated and irradiated state of the material, respectively, with C_{1v}^{eq} being evaluated as in Ref. [19]. We focus on the vacancy exchange mechanism for the chromium mobility in the Fe-Cr system, which is the dominant mechanism in the Fe-12.5%Cr alloy investigated here.

The emission parameter, w_n , is calculated with taking into account of the contribution of matrix frustration to the free energy of cluster distributions in binary alloys [14, 15]. This effect is typical for concentrated alloys, when the Frenkel's model of ideal cluster gas [5] is not valid and it is necessary to consider the interaction between the clusters according to [15] by means of so-called exclusion volume, $V_{k,n}$, i.e. the number of forbidden atomic sites (or volume normalized by the atomic volume) to a k-mer by an n-mer. In our paper it is suggested to take into account the frustration effect empirically by the use of the thermodynamic free energy expression from CALPHAD [16] with the correction suggested by Bonny et al. [17].

The emission parameter, w_n , finally, is calculated by Eq. (15.6)

$$w_n = \exp\left(-\frac{\Delta\mu}{k_{\rm B}T}\right) \, \exp\left(\frac{4\pi\gamma^{\rm cl,m}\left(R_n^2 - R_{n-1}^2\right)}{k_{\rm B}T}\right) \,,\tag{15.6}$$

15.3 Cluster Dynamics Master Equation

where $\gamma^{cl,m}$ is the specific surface tension of the interface between the Cr cluster (cl) and the matrix (m), R_n is the radius of a Cr cluster of size n, k_B the Boltzmann constant, and $\Delta \mu$ is determined via

$$\Delta \mu = \left(\mu_{\rm Cr}^{\rm m}(C_{1\rm Cr}) - \mu_{\rm Cr}^{\rm cl}\right) \cdot x_{\rm Cr}^{\rm cl} + \left(\mu_{\rm Fe}^{\rm m}(C_{1\rm Cr}) - \mu_{\rm Fe}^{\rm cl}\right) \cdot x_{\rm Fe}^{\rm cl} \,. \tag{15.7}$$

Here μ_{Cr}^{cl} (μ_{Cr}^{m}) and μ_{Fe}^{cl} (μ_{Fe}^{m}) are the chemical potentials of chromium and iron, respectively, in the precipitate cluster (matrix), and $x_{Cr(Fe)}^{cl}$ is the mole fraction of chromium (iron) in the Cr precipitate, which is set equal to 0.95 ± 0.05 according to the assumption of the equality of precipitate and matrix composition at the binodal miscibility curve. Note, that no simple lattice gas (or ideal solution) behavior is imposed here to the dependence of the chemical potential in the matrix on the Cr concentration. Instead the chemical potential of chromium (iron) in both subsystems, matrix and precipitate, is taken from Eq. (15.8)

$$\mu_{\rm Cr(Fe)} = \frac{\partial}{\partial n_{\rm Cr(Fe)}} \left(\left(n_{Cr} + n_{Fe} \right) \frac{G}{N_{\rm A}} \right) , \qquad (15.8)$$

where $n_{Cr}(n_{Fe})$ is the number of chromium (iron) atoms in the respective Fe-Cr subsystem, N_A is the Avogadro number, and G is the total *molar* Gibbs free energy as obtained from the expression used by CALPHAD [16]

$$G = x_{\rm Cr} G_{\rm Cr}^{\rm bcc} + x_{\rm Fe} G_{\rm Fe}^{\rm bcc} + k_B N_A T (x_{\rm Cr} \ln x_{\rm Cr} + x_{\rm Fe} \ln x_{\rm Fe}) + G_{\rm ex}^{\rm bcc} + G_{\rm M}^{\rm bcc} .$$
(15.9)

Here $x_{\rm Cr} (x_{Fe})$ is the chromium (iron) mole fraction – or equivalently, the concentration measured in atoms per site – in the respective Fe-Cr subsystem. $G_{\rm Cr}^{\rm bcc}(G_{\rm Fe}^{\rm bcc})$ is the molar free energy of pure bcc Cr(Fe) as reported in [22], and $G_{\rm M}^{\rm bcc}$ is the magnetic contribution to the molar excess free energy proposed by [23]. A regular solution model is used in [16] for the non-magnetic molar excess free energy $G_{\rm ex}^{\rm bcc}$ in the Fe-Cr system. This expression has been modified by Bonny [17] in order to account for the recently proposed modification of the Fe-rich phase boundary [24] for temperatures well below 800 K.



Figure 15.1: Dose dependence of the free vacancy (SIA) concentrations, C_{1v}^{irr} (C_{1i}^{irr}), and the total number density of SIAC, N_i , for the irradiated Fe-12.5at%Cr alloy according to the TEM experiment [2] and the CD simulations.



Figure 15.2: Dose dependence of the mean radius of the VC and the mean diameter of the SIAC, $(R_v)_{mean}$ and $(2R_i)_{mean}$, for the irradiated Fe-12.5 at%Cr alloy according to the TEM experiment [2] and the CD simulations.

We found that the Redlich-Kister polynomial given in Ref. [17] could equally well be written in following factorized form

$$G_{\rm ex}^{\rm bcc} = x_{\rm Cr} \left(1 - x_{\rm Cr}\right) \cdot \left[20500 - 9.68 \cdot T + L\left(x_{\rm Cr}\right) \cdot \left(1 - \frac{T}{1100}\right)^3 \theta\left(1 - \frac{T}{1100}\right)\right] , \quad (15.10)$$

where

$$L(x_{\rm Cr}) = 8615.407399 + 431.3047159(2x_{\rm Cr} - 1) - 31452.7845(2x_{\rm Cr} - 1)^2 +$$
(15.11)

$$48134.04065 \left(2 x_{
m Cr} - 1
ight)^3 - 23569.11288 \left(2 x_{
m Cr} - 1
ight)^4 - 5625.73983 \left(2 x_{
m Cr} - 1
ight)^5$$

and $\theta(x)$ is the Heaviside function being one for $x \ge 0$ and zero else. All coefficients in Eqs. (15.10) and (15.11) are given in SI units (i.e., in J/mol and K). Relating the ratio w_n between the absorption and emission rates entering Eq. (15.1) to chemical potential differences and deriving these differences from empirical thermodynamic free energy expressions is an empirical way to account for the so-called frustration effects due to higher solute atom and/or cluster concentrations in the system as discussed in Refs. [14, 15]. Again the library solver LSODA has been used to integrate the master equations in order to find the precipitate cluster concentrations C_n for all n up to $N_{max} = 9000$.

15.3.3 Cluster Dynamics Modeling

The results from the CD modelling on the dose dependence of the free vacancy and SIA concentrations, C_{1v}^{irr} and C_{1i}^{irr} , the mean radius of the VC and mean diameter of the SIAC, $(R_v)_{mean}$ and $(2R_i)_{mean}$, the total number density of SIAC, N_i , the volume fraction of the Cr precipitates, $C_{v,Cr}$, and the mean radius of the Cr precipitates, $(R_{Cr})_{mean}$, for Fe-12.5at%Cr alloy are shown in the Figures 15.1-15.4. It was

15.3 Cluster Dynamics Master Equation

found that the CD simulation according to the procedure used in Ref. [19] but with taking into account the chromium effect on the SIA diffusivity reported in [11] allows one to reproduce the experimental TEM data [1] for Fe-12.5at%Cr alloy on N_i exactly (Fig. 15.1) and on $(2R_i)_{mean}$ approximately (Fig. 15.2). A saturation behavior under neutron irradiation is observed for both, C_{1i} and N_i , at doses higher than about 0.006 dpa (Fig. 15.1). The loop diameters $(2R_i)_{mean}$ found in the simulations increase slowly with neutron irradiation and reach 5.74 and 6.25 nm for the neutron doses of 0.6 and 1.5 dpa, respectively (Fig. 15.2), instead of about 6 nm for both doses as observed experimentally [1]. A value of about $1.73 \cdot 10^{21}$ m⁻³ is found in the CD simulation for the number density of the SIAC at the experimental neutron doses of 0.6 and 1.5 dpa. The same value was observed by TEM [1]. The strong peak in the SIAC distribution at diameters of about 0.5 nm (see Fig. 15.3) is observed for all neutron exposures. The value of $(R_v)_{mean}$ increases only slowly up to an irradiation dose of about $6 \cdot 10^{-4}$ dpa. Then it increases faster but does never exceed 0.5 nm (Fig. 15.2), which is the experimental resolution limit of both SANS and TEM techniques. Thus our finding is in line with the fact, that no VC has been detected in the experimental studies [1, 2].



Figure 15.3: Size distributions of self interstitial atom cluster in Fe-12.5%Cr for different irradiation conditions as obtained from the CD simulations.

The Cr precipitates evolution was found to be rather sensitive to the surface tension $\gamma^{cl,m}$ of the interface between the precipitate cluster and the α matrix as well as the rate k at which Cr monomers are absorbed. A value for $\gamma^{cl,m}$ of about 0.17 J/m² and k about 7.94 m⁻¹ are necessary to approximately reproduce the SANS data [2] on the dose dependence of the volume fraction $C_{v,Cr}$ and the mean radius $(R_{Cr})_{mean}$ of the Cr-rich α' precipitates by the CD simulations (Fig. 15.4). The saturation of the simulated $C_{v,Cr}$ values at about 4.0 vol% is observed for the same neutron exposes as the saturation of the N_i values.

CD modeling results on the dose dependence of the free vacancy and SIA concentration, C_{1v} and C_{1i} , the mean radius of VC and mean diameter of SIAC, $(R_v)_{mean}$ and $(2R_i)_{mean}$, total number density of SIAC, (N_{i_total}) , volume fraction of Cr-precipitates, C_{v_Cr} , and average radius of Cr-precipitates, R_{av_Cr} , for Fe-9at%Cr are presented in the Table 15.2.

It was found that CD modeling according to [19] with taking into account the chromium effect on the SIA diffusivity [11] provides the reproduction of experimental TEM data [1] on N_i and $(2R_i)_{mean}$



Figure 15.4: Dose dependence of the volume fraction and mean radius of the Cr precipitates, $C_{v,Cr}$ and $(R_{Cr})_{mean}$, for the irradiated Fe-12.5%Cr alloy according to the TEM experiment [2] and the CD simulations.

Nautron	C [at $=$]]	(\mathbf{D})	C [at =]]	$(\mathbf{D}\mathbf{D})$	M	C	C	D
Neutron	C_{1v} [at -]	$(n_v)_{mean}$	C_{1i} [at -]	$(2n_i)_{mean}$	N _i _total	C_{v_Cr}	C_{v_Cr}	n _{av-Cr}
exposure		[nm]		[nm]	$[1/m^3]$	[%vol]	[%vol]	[nm]
[dpa]							$R \ge 0.5$ nm	
$6 \cdot 10^{-7}$	$16.48 \cdot 10^{-13}$	0.184	$4.71 \cdot 10^{-14}$	0.50	$2.22 \cdot 10^{19}$	0.003	0	0.18
$6 \cdot 10^{-6}$	$6.59 \cdot 10^{-13}$	0.189	$6.24 \cdot 10^{-14}$	0.59	$1.35 \cdot 10^{20}$	0.02	0	0.18
$6 \cdot 10^{-5}$	$1.88 \cdot 10^{-13}$	0.196	$7.18 \cdot 10^{-14}$	0.88	$5.72 \cdot 10^{20}$	0.06	0	0.18
$6 \cdot 10^{-4}$	$4.12 \cdot 10^{-14}$	0.199	$7.65 \cdot 10^{-14}$	1.49	$7.05 \cdot 10^{20}$	0.16	0	0.18
$6 \cdot 10^{-3}$	$1.41 \cdot 10^{-14}$	0.231	$7.65 \cdot 10^{-14}$	2.66	$9.05 \cdot 10^{20}$	0.2	0	0.22
$6 \cdot 10^{-2}$	$4.46 \cdot 10^{-15}$	0.302	$7.65 \cdot 10^{-14}$	4.65	$1.11 \cdot 10^{21}$	0.2	0.003	0.40
0.6	$4.46 \cdot 10^{-15}$	0.330	$7.65 \cdot 10^{-14}$	5.84	$1.57 \cdot 10^{21}$	0.2	0.190	0.84
1.5	$4.46 \cdot 10^{-15}$	0.340	$7.65 \cdot 10^{-14}$	6.35	$1.61 \cdot 10^{21}$	0.2	0.196	1.14
3.0	$4.46 \cdot 10^{-15}$	0.350	$7.65 \cdot 10^{-14}$	6.72	$1.62 \cdot 10^{21}$	0.2	0.198	1.44
6.0	$4.46 \cdot 10^{-15}$	0.362	$7.65 \cdot 10^{-14}$	7.06	$1.62 \cdot 10^{21}$	0.2	0.199	1.81
12	$4.46 \cdot 10^{-15}$	0.380	$7.65 \cdot 10^{-14}$	7.37	$1.63 \cdot 10^{21}$	0.2	0.200	2.28

 Table 15.2: Cluster dynamics simulation results for irradiated Fe-9at%Cr model alloy.

very roughly. The most significant divergence between CD and TEM data [1] is found for $(2R_i)_{mean}$ for irradiation dose about 1.5 dpa: calculating data of $(2R_i)_{mean}$ are about 5.84 nm and 6.35 nm from CD against of experimental $(2R_i)_{mean}$ are about 7nm and 13 nm from TEM.

15.4 Discussion

According to the comparison between kinetic Monte Carlo simulations with CD in [25] the deviation of the cluster system from the ideal gas cluster model [5] must be taken into account in CD scheme, when the

15.5 Conclusions

solute concentration exceeds values of the order of 1% atomic in AlZr alloys. In this case the contribution of configurational entropy with respect to the total free energy of the gas of clusters is determined in [15] via constant exclusion volume V (V here is an integer value measuring the number of lattice sites really occupied by the cluster) or real exclusion volume $V_{k,n}$ ($V_{k,n}$ here is the number of forbidden atomic sites to a k-mer by an n-mer) or individual exclusion volume $V_{k,1}$ ($V_{k,1}$ here is the total volume of cluster, i.e. excluding the solute free layer). Because of the complexity of calculations [25] subject of interest is to estimate apriori the frustration effect in the binary alloys. In [26] it was revealed that the applicability of the concept of the uniform supersaturation with ignoring of the exclusion volume in the cluster system depends not on the absolute value of solute concentration but on the value of dimensionless parameter a defined as

$$a = \frac{C_0 - C_{eq}}{C_{cl}} , \qquad (15.12)$$

where C_0 , C_{eq} and C_{cl} are the initial concentration, solubility limit and concentration of solute atoms in the cluster (precipitate), respectively.

In [26] it is obtained analytically that the small value of parameter a ($a \ll 1$) corresponds to the thin layer of the depletion zone surrounding the cluster, i.e. small value of exclusion volume. This parameter is about 0.002 for Fe-9at%Cr alloy. Hence, one can expect no frustration effect for Fe-9at%Cr alloy and to consider this alloy as dilute Fe-Cr alloy. This statement is confirmed by absence of the interference effect in SANS study [3]. Parameter a is about 0.039 for Fe-12.5a%Cr alloy, for which the interference effect is observed by SANS. Hence, this alloy has to be considered as the concentrated Fe-Cr alloy. On the other hand, values of parameter a as well as of the upper limits of constant exclusion volume estimated from SANS [7] are not so high for irradiated Fe-12.5a%Cr alloy. That's why the taking into account of the frustration effect empirically by the use of the thermodynamic free energy expression [17] is found successful in CD modeling of Cr precipitates in this alloy. The complimentary accounting of the diffusion field effects according to [13] provides the best fit to SANS data for value of the surface tension $\gamma^{cl,m}$ about 0.17 J/m² (instead of 0.028 J/m² in [7], where these effects are ignored). Note that obtained result is in a good agreement with data of $\gamma^{cl,m}$ obtained in [27] by the Cluster Expansion method: 0.218 J/m², 0.155 J/m², and 0.048 J/m² for the coherent interfaces [100], [111] and [110], respectively.

The unsuccessful application of the CD scheme of our study to the irradiated Fe-9at%Cr alloy, which includes the dislocation loops decorated by Cr atoms, shows the necessity to consider the formation and migration of Fe-Cr interstitials as additional link between the CD master equations for the self-defects and the CD master equations for the Cr precipitates in this alloy.

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Cluster dynamic (CD) simulations according to Ref. [19], including the effect of the chromium concentration on the SIA diffusivity [11], are able to reproduce the experimental TEM data [1] for Fe-12.5at%Cr on the SIAC size distribution. A saturation behavior of the total number density of SIAC in neutron irradiated Fe-12.5at%Cr model alloys for neutron exposure greater than 0.006 dpa is predicted. The CD simulations also indicate the presence of VC with radii less than 0.5 nm and a strong SIAC peak with a mean diameter of about 0.5 nm, both invisible in SANS and TEM experiments because of the resolution limits of these techniques.

Ratio of exceeding of solute concentration to the concentration of solute atoms in cluster (precipitate) as well as SANS study can be used to estimate apriori the effect of the exclusion volume in CD simulations of Cr precipitates in Fe-Cr alloys. Taking into account of the frustration effect empirically by the use of the thermodynamic free energy expression [17] is sufficient for CD modeling of Cr precipitates in the irradiated Fe-12.5at%Cr alloy. By adjusting the surface tension between the α matrix and the α' precipitates and the rate at which Cr monomers are absorbed it was possible to reproduce the SANS data [2] for this alloy. The resulting specific interface energy of 0.17 J/m² is in a good agreement with calculations according to the Cluster Expansion method [27].

Taking into account the formation and migration of Fe-Cr interstitial as additional link between the CD master equations for the self-defects and the CD master equations for the Cr precipitates may lead to an improvement of CD results for irradiated Fe-9at%Cr alloy.

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16 A New Approach to Theoretical Modeling of Nucleation Kinetics in Solid Solutions

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Где господствует дух науки, там творится великое и малыми средствами.

Н. И. Пирогов

Where the spirit of science dominates, great things may be achieved by marginal means.

N. I. Pirogov

Abstract

A new method for theoretically describing the nucleation kinetics in solid solutions, which decreases the time of calculations by a factor of several tens, has been developed. This result has been achieved using a combination of the kinetic equation for distributions of clusters with respect to the number of particles and with respect to the radius. The distributions with respect to the number of particles and with respect to the radius have been used for small and large clusters, respectively. The concentration of molecules near the surface of clusters has been determined from the asymptotic solution of the diffusion equation. For subcritical clusters, the concentration of molecules near the cluster surface has been taken to be equal to the average concentration in the solid solution. The results obtained from the calculation of the time dependencies of the increase in the concentration and average radius of clusters agree well with experiment.

16.1 Introduction

In order to analyze nucleation kinetics in solid solutions, different analytical and numerical solutions of kinetic equations are used [1-7]. From our point of view the numerical solutions of kinetic equations are more suitable because they allow one to use a minimal number of additional mathematical assumptions and to take into consideration all physical features of the model.

In our previous works [8-10], the kinetics of CuCl nucleation in a photo-chromic glass was experimentally studied at all stages. We obtained the time dependencies of the amount of a new phase [8], the average radius [9, 10] and concentration of clusters [10], as well as the cluster size distribution functions [9]. When solving the kinetic equation for a distribution of clusters with respect to the number of molecules in a cluster, one has to solve numerically a huge number of equations that increases as the third power with an increase in the maximum radius of the clusters involved. A transition to the description in terms of continuous number of particles [1, 6, 7] can lead to additional errors for small clusters and requests unequal step of net for decreasing the calculation time.

Therefore, we have used kinetic equations for the distribution of clusters with respect to the radii. This equation can introduce significant errors for very small clusters. In order to avoid these errors, for very small clusters we have used the equation for the distribution of clusters with respect to the number of particles. Both solutions are joined together in the region of clusters containing approximately 100 particles. For subcritical clusters, the Knudsen kinetic regime is used that is the monomer concentration near to the surface is set to be equal to the average one in the solution. For supercritical clusters for determination of concentration near the surface of a cluster the asymptotic solution of the diffusion equation is applied. The proposed method decreases the time of calculations by a factor of several tens and makes it possible to perform calculations on a personal computer.

The present work is devoted to comparing the results of the calculation with experimental data. This comparison has demonstrated good agreement. The parameters of the medium, which are significant for the nucleation kinetics, have been estimated.

16.2 Kinetic Equation for the Distribution of Clusters with Respect to their Radii

The formation and growth of clusters are determined significantly by their thermodynamic properties. The Gibbs energy (work) of formation of a cluster of n monomers [1, 2, 4-7] has the following form:

$$\Delta G = -n\Delta\mu + \alpha\sigma n^{2/3} , \qquad \alpha = 4\pi (3\omega/4\pi)^{2/3} , \qquad (16.1)$$

where σ is the surface tension coefficient for the cluster, $\omega = 1/c_L$ is the volume per molecule in the cluster (c_L is the concentration of molecules in a liquid cluster), and $\Delta \mu$ is the difference in the chemical potentials of the substance dissolved in an "infinite" cluster and in a solid solution. Since the concentration of monomers in the glass is very low, the solid solution can be treated as an ideal solution. Then, we can write

$$\Delta \mu = \mu - \mu_c = k_B T \ln(S) , \qquad (16.2)$$

where S is the supersaturation for a flat surface.

The radii of the clusters are given by

$$r_n = \sqrt[3]{\frac{3n}{4\pi c_L}} \,. \tag{16.3}$$

Let us express the work of formation of a cluster through the cluster radius

$$\Delta G = (4/3)\pi r^3 c_L k_B T \ln(S) - 4\pi r^2 \sigma .$$
(16.4)

For the critical radius, the work of cluster formation has a maximum, which leads to the decay of subcritical clusters and to the growth of supercritical clusters:

$$r_c = \frac{2\sigma}{k_B T c_L \ln S} = \frac{2\sigma\omega}{k_B T \ln S} .$$
(16.5)

The critical radius can be found from the condition $c = c_s$, where c_s is the concentration of the saturated vapor over the cluster surface. This concentration can be found using the Kelvin formula [11]

$$c_s = c_\infty \exp\left(\frac{2\sigma\omega}{rk_BT}\right) \ . \tag{16.6}$$

The kinetic equation for the distribution function of clusters with respect to the number of particles has the form [4-7]

$$\frac{\partial f_n}{\partial t} = w_{n-1}^+ f_{n-1} + w_{n+1}^- f_{n+1} - w_n^+ f_n - w_n^- f_n , \qquad (16.7)$$

where f_n is the number of clusters containing *n* particles, w_n^+ is the probability of absorption of one molecule by the cluster per second, and w_n^- is the probability of emission of one molecule by the cluster. We assume that all molecules incident on the cluster surface are absorbed. Then, we have

$$w_n^+ = 4\pi r_n^2 c_1 V_T , \qquad w_n^- = 4\pi r_{n-1}^2 c_s V_T , \qquad (16.8)$$

where c_1 is the concentration of molecules in the vicinity of the cluster surface; V_T is the effective velocity of molecules, which is determined by the diffusion coefficient $D = aV_T$; a is the mean jump length of ions, and $\tau = a/V_T$ is the time of one jump.

Eq. (16.7) is used only for clusters containing no more than m particles. From this equation, we can find all values of f_n , except for f_1 and f_m . The number of free monomers f_1 can be found from the condition that the total number of molecules is constant, and f_m is determined from the solution of the equation for the distribution with respect to the radii. This approach allows us to reduce the time of calculations significantly. In particular, in order to solve the equation for the distribution with respect to the number of particles, one has to solve about 6400 equations if the maximum radius of the considered clusters is 4 nm. In our method, the number of equations is only 300. The distributions are joined when the number of molecules in the cluster is equal to m for the corresponding radius r_0 . For large radii of clusters, the gain (decrease in the number of equations) is even more significant. The number of equations, which should be solved to determine the distribution with respect to the number of the maximum radius, whereas the number of equations required to determine the distribution with respect to the radius increases as only the first power. Equations for radius distributions are given in [1, 2, 5, 6].

For our purposes, we need a kinetic equation for the cluster radius distribution function that most closely corresponds to Eq. (16.7) and allows us to find the values of f(n) at individual sites with a good accuracy for sufficiently small values of n. The coefficients of this equation should be expressed through the coefficients of Eq. (16.7). Therefore, we perform a complete derivation of the kinetic equation for the distribution of molecules with respect to the radii. Let us assume that b_n is the increment of the cluster radius after addition of one molecule. Then, we can write

$$b_n = 1/4\pi r_n^2 c_L , (16.9)$$

$$w_n^+ b_n^+ = c_1 V_T / c_L , \qquad w_n^- b_n^- = c_s V_T / c_L .$$
 (16.10)

We determine the cluster radius distribution function

$$\varphi(r) = \frac{f(n)}{\bar{b}_n} , \qquad (16.11)$$

where f(n) is the distribution function with respect to the number of particles in the cluster. We consider f(n) in the interval $[r - 0.5b_{n-1}, r + 0.5b_n]$; therefore, here, we have $\bar{b}_n = 0.5(b_{n-1} + b_n)$.

The flux of clusters incoming at the lower boundary of this interval is given by

$$J_{+} = -w^{-}(r)\bar{b}_{n}\varphi(r) + w^{+}(r-b_{n-1})\bar{b}_{n-1}\varphi(r-b_{n-1}), \qquad (16.12)$$

the flux of clusters outgoing at the upper boundary of the interval is given by

$$J_{-} = w^{+}(r)\bar{b}_{n}\varphi(r) - w^{-}(r+b_{n})\bar{b}_{n+1}\varphi(r+b_{n}).$$
(16.13)

Here, $r = r_n$ is the radius of the cluster containing n molecules.

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Then, we have $b(\partial \varphi / \partial t) = J_+ - J_-$, or

$$J_{+} - J_{-} = -w^{-}(r)\bar{b}_{n}\varphi(r) + w^{+}(r - b_{n-1})\bar{b}_{n-1}\varphi(r - b_{n-1}) - u^{+}(r)\bar{b}_{n}\varphi(r) + w^{-}(r + b_{n})\bar{b}_{n+1}\varphi(r + b_{n}) .$$
(16.14)

Expanding it into a series, we obtain

$$J_{+} - J_{-} = -b_{n-1} \frac{\partial}{\partial r} \left(w^{+} \bar{b} \varphi \right) + 0.5 b_{n-1}^{2} \frac{\partial^{2}}{\partial r^{2}} \left(w^{+} \bar{b} \varphi \right) + b_{n} \frac{\partial}{\partial r} \left(w^{-} \bar{b} \varphi \right) + 0.5 b_{n}^{2} \frac{\partial^{2}}{\partial r^{2}} \left(w^{-} \bar{b} \varphi \right)$$
(16.15)

Next, we write

$$b_n w_n^+(r) = w(r) + 0.5u(r) , \qquad b_{n-1} w_n^-(r) = w(r) - 0.5u(r) .$$
(16.16)

Under the derivatives, we can leave only the principal terms in *b*; then,

$$w^{+}\bar{b} = w^{+}b^{+} - w^{+}b\frac{\partial b}{\partial r} = w + 0.5u , \qquad w^{-}\bar{b} = w^{-}b^{-} + w^{-}b\frac{\partial b}{\partial r} = w - 0.5u .$$
(16.17)

Here, $b^+ = b_n$ and $b^- = b_{n-1}$.

Substituting Eq. (16.17) into Eq. (16.15) and leaving only the principal terms in b, quadratic for $w\phi$, and first order for $u\phi$, we obtain

$$b\frac{\partial\varphi}{\partial t} = J_{+} - J_{-} = b\frac{\partial b}{\partial r}\frac{\partial}{\partial r}\left(w\varphi\right) + b^{2}\frac{\partial^{2}}{\partial r^{2}}\left(w\varphi\right) - \frac{\partial}{\partial r}\left(u\varphi\right) = b\frac{\partial}{\partial r}b\frac{\partial}{\partial r}\left(w\varphi\right) - \frac{\partial}{\partial r}\left(u\varphi\right) .$$
(16.18)

From here, we obtain the kinetic equation for the distribution of clusters with respect to their radii

$$\frac{\partial\varphi}{\partial t} = \frac{\partial b}{\partial r}\frac{\partial}{\partial r}\left(w\varphi\right) + b\frac{\partial^2}{\partial r^2}\left(w\varphi\right) - \frac{\partial}{\partial r}\left(u\varphi\right) = \frac{\partial}{\partial r}b\frac{\partial}{\partial r}\left(w\varphi\right) - \frac{\partial}{\partial r}\left(u\varphi\right) . \tag{16.19}$$

The quantities w and u are expressed through the physical characteristics of the system: $w = (c_1 + c_s)V_T/c_L$ and $u = (c_1 - c_s)V_T/c_L$.

The growth and decrease in the number of clusters are random processes; therefore, Eq. (16.19) is a Fokker-Planck equation [3]. This equation satisfies the law of conservation of the number of clusters: the total number of clusters within each range of radii changes only at the expense of clusters incoming and outgoing at the boundaries of the interval. The equation contains two contributions: the first contribution describes the diffusion with respect to the radii of clusters, and the second contribution describes the regular change in the cluster radius.

In order to determine c_1 , it is necessary to solve the diffusion equation for c together with solving the equation for growth of the cluster. The diffusion equation in spherical coordinates has the following form (c depends only on r; here r is the radial coordinate) [12]:

$$\frac{\partial c}{\partial t} = \frac{a V_T}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) . \tag{16.20}$$

The boundary conditions for c are as follows: the diffusion flux at the cluster surface is equal to the flux absorbed by the cluster

$$aV_T \left(\frac{\partial c}{\partial r}\right)_R = V_T \left(c_1 - c_s\right) , \qquad (16.21)$$

at infinity, the quantity c tends to the average concentration.

The stationary solution of the diffusion equation introduces an essential error into initial stage of growth of supercritical clusters. Since we are interested in the initial nucleation stage, we use the asymptotic
solution of the diffusion equation from the medium into a sphere of constant radius R, which can be obtained from results in [12]. For the concentration near the cluster surface, it gives

$$c_{1} = c_{0} - \frac{(c_{0} - c_{s})R}{a + R} \left\{ 1 - \frac{1}{\sqrt{\pi}} \left(\frac{R}{a + R} \frac{1}{\sqrt{t}} - \frac{1}{2} \left(\frac{R}{a + R} \frac{1}{\sqrt{t}} \right)^{3} \right) \right\}$$
(16.22)

Here, t is the time determined by the number of jumps and R is the current value of the cluster radius. Ignoring the terms containing time, we obtain a steady-state solution that corresponds to the diffusion approximation for the probabilities of emission and absorption of molecules.

A comparison of this solution with the exact numerical solution of the diffusion equation Eq. (16.20) together with the equation for the growth of a single cluster shows that Eq. (16.22) is a good approximation for times corresponding to more than 200 jumps. The steady state solution introduces a considerable error even for 10000 jumps.

16.3 Results of Computations of the Nucleation Kinetics at 500°C

In the present work, we investigated a photo-chromic glass of the composition $9.3Na_2O-62SiO_2-22B_2O_3-1.8Al_2O_3-2.1SnO_2$, in which 0.6 mol% CuO and 1.7 mol% NaCl were added. The molar mass of the glass is 65.6 g/mol, the density of the glass is 2.34 g/cm³, the refractive index is 1.5, the density of copper chloride CuCl is 3.7 g/cm³, and the molar mass of copper chloride is 99 g/mol. Since the glass can usually absorb no more than 0.7 mol% Cl, the concentration of chlorine ions is approximately equal to the concentration of copper ions. The volume concentration of Cu and Cl ions is equal to 0.13 nm⁻³ in the glass and 22.5 nm⁻³ in the liquid cluster. The volume per molecule is $\omega_L = 0.044$ nm³ in the liquid and $\omega_G = 7.75$ nm³ in the glass.

Aluminoborosilicate glasses of the composition close to our glass have an inhomogeneous structure [13]. They consist of a silica network with rather large inclusions of sodium borate glass. The glass network contains approximately 95 mol% SiO₂. The inclusions contain almost all sodium and approximately 90 mol% B. The sizes of the inclusions are approximately equal to 100 nm [13].

The precipitation of CuCl is due to the decomposition of the complexes [14, 15]

$$[BO_{3/2} Cl] Na \rightarrow [BO_{3/2}] + NaCl$$

$$[BO_{3/2} Cl] Cu \rightarrow [BO_{3/2}] + CuCl$$
.

Molar volumes in the glass are: $SiO_2 - 27 \text{ cm}^3/\text{mol}$, $B_2O_3 - 30 \text{ cm}^3/\text{mol}$, and $Na_2O - 20 \text{ cm}^3/\text{mol}$ [13]. The molar volume of the glass is 28 cm³/mol, including 8.5 cm³/mol of the sodium borate glass. Therefore, the volume fraction of the sodium borate glass in this glass as a whole is equal to 0.3. If CuCl is assumed to be uniformly distributed throughout the glass, the CuCl concentration will be too low, i.e., 0.13 nm⁻³, which is slightly larger than the equilibrium concentration of AgCl in the sodium borate glass [5]. Hence, we assume that CuCl clusters are formed only in the sodium borate part of the glass and their local volume concentration is approximately three times higher than the concentration averaged over the glass. We also assume that the major part of the copper and chlorine ions is also contained in the sodium borate inclusions. These assumptions are essential when we compare calculations with experiments.

We use using a combination of the equations for the distributions with respect to the number of particles in a cluster and with respect to the cluster radii. In this case, we solve the equation for the distribution with respect to the number of particles for clusters with radii smaller than 0.94 nm and the equation for the distribution with respect to the radii for clusters with large radii. We use the standard mean field approximation [5], in which the concentration of monomers is taken to be constant over the entire volume and is determined from the condition of conservation of the total number of molecules. The local changes in the concentration of monomers were taken into account only in the vicinity of the surface of the clusters, because they determine the probability of capture of a molecule by a cluster.

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For supercritical clusters, we use the asymptotic solution to the equation of diffusion from the medium into a sphere. For subcritical clusters, there occur both the decrease in the radius due to walk-off and the increase in the radius due to diffusion in the size space. In this case, it is natural to assume that the concentration near the surface of such clusters is equal to the average concentration of monomers; i.e., we can use the Knudsen kinetic regime. This does not hold in the case of the completion of the second stage of nucleation, when the critical radius rapidly increases and the formation of new clusters stops.

At a specified temperature, the kinetics in a reduced time (taken in jump periods) is determined by two parameters, i.e., the supersaturation and the surface tension coefficient. The parameter of the calculation is the conventional initial supersaturation S_0 , which is determined by the total concentration of CuCl molecules in the glass. The actual supersaturation is determined by the fraction of monomers w_1 , which is always smaller than unity, because a part of the molecules is bound inside the clusters in the equilibrium distribution. The initial value of w_1 is determined after the equilibrium distribution has been found. At times in the range 100–300 jump steps, the equilibrium has already been reached, but the supercritical cluster formation can still be ignored.



Figure 16.1: Time dependencies of (a) (1) the fraction of monomers, (2) the critical radius and (b) (1) the average radius of clusters, (2) the square of the average radius of clusters.

The rate of formation of supercritical clusters at a given temperature is determined by the critical radius. With an increase in the amount of the new phase, the fraction of monomers decreases, which leads to a decrease in the degree of supersaturation $S = w_1 S_0$ and to an increase in the critical radius. As the radius increases, the rate of formation of new nuclei decreases rapidly. While the critical radius is of the order of 0.7–0.8 nm, the formation of nuclei stops. The second stage of nucleation begins, i.e., the stage of the individual growth of nuclei.

Solving the kinetic equation, after the distribution with respect to the radii was found, we calculated the concentration of the observed clusters and their average radius. The radius was averaged taking into account the cluster volume, because, during measurements, the contribution from each cluster is proportional to the number of molecules inside this cluster; i.e. it is proportional to the cluster volume. All clusters with radii larger than the value r_{min} were treated as the observed clusters. In the experiment, the cluster radius was determined from the position of the maximum in the absorption of exciton and the concentration of clusters was determined from interband absorption; in this case, we assumed that all clusters have the same radius. Hence, apart from the actual concentration, we also calculated the conventional concentration, which is equal to the total volume of the observed clusters divided by the volume of a cluster with the average radius.



Figure 16.2: Time dependencies of the concentration of the observed clusters. The solid line is the result of the calculation.



Figure 16.3: Radius distribution functions of (a) the number of clusters and (b) the cluster volume (in arbitrary units). Curves 1 - 10 correspond to the numbers of 5000, 10000 ... 50000 jumps.

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A comparison of the results of the calculation with the experiment shows that this model provides an adequate explanation of the obtained results at least at a given temperature. The best agreement with the experiment was achieved for $S_0 = 5.55$, $\sigma = 0.09$ N/m, and $r_{min} = 0.9$ nm. The values of these quantities are close to those used in [5]: $S_0 = 5.0$ and $\sigma = 0.08$ N/m. For each minute of real time, there are 85 jumps, which correspond to a very small diffusion coefficient. This was also observed in [5], where the diffusion coefficient was taken to be two orders of magnitude smaller than the measured value for the given glass in order to obtain agreement between calculation and experiment. Most likely, this is associated with the fact that the absorption and emission of Cu⁺ and Cl⁻ ions by the cluster are multistage random processes.

Figure 16.1 shows dependencies of the monomer fraction w_1 , the critical radius r_c , the average radius R of the cluster, and the square of the cluster radius on the reduced time. The time is number of jump periods. It can be seen from these plots that, in the experiment, there is a tendency toward earlier retardation of the increase in the cluster radius as compared to that obtained in the calculation. Figure 16.2 shows the time dependence of the conventional concentration of the observed clusters. In the figure the local concentration in sodium borate inclusions in the glass is presented. The actual concentration changes in a similar manner but has slightly larger values. Figure 16.3 shows the radius distribution function of the number of clusters f(r) and the radius distribution function of the cluster volume $f_v(r)$. The times correspond to 5000, 10000 ... 50000 jump periods.

The distribution functions in our model are more symmetric than those reported in [5]; moreover, they decay toward small radii more rapidly and agree better with the experimental data [9]. It can be seen from these plots that the results of the calculations agree well with the experiment. However, it should be taken into account that the measured values do not completely correspond to the calculated ones. In general, the results obtained correspond to the classical theory of nucleation for the first stage and the transition to the second stage.

16.4 Conclusions

In the present paper, we described our work carried out on the analysis of results of experimental investigations of the nucleation kinetics of CuCl in glass. To do it, the experimental data were compared with calculations of the nucleation kinetics. The calculations used a new method by applying a combination of the kinetic equations for the distribution function of clusters with respect to the number of particles and with respect to the radius. The proposed method makes it possible to decrease the time of calculations by a factor of several tens and to use a usual personal computer. For the probability of absorption of a molecule by a cluster, we have used exact expressions, and the concentration of molecules near the surface of the cluster has been found from the asymptotic solution of the diffusion equation. For subcritical clusters, we have used the Knudsen regime; more specifically, the concentration of molecules near the cluster surface is assumed to be equal to the average concentration of monomers. This has allowed us to obtain the distribution of clusters with respect to the radii, which is in better agreement with the experiment, and to accurately describe both the increase in the number of clusters and the increase in their radius. The supersaturation in glass and the surface tension coefficient of the clusters were determined. The calculations performed for the temperature $T = 500^{\circ}$ C agree well with the experiment.

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 17 Formation and Dissolution of Subcritical Nuclei in Solid Solutions Paisiy M. Valov, Valeri I. Leiman, Olga Yu. Derkacheva, Vladimir M. Maksimov, Evgeni S. Markov, and Alexander O. Vinogradov St. Petersburg State Technological University of Plant Polymers, 198095 St. Petersburg, Ivan Chernykh street 4, Russia

> Делай, что можешь, с тем, что у тебя есть, и там, где ты находишься

> > Теодор Рузвельт

Do what you can with what you have and in the place where you are

Theodore Roosevelt

Abstract

Critical radius r_c is experimentally determined in nucleation processes in solid solutions involving preformed nucleation centers. An ensemble of CuCl nano-melt nuclei of average radius R = 1.2 nm is formed in CuCl solution in glass at $T_0 = 500^{\circ}$ C. The radius r_c increases to r_{c1} as the temperature jumps up to $T_1 = 550 - 650^{\circ}$ C. The nuclei of radii $r < r_{c1}$ are turned to subcritical ones and dissolve. A part of the nuclei ranged in $r > r_{c1}$ increases in size further. A share of dissolved nuclei was determined from changes in their concentration. The concentration of the evolved CuCl phase, the concentration N of CuCl particles and average radius R were determined from intrinsic optical absorption spectra of CuCl nano-crystals at room temperature in the range of wavelengths 300 nm - 450 nm. The radius r_{c1} was most accurately determined at the beginning of dissolving at $T_1 = 650^{\circ}$ C. The nucleation time dependence of r_c at T_1 was determined from calculation of nucleation kinetics under double annealing with taking into account the initial size distribution of CuCl particles and experimental r_{c1} value at the initial annealing time at the temperature T_1 . The calculated and experimental dependencies for R and N kinetics are compared and compliance of the results with each other is demonstrated.

17.1 Introduction

The critical radius r_c of particles (clusters) depends on temperature T and supersaturation $S = c/c_{\infty}$

$$r_c = \frac{2\sigma\omega}{k_B T \ln S} , \qquad (17.1)$$

where c is the concentration of dissolved molecules, c_{∞} is the concentration of molecules of new phase saturated vapor above the flat surface, σ is the surface tension coefficient of a new phase particle, ω is the particle volume per molecule. In the nucleation process, r_c changes continuously as a result of changes in c.

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Due to exponential dependence of c_{∞} on temperature $c_{\infty} = c_{\infty}(T)$, the radius r_c depends on temperature especially strongly. For the temperature changing from T_0 to T_1 , the Clausius-Clapeyron equation gives

$$c_{\infty 1}(T_1) = c_{\infty 1}(T_0) \cdot \frac{T_0}{T_1} \exp\left(\frac{L}{R_0} \left(\frac{1}{T_0} - \frac{1}{T_1}\right)\right) , \qquad (17.2)$$

where $c_{\infty 0}$ and $c_{\infty 1}$ are the saturated vapor concentrations at T_0 and T_1 , respectively, R_0 is the universal gas constant, L is the molar heat of evaporation. L is assumed to be constant for the temperature range under consideration. It is not always possible to estimate the r_c -value even at the beginning of the nucleation process as a complete set of parameters in Eq. (17.1) is usually unknown.



Figure 17.1: Absorption spectrum of CuCl NC (curve 1) – annealing at 500°C (3 hours), absorption spectrum of CuCl NC after subsequent annealing at 600°C (40 minutes) (curve 2). Decomposition of curve 2: $Z_{1,2}$ – exciton (curve 3) and Z_3 – exciton (curve 4); band-to-band absorption spectrum (curve 5) and absorption spectrum of residual Cu ions in glass (curve 6). Curve 0 represents the initial spectrum of the glass sample.

Independent experimental estimation of the critical radius is important for the theory of nucleation in solid solution and for its use in materials science. The critical radius determines the rate of supercritical clusters formation of the new phase. Knowledge of the critical radius and its dependence on nucleation time makes it possible to control the nucleation process, its important kinetic parameters such as the average radius and the concentration of clusters. We have proposed earlier [1] the method for formation of new phase subcritical nuclei and their decay observation with the optical absorption technique [2, 3].

Let us assume that the distribution of new phase clusters of the average radius $R > r_{c0}(T_0)$ with insignificant changes in supersaturation is formed in a solid solution sample for the time of the first annealing at the temperature $T = T_0$. When increasing the temperature from T_0 to T_1 , the supersaturation S decreases very rapidly due to the considerable increase in c_{∞} in accordance with Eq. (17.2). According to Eq. (17.1), the decrease in supersaturation S is accompanied by an increase in r_c up to r_{c1} . In that case, a part of clusters with radii $r < r_{c1}$ becomes subcritical and dissolves (decays) but another part of clusters of radii in the range $r > r_{c1}$ keeps on mainly increasing in the second annealing process at the temperature T_1 . The sharp change in cluster concentration upon jumping temperature T up to T_1 and known radius distribution of initial clusters allow estimating r_{c1} at the temperature T_1 at initial (zero) time. Referencing

17.2 Experiment

of the calculated r_{c1} -function to its experimental values increases reliability of calculations of $r_{c1}(t, T)$ and other nucleation parameters.

This work is aimed at experimental determination of the critical radius under temperature jump from T_0 to T_1 and calculation of $r_{c1}(t, T_1)$ relationships using the procedure developed in [4] for calculating nucleation in solid solution.

17.2 Experiment

Copper halide solid solution in glass matrix transparent in the range of intrinsic absorption of CuCl crystals was investigated. The glass of the main composition $9.3Na_2O - 62SiO_2 - 22B_2O_3 - 1.8Al_2O_3 - 2.1SnO_2$ with added 1.7 mol% NaCl and 0.6 mol% CuO were used in the experiments. When annealing the samples at the temperature 500 °C and higher, diffusion processes lead to CuCl phase clustering in the nano-melt form. On cooling the samples, crystallization takes place and results in occurrence of optical absorption of CuCl nano-crystals (NC) in the glass transparency region. The concentration of CuCl phase, the average radius, and the concentration of CuCl particles (clusters) were determined from absorption spectra at room temperature [2, 3, 5]. The initial annealing temperature (T_0) was equal to 500°C and the annealing time comprised 3 hours. The second annealing was carried out at the temperatures 650°C, 600°C, and 550°C. The second annealing time changed from 10 seconds to 60 minutes.



Figure 17.2: Radius distribution of initial CuCl nuclei. The average radius R = 1.2 nm, half-width 2s = 0.3 nm. r_{c1} -critical radius at the 650 °C ($r_{c1} = 1.3$ nm).

As an example, the absorption spectrum of original glass sample (curve 0), the absorption spectrum of initial CuCl nano-crystals formed for the time of the first annealing stage (curve 1), and that of CuCl nano-crystals formed after the second annealing stage at 600 °C during 40 minutes (curve 2) are shown in Fig. 17.1. This figure demonstrates also decomposition of the fundamental absorption spectrum of CuCl nano-crystals into the bands of exciton and band-to-band absorption [3].

The energy (E_{ex}) of $Z_{1,2}$ -exciton and the absorption coefficient (K_{bb}) for band-to-band transitions were determined while decomposing the experimental absorption spectra of CuCl nano-crystals. Using the energy (E_{ex}) of $Z_{1,2}$ -exciton, the average radius R of CuCl nano-crystals was estimated [6]. Then, kinetic curves for increasing K_{bb} , R and changing concentration N of CuCl nano-crystals were plotted [3, 5]. The coefficient K_{bb} is proportional to the concentration of the evolved CuCl phase. The concentration N of CuCl particles was calculated as a ratio of K_{bb} value to absorption of bulk crystal (10^5 cm^{-1}) [6] followed

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by dividing the resulting value on the average volume of particles equal to $4\pi R^3/3$. Radius distribution of nano-crystals was determined with the method of thermal-exciton analysis of kinetics of nano-crystals melting [2, 5] and calculated using Eq. (6) given in [5]. The initial radius distribution f(r) for CuCl nanocrystals obtained after the first annealing stage at 500 °C is shown in Fig. 17.2. The distribution shape is similar to that of the Gauss distribution with maximum at $r_m = 1.2$ nm and width $0.3r_m$.



Figure 17.3: Kinetics of changes in the average radius R of CuCl particles (triangles) and their concentration N(circles) at 550, 600 and 650 °C in the course in nucleation going on in the sample with preformed nuclei.

The time dependencies of the average radius R and the concentration N of CuCl particles for the second annealing stage at the temperatures 550, 600 and 650 °C are shown in Fig. 17.3. When increasing the temperature from 500 °C to 650 °C, a tenfold and more increase in the initial rate of R growth occurs. The twofold increase in R is observed for two minutes. Then, in 10-20 minutes, the radius growth becomes slower. However, not all initial clusters are growing.

From Fig. 17.3 it follows that 80% of initial clusters dissolve (decay) for 5 minutes upon annealing at 650°C. Taking into account their distribution, the critical radius r_c is equal to 1.3 nm at the temperature 650°C because 80% of the total area is cut off under the curve f(r). The clusters dissolve exponentially, in the beginning of the process τ_1 being equal to 0.26 min.; then the process runs slower, with τ_2 being equal to 2.9 min. Rapid dissolution of initial nuclei at 650°C results in 10% decrease in the total amount of CuCl phase for the first minute. Then, because of the growth of undissolved nuclei, the increase in the CuCl phase is observed. The initial CuCl clusters dissolve also exponentially at the temperatures 600° and 550°, with τ_1 being equal to 7.4 and 39.4 minutes, respectively (Fig. 17.3). In this case, there are no any drastic changes in the nucleation process; therefore it is difficult to determine r_c .

17.3 Calculations

The authors have earlier developed the technique for the mathematical computations describing nucleation in solid solutions and the nucleation dynamics has been calculated for CuCl solid solution in glass at the temperature 500 $^{\circ}$ C [4]. In this investigation glass composition and solution parameters were the same. The technique was applied to CuCl phase nucleation in glass when there were temperature jumps. The combined

17.3 Calculations

equation for particle number distribution function and particle radius distribution is used in the calculations. In case that the particle radius is less than 0.94 nm the equation for particle number distribution is solved and in case the radius is larger than the value fixed above the equation for radius distribution is used. The two solutions are joined at the radius 0.94 nm.

The standard kinetic equation (Eq. (6) in [4]) is used for calculating the particle number distribution function and Eq. (16) deduced in [4] is used to calculate radius distribution function. Here the conventional average field model was used; in this model, concentration of monomers was believed to be constant throughout the volume and determined under the condition the total number of molecules CuCl was kept unchanged. Any local changes in monomer concentration were taken into consideration only in proximity to particle surface because they specified the probability of molecule capture by the cluster.

To determine the concentration of monomers close to the nano-droplet surface, asymptotic solution of the diffusion equation into sphere is used. The diffusive change in the concentration of monomers at the particle surface occurs only if the systematic variation of radius is observed for particles of certain size due to drift in the space of sizes. For "subcritical" particles, there is both decrease in radii as a result of the drift and increase in radii due to diffusion in the space of sizes. These processes are of approximately equal probability, with diffusive increase being slightly dominated. In this case, it is natural to assume the concentration at the surface of these particles to be equal to the average concentration of monomers, i.e. to use the kinetic mode. This is irrelevant to the second annealing stage.



Figure 17.4: Calculated (line) and experimental (circles) results demonstrating dissolution of initial CuCl particles of radii $r < r_{c1}$ at 650 °C and increase in the average radius of the particles.

Firstly, the particle distributions obtained at 500°C for 3 hours as well as the share of monomers and values of supersaturation and critical radius for that moment of time were calculated [4]. Then, using Eq. (17.2) and Eq. (17.1), new values of supersaturation and critical radius were calculated for the temperatures 650° C and 550° C of the second annealing and the kinetic equation was further solved at new values of parameters. Calculated r_{c1} values obtained for the time 1 minute at 650° C were matched to the experimental value of this parameter. The molar heat of evaporation was chosen to be in compliance with the experimental results. Because the surface tension coefficient decreases as a rule with increasing temperature its value was also fitted. Calculated and experimental changes in the concentration N when dissolving initial nuclei at 650° C are shown in Fig. 17.4. In the initial part of kinetic curve for dissolving CuCl nuclei of the radii $r < r_{c1}$, the calculated and experimental results are in good agreement.

The calculated increase in the average radius of clusters is in satisfactory agreement with experimental



Figure 17.5: Calculated distribution of CuCl particles. Curve 1 - distribution of initial CuCl nuclei. Curves 1-14 - distribution in nucleation at 600 °C on time 0 - 46 min. $r_{c1} - r_{c14}$ show critical radius of distribution, respectively.

data in the initial curve section however the experimental curve rises more steeply. Then, at large values of time, the calculated values of radius increase more rapidly. This fact could be caused by calculation of concentration close to the cluster surface and the transition from the kinetic mode to diffusive one.

Calculated changes in radius distribution for CuCl particles when initial nuclei of the radii $r < r_{c1}$ are dissolved and nuclei of $r > r_{c1}$ increase are given in Fig. 17.5. The curve 1 describes distribution of initial CuCl nuclei formed in nucleation process at 500 °C for 3 hours. The curves 2 - 14 demonstrate changes in radius distribution of CuCl particles occurring for initial 46 minutes in nucleation at 600°C. By $r_{c1} - r_{c14}$ critical radius, respectively, is shown.

From the calculations it follows (Fig. 17.6) that at the temperature jump from 500° C to 650° C the critical radius at 650° C rises steeply first up to $r_c = 1.65$ nm ($r_c = 0.65$ nm at 500° C), and then decreases drastically to 1.3 nm in compliance with its experimental behavior. The critical radius increases further as supersaturation decreases in nucleation. It is initially observed also a drastic increase in the amount of free monomers due to rapid evaporation of CuCl nuclei of $r < r_{c1}$. When the temperature jumps from 500° C to 550° C, the similar steep rise in the critical radius r_c up to 0.80 nm takes place and upon decrease in its value to 0.75 nm, a slow growth of the radius is further observed. The amount of monomers first increases unevenly and then decreases slowly in the course of nucleation at 550° C.

Calculated r_c values and kinetics of nucleation are in good agreement with the experimental results at the following values of parameters: conditional initial supersaturation $(S_0)S_0 = 5.4$ at 500 °C (the whole of CuCl consists of monomers); surface tension coefficient (σ) $\sigma = 0.092$ at 500 °C and $\sigma = 0.085$ at 650 °C; molar heat (L) of evaporation molecules from melt CuCl in this glass L = 41 kJ/mol.

17.4 Conclusions

A method is proposed and implemented for determining the critical radius r_c at nucleation in solid solution containing preformed new phase nuclei. The r_c -value was obtained for solid solution of CuCl in glass for the point of temperature jump at the second annealing. Calculated relationship between r_c and the second annealing time was obtained as a result of total calculation of the nucleation kinetics with taking



Figure 17.6: Calculated changes in the critical radius (circles) and the concentration of monomers (triangles) in nucleation at 650 °C and 550 °C in a sample involving preformed CuCl nuclei.

into account the known initial size distribution of CuCl particles and experimental r_c -value in the beginning of the second annealing.

The calculated and experimental time dependencies obtained for the average radius and the concentration of CuCl particles under condition of complicated nucleation, namely double annealing of solid solution, were compared. The calculated and experimental results obtained are in good agreement. All the results confirm efficiency of the technique used for calculation of nucleation kinetics [4].

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18 Can We Rigorously Define Phases in a Finite System?

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Ich möchte was drum geben, genau zu wissen, für wen eigentlich die Taten getan worden sind, von denen man öffentlich sagt, sie seien für das Vaterland getan worden.

Georg Christoph Lichtenberg

Abstract

Here we propose a generalized statistical multi-fragmentation model which includes the liquid phase pressure in the most general form. This approach allows us to get rid of the absolute incompressibility in the description of the nuclear liquid. Also the present model employs a very general form of the surface tension coefficient of nuclear fragments. Such a model is solved analytically for finite volumes by applying the Laplace-Fourier transform method to an isobaric ensemble. A complete analysis of the isobaric partition singularities of this model is also performed for finite volumes. It is shown that the real part of any simple pole of the isobaric partition defines the free energy of the corresponding state, whereas its imaginary part, depending on the sign, defines the inverse decay/formation time of this state. The developed formalism allows us to exactly define the finite volume analogs of gaseous, liquid and mixed phases of the class of similar models from the first principles of statistical mechanics and demonstrate the pitfalls of earlier works. The finite width effects for large nuclear fragments and quark gluon bags are also discussed.

18.1 Introduction

The necessity to extend the theory of 1-st order liquid-gas phase transition (PT) is determined both by an academic interest to this problem and by practical purpose to study phase transformations in systems that do not have a thermodynamic limit. The latter are of particular interest for nuclear physics of intermediate energies where the nuclear liquid-gas PT [1, 2, 3] is studied in the presence of the Coulomb interaction. Also recently there is developing a great attention to PTs in finite systems because of the searches for a new state of matter, the quark gluon plasma, and its (tri)critical endpoint in the relativistic collisions of heavy ions [4, 5, 6].

This problem has a long history, but up to now it is not resolved. One of the first attempt of its resolving was advanced by T. Hill [7] whose approach is based on the formulation of thermodynamics of small systems. Hill's ideas were developed further in [8], where the authors claimed to establish a one-to-one

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correspondence between the bimodal structure of the partition of measurable quantity B, known on average, and the properties of the Lee & Yang zeros [9] of this partition in the complex g-plane. However, the analysis of such a definition performed in [10] on the basis of exactly solvable model for finite volumes [11] shows that the definition of phases suggested in [8] cannot be established experimentally under any circumstances. Therefore, although many important aspects of the nuclear liquid-gas PT related to finite volumes of studied nuclear systems are well understood [1, 3, 12] the systematic and rigorous extension of the PT theory to finite systems is just at the very initial stage in spite of too optimistic beliefs as expressed in Ref. [13].

Therefore, here we would like to discuss a powerful mathematical method invented recently [11], the Laplace-Fourier transform (LFT), that allows one not only to solve analytically several statistical models for finite volumes or surfaces, but also to establish a common framework to study the deconfinement PT and nuclear liquid-gas PT in finite systems. LFT was successfully applied to the simplified version of the statistical multi-fragmentation model (SMM) [14, 15] in finite volumes [11], to the analysis of surface partition and surface entropy of large but finite physical clusters for a variety of statistical ensembles [16] and to the exact solution of the gas of quark gluon bags [17] for finite volumes [10]. Furthermore, using the theorems proven in [10, 18] it is possible to straightforwardly apply the exact representation of the finite volume grand canonical partition (GCP) of the gas of quark gluon bags model [10] to other exactly solvable statistical models of the deconfinement PT which were solved recently in thermodynamic limit [19, 20, 21, 22, 23]. Finally, we would like to stress that our approach to study PTs in finite systems is not restricted to the models without long-range Coulomb-like interaction. Our strategy is as follows: to firmly define the phases in finite systems without the long-range interaction, and then to extend this approach to the systems with the Coulomb-like interaction. This work is mainly devoted to the first of these tasks for which the finite volume solution of the simplified version of the SMM (and similar models) is analyzed here. In addition, here we generalize the simplified version of the SMM [14, 15] in order to repair such its defects as an existence of limiting baryonic density and an absence of a (tri)critical endpoint for the values of the Fisher exponent $\tau > 2$ [24, 25].

The work is organized as follows. Section 18.2 is devoted to the formulation of the generalized SMM. Section 18.3 contains an introduction into the LFT technique. The analysis of the singularities of the isobaric partition of the suggested model is given in Section 18.4. In Sections 18.5 and 18.6 we, respectively, discuss the location of the isobaric partition singularities in complex plane for the case without PT and with PT in thermodynamic limit. The finite volume analogs of phases along with the critique of Hill's treatment of 1-st order PT in finite systems are presented in Section 18.6. Finally, Section 18.7 contain our concluding remarks.

18.2 Generalized SMM

The system states in the standard SMM are specified by the multiplicity sets $\{n_k\}$ $(n_k = 0, 1, 2, ...)$ of k-nucleon fragments. The partition function of a single fragment with k nucleons is [1]

$$V\phi_k(T) = V \left(mTk/2\pi\right)^{3/2} z_k$$

where k = 1, 2, ..., A (A is the total number of nucleons in the system), V and T are, respectively, the volume and the temperature of the system, m is the nucleon mass. The first two factors on the right hand side (r.h.s.) of the single fragment partition originate from the non-relativistic thermal motion and the last factor, z_k , represents the intrinsic partition function of the k-nucleon fragment. Therefore, the function $\phi_k(T)$ is a phase space density of the k-nucleon fragment. For k = 1 (nucleon) we take $z_1 = 4$ (4 internal spin-isospin states) and for fragments with k > 1 we use the expression motivated by the liquid drop model (see details in Ref. [1]): $z_k = \exp(-f_k/T)$, with the fragment free energy of the simplified SMM

$$f_k = -W(T) k + \sigma(T) k^{2/3} + (\tau + 3/2)T \ln k , \qquad (18.1)$$

with $W(T) = W_o + T^2/\epsilon_o$. Here $W_o = 16$ MeV is the bulk binding energy per nucleon. T^2/ϵ_o is the contribution of the excited states taken in the Fermi-gas approximation ($\epsilon_o = 16$ MeV). $\sigma(T)$ is the

18.2 Generalized SMM

temperature dependent surface tension parameterized in the following relation

$$\sigma(T) = \sigma_{\rm o} \left[\frac{(T_c^2 - T^2)}{(T_c^2 + T^2)} \right]^{5/4}$$
(18.2)

with $\sigma_0 = 18$ MeV and $T_c = 18$ MeV ($\sigma = 0$ at $T \ge T_c$). The last contribution in Eq. (18.1) involves the Fisher's term with dimensionless parameter τ . The free energy Eq. (18.1) does not contain symmetry and Coulomb contributions which are neglected. Hence it is called a simplified version of the SMM which was suggested and studied numerically in Refs. [14, 15]. However, its investigation appears to be of principal importance for studies of the liquid-gas phase transition in finite systems.

From an exact analytical solution of the simplified SMM [24] it follows that the baryonic density has a maximum value max $\rho = 1/b = \rho_0 = 0.16 \text{ fm}^{-3}$ in the limit $\mu \to \infty$ (here ρ_0 is the normal nuclear density). This, however, contradicts results of experiments on heavy ion collisions [26] in which the nuclei can be compressed to much higher densities. In order to avoid such a behavior we generalize the SMM to the GSMM which includes the pressure of the liquid phase $p_l(T, \mu)$ in a general form. Then the free energy of the fragments with k > 1 reads as

$$f_k^G = \mu \, k - p_l(T,\mu) \, b \, k + \sigma(T) \, k^{2/3} + (\tau + 3/2) T \ln k \,, \tag{18.3}$$

where the pressure of a liquid phase is (at least) a double differentiable function of its arguments that contains the temperature dependent binding energy W(T). Also it is assumed that the function $p_l(T, \mu)$ reproduces all the typical properties of a liquid phase. An extremely important property of the GSMM is that the liquid phase equation of state $p_l(T, \mu)$ can be taken from some microscopic models including the mean-field ones, but the resulting model will be a truly statistical one since the analytical properties of the isobaric partition singularities remain unmodified in this case.

The GSMM nucleons are considered as in the SMM. Note that the pressure of a liquid phase should approach the asymptotics $p_l \sim T^2$ for $T \to \infty$ and $p_l \sim \mu^2$ for $\mu \to \infty$ to respect a causality condition [27]. Therefore, the simplest parameterization of the liquid phase pressure which at low densities recovers the usual SMM result and at high densities obeys such asymptotics can be written as follows

$$p_l(T,\mu) = \frac{\mu(1+a\,\mu) + W(T)}{b} , \qquad (18.4)$$

where a positive constant a > 0 has to be fixed by the condition that at low densities it behaves as $a|\mu| \ll 1$. However, in what follows we study the most general form of the liquid phase pressure.

In addition to the new parameterization of the free energy of the k-nucleon fragment Eq. (18.3) we propose to consider a more general parameterization of the surface tension coefficient

$$\sigma(T) = \sigma_{\rm o} \left| \frac{T_c - T}{T_c} \right|^{\zeta} \operatorname{sign}(T_c - T) , \qquad (18.5)$$

with $\zeta = \text{const} \ge 1$ and $T_c = 18$ MeV. In contrast to the Fisher droplet model [28] and the SMM [1], the GSMM surface tension Eq. (18.5) is negative above the critical temperature T_c . It is necessary to stress that there is nothing wrong or unphysical with negative values of surface tension coefficient Eq. (18.5), since $\sigma k^{\frac{2}{3}}$ in Eq. (18.3) is the surface free energy of the fragment of mean volume b k and, hence, as any free energy, it contains the energy part e_{surf} and the entropy part s_{surf} multiplied by temperature T [28]. Therefore, at low temperatures the energy part dominates and the surface free energy is positive, whereas at high temperatures the number of fragment configurations with large surface drastically increases and it exceeds the Boltzmann suppression and, hence, the surface free energy becomes negative since $s_{surf} > \frac{e_{surf}}{T}$. By this reason negative values of the surface tension coefficient were recently employed in a variety of exactly solvable statistical models for the deconfinement PT [19, 20, 21, 29]. For the first time this fact was derived within the exactly solvable models for surface deformations of large physical clusters [16]. Very recently two of us derived a relation between the surface tension of large quark gluon bags and the string tension of two static color charges measured by the lattice QCD [30] from which it was possible to conclude that at high temperatures the surface tension coefficient of quark gluon bags should be negative [30, 31].

Furthermore, a thorough analysis of the temperature dependence of the surface tension coefficient in ordinary liquids [33, 32] shows not only that the surface tension coefficient approaches zero, but, in contrast to the widespread beliefs, for many liquids the full T derivative of σ does not vanish and remains finite at T_c : $\frac{d\sigma}{dT} < 0$ [32]. Therefore, just the naive extension of these data to the temperatures above T_c would lead to negative values of surface tension coefficient at the supercritical temperatures. On the other hand, if one, as usually, believes that $\sigma \equiv 0$ for $T > T_c$, then it is absolutely unclear what physical process can lead to simultaneous existence of the discontinuity of $\frac{d\sigma}{dT}$ at T_c and the smooth behavior of the pressure's first and second derivatives at the cross-over. Therefore, we conclude that negative values of the surface tension coefficient at supercritical temperatures at how provide the surface tension coefficient at supercritical temperatures.

The existence of negative values of the surface tension coefficient in Eq. (18.5) leads to entirely new result for the GSMM compared to that one of the SMM for $\tau > 2$. Thus, for $\tau > 2$ the SMM predicts the existence of the 1-st order PT up to infinite values of T [18, 24, 25]. Clearly, such a result does not correspond to the experimental findings and is usually understood as a pitfall of this model. However, the negative values of σ in Eq. (18.5) lead to a different result in the GSMM. Using the technique developed in [19, 29] it is easy to show that in this case there is a cross-over for $T > T_c$ and, hence, for $\tau > 2$ the GSMM has a critical point at $T = T_c$.

18.3 The Laplace-Fourier Transformation Technique

To evaluate the grand canonical partition (GCP) of the GSMM for finite volumes first we define the canonical partition function (CPF) of nuclear fragments. The latter has the following form:

$$Z_A^{id}(V,T) = \sum_{\{n_k\}} \left[\prod_{k=1}^A \frac{[V \phi_k(T)]^{n_k}}{n_k!} \right] \delta(A - \sum_k k n_k) \,.$$
(18.6)

In Eq. (18.6) the nuclear fragments are treated as point-like objects. However, these fragments have nonzero proper volumes and they should not overlap in the coordinate space. In the excluded volume (van der Waals) approximation this is achieved by substituting the total volume V in Eq. (18.6) by the free (available) volume $V_f \equiv V - b \sum_k kn_k$, where b is eigen volume of nucleon. Therefore, the corrected CPF becomes: $Z_A(V,T) = Z_A^{id}(V - bA,T)$.

The calculation of $Z_A(V,T)$ is difficult due to the constraint $\sum_k kn_k = A$. This difficulty can be partly avoided by evaluating the GCP function:

$$\mathcal{Z}(V,T,\mu) \equiv \sum_{A=0}^{\infty} \exp\left(\frac{\mu A}{T}\right) Z_A(V,T) \Theta(V-bA) , \qquad (18.7)$$

where μ denotes a chemical potential. Nevertheless, the calculation of \mathcal{Z} is still rather difficult. The summation over $\{n_k\}$ sets in Z_A cannot be performed analytically because of additional A-dependence in the free volume V_f and the restriction $V_f > 0$. This problem was resolved [24] by the Laplace transformation method to the so-called isobaric ensemble [17].

To study the PT in finite systems here we consider a more strict constraint $\sum_{k}^{K(V)} k n_k = A$, where the size of the largest fragment $K(V) = \alpha V/b$ cannot exceed the total volume of the system (the parameter $\alpha \leq 1$ is introduced for convenience). The case K(V) = const considered in [34] is also included in our treatment. A similar restriction should be also applied to the upper limit of the product in all partitions $Z_A^{id}(V,T), Z_A(V,T)$ and $\mathcal{Z}(V,T,\mu)$ introduced above (how to deal with the real values of K(V), see [11]).

18.4 Isobaric Partition Singularities

Then the model with such a constraint, the CGSMM, cannot be solved by the Laplace transform method, because the volume integrals cannot be evaluated due to a complicated functional V-dependence. However, the CGSMM can be solved analytically with the help of the following identity [11]

$$G(V) = \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{2\pi} e^{i\eta(V-\xi)} G(\xi), \qquad (18.8)$$

which is based on the Fourier representation of the Dirac δ -function. The representation Eq. (18.8) allows us to decouple the additional volume dependence and reduce it to the exponential one, which can be dealt with by the usual Laplace transformation in the following sequence of steps

$$\hat{\mathcal{Z}}(\lambda, T, \mu) = \int_{0}^{\infty} dV \, e^{-\lambda V} \, \mathcal{Z}(V, T, \mu) = \int_{0}^{\infty} dV' \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{2\pi} \, e^{i\eta(V'-\xi)-\lambda V'} \times \\
\sum_{\{n_k\}} \left[\prod_{k=1}^{K(\xi)} \frac{1}{n_k!} \left\{ V' \, \phi_k(T) \, e^{\frac{(\mu-(\lambda-i\eta)bT)k}{T}} \right\}^{n_k} \right] \Theta(V') = \\
\int_{0}^{\infty} dV' \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{2\pi} \, e^{i\eta(V'-\xi)-\lambda V'+V'\mathcal{F}(\xi,\lambda-i\eta)} \,.$$
(18.9)

After changing the integration variable $V \to V' = V - b \sum_{k}^{K(\xi)} k n_k$, the constraint of Θ -function has disappeared. Then all n_k were summed independently leading to the exponential function. Now the integration over V' in Eq. (18.9) can be straightforwardly done resulting in

$$\hat{\mathcal{Z}}(\lambda, T, \mu) = \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{2\pi} \frac{e^{-i\eta\xi}}{\lambda - i\eta - \mathcal{F}(\xi, \lambda - i\eta)} , \qquad (18.10)$$

where the function $\mathcal{F}(\xi, \tilde{\lambda})$ is defined as follows

$$\mathcal{F}(\xi,\tilde{\lambda}) = \sum_{k=1}^{K(\xi)} \phi_k(T) \ e^{\frac{(\mu - \tilde{\lambda} bT)k}{T}} = \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} \left[z_1 \ e^{\frac{\mu - \tilde{\lambda} bT}{T}} + \sum_{k=2}^{K(\xi)} k^{-\tau} e^{\frac{(p_l(T,\mu) - \tilde{\lambda} T)bk - \sigma k^{2/3}}{T}} \right].$$
(18.11)

This result generalizes the finite volume solution of the simplified SMM obtained in [11, 10].

As usual, in order to find the GCP by the inverse Laplace transformation, it is necessary to study the structure of singularities of the isobaric partition Eq. (18.11).

18.4 Isobaric Partition Singularities

The isobaric partition Eq. (18.11) of the CGSMM is, of course, more complicated than its SMM analog found in thermodynamic limit [24] because for finite volumes the structure of singularities in the CGSMM is much richer than in the SMM, and they match in the limit $V \rightarrow \infty$ only. To see this let us first make the inverse Laplace transform:

$$\mathcal{Z}(V,T,\mu) = \int_{\chi-i\infty}^{\chi+i\infty} \frac{d\lambda}{2\pi i} \,\hat{\mathcal{Z}}(\lambda,T,\mu) \, e^{\lambda V} = \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{2\pi} \int_{\chi-i\infty}^{\chi+i\infty} \frac{d\lambda}{2\pi i} \, \frac{e^{\lambda V - i\eta\xi}}{\lambda - i\eta - \mathcal{F}(\xi,\lambda - i\eta)} = \int_{-\infty}^{+\infty} \frac{d\xi}{2\pi} \int_{-\infty}^{+\infty} \frac{d\eta}{2\pi} e^{i\eta(V-\xi)} \sum_{\{\lambda_n\}} e^{\lambda_n V} \left[1 - \frac{\partial \mathcal{F}(\xi,\lambda_n)}{\partial \lambda_n}\right]^{-1}, \quad (18.12)$$

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where the contour λ -integral is reduced to the sum over the residues of all singular points $\lambda = \lambda_n + i\eta$ with n = 1, 2, ..., since this contour in the complex λ -plane obeys the inequality $\chi > \max(\operatorname{Re}\{\lambda_n\})$. Now both remaining integrations in Eq. (18.12) can be performed, and the GCP becomes

$$\mathcal{Z}(V,T,\mu) = \sum_{\{\lambda_n\}} e^{\lambda_n V} \left[1 - \frac{\partial \mathcal{F}(V,\lambda_n)}{\partial \lambda_n} \right]^{-1},$$
(18.13)

i.e. the double integral in Eq. (18.12) simply reduces to the substitution $\xi \to V$ in the sum over singularities. In [11] this remarkable result was formulated as a theorem, which now is generalized to more complicated forms of the liquid phase pressure.

The simple poles in Eq. (18.12) are defined by the equation

$$\lambda_n = \mathcal{F}(V, \lambda_n) \,. \tag{18.14}$$

In contrast to the usual SMM [24] the singularities λ_n are (i) volume dependent functions, if K(V) is not constant, and (ii) they can have a non-zero imaginary part, but in this case there exist pairs of complex conjugate roots of Eq. (18.14) because the GCP is real.

Introducing the real R_n and imaginary I_n parts of $\lambda_n = R_n + iI_n$, we can rewrite Eq. (18.14) as a system of coupled transcendental equations

$$R_n = \sum_{k=1}^{K(V)} \tilde{\phi}_k(T) \, e^{\frac{Re(\nu_n)\,k}{T}} \cos(I_n bk) \,, \tag{18.15}$$

$$I_n = -\sum_{k=1}^{K(V)} \tilde{\phi}_k(T) \ e^{\frac{Re(\nu_n) k}{T}} \sin(I_n bk) \,, \tag{18.16}$$

where we have introduced the set of the effective chemical potentials $\nu_n \equiv \nu(\lambda_n)$ with

$$\nu(\lambda) = p_l(T,\mu)b - \lambda bT ,$$

and the reduced distributions

$$\tilde{\phi}_1(T) = \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} z_1 \exp(((\mu - p_l(T, \mu)b)/T))$$

and

$$\tilde{\phi}_{k>1}(T) = \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} k^{-\tau} \exp(-\sigma(T) k^{2/3}/T)$$

for convenience.

Consider the real root $(R_0 > 0, I_0 = 0)$, first. Similarly to the SMM, for $I_n = I_0 = 0$ the real root R_0 of the GSMM exists for any T and μ . Comparison of R_0 from Eq. (18.15) with the expression for vapor pressure of the analytical SMM solution [24] indicates that TR_0 is a constrained grand canonical pressure of the mixture of ideal gases with the chemical potential ν_0 . As usual, for finite volumes the total mechanical pressure [7] differs from TR_0 . Equation (18.16) shows that for $I_{n>0} \neq 0$ the inequality $\cos(I_n bk) \leq 1$ cannot simultaneously become an equality for all k-values. Then from Eq. (18.15) one obtains (n > 0)

$$R_n < \sum_{k=1}^{K(V)} \tilde{\phi}_k(T) e^{\frac{Re(\nu_n)k}{T}} \quad \Rightarrow \quad R_n < R_0,$$
(18.17)

where the second inequality Eq. (18.17) immediately follows from the first one. In other words, the gas singularity is always the rightmost one. This fact plays a decisive role in the thermodynamic limit $V \to \infty$.



Figure 18.1: A graphical solution of Eq. (18.16) for T = 10 MeV and $\tau = 1.825$ for the typical SMM parameterization of the surface tension coefficient by Eq. (18.1). Note, however, that qualitatively the same picture remains valid for any parameterization of the surface tension coefficient. The l.h.s. (straight line) and r.h.s. of Eq. (18.16) (all dashed curves) are shown as the function of dimensionless parameter $I_1 b$ for the three values of the largest fragment size K(V). The intersection point at (0; 0) corresponds to a real root of Eq. (18.14). Each tangent point with the straight line generates two complex roots of Eq. (18.14).

The interpretation of the complex roots $\lambda_{n>0}$ seems to be less straightforward and, hence, in this case we follow the line of arguments suggested in Ref. [11]. According to Eq. (18.13), the GCP is a superposition of the states of different free energies $-\lambda_n VT$. Strictly speaking, $-\lambda_n VT$ has a meaning of the change of free energy, but we will use the traditional term for it. For n > 0 the free energies are complex. Therefore, $-\lambda_{n>0}T$ is the density of free energy. The real part of the free energy density, $-R_nT$, defines the significance of the state's contribution to the partition: due to Eq. (18.17) the largest contribution always comes from the gaseous state and has the lowest value of the real part of free energy, i. e. $-R_{n>0}T$, are thermodynamically metastable. For infinite volume they should not contribute unless they are infinitesimally close to $-R_0T$, but for finite volumes their contribution to the GCP may be important.

As one can see from Eqs. (18.15) and (18.16), the states of different free energies have different values of the effective chemical potential ν_n , which is not the case for infinite volume [24], where there exists a single value for the effective chemical potential. Thus, for finite V the states which contribute to the GCP Eq. (18.13) are not in a true chemical equilibrium.

The meaning of the imaginary part of the free energy density becomes clear from Eqs. (18.15) and (18.16): as it is seen from Eq. (18.15) the imaginary part $I_{n>0}$ effectively changes the number of degrees of freedom of each k-nucleon fragment ($k \leq K(V)$) contribution to the free energy density $-R_{n>0}T$. It is clear, that the change of the effective number of degrees of freedom can occur virtually only and, if $\lambda_{n>0}$ state is accompanied by some kind of equilibration process. Both of these statements become clear, if we recall that the statistical operator in statistical mechanics and the quantum mechanical evolution operator are related by the Wick rotation [35]. In other words, the inverse temperature can be considered as an imaginary time. Therefore, depending on the sign, the quantity $I_n bT \equiv \tau_n^{-1}$ that appears in the trigonometric functions of Eqs. (18.15) and (18.16) in front of the imaginary time 1/T can be regarded as the inverse decay/formation time τ_n of the metastable state which corresponds to the pole $\lambda_{n>0}$ (for more details see next sections and [11]).

Such an interpretation of τ_n naturally explains the thermodynamic metastability of all states except

the gaseous one: the metastable states can exist in the system only virtually because of their finite decay/formation time, whereas the gaseous state is stable because it has an infinite decay/formation time.

18.5 No Phase Transition Case

It is instructive to treat the effective chemical potential $\nu(\lambda)$ as an independent variable instead of μ . In contrast to the infinite V, where the upper limit $\nu \leq 0$ defines the liquid phase singularity of the isobaric partition and gives the pressure of a liquid phase $p_l(T, \mu) = TR_0|_{V\to\infty}$, for finite volumes and finite K(V) the effective chemical potential can be complex (with either sign for its real part) and its value defines the number and position of the imaginary roots $\{\lambda_{n>0}\}$ in the complex plane. Positive and negative values of the effective chemical potential for finite systems were considered within the Fisher droplet model [36], but, to the best of our knowledge, its complex values have been discussed for the first time in [11]. From the definition of the effective chemical potential $\nu(\lambda)$ it is evident that its complex values for finite systems exist only because of the excluded volume interaction, which is not taken into account in the Fisher droplet model [28].

As it is seen from Fig. 18.1, the r.h.s. of Eq. (18.16) is the amplitude and frequency modulated sine-like function of dimensionless parameter $I_n b$. Therefore, depending on T and $\operatorname{Re}(\nu)$ values, there may exist no complex roots $\{\lambda_{n>0}\}$, a finite number of them, or an infinite number of them. In Fig. 18.1 we showed a special case which corresponds to exactly three roots of Eq. (18.14) for each value of K(V): the real root $(I_0 = 0)$ and two complex conjugate roots $(\pm I_1)$. Since the r.h.s. of Eq. (18.16) is monotonously increasing function of $\operatorname{Re}(\nu)$, it is possible to map the $T - \operatorname{Re}(\nu)$ plane into regions of a fixed number of roots of Eq. (18.14). For fixed T-value each curve in Fig. 18.2 divides the $T - \operatorname{Re}(\nu)$ plane into three parts: for $\operatorname{Re}(\nu)$ -values below the curve $\operatorname{Re}(\nu_1(T))$ there is only one real root (gaseous phase), for points on the curve $\operatorname{Re}(\nu) = \operatorname{Re}(\nu_1(T))$ there exist three roots, and above the curve $\operatorname{Re}(\nu_1(T))$ there are five or more roots of Eq. (18.14). Although Fig. 18.2 corresponds to the usual SMM parameterization of the surface tension coefficient, the picture is qualitatively the same for general parameterization of σ whereas its modifications are discussed below.

For constant values of $K(V) \equiv K$ the number of terms in the r.h.s. of Eq. (18.16) does not depend on the volume and, consequently, in thermodynamic limit $V \to \infty$ only the rightmost simple pole in the complex λ -plane survives out of a finite number of simple poles. According to the inequality Eq. (18.17), the real root λ_0 is the rightmost singularity of isobaric partition Eq. (18.10). However, there is a possibility that the real parts of other roots $\lambda_{n>0}$ become infinitesimally close to R_0 , when there is an infinite number of terms which contribute to the GCP Eq. (18.13).

Let us show now that even for an infinite number of simple poles in Eq. (18.13) only the real root λ_0 survives in the limit $V \to \infty$. For this purpose consider the limit $\operatorname{Re}(\nu_n) \gg T$. In this limit the distance between the imaginary parts of the nearest roots remains finite even for infinite volume. Indeed, for $\operatorname{Re}(\nu_n) \gg T$ the leading contribution to the r.h.s. of Eq. (18.16) corresponds to the harmonic with k = K, and, consequently, an exponentially large amplitude of this term can be only compensated by a vanishing value of $\sin(I_n bK)$, i.e. $I_n bK = \pi n + \delta_n$ with $|\delta_n| \ll \pi$ (hereafter we will analyze only the branch $I_n > 0$), and, therefore, the corresponding decay/formation time $\tau_n \approx K[\pi nT]^{-1}$ is volume independent.

Keeping the leading term on the r.h.s. of Eq. (18.16) and solving for δ_n , one finds

$$I_n \approx \frac{\pi n + \delta_n}{b K(v)}, \qquad (18.18)$$

$$\delta_n \approx \frac{(-1)^{n+1}\pi n}{Kb\,\tilde{\phi}_K(T)} \, e^{-\frac{\operatorname{Re}(\nu_n)\,\mathrm{K}}{T}},\tag{18.19}$$

$$R_n \approx (-1)^n \tilde{\phi}_K(T) \, e^{\frac{\operatorname{Re}(\nu_n)\,\mathrm{K}}{T}}, \qquad (18.20)$$

where in the last step we used Eq. (18.15) and condition $|\delta_n| \ll \pi$. Since for $V \to \infty$ all negative values of



Figure 18.2: Each curve separates the $T - \text{Re}(\nu_n)$ region of one real root of Eq. (18.14) (below the curve), three complex roots (at the curve) and five and more roots (above the curve) for three values of K(V) and the same parameters as in Fig. 18.1.

 R_n cannot contribute to the GCP Eq. (18.13), it is sufficient to analyze even values of n which, according to Eq. (18.20), generate $R_n > 0$.

Since the inequality Eq. (18.17) can not be broken, a single possibility, when $\lambda_{n>0}$ pole can contribute to the partition Eq. (18.13), corresponds to the case $R_n \to R_0 - 0^+$ for some finite *n*. Assuming this, we find $\operatorname{Re}(\nu(\lambda_n)) \to \operatorname{Re}(\nu(\lambda_0))$ for the same value of μ .

Substituting these results into equation Eq. (18.15), one gets

$$R_n \approx \sum_{k=1}^K \tilde{\phi}_k(T) \ e^{\frac{\operatorname{Re}(\nu(\lambda_0)) \ k}{T}} \cos\left[\frac{\pi nk}{K}\right] \ll R_0 \,.$$
(18.21)

The inequality Eq. (18.21) follows from the equation for R_0 and the fact that, even for equal leading terms in the sums above (with k = K and even n), the difference between R_0 and R_n is large due to the next to leading term k = K - 1, which is proportional to

$$e^{\frac{\operatorname{Re}(\nu(\lambda_0))(\mathrm{K}-1)}{T}} \gg 1$$
.

Thus, we arrive at a contradiction with our assumption $R_0 - R_n \rightarrow 0^+$, and, consequently, it cannot be true. Therefore, for large volumes the real root λ_0 always gives the main contribution to the GCP Eq. (18.13), and this is the only root that survives in the limit $V \rightarrow \infty$. Thus, we showed that the model with the fixed size of the largest fragment has no phase transition because there is a single singularity of the isobaric partition Eq. (18.10), which exists in thermodynamic limit. However, for the finite systems we can also define the analog of the metastable mixed phase which corresponds to a finite number of complex conjugate solutions $\lambda_{n>0}$. Clearly, in the thermodynamic limit the contribution of these metastable states into all physical quantities disappears. The equation $\operatorname{Re}(\nu) = \operatorname{Re}(\nu_1(T))$ defines the boundary between the finite volume analogs of the gaseous and mixed phases in $T - \operatorname{Re}(\nu)$ and $T - \mu$ planes.

18.6 Finite Volume Analogs of Phases

If K(V) monotonically grows with the volume, the situation is different. In this case for a positive value of $\operatorname{Re}(\nu) \gg T$ the leading exponent in the r.h.s. of Eq. (18.16) also corresponds to a largest fragment, i.e. to

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k = K(V). Therefore, we can apply the same arguments which were used above for the case K(V) = K = const and derive similarly Eqs. (18.18)–(18.20) for I_n and R_n . From the relation $I_n \approx \frac{\pi n}{b K(V)}$ it follows that, when V increases, the number of simple poles in Eq. (18.12) also increases and the imaginary part of the closest to the real λ -axis poles becomes very small, i.e $I_n \to 0$ for $n \ll K(V)$, and, consequently, the associated decay/formation time $\tau_n \approx K(V)[\pi nT]^{-1}$ grows with the volume of the system. Due to the fact that $I_n \to 0$, the inequality Eq. (18.21) cannot be established for the poles with $n \ll K(V)$. Therefore, in contrast to the previous case, for large K(V) the simple poles with $n \ll K(V)$ will be infinitesimally close to the real axis of the complex λ -plane.

In this case from Eq. (18.20) one obtains

$$TR_n \approx p_l(T,\mu) - \frac{T}{K(V)b} \ln \left| \frac{R_n}{\tilde{\phi}_K(T)} \right|$$

$$\approx p_l(T,\mu) - \frac{\sigma}{[K(V)]^{\frac{1}{3}}b} - T \left[\frac{\ln \left| \left(\frac{2\pi}{mT}\right)^{\frac{3}{2}} R_n \right| + \tau \ln K(V)}{K(V)b} \right]$$
(18.22)

for $\operatorname{Re}(\nu) \gg T$ and $K(V) \gg 1$. Thus, from Eq. (18.22) one can clearly see that for an infinite volume an infinite number of simple poles moves toward the real λ -axis to the vicinity of liquid phase singularity $\lambda_l = p_l(T, \mu)/T$ of the isobaric partition [24] and generates an essential singularity of function $\mathcal{F}(V, p_l/T)$ in Eq. (18.11) *irrespective to the sign of the liquid phase pressure* $p_l(T, \mu)$. As we showed above, the states with $\operatorname{Re}(\nu) \gg T$ become stable because they acquire infinitely large decay/formation time τ_n in the limit $V \to \infty$. Therefore, these states should be identified as a liquid phase for finite volumes as well. Such a conclusion can be easily understood, if we recall that the partial pressure TR_n of Eq. (18.22) corresponds to a single fragment of the largest possible size. Moreover, as one can see from the leading terms on the r.h.s. of Eq. (18.22) the partial pressure TR_n contains both the liquid phase and the surface contributions for a spherical fragment of the mean radius $[K(V)b]^{\frac{1}{3}}$. In fact, the above results remain valid under a weaker condition $\operatorname{Re}(\nu) K(V) \gg T$ since such an inequality allows one to establish the approximation Eq. (18.20).

Now it is clear that each curve in Fig. 18.2 is the finite volume analog of the phase boundary $T - \nu$ for a given value of K(V): below the phase boundary there exists a gaseous phase, but at and above each curve there are states which can be identified with a finite volume analog of the mixed phase, and, finally, if $\operatorname{Re}(\nu)/T \to \infty$ there exists a liquid phase. Again as in the previous section the equation $\operatorname{Re}(\nu) = \operatorname{Re}(\nu_1(T))$ defines the boundary between the finite volume analogs of the gaseous and mixed phases in $T - \operatorname{Re}(\nu)$ and $T - \mu$ planes. Clearly, for finite V the solution of this equation $\mu_c(T, V)$ depends on T and V.

Although the calculations depicted in Fig. 18.2 were made for $\sigma(T) \ge 0$ and for finite values of the effective chemical potential $\text{Re}(\nu)$ the shown results can be qualitatively explained using Eq. (18.22) in the limit $\text{Re}(\nu)\text{K}(V)/T \to \infty$. Indeed, from Eq. (18.22) one finds

$$\operatorname{Re}(\nu_{n}) \approx \frac{\sigma}{[K(V)]^{\frac{1}{3}}} + T \left[\frac{\ln \left| \left(\frac{2\pi}{mT}\right)^{\frac{3}{2}} R_{n} \right| + \tau \ln K(V)}{K(V)} \right],$$
(18.23)

from which one obtains $\operatorname{Re}(\nu_n) > 0$ for finite K(V) values (compare to Fig. 18.2), if $|\left(\frac{2\pi}{mT}\right)^{\frac{3}{2}}R_n| \gg 1$ and $\sigma \geq 0$. If, however, the surface tension coefficient gets negative, i.e. $\sigma < 0$ for $T > T_c$, then for sufficiently large values of K(V) one can find that $\operatorname{Re}(\nu_n) < 0$, i.e. in this case the finite volume analog of phase boundary can demonstrate another behavior than that one shown in Fig. 18.2. For $T = T_c$, the surface tension coefficient vanishes and from Eq. (18.23) we get

$$\operatorname{Re}(\nu_n)\Big|_{T=T_c} \approx \frac{T_c}{K(V)} \left[\ln \left| \left(\frac{2\pi}{mT_c} \right)^{\frac{3}{2}} \frac{p_l(T_c, \mu)}{T_c} \right| + \tau \ln K(V) \right],$$
(18.24)

where in the last step of derivation we replaced R_n by the leading term from the r.h.s. of Eq. (18.22). This result shows that (i) at $T = T_c$ the deviation of the partial pressure TR_n from the liquid phase pressure

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decreases faster as function of K(V) than for other temperatures, but at the same time (ii) for large K(V) this deviation still decreases slower than the imaginary part I_n . For a quantitative example let us choose μ in such a way that the first term on the r.h.s. of Eq. (18.24) disappears, i.e. for

$$\operatorname{Re}(\nu_n)\Big|_{T=T_c} \approx \frac{T_c \tau}{K(V)} \ln K(V)$$
.

Then for $\tau = 1.825$ one finds $\operatorname{Re}(\nu_n)|_{T=T_c} \approx 7.56$ MeV for K(V) = 10, $\operatorname{Re}(\nu_n)|_{T=T_c} \approx 4.92$ MeV for K(V) = 20, $\operatorname{Re}(\nu_n)|_{T=T_c} \approx 3.72$ MeV for K(V) = 30, and $\operatorname{Re}(\nu_n)|_{T=T_c} \approx 1.5$ MeV for K(V) = 100. From Fig. 18.2 one can see that, although our estimate of $\operatorname{Re}(\nu_n)|_{T=T_c}$ for K(V) = 10 is about 2.5 MeV below its value found numerically, the corresponding estimates for K(V) = 20 and K(V) = 30 obtained from Eq. (18.24) are in a very good agreement with the results of the numerical evaluation.

When there is no phase transition, i.e. K(V) = K = const, the structure of simple poles is similar, but, first, the line which separates the gaseous states from the metastable states does not change with the system volume, and, second, as shown above, the metastable states will never become stable. Therefore, a systematic study of the volume dependence of free energy (or pressure for very large V) along with the formation and decay times may be of a crucial importance for experimental studies of the nuclear liquid gas phase transition.

The above results demonstrate that, in contrast to Hill's expectations [7], the finite volume analog of the mixed phase does not consist just of two pure phases. The mixed phase for finite volumes consists of a stable gaseous phase and the set of metastable states which have different values of free energy. Moreover, the difference between the free energies of these states is not the surface-like, as Hill assumed in his treatment [7], but the volume-like as we have seen. Furthermore, according to Eqs. (18.15) and (18.16), each of these states consists of the same fragments, but with different weights. As was shown above for the case $\text{Re}(\nu) \gg T$, some fragments that belong to the states, in which the largest fragment is dominant, may, in principle, have negative weights (effective number of degrees of freedom) in the expression for $R_{n>0}$ Eq. (18.15). This can be understood easily because higher concentrations of large fragments can be achieved at the expense of the smaller fragments and is reflected in the corresponding change of the real part of the free energy $-R_{n>0}VT$. Therefore, the actual structure of the mixed phase at finite volumes is more complicated than was expected in earlier works.

Here it is necessary to add a few remarks about the description of the deconfinement PT on the basis of statistical models [19, 20, 21, 29] that were solved recently in thermodynamic limit. The finite volume solution of the models [19, 20, 21, 29] can be straightforwardly found using the LFT developed in [10, 11]. Recently, however, the importance of finite width of heavy/large quark gluon plasma bags was realized [21, 22, 23]. Both the theoretical estimates [22, 23] and the analysis of the asymptotic Regge trajectories of non-strange mesons [37] indicate that the width of the quark gluon bag of the volume V with the mass M being heavier than $M_0 \approx 2.5$ GeV is $\Gamma = \gamma(T) \sqrt{\frac{V}{V_0}}$ (here $V \ge V_0 = 1$ fm³). Since even at T = 0the value $\gamma(T = 0) \approx 400$ MeV is large, we conclude that the short life-time $t_{life}(V) = 1/\Gamma(V)$ of such bags can, in principle, modify our conclusions about the metastable states $\lambda_{n>0}$. This is so because in the SMM and the GSMM the fragments are implicitly assumed to be stable and, hence, their life-time is set to be infinite while in reality there is the region of stability of nuclear fragments outside of which the nucleus life-time is extremely short. A similar situation is found with large/heavy quark gluon bags although the instability of nuclei is due to the Coulomb interaction whereas the short life-time of the bags should be attributed to such a property of strongly interacting matter as the color confinement [21, 30, 31].

Now it is clear that, if the individual life-time of the largest bag $t_{life}(V)$ in the volume V is larger than the collective decay/formation time of the state $\lambda_{n>0}$ which for quark gluon bags is $\tilde{\tau}_n \approx \frac{V}{V_0 \pi n T}$ [10], then the largest bag can be considered as a stable one during the course of collective decay/formation process, i.e. $t_{life}(V) \geq \tilde{\tau}_n$. Otherwise the process of collective decay or formation of the state $\lambda_{n>0}$ cannot ever be completed because the largest bag ceases its existence much earlier. Note that under such conditions one can hardly expect an existence of thermal equilibrium in the system of shortly living particles. Therefore, the inequality $t_{life}(V) \ge \tilde{\tau}_n$ sets some constraints on the applicability range of the above analysis to the short-living bags

$$\left[\frac{V}{V_0}\right]^{\frac{3}{2}} \leq \frac{\pi T}{\gamma(T)} n.$$
(18.25)

This inequality can be used as an estimate for the volume of largest bags in a finite system, if n and T are known. For instance, if $\gamma(T) = \gamma(T = 0) = \text{const}$, then one obtains

$$\frac{V}{V_0} \le \left[\frac{\pi T}{\gamma(T=0)} n\right]^{\frac{2}{3}} .$$

Alternatively, Eq. (18.25) can be used to estimate the range of temperatures for given n since $V/V_0 \ge 1$. Using the last inequality one can rewrite Eq. (18.25) as $n \ge \frac{\gamma(T)}{\pi T}$. Substituting into the last result the following expression for $\gamma(T)$

$$\gamma(T) = \sqrt{2V_0 \, a \, T T_H^2 (T^2 + T T_H + T_H^2)}$$

that was predicted in [22], where $T_H \approx 160 \text{ MeV}$ is the Hagedorn temperature and $a = \frac{37}{90}\pi^2$ for SU(3) color group with two quark flavors, we find $n \ge 1$ for $T \ge 500$ MeV and $n \ge 2$ for $T \ge 1120$ MeV. These estimates show that at LHC energies we can expect an existence of metastable states which are described within the developed approach.

18.7 Conclusions

In this work we generalized the SMM to GSMM and included into it the nuclear liquid phase pressure of the most general form. This allowed us to get rid of the absolute incompressibility of the nuclear liquid. Also in this model we introduced very general form of the surface tension coefficient which enabled us to repair another pitfall of the simplified SMM related to the absence of critical endpoint in this model for $\tau > 2$. The LFT method was applied to the constrained GSMM and this model was solved analytically for finite volumes.

It is shown that for finite volumes the GCP function can be identically rewritten in terms of the simple poles of the isobaric partition Eq. (18.10). The real pole λ_0 exists always and the quantity $T\lambda_0$ is the CGC pressure of the gaseous phase. The complex roots $\lambda_{n>0}$ appear as pairs of complex conjugate solutions of Eq. (18.14). As we discussed, their most straightforward interpretation is as follows: $-T\text{Re}(\lambda_{n>0})$ has a meaning of the free energy density, whereas $bT\text{Im}(\lambda_{n>0})$, depending on sign, gives the inverse decay/formation time of such a state. The gaseous state is always stable because its decay/formation time is infinite and because its free energy is minimal. The complex poles describe the metastable states for $\text{Re}(\lambda_{n>0}) \ge 0$ and mechanically unstable states for $\text{Re}(\lambda_{n>0}) < 0$.

We studied the volume dependence of the simple poles and found a dramatic difference in their behavior in case with PT and without it. For the former one the found representation allows one to define the finite volume analogs of phases unambiguously and to establish the finite volume analog of the $T - \mu$ phase diagram (see Fig. 18.2). At finite volumes the gaseous phase exists, if there is a single simple pole, the mixed phase corresponds to three and more simple poles, whereas the liquid is represented by an infinite amount of simple poles at highest possible particle density (or $\mu \to \infty$).

As we showed, for given T and μ the states of the mixed phase which have different Re(λ_n) are not in a true chemical equilibrium for finite volumes. This feature cannot be obtained within the Fisher droplet model due to lack of the hard core repulsion between fragments. This fact also demonstrates clearly that, in contrast to Hill's expectations [7], the mixed phase is not just a composition of two states which are the pure phases. As we showed, the mixed phase is a superposition of three and more collective states, and each of them is characterized by its own value of λ_n . Because of that the difference between the free energies of these states is not the surface-like, as Hill argued [7], but the volume-like.

18.7 Conclusions

A detailed analysis of the isobaric partition singularities in the $T - \text{Re}(\nu)$ plane allowed us to define the finite volume analogs of phases and study the behavior of these singularities in the limit $V \rightarrow \infty$. Such an analysis opens a possibility to rigorously study the nuclear liquid-gas PT and the deconfinement PT directly from the finite volume partition. This may help to extract the phase diagram of strongly interacting matter from the experiments on finite systems (nuclei) with more confidence. The conditions of the model applicability to the description of the short-living quark gluon plasma bags are also discussed.

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19 Three-dimensional Calculation of Inhomogeneous Structure in Low-Density Nuclear Matter

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When a man in the beginning of his life is ignorant of everything, he has no scruples, finds no obstacles, no inhibitions. But after a while he starts to learn, and becomes timid, cautious, and begins to feel something choking in his mind, which prevents him from going ahead as he used to before he had any learning. Learning is needed, but the point is not to become its slave. You must be its master, so that you can use it when you want it.

Yagyu Munemori (1571-1646) (as interpreted by D. T. Suzuki)

Abstract

In low-density nuclear matter which is relevant to the crust region of neutron stars and collapsing stage of supernovae, non-uniform structures called "nuclear pasta" are expected. So far, most works on nuclear pasta have used the Wigner-Seitz cell approximation with ansatz about the geometrical structures like droplet, rod, slab and so on. We perform fully three-dimensional calculation of non-uniform nuclear matter for some cases with fixed proton ratios and in beta-equilibrium based on the relativistic mean-field model and the Thomas-Fermi approximation. In our calculation typical pasta structures are observed. However, there appears some difference in the density region of each pasta structure.

19.1 Introduction

In 1934, W. Baade and F. Zwicky proposed the existence of neutron stars only one year after the discovery of neutron. Estimating the binding energy of neutron stars, they predicted that neutron stars are made by supernova explosions. Neutron star had been an imaginary object for 30 years, until pulsars were discovered by J. Belle and A. Hewish in 1967. Neutron star has a radius of about 10 km and the mass about 1.4 times of the sun, and consists of four parts [1]. The region around 0.3km from outside is called "outer crust", where Fe nuclei are expected to form a Coulomb lattice. Around 0.3 - 1km is called "inner crust" with a density about 0.3-0.5 ρ_0 . There are neutron-rich nuclei in lattice and dripped neutrons in a superfluid state. Two central regions with higher density are called "outer core" and "inner core", where speculated

are proton super-conductivity, neutron super-fluidity [2], meson condensations [3], hyperon mixture [4], or quark states [5, 6].

The transition of matter composition with the change of density inside neutron stars causes a question: does it change continuously or suddenly? A sudden change of matter property is generally accompanied by a first-order phase transition which causes an appearance of the mixed phase.

Ravenhall et al. [7] suggested the existence of non-uniform structures of nuclear matter, i.e., the structured mixed phase. They suggested five types of structures as droplet, rod, slab, tube, and bubble. Due to its geometrical shapes which depend on the density, we call it "nuclear pasta" like spaghetti and lasagna etc [7, 8]. Many workers have suggested the existence of pasta structures in low-density nuclear matter, relevant to the crust region of neutron stars and the collapsing stage of supernovae. The existence of the pasta structures at the crust of neutron stars may not influence on the bulk property and structure of neutron stars. However, it should be important for the mechanism of glitch, the cooling process of neutron stars, and the thermal and mechanical properties of supernova matter.

The pasta structures presented by Ravenhall have geometrical symmetries. So we can treat the system with the Wigner-Seitz (WS) cell approximation. Because of the convenience, the WS cell approximation has been very often used. But there may be some shortcomings. First, the existence of some kinds of structures other than the typical pasta structures were suggested. For example, in compressive process of matter, two droplets connect with each other and form dumbbell-like pieces [9]. Other examples are double diamond [10, 11] and gyroid [11] shapes of matter suggested by using compressible liquid-drop model. These shapes cannot exist as a ground state at zero temperature, so they might exist in supernova matter at finite temperatures. Such structures are impossible to be described by the WS approximation. It is worth trying to calculate without any approximation whether or not these structures exist as a ground state or an excited state.

19.2 Method

19.2.1 Relativistic Mean Field Theory

There are several approaches for studying pasta structures in the literature, as liquid-drop model [7, 11], Thomas-Fermi model [12, 13], Hartree-Fock [14], quantum molecular dynamics (QMD) [15, 9], relativistic mean field model (RMF) [16, 17]. In the studies using liquid-drop model and RMF model, always used was the Wigner-Seitz (WS) cell approximation, where only the typical pasta structures are considered. QMD calculation does not assume any specific structure of baryons. But uniform electron distribution, though it should be almost uniform, is assumed. The Thomas-Fermi calculation in Ref. [12] and HF calculation [14] used the periodic boundary condition and did not assume any geometrical symmetry in structure. However, the size of the periodic cell was not large enough for quantitative discussion.

In this paper, we use the Thomas-Fermi approximation for baryons with interaction by the RMF model. This model is not only simple for numerical calculation but also quantitatively reliable for the properties of finite nuclei and the saturation property of matter.

We start from the simple Lorentz-scalar Lagrangian with nucleons, electrons and σ , ω , ρ -mesons as follows,

$$L = \bar{\psi} \left[i\gamma^{\mu}\partial_{\mu} - m_{N}^{*} - g_{\omega N}\gamma^{\mu}\omega_{\mu} - g_{\rho N}\gamma^{\mu}\boldsymbol{\tau}\cdot\boldsymbol{R}_{\mu} - e\frac{1+\tau_{3}}{2}\gamma^{\mu}A_{\mu} \right]\psi + \frac{1}{2}(\partial_{\mu}\sigma)^{2} - \frac{1}{2}m_{\sigma}^{2}\sigma^{2} - U(\sigma) - \frac{1}{4}\omega_{\mu\nu}\omega^{\mu\nu} + \frac{1}{2}m_{\omega}^{2}\omega_{\mu}\omega^{\mu} - \frac{1}{4}\boldsymbol{R}_{\mu\nu}\boldsymbol{R}^{\mu\nu} + \frac{1}{2}m_{\rho}^{2}\boldsymbol{R}_{\mu}\boldsymbol{R}^{\mu} - \frac{1}{4}F_{\mu\nu}F^{\mu\nu} + \bar{\psi}_{e}[i\gamma^{\mu}\partial_{\mu} - m_{e} + e\gamma^{\mu}A_{\mu}]\psi_{e} , \qquad (19.1)$$

where the effective mass is written as $m_N^* = m_N - g_{\sigma N} \sigma$, and the potential energy of sigma meson

$$U(\sigma) = \frac{1}{3} b m_N (g_\sigma \sigma)^3 - \frac{1}{4} c (g_\sigma \sigma)^4 .$$

19.2 Method

From the variational principle for this Lagrangian, we get equations of motion for nucleons, σ , ω , ρ -mesons and the Coulomb potential as follows:

$$\left[i\gamma^{\mu}\partial_{\mu} - m_{N}^{*} - g_{\omega N}\gamma^{\mu}\omega_{\mu} - g_{\rho N}\gamma^{\mu}\boldsymbol{\tau}\cdot\boldsymbol{R}_{\mu} - e\frac{1+\tau_{3}}{2}\gamma^{\mu}A_{\mu}\right]\psi = 0, \qquad (19.2)$$

$$\partial_{\mu}\partial^{\mu}\sigma - \left(\bar{\psi}g_{\sigma N}\psi - m_{\sigma}^{2}\sigma - \frac{dU}{d\sigma}\right) = 0, \qquad (19.3)$$

$$-\partial_{\mu}\omega^{\mu\nu} - \left(-g_{\omega N}\bar{\psi}\gamma^{\nu}\psi + m_{\omega}^{2}\omega^{\nu}\right) = 0, \qquad (19.4)$$

$$\partial_{\mu} \mathbf{R}^{\mu\nu} + m_{\rho}^{2} \mathbf{R}^{\nu} = g_{\rho N} \bar{\psi} \boldsymbol{\tau} \gamma^{\nu} \psi , \qquad (19.5)$$

$$\nabla^2 A_0 = e^2 \left(\bar{\psi} \gamma^0 (1 + \tau_3) / 2\psi - \bar{\psi}_e \gamma_0 \psi_e \right) = e^2 \hat{\rho}_{ch} .$$
(19.6)

By the mean-field approximation for meson fields and the static approximation for electric field, we have

$$\langle \sigma \rangle = \sigma , \qquad \langle \omega^{\mu} \rangle = \delta^{\mu,0} \omega_0 , \qquad \langle R_a^{\mu} \rangle = \delta^{\mu,0} \delta_{a,3} R_0 , \qquad V = \langle A_0 \rangle .$$

The bracket $\langle \ldots \rangle$ represents the expectation value in the ground-state of nuclear matter, and we assume the space and time-reversal symmetries for this state. ω and ρ mesons cannot have finite value in space components. Therefore we finally get the equations for mesons as follow

$$-\nabla^2 \sigma + m_\sigma^2 \sigma = -\frac{dU}{d\sigma} + g_{\sigma B} \langle \bar{\psi}\psi \rangle$$
(19.7)

$$-\nabla^2 \omega_0 + m_\omega^2 \omega_0 = g_{\omega N} (\rho_p + \rho_n) \tag{19.8}$$

$$-\nabla^2 R_0 + m_R^2 R_0 = g_{\rho N} (\rho_p - \rho_n) \tag{19.9}$$

By the Thomas-Fermi approximation at zero temperature, momentum distributions of nucleons have stepfunctional forms and plane-wave solutions for Dirac equation. Scalar density and density of nucleons

$$\rho_s = \sum_{i=1}^{A} \bar{\psi}_i(x) \psi_i(x) , \qquad \rho = \sum_{i=1}^{A} \psi_i(x)^{\dagger} \psi_i(x)$$

are written using ψ_i $(i = 1, 2, \dots, A)$ as

$$\rho = 2 \int_0^{k_F} \frac{d^3k}{(2\pi)^3} \frac{M^*}{E_k^*} \sum_s u^{\dagger}(k,s) u(k,s) = 4 \int_0^{k_F} \frac{d^3k}{(2\pi)^3} = \frac{2k_F^3}{3\pi^2} , \qquad (19.10)$$

$$\rho_s = 2 \int_0^{k_F} \frac{d^3k}{(2\pi)^3} \frac{M^*}{E_k^*} \sum_s \bar{u}(k,s) u(k,s) = 4 \int_0^{k_F} \frac{d^3k}{(2\pi)^3} \frac{M^*}{E_k^*} , \qquad (19.11)$$

and the electron density is given as $\rho_e \equiv -\int d^3x \langle \bar{\psi}_e \gamma_0 \psi_e \rangle < 0$. The energy density of nuclear matter is obtained by the energy-momentum tensor and putting $(\mu, \nu) = (0, 0)$, as

$$\hat{T}_{\rm RMF}^{00} = \langle \psi^{\dagger} \left[-i\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \beta m_N^* + g_{\omega N} \omega_0 + g_{\rho N} R_0 + e \frac{1 + \tau_3}{2} V \right] \psi \rangle
+ \frac{1}{2} (\nabla \sigma)^2 + \frac{1}{2} m_{\sigma}^2 + U(\sigma)
- \frac{1}{2} (\nabla \omega_0)^2 - \frac{1}{2} m_{\omega}^2 \omega_0^2 - \frac{1}{2} (\nabla R_0)^2 - \frac{1}{2} m_{\rho}^2 R_0 - \frac{1}{2} (\nabla V)^2
+ \langle \psi_e^{\dagger} \left[-i\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \beta m_e - eV \right] \psi_e \rangle.$$
(19.12)



Figure 19.1: (a) Binding energy and (b) pressure without the contribution of electrons. Red line corresponds to the case of proton ratio $Y_p = 0.5$ and green, blue, purple, sky blue and yellow correspond to 0.4, 0.3, 0.2, 0.1 and 0, respectively.

Therefore, we get the total energy in the form

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$$E = 2 \sum_{n,p \in F} \sqrt{k^2 + m_N^{*2}} + \int d^3x \left[\frac{1}{2} (\nabla \sigma)^2 + \frac{1}{2} m_\sigma^2 \sigma^2 + U(\sigma) \right] + \int d^3x \left[\frac{1}{2} (\nabla \omega_0)^2 + \frac{1}{2} m_\omega^2 \omega_0^2 + \frac{1}{2} (\nabla R_0)^2 + \frac{1}{2} m_\rho^2 R_0^2 \right] + \int d^3x \left[-\frac{1}{2} (\nabla V)^2 \right] + E'_e$$

$$E'_e = \int d^3x \left[\frac{2}{(2\pi)^3} \int_0^{k_F^{(e)}} 4\pi k^2 dk \sqrt{k^2 + m_e^2} - eV(-\rho_e) \right]$$
(19.13)

$$= \int d^3x \left[\frac{(\mu_e - V)^4}{4\pi^2} - V\rho_e \right] \qquad \left(\mu_e \approx k_F^{(e)} + V \right) .$$
(19.14)

Table 19.1: Parameter set.

$g_{\sigma N}$	$g_{\omega N}$	$g_{ ho N}$	b	с	$m_{\sigma}({ m MeV})$	$m_{\omega} ({ m MeV})$	$m_{ ho}({ m MeV})$
6.3935	8.7207	4.2696	0.008659	0.002421	400	783	769

We use the same parameter set of Ref. [16], which reproduces the saturation property of nuclear matter (Fig. 19.1), and the binding energies and the proton mixing ratios of finite nuclei. We list the parameter set in Table 19.1.

19.2.2 Numerical Calculation

To simulate infinite matter, we employ a periodic boundary condition to the calculation cell with a cubic shape. Desirable cell size is large as possible. We divide the cell into grid points. The density distributions

19.3 Results

and the meson-field profiles are represented by their local values on the grid points. Given are the average densities of protons, neutrons and electrons, but density distributions are randomly provided. The suitable density distributions and fields are searched for.

The meson fields and the Coulomb potential are obtained by solving the equations of motion Eqs. (19.3)-(19.6). To obtain the density distributions of nucleons and electrons we introduce local chemical potentials. The equilibrium state is determined so that the chemical potentials are independent of the position. An exception is the region with a particle density equals to zero, where the chemical potential of that particle becomes higher.

$$\mu_{p} = \sqrt{(3\pi^{2}\rho_{p}(\boldsymbol{r}))^{2/3} + (m_{N}^{*}(\boldsymbol{r}))^{2}} + g_{\omega N}\omega_{0}(\boldsymbol{r}) + g_{\rho N}R_{0}(\boldsymbol{r}) - V(\boldsymbol{r}) , \qquad (19.15)$$

$$\mu_{n} = \sqrt{(3\pi^{2}\rho_{n}(\boldsymbol{r}))^{2/3} + (m_{N}^{*}(\boldsymbol{r}))^{2} + g_{\omega N}\omega_{0}(\boldsymbol{r}) - g_{\rho N}R_{0}(\boldsymbol{r})}, \qquad (19.16)$$

$$\mu_{e} = (3\pi^{2}\rho_{e}(\mathbf{r}))^{1/3} + V(\mathbf{r}) . \qquad (19.17)$$

Starting from given density distributions, we repeat the following procedures to attain uniformity of chemical potentials.

- 1. Calculate the chemical potentials on all of the grid points.
- 2. Compare chemical potentials on the neighbor six grid points.
- 3. If the chemical potential of the point under consideration
- is larger than that of another, give some part of the density to
- the other grid point.

19.2.3 Coulomb Energy

In the Coulomb and electron energies Eqs. (19.14), we consider the energy only within the calculating cell without interaction with the neighbors. Therefore we do not include the Coulomb energy of the higher order, although we solve the Poisson equation completely. The dipole interaction, which gives the largest contribution among the higher order interactions, comes up to 5% of the Coulomb energy. So we subtract the dipole moment of the electric field by carrying out a translation of the coordinate so that the dipole moment of charge density in the cell diminishes.

19.3 Results

We calculate three-dimensional structures of low-density nuclear matter at zero temperature and obtain the energy or pressure as function of density, i.e. the equation of state (EOS). In this report, let us first demonstrate the cases with the fixed proton mixing ratio, $Y_p \equiv N_p/N_B$, and then with beta-equilibrium. Particularly, we set the proton mixing ratio equal to $Y_p = 0.5$, 0.3 and 0.1. This choice has been made because these cases should be the ones of typical nuclear matter, relevant for the supernova core, and for protoneutron stars.

In some of the previous works which have used the WS cell approximation, nuclear matter might be enforced to have some typical pasta structures. In reality, however, there might appear some intermediate shapes in the density regions where structure changes. With the WS cell approximation, the cell size which gives the minimum energy density has been calculated [16]. To save the computational effort, we make use of that size of the WS cell for the size of our cell with a periodic boundary condition.

First, we show the result for symmetric nuclear matter with a proton mixing ratio $Y_p = 0.5$ in Fig. 19.2. Panels (a), (b), (c), (d), (e), and (f) correspond to droplet, rod, slab, tube, bubble and uniform state, respectively. In our calculation, all of the typical pasta structures are seen.

The binding energy, the total pressure and the baryon partial pressure are presented in Fig. 19.3. The line with colors, dashed line and dots correspond to the results with the WS cell approximation, the case of



Figure 19.2: Proton density distribution for symmetric nuclear matter ($Y_p = 0.5$). Red color corresponds to the highest density 0.08 fm⁻³, and blue corresponds to 0 fm⁻³.

uniform matter, and our results by the three-dimensional calculation, respectively. The density region with numbers $1, 2, \ldots, 6$ separated with vertical dashed lines indicate that the structures in Fig. 19.2 (a), (b), \ldots , (f) appear. Note that the density range for each pasta structure is slightly different from the previous study with the WS cell approximation.



Figure 19.3: EOS of matter with $Y_p = 0.5$. (a) Energy per nucleon obtained by the present calculation (colored circles) compared with the results of Ref. [16]. (b) Total pressure and (c) baryon partial pressure. Black dotted lines in (a), (b) and (c) show the cases of uniform matter.

19.3 Results

Next, we show the result for proton mixing ratio $Y_p = 0.3$. in Fig. 19.5. The cell size is set to be the same as in Ref. [16]. The difference between two results is that the bubble structure does not appear in the present calculation. Comparing the cases of $Y_p = 0.5$ and 0.3, the upper limit of the density where



Figure 19.4: Same as Fig. 19.2 for $Y_p = 0.3$. But the density range from blue to red is 0 to 0.075 fm⁻³.



Figure 19.5: Same as Fig. 19.3 for $Y_p = 0.3$.

non-uniform structures appear is different.

In the case of symmetric nuclear matter, the density region of non-uniform matter roughly corresponds to the spinodal region, where $(dP/d\rho_B) < 0$, while the non-uniform region is slightly wider than the spinodal region for $Y_p = 0.3$. This may be because the symmetric nuclear matter behaves congruently (phase transition in a single chemical component), while the liquid-gas mixed phase in matter with $Y_p = 0.3$ is non-congruent and the values of Y_p in two phases are generally different. Therefore the instability of



Figure 19.6: Same as Fig. 19.2 for $Y_p = 0.1$. The density range from blue to red is 0 to 0.05 fm⁻³.

uniform matter is determined not only by the compressibility of uniform matter but also by the chemical composition of the mixed phase to be formed. In Fig. 19.7, we show the baryon density dependence of



Figure 19.7: Same as Figs. 19.3 and 19.5 for $Y_p = 0.1$.

binding energy, total pressure, and baryon partial pressure. We use the lines and dots in non-uniform structures of only droplet, rod, and slab appear.

To compare quantitatively our calculation with the WS cell approximation, we show the cell and the structure size in Fig. 19.8. Upper and lower lines represent the cell and the structure size in one cell,


Figure 19.8: Comparison of the cell and the structure size with WS approximation and three-dimensional calculation $(Y_p = 0.3)$. Line with colors: WS approximation, Dots: Three-dimensional calculation. Upper line with color R_{cell} : cell size, bottom line with color R_d : Non-uniform structure size.



Figure 19.9: Density distributions of nucleons and electron in the case of beta-equilibrium. The left panel (a) shows the result reported in Ref. [16] with WS approximation. The horizontal axis is the distance from the center of the cell, and the vertical axis densities of nucleons and electron.

respectively. Non-uniform structure size is defined by way of a density fluctuations as

$$R = \begin{cases} R_w \frac{\langle \rho_p \rangle^2}{\langle \rho_p^2 \rangle}, & \text{(for droplet, rod and slab)} \\ \\ R_w \left(1 - \frac{\langle \rho_p \rangle^2}{\langle \rho_p^2 \rangle} \right), & \text{(for tube and bubble)} \end{cases}$$
(19.18)

We show in Fig. 19.8 the size of the cell and the non-uniform structure. The density where each pasta structure appears is mostly in agreement with Ref. [16]. However, there are large differences in the transient region of pasta structures.

In our calculation, we set, as the initial condition, the density distributions of fermions (nucleons and

electron) and mesons randomly. So, the converged density distribution sometimes are trapped in local minimum states particularly at the density region where structure changes.

Let us discuss the case of beta-equilibrium at zero temperature, which is relevant to the realistic neutron star matter.



Figure 19.10: Energy, pressure, and Y_p of matter in beta-equilibrium.

In Figs. 19.9 and 19.10, we present density distributions by the WS cell approximation and the present three-dimensional calculation. While some pasta structures appeared for fixed proton mixing ratio, only the droplet structure appears for the beta-equilibrium case. This result is qualitatively the same as in the WS cell approximation.

Nuclear matter in the crust region of neutron stars includes a very small fraction of protons and electrons. So the contribution to the energy and pressure comes almost from neutrons and a little from protons and electrons. Consequently the binding energy and pressure of uniform matter are almost the same as those of non-uniform matter. The proton mixing ratio Y_p , however, is significantly different between uniform and no-uniform cases. Though it approaches to zero in the zero-density limit for uniform matter, there is a steep rise for non-uniform matter. It approaches to approximately 0.5, which corresponds to a neutral atom in the low-density limit.

19.4 Conclusion

We have performed the three-dimensional calculations for low-density nuclear matter and presented first results, based on relativistic mean-field theory and Thomas-Fermi approximation. For some fixed proton

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19.4 Conclusion

mixing ratios and for β -equilibrium nuclear matter, we have obtained non-uniform structures and the relevant EOS. The observed structures are typical "pasta" structures, which were previously studied with the WS cell approximation. For $Y_p = 0.5$, all of the typical pasta structures appeared. For $Y_p = 0.3$ and 0.1, however, some of the pasta structures did not appear. The density region for each type of pasta structure was also different between the WS cell approximation and the three-dimensional calculation.

These may be due to the difference of the shapes of the cell. The WS cell for droplet, rod, slab, tube and bubble structures are sphere, cylinder, plate, cylinder and sphere, respectively. On the other hand, the cubic cell is used in the three-dimensional calculation. In any way, it is desirable to avoid the effects of the shape of the used cell. We therefore are planning to enlarge the cubic cell so that several periods of structures can emerge in it.

For β -equilibrium, we got only the droplet structure. This result is qualitatively the same as the one with the WS cell approximation. However, we cannot definitely state that nuclear matter in β -equilibrium has only droplet shapes, because other works with different interaction have observed pasta structures other than droplet. In β -equilibrium, proton mixing ratio is largely different from that in uniform matter. It tends to zero for uniform matter at zero-density limit, while it increases in the case of non-uniform matter, and the asymptotic value should be 0.5 which represents atoms.

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20 On "Smoothing" of First Order Phase Transition in Small Systems Alexander L. Tseskis⁽¹⁾, Naoum M. Kortsensteyn⁽²⁾, and Jürn W. P. Schmelzer⁽³⁾

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Any physical theory is always provisional,

in the sense that is only a hypothesis: you can never prove it.
No matter how many times the results of experiments agree with some theory, you can never be sure that the next time the results will not contradict the theory.
On the other hand, you can disprove a theory by finding even a single observation that disagrees with the predictions of the theory.
A philosopher of science, Karl Popper, has emphasized, a good theory is characterized by the fact that it makes a number of predictions that could in principle be disproved or falsified by observation.
Each time new experiments are observed to agree with the predictions the theory survives, and our confidence in it is increased; but if ever a new observation is found to disagree, we have to abandon or modify the theory. At least that is what is supposed to happen, but you can always question the competence of the person who carried out the observation.

However, one cannot really argue with a mathematical theorem.

Stephen W. Hawking

Abstract

The influence of the size of the system on first-order phase transitions (induced by an external field) is discussed for a system with Landau Effective Hamiltonian (LEH). It is shown that, at a sufficient decrease of the linear size of the system, the first-order transition disappears and a continuous behavior of the averaged value of the order parameter is found instead of a sharp jump at zero external field.

20.1 Introduction

It is usually believed that all the thermodynamic quantities of macroscopic systems can be computed on the basis of statistical considerations, and the accuracy of such a computation depends on the number of particles in the considered system. As long as the system includes large enough numbers of particles the relative deviations (fluctuations) of the corresponding values from the calculated averaged values in infinite systems (thermodynamic limit) are negligibly small. These deviations originate from the fluctuations of different physical parameters and tend to zero when the number of particles of the system (or its volume at a given density) tends to infinity. The corresponding dependence of

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the values of the physical quantities on the size of the system gives rise to a certain approach – the Finite-Size Scaling (FSS) – which describes mentioned above variations [1].

It turns out that, at second-order phase transitions, FSS leads to a result according to which all the infinite (in the bulk) quantities become finite in a finite system, in other words, the corresponding calculations do not lead to any singularity. Singularities manifest themselves only at the thermodynamic limit; therefore FSS must include a sort of asymptotic formulae allowing one the passage from the description of a finite system to the description of an infinite one (see, for instance [2]).

Unfortunately, the corresponding relations (as far as being obtained!) are valid only in the case of a large number of particles (or large volume) of a finite system, so that if this number is small enough one has to use certain numerical calculations (a simple example of such calculations was given in [3] in connection with second-order transitions in the model with LEH).

It is obvious that finite size effects are, generally speaking, manifest themselves not only in the case of secondorder transitions but also at first-order transitions. Moreover, according to the known theorems by Yang and Lee [4] the first-order transition, with characteristic jumps of some of the thermodynamic parameters of different phases, can occur only in an infinite system. Therefore, one can expect that a first-order transition must be also smoothed when the size of the system is finite or can even disappear in small enough systems. Of course, one of the most interesting situations that should be investigated is namely the case of a van der Waals system directly corresponding to the Yang-Lee theorem. This is possible for instance within the framework of Molecular Dynamics (MD) simulations and presents certain difficulties. On the other hand there exists an example of first-order transition in a much simpler model system, namely, one can consider first-order transitions induced by an external field within the framework of the statistics with LEH. The corresponding calculations allow one, as it is shown below, to clarify characteristic features of the influence of the (decreasing) size of the system on the first-order phase transition. The results of these calculations and discussion are given in the next section of this work.

20.2 First-Order Transition in a System with LEH

We consider below a system with LEH [5] in its simplest form with only zero mode components of the fluctuations being taken into account. At this condition, LEH takes the form

$$H = at\eta^2 V + b\eta^4 V - \eta h V , \qquad (20.1)$$

where η and h are order parameter and external field, respectively, t is a temperature difference, $t = T - T_c$, T_c is the critical temperature, $V = L^3$ is volume of the system, a and b are constant parameters describing specific features of the system under consideration. At the absence of the external field, such a system undergoes a second-order phase transition; taking into account order parameter fluctuations leads to known singularities of the respective transition.

If the external field is not equal to zero, the behavior of the averaged value of the order parameter, $\langle \eta \rangle$, becomes quite different at different temperatures. Namely, at t > 0 the averaged value of the order parameter as a function of the external field is continuously passing through the origin of the coordinate system (see Fig. 20.1). At t < 0 a finite jump of this function appears when the external field becomes zero, so that this transition becomes a first-order parameter fluctuations, in this way Eq. (20.1) coincides literally with the free energy of the system [5] expressed in terms of the averaged value of the order parameter. At the same time, it is important to verify whether the order parameter fluctuations - playing a decisive role in second-order transitions - do also affect this first-order transition.

In order to do it one has to consider the averaged value of the order parameter averaging over Gibbs distribution with a Hamiltonian given by Eq. (20.1),

$$\langle \eta \rangle = \frac{\int \eta \exp\left\{-\frac{H}{T_c}\right\} d\eta}{\int \exp\left\{-\frac{H}{T_c}\right\} d\eta} \,. \tag{20.2}$$

The form of H, given with Eq. (20.1), shows that the larger is the value of the order parameter fluctuation the stronger is its influence on the averaged value of the order parameter. At the same time, at $h \rightarrow 0$ and small t the system is inside fluctuation region. Therefore, in order to clarify how the considered transition depends on the size of the system, it is necessary to connect the order parameter fluctuations with this size.



Figure 20.1: Demonstration of the absence of first-order transition at positive t (at this condition, due to fluctuations, the slope of the curves also decreases with the decrease of the system size)

Such computation can be done qualitatively by consideration the FSS properties of the susceptibility of the system,

$$\chi = \left\langle \int \eta^2 dV \right\rangle \,. \tag{20.3}$$

According to commonly employed approach, this quantity diverges as $|t|^{-\gamma}$ at the thermodynamic limit. By taking into account the finite size of the system one is to remedy such a relation in order to avoid singularities of this quantity (and all the other physical parameters).

Despite the fact that the corresponding asymptotic (finite but large size of the system) formulae can be rigorously obtained only for certain discrete models (for example, the two-dimensional Ising model [2]) their generalization is formally and physically obvious. For any singular quantity, G, it reads

$$G \equiv G\left(t^2 + \frac{1}{L^{\Delta}}\right) . \tag{20.4}$$

The function, G, in Eq. (20.4) is singular at zero argument, and the exponent Δ depends on the form of the model Hamiltonian. As it is shown in [2] the exponent Δ can be expressed via the critical indices so that for t = 0 it reads

$$\chi \sim L^{\gamma/\nu}$$
 or $\eta \sim L^{(\gamma-\nu d)/2\nu}$. (20.5)

Here ν is the exponent of the correlation length and d is the spatial dimension.

It is obvious that the sign of the exponent in the relation for η is negative so that the characteristic value of the fluctuation of the order parameter increases with the decrease of the system size. Despite this result follows from an asymptotic formula (valid for large L) it can be extended and applied qualitatively to the description of a system of an arbitrary size, so that one can expect that fluctuations namely in small systems significantly affect phase transition and can change its form.

Of course, given above speculations reflect namely the properties of second order phase transitions (do not forget that they follow from certain FSS considerations of the two-dimensional Ising model!); at the same time, it is clear that the influence of statistical fluctuations presents a phenomenon of common character, and therefore one can expect that the fluctuations manifest themselves also at first-order transitions. Such expectations are confirmed by the calculations of the average value of the order parameter at t < 0 according to Eq. (20.2).

Calculations are carried out at $a = b = T_c = 1$. The corresponding results are presented on Fig. 20.2. It is seen that at large size of the system, L = 2000, order parameter fluctuations do not affect the first-order transition (black curve). At smaller values of the size of the system this first-order transition disappears and it is easy to see that the



Figure 20.2: Smoothing of first-order phase transition at the decrease of the size of the system

smaller is system size the less is the slope of the curve presenting the dependence of the averaged order parameter on the external field. For comparison the results of the same calculations for positive t are given on Fig. 20.1. As it is bound to be there is no first-order transition at this value of the temperature but the effect of the fluctuations is also seen as the decrease of the slope of the curves at the decrease of L.

20.3 Conclusions

The results given above show, in principle, that the manifestation of phase transitions (and its type) is defined not only by the type of the Hamiltonian but also by the size of the system. Namely, we shown that first-order phase transitions (induced by an external field) in a system with LEH takes place at large sizes of the system and disappears at small enough sizes.

It is not obvious beforehand if such a conclusion can be extended to other types of interaction, for instance van der Waals type potentials. On the other hand, there are clear physical reasons for the growth of fluctuations in response to the decrease of the system size. Really, the smaller is the size of the system the less is the possibility to divide it into a large number of small (but macroscopic!) non-interacting subsystems and consequently deviations of different physical parameters from their mean values are not small. Such fluctuations are to be especially strong in the vicinity of the transition point (gas-liquid transition) where one of the phases converts to another one (so that density and energy fluctuations are valuable). Because energy fluctuations are responsible for specific heat behavior it is possible to believe that this parameter undergoes certain deviations from its usual form in the bulk. Moreover, these strong fluctuations can affect also the transition temperature as such so that corresponding deviations of the physical parameters from their bulk values just give its new position.

It is to be emphasized in conclusion that such affirmations can be confirmed for instance by certain numerical simulations.

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21 Theory and Experiment in Second-Order Phase Transitions and Critical Phenomena: The Case of Pure Liquids

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Some would like to understand what they believe in, some, to believe in what they understand.

Stanislaw Jerzy Lec

Abstract

The paper deals with some unresolved problems in the physics of critical phenomena. Precision experiments, carried out on pure liquids, show that, first, in the immediate vicinity of the critical point of pure liquids a transition (the second crossover) from the Ising critical behavior to the mean-field, classical, critical behavior is discovered. Second, a transition in the opposite direction (first crossover) that is expected far from the critical point in pure liquids is not experimentally observed at all. As a further test of the applicability of the 3-dimensional Ising model for the description of the critical behavior of pure liquids recently established by the author quasi-universal correlations "amplitude critical exponent" have been used. On the example of critical amplitudes combinations R_{γ}^{+} and R_{ε}^{*} it is shown that the existence of such correlations gives a new approach to the verification of the universality of such combinations proposed by the theory, providing a unique opportunity to apply for this test the entire array of existing experimental data. The use in these correlations of experimentally determined values of critical exponents leads to values of universal constants R_{χ}^+ and R_{ξ}^* , almost coinciding with the theoretical ones. On the contrary, if for the same correlations one uses values of critical indices corresponding to the 3-dimensional Ising model, then values of these combination turn out to be almost by a factor of $1.5 \div 2$ less than their theoretical values. Thus, the test of the Ising model with respect to its adequacy in describing properties of real pure fluids in this case leads to negative results too. All facts of inconsistencies of real systems critical behavior with their consequences concerning the applicability of the 3-dimensional Ising model, outlined in the article, will apparently demand from the modern theory of critical phenomena a certain correction, at least, with respect to the description of pure liquids.

21.1 Introduction

In his famous work of the mid-forties of last century [1], Onsager was able to show that the specific heat of the twodimensional Ising model, the so-called "nearest-neighbor" model, with explicitly involving only short-range forces, exhibits a logarithmic divergence at the critical point. Since that times, the Ising model has become *de facto* the main theoretical model of critical behavior of all those objects (pure liquids, solutions of binary alloys and anisotropic ferroand antiferromagnets), which fall into the same class of universality.

An alternative approach to this problem was presented, as it is well-known, by van der Waals already for about 50 years before the appearance of the Ising model. All van der Waals-like theories have the same important feature: the attraction forces between molecules, providing a cooperative effect, are assumed to be of a long-range type. As a result, since the theory of this type is equivalent to a model with infinite range of interaction, they have a common name of mean-field (or "self-consistent"-field) theories. This notation is borrowed from the theory of P. Weiss. These theories predict exactly the same singularities for the transition point [2]. Theories of this type, in contrast to the Ising model, do not take into account the increasing role of fluctuations in the system as it approaches the critical point.

A decisive role in the theory and practice of critical phenomena play critical indices imposed even by van der Waals. To each model of critical behavior corresponds a certain set of their numerical values (see Table 21.1, where critical indices β , γ , δ , and ν are given according to their generally accepted meaning [3]).

21 Second-Order Phase Transitions and Critical Phenomena

Table 21.1: Examples of the critical exponents.

Model	Critical indices							
Widdei	β	γ	δ	ν				
Mean-field	0.5	1.0	3.0	0.5				
3d-Ising	0.325	1.242	4.82	0.63				

As it is well known, in the asymptotic vicinity of the critical point various physical quantities can theoretically be represented by simple power-law relationships (see, for example [3])

$$f_i(x) = \Lambda_i x_i^{\lambda_i} , \qquad (21.1)$$

where x is the relative distance from the critical point for one of the thermodynamic variables (e.g., temperature or density), Λ_i and λ_i are the critical amplitudes and critical exponents, respectively.

The world literature on critical phenomena has accumulated a large amount of theoretical and experimental data confirming the applicability of the Ising model, and hence the fluctuational approach to the description of critical phenomena in **idealized** and similar systems. At the same time, the difficulties associated with the study of real non-idealized systems, whose heterogeneity is caused by the presence of boundaries, flows, external fields, etc., were, however, too serious. They are so severe that V. L. Ginzburg went on to regard the problem of phase transitions and critical phenomena as an unresolved century problem [4] even after the 1982 Nobel Prize was awarded to K. G. Wilson *"for the creation of the theory of critical phenomena"*. One of the open problems in this theory is connected with the so-called second crossover.

21.2 Second Crossover

It is known that in the course of approaching the critical point the development of large-scale fluctuations is accompanied by a continuous growth in the susceptibility of the "critical" systems to all sorts of disturbances (see, e.g. [5]). In this case, any effect (gravity and/or Coulomb field, gradients, impurities, the presence of boundaries, etc.) arbitrarily weak under normal conditions, ultimately will become a factor of primary importance [6]. As a result, any system as it approaches the critical point will behave more and more different as compared to the ideal model of its critical behavior. This kind of behavior, in turn, means that in the immediate vicinity of the critical point any real system must be regarded as non-ideal [6]. Note that the notation "immediate neighborhood" here refers to a region near to the critical point, where the influence of various "fields" in the experiments of high sensitivity and accuracy is becoming noticeable.

It is obvious that in the absence of a complete theoretical description of critical behavior of non-ideal systems the determining method of analysis has to be assigned to experiments in the nearest neighborhood of the critical point. Unfortunately the percentage of high-precision, complex, studies on the direct experimental investigation of thermodynamic properties of real systems, where the influence of various disturbing factors is not completely been eliminated, is extremely small. Nevertheless, as a result of precisely such a kind of research, new peculiarities of the critical behavior not predicted by existing theory were discovered [7, 8]. It turned out that in the immediate vicinity of the critical point, as paradoxical as this conclusion may occur, pure liquids demonstrate the van der Waals-like behavior with its inherent values of critical indices (Fig. 21.1) [7-10]. From the very beginning, such a sharp change of critical behavior has been explained by the gravitational effect [7, 8], later this idea has received further experimental confirmation [9, 10], and as a result the transition itself was denoted as "second crossover" [6, 11].

21.3 First Crossover

With respect to the first crossover – the transition from mean-field-like critical behavior to the Ising-like (fluctuational)one whose position is determined by the Ginzburg criterion [12] – our analysis (see below) of available in literature precision (p, ρ, T) -data showed that this crossover in pure liquids has not been experimentally observed [6].

In recent years the group of W. Wagner (Bochum, Germany) carried out precision (p, ρ, T) -experiments in a wide range of state parameters, including the close vicinity of the critical point, on a set of pure substances. Using the



Figure 21.1: Second crossover for pure SF₆ (\circ , \bullet , \bigtriangledown) and CO₂ (\blacktriangledown). Data for β and γ refer to the ranges $\tau < 0$ and $\tau > 0$, respectively ($\tau = (T/T_c) - 1$, T_c is the critical temperature). The piezometer height was equal to 8 mm (\circ , \bullet) and 30 mm (\bigtriangledown , \blacktriangledown). For convenience, experimental points are connected by dashed lines (for details, see [6, 11]).



Figure 21.2: Generalized coexistence curves for ethylene, argon, methane, and sulfur hexafluoride: $B = (1814 \pm 0.008)$, $\beta = (03498 \pm 0.0014)$ (for details, see [6]).

experimental results of some of these studies, we constructed the generalized temperature dependencies in a double logarithmic scale for the coexistence curve and the isothermal compressibility in the single-phase region for several



Figure 21.3: Generalized compressibility for ethylene, argon, methane, and sulfur hexafluoride: $\Gamma = (0087 \pm 0.004)$, $\gamma = (1144 \pm 0.013)$ (for details, see [6]).

pure liquids (Figs. 21.2 and 21.3, [6]). This type of analysis, allowing one to determine the effective critical exponents, is a very effective tool for studying the crossover behavior. The absence of any kinks on the curves obtained indicates that in an experiment on pure real liquids one cannot, as strange as it seems, find the transition to mean-field behavior at any distance from the critical point. The effective critical exponents $\beta = (0.3498 \pm 0.0014)$ and $\gamma = (1.144 \pm 0.013)$ have values that differ from both the classical and Ising values. At the same time as the "left" boundaries of the temperature range at each of the plots (Figs. 21.2 and 21.3) almost coincide with the beginning of transition in the area of the second crossover, it can be argued that – for real pure fluids – the "Ising" range, if it exists at all, is extremely narrow. Similar results were obtained for the critical isotherm [6].

It is interesting to note that a similar behavior of critical exponents was found already at the end of the 19th century by J. E. Verschaffelt, who was working at the van der Waals and Kamerlingh Onnes laboratories. His measurements of the coexistence curve of pure CO₂ showed that the critical exponent β retains its value constant ($\beta = 0.3434$) over a wide temperature range, i.e., $0.4^{\circ}C < T_c - T < 68^{\circ}C$ [13]. Against this background even more surprising is the fact that nowadays there is developed a theoretical direction aimed at a detailed investigation of the "first crossover" manifestations in the framework of the Ising model (see, for example [14] and references cited therein).

21.4 "Critical Exponent" – Critical Amplitude" Correlations

As a result of data analysis of both (p, ρ, T) -studies and results on light scattering experiments near to the pure liquid critical points by the author were first established correlations between $\beta - B$; $\gamma - \Gamma$; $\delta - D$ and $\xi_0 - \nu$, i.e., between the critical exponents and amplitudes involved in the description of the coexistence curve, the isothermal compressibility in the single-phase region, the critical isotherm and the correlations for the coexistence curve $(B \cdot \beta^{-b} = b_0)$ [15], isothermal compressibility in the single-phase region $(\Gamma \cdot \gamma^{-g} = g_0)$ and the critical isotherm $(D \cdot \delta^{-d} = d_0)$ [16] as well as for the correlation length $(\xi_0^* \cdot \nu^j = j_0)$ [6]. Figure 21.4 gives an example of one of these dependencies.

It is known that the general thermodynamic and statistic foundations obtained employing the assumption of the similarity hypothesis lead to the existence of a certain set of universal, model independent relations between the critical exponents, for example,

$$\beta(\delta-1) = \gamma . \tag{21.2}$$



Figure 21.4: Correlation between critical amplitude (Γ) and index (γ) for the isothermal compressibility in the single phase region (for details see [6]).

Along with such dependencies, some combinations of critical amplitudes are also universal [17], even though they themselves, in contrast to the indices, are not universal. The numerical values of these relations are also clearly associated with a class of universality of the system, and, therefore, their careful experimental determination is no less important than the knowledge of the critical indices. Among these relations the most informative and most reliable seems to us to be the relation

$$R_{\gamma}^{+} = \Gamma D B^{\delta - 1} \,. \tag{21.3}$$

In the case of three-dimensional Ising model we have the value $R_{\chi}^+ = 1.60$ with the method of ε -expansion, and $R_{\chi}^+ = 1.75$ for the high-temperature expansion method (see, e.g. [17]). For an independent verification of the universality of this relation in the case of real systems, it is necessary to investigate the behavior of all the required thermodynamic properties within the same experiment. Well-known difficulties of investigation of the critical region explain the small number of available experimental values of R_{χ}^+ .

Availability of four quasi-universal correlations allows one to offer a correct method of testing of the universality not only of above mentioned relation $R_{\chi}^+ = \Gamma DB^{\delta-1}$ but also of the dependence

$$R_{\xi}^{*} = \xi_{0}^{*} \left(\frac{B^{2}}{\Gamma}\right)^{1/3}$$
(21.4)

not using the results of only a single experiment, as it is usually done, but on the basis of these correlations, i.e., on the basis of a large body of existing experimental thermodynamic data.

21.5 Test of the Ising Model

The application of quasi-universal correlations makes it possible to present the universal relation $R_{\chi}^{+} = \Gamma D B^{\delta-1}$ as

$$R_{\chi}^{+} = \Gamma D B^{\delta - 1} = g_0 \gamma^{-g} \cdot d_0 \delta^d \cdot (b_0 \beta^b)^{\delta - 1} , \qquad (21.5)$$

where the numerical values of a set of "universal" constants are given by

$$b = 4.30 \pm 0.22 , \qquad b_0 = 178 \pm 40 ,$$

$$g = 7.15 \pm 0.16 , \qquad g_0 = 0.23 \pm 0.01 ,$$

$$d = 8.48 \pm 0.15 , \qquad d_0 = (8.2 \pm 1.5) \cdot 10^{-6} .$$
(21.6)

This set of constants was determined on the basis of a whole set of experimental data presented for each thermodynamic property under study in the form of a graphical dependence as shown in Fig. 21.4 for the isothermal compressibility in the single-phase region [15, 16]. Substituting into Eq. (21.5) the values of all the necessary constants Eq. (21.6) makes it possible to calculate the value of the universal combination of amplitudes R_{χ}^+ . To fix the values of critical indices, connected with each other by the universal relation Eq. (21.2), is required as a prerequisite.

Logically noncontradictory such determination can be performed in two ways. First, it may be done by employing a theoretical set of data corresponding to the three-dimensional Ising model: $\beta = 0.325$, $\gamma = 1.242$ and $\delta = 4.82$ (see Table 21.1). Second, one can use the values obtained independently in the same experiment on the same sample of high purity. A (p, ρ, T) -experiment on SF₆ [6-8], whose purity was not worse than 99.9995%, answered to all requirements for experiments of this kind. The obtained in the course of the experiment results – $\beta = 0.3508 \pm 0.0013$, $\gamma = 1.16 \pm 0.03$ and $\delta = 4.30 \pm 0.01$ [6–8] – are in excellent agreement with Eq. (21.2).

The first method of calculation leads to a value $R_{\chi}^+ = 0.94$, significantly different from the theoretical estimate, again indicating that values of critical indices corresponding to this model can be regarded only as a zeroth order approximation to the situation typical to real liquids. In the second case, we obtain the value $R_{\chi}^+ = 1.44$, which is close to both its theoretical RG-value ($R_{\chi}^+ = 1.6$) and the value $R_{\chi}^+ = 1.48 \pm 0.05$, which gives the substitution values of the amplitudes ($B = 2.054 \pm 0.021$, $D = 1.70 \pm 0.01$) [8] and refined $\Gamma = 0.081 \pm 0.001$ [6], conjugated with the critical indices values mentioned for SF₆, directly into the relation $R_{\chi}^+ = \Gamma DB^{\delta-1}$.

In addition we see that in Fig. 21.4, where a log-log scale for correlation between the amplitude (Γ) and the exponent (γ) for the isothermal compressibility in the single-phase region near the critical points of several pure substances is presented, there are no points corresponding to the value of $\gamma = 1.24$, a result known from the three-dimensional Ising model. Note, however, that lower values of the exponent [17] – $\gamma = 1.20$ ($\Gamma = 0.065$) and $\gamma = 1.21$ ($\Gamma = 0.061$) – resulting from the application of various theoretical models to describe the experimental data in the neighborhood of the CO₂ critical point, quite well fit into the overall picture (Fig. 21.4).

As for the other universal constant R_{ξ}^* , for its presentation in the form similar to Eq. (21.5) the results of direct measurement of thermal conductivity [18] and static light scattering (see details in [6]) for pure ammonia were used. The analysis of these data led in the relation $\xi_0^* \cdot \nu^j = j_0$ to the following parameters

$$j = 6.26 \pm 0.06$$
, $j_0 = (7.34 \pm 0.03) \cdot 10^{-3}$. (21.7)

After that, for $R_{\xi}^* = \xi_0^* \cdot (B^2/\Gamma)^{1/3}$, we have

$$R_{\xi}^{*} = j_{0}\nu^{-j} \cdot (b_{0}\beta^{b})^{2/3} \cdot (g_{0}\gamma^{-g})^{-1/3} .$$
(21.8)

Taking into account for NH₃ the values $\gamma = (1.176 \pm 0.025)$ and $\nu = (0.606 \pm 0.002)$ [6], we obtain $R_{\xi}^* = 0.665$. These results agree well with both theoretical values: the ε -expansion gives for the three-dimensional Ising model the value $R_{\xi}^* = 0.668$, and the high-temperature expansion method yields $R_{\xi}^* = 0.654$ (see, e.g., [17]). On the other hand, the substitution into Eq. (21.8) of the critical exponents (β , γ , ν) corresponding to the three-dimensional Ising model leads to $R_{\xi}^* = 0.456$, which is almost by a factor of 1.5 less than any theoretical value of R_{ξ}^* .

21.6 Conclusions

Precision experiments, carried out on pure liquids, show that

- in the immediate vicinity of the critical point under conditions of anomalously increasing system compressibility a transition to the mean-field-like critical behavior (the second crossover) is observed. To our opinion, this transition is induced by the influence of internal gravitational effects [6–8]. In the Ising model the second crossover does not occur;
- the transition in the opposite direction (first crossover), which was supposed to happen as far as removing the system from the critical point, is not observed;

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21.6 Conclusions

- the critical exponents of the system keep for several decades of change in the relative density and (or) temperature any of their values, which occur immediately after system departure from the region of the second crossover;
- between the critical amplitudes and critical indices there are quasi-universal correlations of power type what is interesting not only itself, but also allows one to the system of criteria assessing of experimental data quality to be more complete;
- the existence of such correlations gives a new approach to the verification of the universality of combinations of critical amplitudes R_{χ}^+ and R_{ξ}^* , proposed by the theory, providing a unique opportunity to apply for this test the entire array of experimental data;
- the use in these correlations of experimentally determined values of critical exponents leads to the values of universal constants R⁺_χ and R^{*}_ξ, almost coinciding with the theoretical ones. On the contrary, if for the same correlations one uses values of critical indices corresponding to the 3-dimensional Ising model, then R⁺_χ and R^{*}_ξ values turn out to be almost by a factor of 1.5 ÷ 2 less than their theoretical values. Thus, the test of the Ising model on the adequacy of describing properties of real pure fluids in this case too leads to negative results.

All of the above mentioned conclusions would, evidently, require from the modern theory of critical phenomena a certain correction, at least, when applied to pure liquids.

Once in one of his lectures, Richard Feynman (Nobel Prize Laureate in Physics (1965)) with humor which never left him and at the same time as always wonder exactly noticed: *There is always the possibility of proving any definite theory wrong; but notice that we can never prove it right. Suppose that you invent a good guess, calculate the consequences, and discover every time that the consequences you have calculated agree with experiment. The theory is then right? No, it is simply not proved wrong [19].*

This quote of Richard Feynman is fully applicable to the situation in the physics of phase transitions and critical phenomena. On this subject, thousands of papers were published, most of them with the aim to experimentally confirm the conclusions of the modern theory of critical phenomena for an idealized model. Here we presented an alternative approach to the problem under discussion.

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22 Asymmetry of Heterophase Fluctuations in Nucleation Theory Vitaly B. Rogankov

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> Alles was du sagst, sollte wahr sein. Aber nicht alles was wahr ist, solltest du auch sagen.

Voltaire

Abstract

The orthodox theory of an equilibrium transition between two infinite homogeneous phases of gas (g) and liquid (l) developed by Gibbs fails just where its application is most important for a real fluid. To describe quantitatively the regions of criticality, located around the actual critical point (T_c, P_c, ρ_c) and metastability, located inside the actual coexistence-curve $[P_{\sigma}(T), \rho_g(T), \rho_l(T)]$ one has to use the symmetric models of asymptotic scaling behavior and interfacial density profile $\rho(z)$, respectively. Although the concept of symmetry has a great heuristic value it cannot be considered as fully satisfactory in application to real systems in finite volumes. The study of formation and growth of α -nuclei in the ambient metastable β -phase requires the reliable estimates of the local properties for both constituents which the Gibbs' theory does not provide. This work is an attempt to develop the alternative thermodynamically-consistent model of predictions based on the input coexistence-curve data including the parameters of critical point.

22.1 Introduction

One may find the mean-field (MF) conjectures about the near-critical behavior of fluids in the fundamental thermodynamic books of Rowlinson [1] for local potentials and Krichevskii [2] for caloric EOSs represented by the truncated Taylor expansions. The assumptions of *analyticity and symmetry* for an internal energy e(v, T) in a pure substance

$$e_g = e_l + \left(\frac{\partial e}{\partial v}\right)_T^l (v_g - v_l) + \frac{1}{2} \left(\frac{\partial^2 e}{\partial v^2}\right)_T^l (v_g - v_l)^2 + \dots , \qquad (22.1)$$

$$v_g - v_l = 2 \ (v_c - v_l) \tag{22.2}$$

are adopted exclusively on an ad hoc basis. The standard assumption of *additivity* along the tie-lines at $(P_{\sigma}, T) = \text{const}$

$$e = \frac{v_g - v}{v_g - v_l} e_l + \frac{v - v_l}{v_g - v_l} e_g$$
(22.3)

ignores, completely, the influence of interfacial energy and surface tension, γ , on the local structure of metastability.

To go beyond the MF-oversimplifications, authors [3-5] developed the generalized Gibbs' (GG)-approach based on the following form of a local-equilibrium (LE) hypothesis

$$P_{\alpha} - P_{\beta} = s_{\alpha} \rho_{\alpha} \left(T_{\alpha} - T_{\beta} \right) + \rho_{\alpha} \left(\mu_{\alpha} - \mu_{\beta} \right) + 2\gamma / R_{c\alpha} .$$
(22.4)

It is related to the critical spherical-cluster of radius $R_{c\alpha}$ and contains the complex surface-tension functional, $\gamma(\rho_{\alpha}, s_{\alpha}; \rho_{\beta}, s_{\beta})$. To avoid the presence of unmeasurable difference

$$\mu_{\beta} - \mu_{\alpha} = (3/R_{c\alpha}) \left(\frac{\partial \gamma}{\partial \rho_{\alpha}} \right)$$

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one may use the equivalent form of LE-hypothesis

$$P_{\beta} = T_{\beta} \frac{s_{\beta} - s_{\alpha}}{v_{\beta} - v_{\alpha}} - \frac{e_{\beta} - e_{\alpha}}{v_{\beta} - v_{\alpha}} + \frac{2\gamma v_{\alpha}}{(v_{\beta} - v_{\alpha}) R_{c\alpha}} , \qquad (22.5)$$

in which an appearance of the factor $v_{\alpha}/\left(v_{\beta}-v_{\alpha}
ight)$ is essential for the concept of asymmetry.

The present author has developed [6-9] the model of fluctuation thermodynamics (FT) based on the thermodynamicallyconsistent system of homophase and heterophase equalities at any coexistence-curve (CXC)-state

$$P_{j} = T_{j} \left(\frac{\partial P}{\partial T}\right)_{\rho_{j}} + \rho_{j}^{2} \left(\frac{\partial e}{\partial \rho}\right)_{T_{j}} = T_{j} \left(\frac{\partial s}{\partial v}\right)_{T_{j}} - \left(\frac{\partial e}{\partial v}\right)_{T_{j}}, \qquad (22.6)$$

$$P_{\sigma} = T \frac{dP_{\sigma}}{dT} + \rho_l \rho_g \frac{e_l - e_g}{\rho_l - \rho_g} = T \frac{s_g - s_l}{v_g - v_l} - \frac{e_g - e_l}{v_g - v_l} , \qquad (22.7)$$

$$B_{T_j} = \frac{1}{\rho_j \, k \, T_j \, \chi_{T_j}} = v_j^2 \left\{ \left[\frac{\partial^2 \left(e/kT \right)}{\partial v^2} \right]_{T_j} - \left[\frac{\partial^2 \left(s/k \right)}{\partial v^2} \right]_{T_j} \right\} \,, \tag{22.8}$$

where the subscript $j = (\alpha, \beta)$ is introduced to separate the heterophase aggregates from their two-phase counterparts i = (g, l). The second equality Eq. (22.7) accumulates the Maxwell's and Clapeyron's conditions. It can be compared with the GG-Eq. (22.5) to conclude that the former is the limiting macroscopic form of the latter at any subcritical temperature, $\overline{T} = (1 - T/T_c) \ge 0$, including the critical point (CP) itself.

The differential form of Second Law described by Eq. (22.8) for an isothermal modulus, B_T , admits finite (nonzero) values of second derivatives at the ordinary points of spinodal, $B_T = 0$. One should not miss the distinction between the isothermal derivatives of caloric EOSs from Eq. (22.8) and those for the local thermodynamics potential, e(v, s). At the classical spinodal determined as an envelope for the families of isochors and isoentrops by the Gibbs' conditions

$$\left(\frac{\partial P}{\partial T}\right)_{v} = \left(\frac{\partial P}{\partial T}\right)_{s} = \frac{dP_{sp}}{dT} \qquad (a)$$

$$e_{ss}e_{vv} = e_{sv}^{2} \qquad (b)$$
(22.9)

both requirements of strong divergence, $\chi_T \to \infty$ and $C_p \to \infty$, are fulfilled. At the actual (non-classical) CP the additional conditions for the weak divergence, $C_v \to \infty$ ($e_{ss} = 0$) and $\chi_s \to \infty$ ($e_{vv} = 0$), are connected with the spinodal equality, $B_T = 0$, too.

On the other hand, there is the essential difference between the van der Waals (vdW) definition of a classical CP by two isothermal derivatives of thermal EOS, $P_v^c = P_{vv}^c = 0$ and that for the second-order phase transition in which the second derivative, $P_{vv}^{so} \neq 0$ and C_v is finite. Rowlinson [1] discussed the experimental determination of classical CP as a combination of two requirements

- 1. it is the state at which the i-densities become equal, $\rho_g = \rho_l = \rho_c$;
- 2. it is also the highest set of (T_c, P_c) -values at which $P_v^c = 0$ (firstly, without the additional stability-constraints on $P_{vv}^c = 0$ and $P_{vvv}^c < 0$ implied by the vdW-EOS).

A meaningful note was [1] that " $C_p \to \infty$ and the sharp increase of C_v make it hard to reach thermal equilibrium [as well as] even slow changes of P are more nearly adiabatic then isothermal and cyclic changes leads to hysteresis". The standard analysis of stability requires that $e_{sv} = (\partial T/\partial v)_s < 0$ below and near CP but it is so only for the g-phase branch $v_g(T)$ along CXC.

The local description of the *liquid region* below T_c used by FT-model is not MF-one because the third term of RHS in Eq. (22.1) is adopted to be zero. Simultaneously, it can be still called "classical" since the same condition is fulfilled in the original vdW-EOS. The most appropriate for the study of (g,l)-asymmetry FT-EOS has been proposed [6, 7] on the base of Eqs. (22.6)-(22.8) and the measurable input CXC-data *without any adjustable parameters* as

$$Z_{FT} - 1 = \frac{b(T)\rho - c(T)}{1 - b(T)\rho} - \frac{a(T)\rho}{kT}, \qquad (22.10)$$

$$a(T) = \frac{P_{\sigma} \left(A_{\sigma} - 1\right)}{\rho_{l} \rho_{g}} = -\frac{e_{l} - e_{g}}{\rho_{l} - \rho_{g}} = -\left(\frac{\partial e}{\partial \rho}\right)_{T}^{l} , \qquad (22.11)$$

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$$b(T) = \frac{A_{\sigma} - 2}{(\rho_l + \rho_g) (A_{\sigma} - 1)} , \qquad (22.12)$$

$$1 - c(T) = Z_l \left[1 + \frac{\rho_l \left(A_\sigma - 1 \right)}{\rho_g} \right] (1 - b\rho_l) , \qquad (22.13)$$

where

$$A_{\sigma} = \left(\frac{T}{P_{\sigma}}\right) \left(\frac{dP_{\sigma}}{dT}\right)$$

and

$$Z_l = \frac{P_\sigma}{(\rho_l kT)}$$

The last equality from Eq. (22.11) can be compared with the MF-equation, Eq. (22.1)

$$e_g = e_l + \frac{v_l}{v_g} \left(\frac{\partial e}{\partial v}\right)_T^l \left(v_g - v_l\right) \,. \tag{22.14}$$

The appearance of the (v_l/v_g) -factor in the FT-coefficient a(T) in Eq. (22.11) is the sign of CXC-asymmetry. It is inherently close to that from the GG-estimate in the γ -dependent term of Eq. (22.5). Another distinctive feature of the asymmetric approach is that the modulus B_{T_j} from Eq. (22.8) is connected [10] with the spatial integral of a finite-range direct correlation function $c(r; \rho, T)$. It controls the coefficient c_o in the standard square-gradient theory of density profile.

22.2 Non-Classical Spinodal and Near-Critical Anomalous Nucleation in Gas Phase

The quantitative prediction of a spinodal, consistently with the measurable thermal CXC-data, is an important ingredient in any study of nucleation and spinodal decomposition. The distinction of a physical scenario for these phenomena becomes especially essential near CP where the long-range, $r \leq \xi$, and long-time, $t \leq \tau$, equilibration of LE-states is observable. The known approach to investigate the above distinction by computer simulation is the *instantaneous quench* [11] of a preliminarily equilibrated (*N*,*V*,*E*)-system from a one-phase initial state to the metastable or unstable regions located within the CXC. Unfortunately, this method provides the detailed density morphology and describes reliably the time evolution only if the "temperature distance" $T_c - T > 0$ at a quench is significant.

Another possibility to achieve the near-critical metastable and unstable regions can be realized by the laboratory experiment as the shock-wave of expansion [12, 13]. The concept is similar to the just described because one must fastly quench the equilibrium system into the vicinity of CP. Zeldovich has supposed [12] that the distribution of classical LE-states can be formed quickly at $t \le t_c$ in the small open subvolumes $\sim r^3 \le r_c^3$ (r_c - an effective cut-off radius of direct interactions) at the initial *adiabatic* stage of equilibration. As a consequence, one has to observe the restoration of the MF-type EOS at these molecular scales r_c , t_c

$$P - P_c = a \left(T - T_c \right) + b \left(\rho - \rho_c \right) \left(T - T_c \right) + c \left(\rho - \rho_c \right)^3 , \qquad (22.15)$$

which is in contradiction to the experimental near-critical data [14] obtained mainly for the mesoscopic scales, $\sim r^3 \leq \xi^3$ and $t \leq \tau$ ($\xi_c \to \infty, \tau_c \to \infty$).

Novikov [13] has developed the phenomenological MF-type EOS for the same region

$$P - P_c = a \left(T_c - T\right) + b \left(v_c - v\right)^2 \left(T_c - T\right) + c \left(T_c - T\right)^{5/3} + d \left(v_c - v\right)^5$$
(22.16)

based exclusively on the classical Gibbs' description of the heterophase states [15]. There are, however, some distinctive features of such an approach. By contrast to MF-expansion which requires, in addition to Eq. (22.4) for volumes, the complete symmetry of caloric CXC-properties [2]

$$e_g - e_l = 2(e_c - e_l)$$
, $s_g - s_l = 2(s_c - s_l)$ (22.17)

both these consequences of Eq. (22.3) are not fulfilled at the thermodynamically consistent consideration. This is the main reason for an appearance of non-analytic contribution $\sim (T_c - T)^{5/3}$ in Eq. (22.16) and the respective divergence

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in the second derivative $(d^2 P_{\sigma}/dT^2)_c$ of the vapor-pressure and spinodal curves (which are confluent at CP) with the common exponent, $\theta = -1/3$. It is worthwhile to note that the similar exponent in Eq. (22.15) is even larger, i.e., $\theta = -1/2$, while in the framework of scaling theory one obtains $\theta = -\alpha = -0.11$ [14] (see also Section 22.3).

The important result obtained as a development of Gibbs' analysis of stability is the proved necessity [13] to use different sets of coefficients (a,b,c,d) in Eq. (22.16) for the coexisting (g,l)-phases. The failure of a global EOS-concept is connected with the hypothesis of homogeneity in the thermodynamic limit. If the whole (N,V,E)-system is treated as a homogeneous one the statistical mechanics [16] always predicts subcritical isotherms $T \leq T_c^o$ of vdW-type independently of the accuracy provided by the molecular model or by simulations. To avoid this restriction one may, at least, omit the concept of global vdW-type EOS.

This approach realized in the framework of FT-model (Section 22.1) predicts an unwanted shape of non-classical spinodal (NSP) shown for CO_2 and H_2O in Figs. 22.1 and 22.2 together with its classical counterpart (SP). To obtain the latter, the classical thermodynamically-consistent variant of FT-EOS (Eq. (22.10)) (named below by the WMG (van der Waals-Maxwell-Gibbs)-abbreviation to separate it from the MF-approximations) has been used. It is based on the following sequence of steps. One must, firstly, solve the transcendental equation for the given ratio of *T*-dependent coexisting densities (factor of CXC-asymmetry)

$$\frac{\rho_g}{\rho_l} \equiv \varphi_{\sigma}(T) = \frac{1 + y(x)e^{-x}}{1 + y(x)e^x} , \qquad (22.18)$$

in which the universal CXC-function *y*(*x*) is known [6, 8] and *x* is the *classical WMG-disorder parameter* of the entropy difference from Eqs. (22.5) and (22.7)

$$x = (s_g - s_l)^o / 2k . (22.19)$$

In contrast, the *actual non-classical disorder parameter* is measurable and can be determined by the Clapeyron equation for the reduced slope A_{σ} from Eqs. (22.11)-(22.13)

$$A_{\sigma}(T) = \frac{T(s_g - s_l)}{P_{\sigma}(v_g - v_l)} = \frac{(h_g - h_l)\rho_g\rho_l}{P_{\sigma}(\rho_l - \rho_g)} .$$
(22.20)

The next step is the consistent evaluation of classical WMG-excluded volume $b^{\circ}(T)$ in the coexisting *i*-phases

$$v_g(T)/b^o(T) - 1 = y(x)e^x$$
, $v_l(T)/b^o(T) - 1 = y(x)e^{-x}$. (22.21)

One may compare it with the actual non-classical coefficient b(T) from Eq. (22.12). The other classical WMGcoefficients $A^o_{\sigma}(T)$, $a^o(T)$, $c^o(T)$ are determined by the FT-EOS', Eqs. (22.11)-(22.13). In particular, the cohesive classical coefficient $a^o(T)$ depends now upon CXC-diameter ρ_d but not on the actual reduced slope $A_{\sigma}(T)$ from Eqs. (22.11)-(22.13)

$$a^{o}(T) = \frac{P_{\sigma}}{\rho_{l}\rho_{g} \left[1 - 2b^{o}(T)\rho_{d}\right]} \,. \tag{22.22}$$

As a result, one obtains *two alternative sets* of classical WMG-coefficients $(a^o, b^o, c^o, A^o_{\sigma})$ and non-classical FT-EOScoefficients (a, b, c, A_{σ}) which both are completely consistent with the input CXC-data $(\rho_g, \rho_l, P_{\sigma})$ at each subcritical temperature $T \leq T_c$.

We have used the accurate experimental (smoothed) CXC-data measured by Wagner et al. for CO_2 [17] and H_2O [18] as well as by Douslin and Harrison for C_2H_6 [19] below to calculate the above sets of coefficients. Then, an universal combination of the NSP and SP, respectively has been predicted for CO_2 (Fig. 22.1) and H_2O (Fig. 22.2) by the system of SP-equalities

$$P_{sp} = a(T)\rho_{sp}^2 \left[1 - 2b(T)\rho_{sp}\right], \qquad (22.23)$$

$$RT [1 - c(T)] = 2a(T)\rho_{sp} [1 - b(T)\rho_{sp}]^2 .$$
(22.24)

Any adjustable parameters are absent in the described procedure of prediction.

It is obvious from Fig. 22.2b that the reentrant shape $P_{sp}^{l}(T)$ of SP for water can be predicted independently of the concept of *pseudospinodal* used by Speedy [20]. Another impressive fact is the excellent agreement in Figs. 22.1 and 22.2 of SP predicted by the WMG-coefficients with that obtained by Kraska et al. [21-23]. These authors have emphasized "the enormous computational effort for (MD) simulations using the electrostatic CO₂-model" and, all the more, even for those based on the oversimplified H₂O-model but, at the same time, have found *the obvious similarity*



Figure 22.1: Classical (WMG)- and non-classical (FT-EOS)-spinodals predicted for carbon dioxide; the input CXC-data [17] are shown by lines.

with the results of simulations for the simplest Ar-model. This similarity for many other substances and the reliable prediction of a liquid's spinodal branch up to the CP itself are demonstrated by FT-model without any efforts on the base of exclusively measurable CXC-data for all above numerated substances.

The most striking distinction between NSP and SP is observable for g-phase in which the narrow strip of anomalous



Figure 22.2: Classical (WMG)- and non-classical (FT-EOS)-spinodals predicted for water; the input CXC-data [18] are shown by lines.

negative compressibility arises in the near-critical range, $\overline{T} \leq 2 \cdot 10^{-2}$. A gas' NSP-branch becomes tangential to the vapor-pressure $P_{\sigma}(T)$ at the certain temperature located near but still below T_c where the standard supersaturation is, $P_{sp}^g/P_{\sigma} = 1$ (Figs. 22.1c and 22.2c). Above this point, the P_{sp}^g/P_{σ} value is again larger than unity and the anomalous



Figure 22.3: Global asymmetry of the classical liquid and the non-classical gas for C_2H_6 predicted along the isotherms: 1) 248.15K; 2) 273.15K; 3) 298.15K; 4) 303.15K; 5) 304.15K; 6) 305.25K; 7) 305.33K (Empty squares: predictions by FT-EOS and WMG; Full squares: experimental single-phase data obtained by Douslin and Harrison [19]; CP is the actual critical point, MCP is the metastable critical point).

hump arises on the near-critical isotherms (four of them (4-7) are shown in Fig. 22.3 for C_2H_6 predicted by the non-classical FT-EOS.

Formally, spinodal decomposition becomes possible in the LE-states located outside the measurable g-branch $\rho_g(T)$ of CXC. However, it is hardly possible to observe this dynamical process by the laboratory experiments since the initial g-phase is unstable only for all infinitesimal density variations having a wavelength greater than some critical wavelength, $\lambda \ge \lambda_c \approx \xi$ [11, 24]. Simultaneously, the mesoscopic fluctuations are highly probable in the described pseudo-metastable g-phase with any intermediate wavelength, $r_c < \lambda < \xi$. The respective physical scenario is here nucleation but its anomalous nature (based on the great value of correlation length ξ near CP) requires the study and confirmation by computer experiments.

It is also interesting to compare the predicted here static inhomogeneities with the ones described by the hydrodynamic theory of spinodal decomposition in a fluid phase [24]. It accounts for stochastic fluctuations and *incorporates a non-local driving force through the pressure gradient dependence*. The principal distinctions of FT-model [9] from the generalized vdW-approximation used by Koch et al. [11, 24] are the different regions of applicability and the adopted models of a fluid. If the former emphasizes the asymmetric nature of g- and l-phases, the latter uses the perturbationtype modification of the vdW-theory based on the reference hard-sphere model. The same authors [24] have compared, in particular, the MD-simulated behavior of a Lennard-Jones fluid [11] quenched to the middle of unstable region from $T_a^c = 2.0$ to $T^* = 0.8$ ($T_c^* = 1.36$) along the critical isochor $\rho_o^c = \rho_c^*$.

The natural question is then "can the predicted NSP be trusted?" taking into account the asymptotic (monotonous) behavior of the critical isotherm T_c [14]

$$\bar{P}_i \equiv 1 - P_i \left(T_c, \rho \right) / P_c = \pm D_o \left| \bar{\rho}_i \right|^\delta \tag{22.25}$$

and the topmost symmetric part of CXC

$$\Delta \bar{\rho} \equiv (\rho_l - \rho_g) / 2\rho_c = B_o \bar{T}^\beta . \tag{22.26}$$

The simple argument to approve the positive answer follows from the comparison of Eq. (22.26) with the thermodynamicallyconsistent definition of the same quantity $\Delta \bar{\rho}$ used in this work

$$\Delta\bar{\rho} = \frac{(s_g - s_l)\,\rho_g}{2k\rho_c A_\sigma(T)Z_l(T)} \,. \tag{22.27}$$

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Figure 22.4: Two asymmetric manifolds of classical liquid and non-classical gas tied along the split dew-bubble curve of interface at subcritical temperatures (a weak direction in the Griffiths-Wheeler's sense); a fluid region above T_c is subdivided presumably by the strong direction of non-classical (dotted curve) critical isobar P_c onto the subregions of supercritical fluid (located up to the also strong direction of classical (dashed curve) critical isotherm T_c) and non-classical gas. The predicted by FT-EOS novel form of (P, T)-diagram is based on the actual CXC- and CP-data of a substance but it is represented here schematically.

One may obtain the same value of *heterophase order parameter* $\Delta \bar{\rho}$ for two possible (non-classical and classical) combinations of *heterophase disorder parameter* $(s_g - s_l)/2k$ with the respective reduced slope $A_{\sigma}(T)$. This possibility is confirmed by the described here FT-model's formalism and is illustrated in Fig. 22.4 for C₂H₆.

The additional $P_{\sigma}^{o}(T)$ -branch located near the input one $P_{\sigma}(T)$ has been evaluated by the numerical integration of $A_{\sigma}^{o}(T)$ -values. At the actual CP there are two alternative variants of critical FT-EOS' non-classical and classical coefficients

$$a_{c} = P_{c} \left(A_{c} - 1\right) / \rho_{c}^{2}, b_{c} = \left(A_{c} - 2\right) / \left[2\rho_{c} \left(A_{c} - 1\right)\right], 1 - c_{c} = Z_{c} A_{c}^{2} / \left[2\left(A_{c} - 1\right)\right],$$
(22.28)

$$a_c^o = 3P_c/\rho_c^2$$
, $b_c^o = 1/3\rho_c$, $1 - c_c^o = Z_c/Z_c^o$. (22.29)

The ones belonging to the latter set can be obtained from the former set by the discontinuous change in the reduced slope from the actual slope A_c to the classical slope $A_c^o = 4$.

The spectacular confirmation of (g,l)-asymmetry has been demonstrated by the extrapolation of WMG-critical isotherm, T_c , into the g-range $\rho \leq \rho_c$

$$P(T_c, \rho) = \frac{\rho R T_c \left(1 - c_c^o\right)}{1 - b_c^o \rho} - a_c^o \rho^2$$
(22.30)

as well as of the FT-EOS-critical isobar P_c into the *l*-range $\rho \ge \rho_c$

$$P_c(T,\rho) = \frac{\rho RT \left[1 - c(T)\right]}{1 - b(T)\rho} - a(T)\rho^2 .$$
(22.31)

One obtains two evident envelopes of the classical WMG-isotherms, $T \leq T_c$, and non-classical FT-EOS-isobars, $P \leq P_c$, respectively.

In contrast to a variety of global-EOS-models of phase transition, the developed approach based on the measurable input CXC data $[P_{\sigma}(T), \rho_g(T), \rho_l(T)]$ predicts reliably the single-phase and metastable properties up to the region

22.3 Surface Tension and Density-Factor of CXC-Asymmetry

of CP. At the same time, the predicted asymmetry of classical $(s_g - s_l)^o / 2k$ and non-classical (actual) disorder parameter $(s_g - s_l) / 2k$ generalizes the concept of asymmetry between the *homophase disorder parameters* $(s_g - s_c)$ and $(s_c - s_l)$ demonstrated by the MF-consideration [13]. The important consequences of this generalization for the description of heterophase fluctuations are obvious. Indeed, one obtains the consistent asymmetric estimates of heat which is required either to form the bubbles in a *l*-phase, $T(s_g - s_l)^o > 0$, or to form the drops in a *g*-phase, $T(s_g - s_l)^o < 0$.

An appearance of second (metastable) CP shown in Figs. 22.1-22.4 and located near the actual CP at the different values, P_c^m , ρ_c^m but at the same critical temperature, $T_c^m = T_c$, is a consequence of local FT-EOS. It gives the novel information about the interrelation between the classical vdW-definition of CP by two equalities, $P_v^c = P_{vv}^c = 0$, and the standard one [16] adopted for the second-order phase transitions. The latter is called here a metastable CP (MCP) which is connected with an actual CP by the unstable part of critical isotherm predicted by FT-EOS. Benguigui [25] discussed the similar interrelation between CP and MCP for the phase transitions in ferro-magnetics and ferro-electrics.

22.3 Surface Tension and Density-Factor of CXC-Asymmetry

The role of classical vdW-type spinodal determined by the constrained form of Eq. (22.8) $B_{T_j} = 0$ for any global EOS as the deterministic boundary of metastability must be specified. The local-density fluctuations become unbounded at its points only if one tries to use the Gaussian-type (GT)-description when the second moment $\langle (\delta \rho)^2 \rangle$ is really infinite [16]. There are many signs that the dynamics of nucleation growth is non-linear and one should not expect the GT-approach to be valid. Although it no longer applies, more complicated classical distributions of fluctuations (an Airy density at a marginal type steady-state of spinodal and a Pearcey density at a critical state) become appropriate. It was shown [9] that the GT-distribution must be replaced by the above densities in which the isothermal compressibility χ_{T_j} is large but finite (and, respectively, the bulk modulus B_{T_j} is small but also finite).

At first sight, to elucidate the details of characteristic scales, r_c , $R_{c\alpha}$, and ξ , it is naturally to apply a combination of scaling theory [14] and a homogeneous-nucleation theory [26]. However, the former realizes the non-analytic approach to the Ising-like (IL)-systems and its extrapolation into the metastable regions is ill-defined. On the other hand, the latter uses the analytic GT-approximation [16] and its predictions become especially questionable at the extrapolation for the heterophase fluctuations. This is a direct consequence of the highly-modelistic (i.e. qualitative by nature) consideration based on the usage of unmeasurable chemical potential. Its model for the coexisting (g,l)-phases as well as for their analytic metastable extensions, $\mu_g(P,T)$ and $\mu_l(P,T)$, respectively, may turn out inconsistent if the concept of global EOS fails. It is important to emphasize here that such an inconsistency can reveal the significant physical distinctions (asymmetry) of metastability in the above phases.

To illustrate this statement let me remind that a relative concentration of homogeneous liquidus clusters containing n particles in the ambient metastable vapor β -phase depends presumably on the supersaturation, $P/P_{\sigma}(T)$ [26], as

$$\frac{C_n}{C} \approx \left(\frac{P}{P_{\sigma}}\right)^n \exp\left[-\frac{4\pi\gamma(T)}{kT} \left(\frac{3v_l n}{4\pi}\right)^{2/3}\right] \,. \tag{22.32}$$

Weakliem and Reiss [27] have demonstrated that at very small values *n* the factor $(P/P_{\sigma})^n$ becomes ill-founded. It is argued, implicitly, that the *n*-cluster must have a minimum effective radius

$$R_{m\alpha} = [3v_l(T)n/4\pi]^{1/3}$$

in order to exist at given external conditions (P,T). It seems, however, that the use itself of two fixed fields (P,T) at the investigation of heterophase fluctuations is the certain restriction. Obviously, any choice of the standard $(V;\mu,T)$ or (N;P,T)-ensembles with two fixed external fields does not determine comprehensively the state of two-phase [1] i = (g, l) or, generally, heterophase $j = (\alpha, \beta)$ assembly. Both pairs of thermodynamically conjugated intensive variables $(\rho, \sigma = \rho s)$ or (v,s) can vary within given CXC-limits without changing of the fixed fields, (μ,T) or (P,T), respectively. Additionally, the observable existence of bimodal distributions of LE-fields in the molecular scales makes the standard statistical mechanics and the GT-fluctuation theory [16] inapplicable. The thermodynamic insight can be gained by the method of present work in which the striking asymmetry between the nucleation phenomena in vapor and liquid becomes evident.

The distinctions between the classical (MF, GT) and non-classical (IL) scaling structures of fluctuations have important implications for many problems of the nucleation theory [28]. An existence of the reentrant shape of pseudospinodal in the near-MF-systems provides, for example, the reasonable explanation of the formation of glasses in

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supercooled liquids. Speedy has shown for the low-temperature region of water [20] that the above conjectural limit of stability corresponds to the power-law divergences of the response functions with the common pseudospinodal exponent $\gamma = 1/2$ along any subcritical isobar

$$\chi_T \sim \alpha_P \sim C_P \sim [T_{sp}(P) - T]^{-1/2}$$
 (22.33)

It has been demonstrated by Fig. 22.2b that the reentrant shape of *classical WMG-spinodal* can be obtained without any appeals to the concept of *pseudospinodal* and to the respective analytic expansion adopted by Speedy [20] for the local EOS of liquid water. As a result, the term pseudo-MF-systems (PMF) is preferable below instead of conventional one, near-MF-systems [28]. Moreover, the main difference between the MF- and PMF-systems adopted here is that all hyperscaling exponents of latter ones (ν , η , μ) are larger than even those in IL-systems while the respective scaling sets (α , β , γ , δ) are coincided. The spatial structure and type of fluctuations close to spinodal are different in the universal classes of (*N*, *V*,*E*)-systems represented in Table 22.1 where the scaling arguments [14] have been used for separation.

Table 22.1: Universal classes of criticality: * the relation $(\mu/\nu) = 2$ is not fulfilled $(T \le T_c)$, ** only if the relation $(\mu/\nu) = 2$ is fulfilled $(T \ge T_c)$, *** logarithmic divergence.

Туре	scaling		hyperscaling							
	α	β	γ	δ	ν	η	μ			
	3/2 - 1aw	$3/2 - \text{law} \ (\beta \ \delta = \gamma + \beta = 3/2) \ [9]$								
MF	0	1/2	1	3	1/2	0**	3/2*			
GT	1/2	1/2	1	3	1/2	0**	1			
PMF	0	1/2	1	3	2/3	1/2	4/3			
IL	1/6	1/3	7/6	9/2	11/18	1/11	11/9			
	ε – expanded	nsion resu	Its $(d = 3)$	[14]						
IL	0.110	0.326	1.239	4.80	0.630	0.033	1.26			
	$5/3 - \text{law} \ (\beta \ \delta = \gamma + \beta = 5/3)$									
MF5	0***	1/3	4/3	5	2/3	0**	4/3			

One may consider the appropriate set of the hyperscaling PMF-exponents introduced in [9] in the framework of 3/2-law as an alternative to the standard MF-one. Consequently, the supposed divergence of coefficient c_o in the vdW square-gradient theory of interface [29]

$$\beta = \rho f = \beta_{vdW} \left(\rho, T\right) + \left(c_o/2\right) \left(\vec{\nabla}\rho\right)^2 \tag{22.34}$$

is here much stronger

$$\eta \nu = 1/3 (PMF) \gg 1/18 (IL - (3/2) - \text{law}) > 0.02 (IL)$$

than the conventional one for the IL-type [28]. All these discrepancies with the vdW-concept (in which c_o is a positive constant independent on the state variables (ρ , T)) do not necessarily indicate a breakdown of the vdW-approximation, Eq. (22.34). In contrast, it might well be a consequence just of the Widom's interpretation [29] based on the determination of a second moment

$$c_o = -\frac{1}{6} \int r^2 U(r) d\vec{r} \approx \frac{1}{6} \int r^2 \left[kTc(r) \right] d\vec{r}$$
(22.35)

by the Ornstein-Zernike's direct correlation function. This approach replaces the vdW-contribution β_{vdW} in Eq. (22.34) by the original Widom's scaling EOS ($\beta = -P + \mu \rho$).

To test the consistency of a spinodal prediction far away from CP one may use the set of reliable semi-empirical correlations developed for the surface tension γ by the principle of corresponding states (PCS) [30]. The main independently-determined factor is here the difference of pressures between the liquid branch of classical spinodal, $\bar{P}_{sp}^{l} = 1 - P_{sp}^{l}/P_{c}$, and the saturated-vapor curve, $\bar{P}_{\sigma} = 1 - P_{\sigma}/P_{c}$. The best, from my viewpoint, variant of such a correlation is provided by the known Furth-Skripov's equation ($C_{o} \approx 1$)

$$\bar{P}_{sp}^{l} - \bar{P}_{\sigma} = \frac{C_{o}}{P_{c}} \frac{\gamma^{3/2}}{\left(kT\right)^{1/2}} \left(1 - \frac{\rho_{g}}{\rho_{l}}\right)^{-1}$$
(22.36)

in which the asymmetric factor (Section 22.1) is represented explicitly. Since it is desirable to obtain the conclusions without introducing any adjustable coefficients, the equality, $C_o = 1$ has been used below.

Filippov [30] has developed the consistent PCS-variant of description

$$\bar{P}_{sp}^{l} - \bar{P}_{\sigma} = (C_1 - C)\,\bar{T}^{\beta\sigma} \tag{22.37}$$

based on the system of postulated equations with the common reduced slope, $A_c = B_o^{1/\beta}$ at CP

$$\bar{P}_{sp}^{l} = B_{o}^{l/\beta}\bar{T} + C_{1}\bar{T}^{\beta\delta}, \ \bar{P}_{\sigma} = A_{c}\bar{T} + C\bar{T}^{\beta\delta}.$$

$$(22.38)$$

By comparison of Eqs. (22.36) and (22.37) one obtains the equality

$$\mu = 2(2 - \alpha)/3, \qquad (22.39)$$

which is exactly satisfied in any hyperscaling system from Table 22.1. It is fulfilled also in the MF5 [13] but not in the MF3 [12] systems. Unfortunately, any estimate of C_1 in Eq. (22.38) is rather arbitrary.

To elucidate the problem of consistency we have also tested by scaling arguments the correlation recently proposed by Kraska et al. [21-23] for a phenomenological prediction of $\bar{P}_{sp}^l(\bar{T})$

$$\bar{P}_{sp}^{l} - \bar{P}_{\sigma} = \frac{3}{2P_{c}} \frac{\gamma}{l} , \qquad (22.40)$$

where l(T) is the actual thickness of interfacial layer. Let us assume the asymptotic single-power-laws in accordance with the Widom's concept of interface [29]

$$l = \xi = \xi_o \bar{T}^{-\nu} , \qquad \gamma = \gamma_o \bar{T}^{\mu} . \tag{22.41}$$

This assumption provides the IL-asymptotic behavior of second derivative

$$\frac{d^2 \left(\bar{P}_{sp}^l - \bar{P}_{\sigma} \right)}{d\bar{T}^2} = \frac{3\gamma_o}{2P_c\xi_o} \left(2 - \alpha \right) \left(1 - \alpha \right) \bar{T}^{-\alpha} , \qquad (22.42)$$

if one takes into account the scaling equalities

$$\mu + \nu = \gamma + 2\beta = 2 - \alpha \,. \tag{22.43}$$

However, Kraska et al. [21] have developed the correlation Eq. (22.40) far away from CP where its comparison with the Furth-Skripov's Eq. (22.36) gives

$$\xi_o = \frac{3B_o\rho_c}{\rho_l(T)} \left(\frac{kT}{\gamma_o}\right)^{1/2} \bar{T}^\beta \equiv \xi_o^o(T)\bar{T}^\beta , \qquad (22.44)$$

if the hyperscaling equality (see Table 22.1) is also fulfilled

$$\mu = 2\nu . \tag{22.45}$$

One must conclude paradoxically that the asymptotic subcritical behavior of the thickness and correlation length is somehow elusive in this approximation

$$l = \xi = \xi_o^o(T)\bar{T}^{\beta-\nu} \,. \tag{22.46}$$

It can be even non-divergent for the GT-systems in which $\beta = \nu$.

This discrepancy may be eliminated by the natural, from my viewpoint, generalization of Eq. (22.40) in accordance with Eqs. (22.36)-(22.39)

$$\bar{P}_{sp}^{l} - \bar{P}_{\sigma} = \frac{3}{2P_{c}} \frac{\gamma}{l} \left(1 - \frac{\rho_{g}}{\rho_{l}} \right)^{-1} .$$
(22.47)

It gives the prediction of spinodal \bar{P}_{sp}^l supposed by Kraska et al. [21-23] far away from CP (where $\rho_g \ll \rho_l$) and, simultaneously, it provides the consistent *T*-dependent estimate of amplitude ξ_o from Eq. (22.41)

$$\xi_o = \frac{3}{2} \left(\frac{kT}{\gamma_o}\right)^{1/2} \,. \tag{22.48}$$

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It is interesting to compare the proposed here phenomenology with the interpretation of Tolman's length Δ , the curvature-correction coefficient for the surface tension

$$\gamma(R,T) = \gamma(T)\left(1 - 2\Delta/R\right) \tag{22.49}$$

developed, recently, by Wang and Anisimov [31] in the framework of complete scaling. Authors [31] have obtained an approximation

$$\Delta \approx \mp \xi_o \left[\frac{3a_3}{2(1+a_3)} B_o \bar{T}^{\beta-\nu} - b_2 \frac{\beta B_o}{\Gamma_o^-} \bar{T}^{1-\alpha-\beta-\nu} \right] , \qquad (22.50)$$

where \mp corresponds to a liquid droplet or to a vapor bubble, respectively, and a_3 -coefficient is zero in the revised (incomplete) scaling where only b_2 -coefficient is essential. The amplitude ξ_o from Eq. (22.41) corresponds to a universal ratio, $\xi_o^- = \xi_o^+/1.96$, and it can be expressed by the two-scale-factor universality [32] as

$$\xi_o^- = \left(\frac{U^- k T_c}{\gamma_o}\right)^{1/2} \,, \tag{22.51}$$

where U^- as well as the above value 1.96 are universal dimensionless numbers.

Table 22.2: Comparison of characteristic microscopic scales at CP.

Substance	Ne	N ₂	Ar	O ₂
$T_c, K/\gamma_o, dyn/cm$	44.8/15.1	126/28.4	150.7/36.31	154.3/38.4
ξ_o , nm, Eq. (22.48)	0.304	0.371	0.359	0.353
d_{LJ} , nm, [33]	0.278	0.371	0.341	0.346

One may compare these local near-critical estimates, expressed by Eqs. (22.49)-(22.51), with the global description represented by Eqs. (22.44), (22.46), and (22.48). The relatively weak divergence in Eq. (22.46) is related to the correlation length ξ and/or thickness of the interface l itself while that in Eq. (22.50) corresponds to the contribution in the Tolman's length Δ from the complete scaling [31]. The above supposition to use directly the density-factor of asymmetry in Eq. (22.47) provides the *T*-dependent estimate of ξ_o by Eq. (22.48). It is asymptotically consistent with its estimate obtained by Anisimov and Sengers [32]. The quantitative estimates obtained by the input γ_o -data at $\mu = 11/9$ from [33] are represented in Table 22.2. The effective diameter d_{LJ} of the Lennard-Jones (12/6) potential based on the second-virial coefficient is taken here from [33] to emphasize the presumable physical sense of ξ_o in Eq. (22.48). It is the certain energetically preferable distance between neighboring particles of an interfacial layer.

22.4 Conclusions

In the meaningful consideration of interface Stillinger [34] has introduced the known model of an *inherent density* profile for temperature T taken well below T_c . The Gibbs dividing-surface concept has been extended to accommodate the molecular scale fluctuations ("capillary waves"). The influence of the non-zero gravitational field is the main factor which replaces the one-dimensional $\mu_{\sigma}(T)$ -dependence by the narrow two-dimensional region [34] in the thermodynamic field space. The similar consistent shape of a split $P_{\sigma}(T)$ -dependence can be obtained by the numerical integration of the predicted, independently, WMG-slope $A^o_{\sigma}(T)$. It is shown in Fig. 22.4 and brings the strong resemblance with the dew-bubble curve at constant concentration in mixtures. The differences of local fields in the nucleation phenomena adopted by the GG-approach in Eq. (22.4) are confirmed by the above thermodynamically-consistent consideration.

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23 Clustering of Global Events in Modern History of the Earth

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> In nature we never see anything isolated, but everything in connection with something else which is before it, beside it, under it and over it.

> > Johann Wolfgang von Goethe

Abstract

We examine the correlations between different temporal (1895 – 2008 years) series of global parameters (energies of catastrophic earthquakes for whole Earth and separate regions; on the sea surface and land air temperatures; length of day; coordinates of the mean rotation axis; sunspot numbers) and try to explain their origin. We have discovered two clusters within this set of parameters. One of them contains energies of catastrophic earthquakes for the whole Earth and separate regions that evidences a temporal synchronism of strong earthquakes in different regions of the Earth. The slowdowns of the Earth rotation are weakly correlated with the earthquake energies. The second cluster contains the mean sea surface and global air temperatures; shifts of the Earth axis and solar activity indicators. Global climate warming is accompanied by stable drift of the Earth axis along the longitude $66^{\circ} \pm 3^{\circ}W$ to North America. The slowdown of this drift correlates with strength of earthquake energies. The modal coordinates of catastrophic earthquakes in continental and oceanic crust of the West hemisphere and continental crust of the East hemisphere are in agreement with this direction. Within the temporal interval of 80 years, we have estimated the recurrence steps of different global events connected with cosmic and endogenous factors, as well as their temporal sequences. We ground an assumption on connection between the natural part of the climate warming and strengthening of endogenous term flow and its accumulation by the ocean.

23.1 Introduction

The appearance of new more precise data on variations of the natural environment global parameters allows one to specify the interconnections between them and to estimate in more details the contributions of endogenous and cosmic factors. Amongst these parameters, the most significant ones are episodic but catastrophic earthquakes and warm regime of atmosphere which indicates a stable trend to climate warming in the current epoch.

The prediction of time and place of catastrophic earthquakes is the main problem of current seismic studies. However it is difficult because we have no clear conception about the nature of generic factors and their recurrence step. The annual numbers of such earthquakes are rather small (not more the first tens) and vary from time to time with a difficultly establishing regularity. However, during a few tenth years within the past twentieth century the flashes of the strong earthquakes were observed for the Earth as a whole and separate regions which question the hypothesis of seismic regime stationarity (see, e.g., [1]). After smoothing the data for the above period, the authors [1] could reveal the linear statistical correlation with r = 0.734 between the average length of solar activity cycle (measured by Wolf numbers) and the time range between the earthquakes with magnitudes larger than seven.

The authors of paper [2] have indicated the absence of correlations between the number of strong earthquakes and the Earth angular velocity, contrary to popular belief, this correlation is observed only for rather weak earthquakes (M > 4.0). However, they have found a positive correlation $(r = 0.42 \pm 0.17)$ between a number of strong earthquakes (M > 5.5) and the module of temporal derivative of the Earth rotation frequency for the range 1964 – 1988 years, explaining this result by growth of stresses in the Earth crust at accelerations and decelerations of the Earth rotation. Authors of paper [3] indicate the connection between the strong earthquakes in Kamchatka ($M \ge 7.5$) and maxima and minima of solar activity cycle defined by Wolf numbers. In papers [4, 5] and others, the authors justify the trigger mechanism of the earthquakes due to variations of the air masses pressure to the Earth surface because of atmospheric circulation, which is largely in agreement with solar activity at extreme values of the Wolf numbers.

In the present work, we continue to study different correlations between the gross amount earthquakes energy logarithm for high magnitude earthquakes (M > 6) during the year, as for the whole Earth, as in separate regions, as well as the mean annual length of day, shifts of the geographic pole positions along the directions X and Y (Greenwich meridian and 90° west longitude, correspondingly), Wolf numbers, and global temperature variations for land air and sea surface. The data for earthquake magnitudes were taken from [6], the ones for length of day were taken from [7] for the period till 1998 and from [8] after this until 2009, the shifts of geographic pole coordinates were taken from [9], the Wolf numbers were extracted from [10], the mean annual land air temperatures were taken from [11], and the temperatures of sea surface were taken from [12].

Table 23.1: Statistical parameters for distribution of geographic coordinates (in degrees) of the largest earthquakes during 1893 - 2008. Note: *N* is the number of the earthquake events.

Hemisphere	Region	N		Mean	Std. Dev.	Mode
	Whole	1316	Latitude	21	23	39
			Longitude	102	49	122
East	Land	854	Latitude	23	23	36
			Longitude	91	49	70
	Sea	463	Latitude	18	24	40
			Longitude	122	43	142
	Whole	525	Latitude	6	27	17
			Longitude	-102	36	-71
West	Land	335	Latitude	6	24	17
			Longitude	-98	33	-71
	Sea	190	Latitude	7	30	17
			Longitude	-108	40	-71

In order to estimate the earthquake energy we have used the relationship [13]

$$\log E = 4.4 + 1.5M , \tag{23.1}$$

where E is the energy at the Earth surface in Joules, and M is its magnitude. We have employed the data on earthquake localizations and their magnitudes during the time interval from 1893 till 2008. We have included into the statistics the data for 1841 earthquakes which have measured magnitudes.

In order to reveal the peculiarities of earthquake reactions to possible external perturbations in separate regions of the Earth, we have considered the North and South hemispheres delineated by equator, the East and West hemispheres delineated by Mid-Atlantic and Eastern Pacific abyssal faults, as well as the territories occupied by land and ocean. The statistical parameters for distributions of catastrophic earthquake coordinates are given in Table 23.1 separately for the East and West hemispheres. The average values of these coordinates have rather high root-mean-square deviations due to the initiation of the earthquakes by many factors having no the same space localization. Therefore in Table 23.1 we give also the modal coordinates describing the most often coordinates of catastrophic earthquake localizations.

23.2 Correlations

23.2 Correlations

We have calculated the paired correlation coefficients between the above mentioned parameters and have carried out the factor analysis in the principal component model [14] with the purpose to find the partial groups of interrelated variables. Taking into account a high variability of the mean annual data for earthquake energies, as well as the air and water temperatures, we have used the results of averaging by five years window.

The correlation coefficients are given in Table 23.2. Here and therein in Table 23.3, we use the following notations for mean annual data: Yr are years, W are Wolf numbers (indicator of solar activity), LOD is length of day, X and Y are the pole coordinates, ST is sea surface temperature of ocean, GT is land air temperature, Ws, Es, Nr, St, Se, Ln, and Er are the energy releases for the earthquakes in different hemispheres (West, East, North, and South), in ocean, land, and the Earth as a whole.

Table 23.2: Coefficients of the paired linear correlation between mean annual quantities of different parameters for the Earth as whole and its separate regions during 1895 – 2006. Note: Correlation coefficients with their modules not less 0.24 differ from zero with a confident probability 99%. All coefficients excluding the diagonal ones were multiplied by 100.

	Yr	w	LOD	x	Y	ST	GT	Ws	Es	Nr	St	Se	Ln	Er
Va	1	20	24	80	05	00	80	22	40	50	10	27	56	42
W	20	50	-24	20	95	90	22	-35	-49	-30	-10	-27	-30	-45
N N	50	1	-15	50	21	27	25	-/	-50	-55	9	-40		-17
LOD	-24	-15	1	-20	-16	-42	-37	22	25	24	11	19	20	19
X	89	30	-20	1	85	78	77	-31	-46	-47	-13	-28	-52	-42
Y	95	27	-16	85	1	86	86	-38	-47	-49	-17	-26	-59	-45
ST	90	27	-42	78	86	1	96	-33	-37	-43	-12	-21	-46	-35
GT	89	23	-37	77	86	96	1	-33	-31	-39	-8	-19	-45	-33
Ws	-33	-7	22	-31	-38	-33	-33	1	31	55	71	40	69	81
Es	-49	-30	25	-46	-47	-37	-31	31	1	87	15	70	62	74
Nr	-50	-33	24	-47	-49	-43	-39	55	87	1	16	76	64	86
St	-10	9	11	-13	-17	-12	-8	71	15	16	1	13	61	57
Se	-27	-48	19	-28	-26	-21	-19	40	70	76	13	1	23	61
Ln	-56	0	20	-52	-59	-46	-45	69	62	64	61	23	1	85
Er	-43	-17	19	-42	-45	-35	-33	81	74	86	57	61	85	1

Table 23.3: Factor loadings on the variations of the mean annual parameters and the factor dispersions (D). Note: The factor loadings with their modules not less 0.24 differ from zero with a confident probability 99%.

Factors	1	2	3	4
Yr	0.95	-0.21	-0.02	0.13
W	0.36	0.33	-0.74	0.22
LOD	-0.37	-0.04	0.23	0.89
X	0.88	-0.15	-0.02	0.18
Y	0.93	-0.19	0.05	0.20
ST	0.90	-0.36	-0.12	-0.06
GT	0.90	-0.36	-0.12	-0.06
Se	-0.42	-0.74	0.32	-0.05
Ln	-0.69	-0.31	-0.59	0.06
Er	-0.62	-0.66	-0.38	0.03
D, %	55	15	12	9

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According to Table 23.2, variations of the mean annual energy of earthquakes are synchronized in different regions at high confidence level, and for most cases they are in agreement with this parameter for the Earth as a whole. The only earthquakes in the South and North hemispheres are exceptions, as well as a significant correlation is not observed between the land and ocean. The annual variations of the Wolf numbers show a weak positive correlation with variations of the Earth axis coordinates, and variations of the sea surface and the land air temperatures. The Wolf numbers have stronger but negative correlation with annual variations of the earthquake energies in the East and North hemispheres, as well as in the ocean. This result is due to an agreement between the maxima of temporal earthquake energy distributions and solar activity minima in several cases for the above mentioned regions. The Earth rotation rate has a reliable, but not high negative correlation with the earthquake energy in the East and North hemispheres, as well as the higher positive correlation with the sea surface and the land air temperatures.

The air and water temperatures are closely correlated between each other and have a negative correlation with the earthquake energy releases in the West, East, North hemispheres, and the Earth as a whole. The strongest negative correlation is observed between the above temperatures and the land earthquakes. Amongst the hemispheres under considerations, the South hemisphere has the least part of the land, and such correlation is not observed for this hemisphere.

The shifts of X and Y coordinates of the Earth axis have rather strong positive correlation between each other and with the sea surface and the land air temperature variations. Amongst the coordinates, the variations of Y have the strongest correlation with the air and water temperatures. The variations of mean annual Earth axis drift have a highly reliable correlation with the earthquake energies for the most of the Earth regions, excluding the South hemisphere. Especially the land earthquakes are specified, which energy does mostly correlate (r = -0.59) with decreasing of the Earth axis drift. If we delete from the sample under study the Chile event of 1960 with abnormally high magnitude (9.5 balls), the correlation coefficient between the above indicators for the land increases till -0.72.

During the time under consideration we observe a close positive correlation between time on one hand, and the sea surface and the land air temperature and the Earth axis shifts on other hand. It is caused by the climate warming and stable drift of the Earth axis geographic coordinates along the meridian $70^{\circ}W$. A weaker negative correlation is revealed between the time and mean annual energies of land earthquakes, which provides also similar negative correlation with the earthquake energies in the East, North hemispheres, and the Earth as a whole. The Wolf numbers and solar activity have high reliable, but weak correlation with time.

A scheme of positive correlation connections (Fig. 23.1) that is constructed by using the data of Table 23.2, shows an existence of two clusters in the set of parameters under consideration. One cluster contains the earthquake energies for the Earth as whole and separate regions. That evidences a temporal synchronization of large earthquake flashes in different Earth regions. The slowdowns of the Earth rotation correlate with the earthquake energies weakly. The second cluster contains the mean annual air and water temperatures increasing with time, as well as the Earth axis coordinate shifts with which an solar activity indicator does weakly correlate. Thus the climate warming is accompanied by a stable drift of the Earth axis.

As the most reliable differences in the structure of correlation interconnections between the earthquake energies in different Earth regions are caused by fractions of the land and ocean areas, the subsequent estimation of partial correlations by factor analysis principal component method will be carried out using the data only for the indicated regions (Table 23.2). We can see from Table 23.2 that for the first factor one covariant group is formed (with very high dispersion of 55%) by annual dates, land air and sea surface temperatures, the Earth axis coordinate shifts, and the Wolf numbers. The second group (that has a negative correlation with the first one) includes the earthquake energy variations at the land, ocean, and the Earth as a whole, as well as the length of day variations. This factor indicates an agreement between the earth rotation slowdown and the earthquake energies synchronized with reduction of the Earth axis drift and the land air and sea surface temperatures decreasing at the solar activity decrease expressed by the Wolf numbers. The negative correlation between the length of day and solar activity may be explained by zonal transfer of air masses which leads to the Earth rotation acceleration. The lowering of the land air and sea surface temperatures may be connected with gain of meridional air mass transfer [15] that is more active in the periods of the Earth rotation slowdown.

The second factor has the less dispersion (15%) and indicates the agreement between the earthquake energy variations in the ocean and the Earth as whole and the air and water temperature variations within the periods of small solar activity in some cases, at the absence of the correlation with them for other parameters under study. The interconnections revealed in this factor may be considered as a result of water and air heating effect on ordering of the earthquake events in the ocean. The third factor having the dispersion of 12% has revealed a rather weakly expressed component of correlation interaction which reflects predominantly the synchronization between the land earthquake energies and solar activity. The fourth factor (D = 9%) has predominantly revealed a length of day indicator which has no an agreement with other parameters.



Figure 23.1: Scheme of positive correlation interconnections between the mean annual quantities of global parameters. See the symbols in the text.

The factor analysis results indicate an ambiguity of interconnection between the warm atmosphere regime and earthquake energies. Its dominant component is the positive correlation between increasing the earthquake energies at the land, oceanic bottom, the Earth as a whole and cooling of the land air and oceanic water during low solar activity. The opposite positive correlation between increasing the earthquake energies at the ocean territory and the Earth as a whole and heating of the land air and water in the ocean surface during low solar activity is revealed to a less degree, it is explained by increasing the friction at the boundary between water and oceanic bottom.

The above correlations summarize a complicated superposition of interconnections reflecting not only the interaction peculiarities between the analyzed parameters during the time interval under study, but also generated by different inertia processes. Therefore we will calculate the correlation coefficients between the above parameters using different temporal shifts, as well as the autocorrelations.

23.3 Time Series of Correlation Coefficients

Autocorrelations of the indicators under study during the period 1895 - 2006 years have allowed us to reveal the recurrence cycles for variations of these indicators within the time interval, at least, of 80 years, within which we have rather low uncertainties of correlation coefficients. The recurrence of the Earth rotation slowdown with a step of about 68 years is seen in Fig. 23.2 for length-of-day variations at high confidence level. The bars here and therein give the errors of the correlation coefficients. The autocorrelations for the Earth axis coordinate (X and Y) variations do decrease with time. However, clear variations of the correlation coefficient at this trend background are also observed. They are better seen for coordinate X and have a cycle of 6 - 7 years (Fig. 23.3). This periodicity may be caused by the



Chandler component of the Earth rotation which is connected with solar perturbations in orbital motions of the Moon and Earth around the center-of-mass of the system Earth-Moon [16].

Figure 23.2: Autocorrelation for the variations of the length-of-day (LOD) within the interval 1895 – 2006. Here and on other similar plots, over the symbols of the correlation coefficients are indicated the years of their maxima.

The autocorrelations of the Wolf numbers during 1895 - 2006 years have the recurrence with the step 10 - 11 years, which is connected with the well-known "11-year" solar activity cycle (Fig. 23.4). The positive maximal correlation coefficients in this plot are formed at the values of temporal shift when one has the most agreed changes of solar activity variations, and the negative correlations are found when this shift leads to combination of maxima and minima in solar activity. However during long-term range of 1700 - 2008 years (Fig. 23.5), the oscillations of the autocorrelation coefficients have increasing of this step from 10 to 12 years, and 12-year activity cycle repeats after approximately (65 ± 12) years. The plots of autocorrelation changes for the land air and sea surface temperature variations are similar and have the agreed appreciable maxima within 45 - 46 and 60 - 67 years (Fig. 23.6). In addition, the temperature changes of the air show rather weak one-step component of 7-year periodicity.



Figure 23.3: Autocorrelation for the variations of the Earth axis pole geographic coordinates during 1895 – 2006.


Figure 23.4: Autocorrelation for the Wolf number variations during 1895 – 2006. Here and on other similar plots, under the symbols of the correlation coefficients are indicated the years of their minima.



Figure 23.5: Autocorrelation for the Wolf number variations during 1700 – 2008.

The autocorrelation curves for annual variations of the earthquake energies have the maxima which evidence high confident cycles of 54 years and not so confident recurrences with a step of 8 years (possibly connected with Chandler cycle) and 61 years (Fig. 23.7). The earthquake energies for oceanic regions have rather weak cycles agreed with solar activity (see Figs. 23.8 and 23.4) and more confident recurrence with a step of 54 years, which is also registered for the land earthquakes (see Figs. 23.7 and 23.8). The autocorrelations for the earthquake energies at the Earth surface are mostly defined by the recurrence for the land earthquakes (see Figs. 23.7 and 23.9).

The recurrence of the earthquake energies with a step of ~ 8 years is possibly connected with the Chandler cycle, and the ones with steps of 46 and 61 years are agreed with principal phases of land air and sea surface temperature periodicities (see Fig. 23.6). This is important evidence of lunar and solar tides, as well as the effects of atmosphere and ocean fluctuations on ordering the catastrophic earthquakes in time. However, there is a cycle of 54 years in the earthquakes, which has no analogues in variations of other parameters under study.

Due to a delayed character of the response from condensed Earth shells (lithosphere and hydrosphere) to variations of cosmic and endogenous factors, the establishment of cause-effect interconnections in the chain of global events is



Figure 23.6: Autocorrelation for the mean annual of the land air (circles) and sea surface (squares) temperatures during 1895 – 2006.



Figure 23.7: Autocorrelation for the variations of the mean annual earthquake energies of the land earthquakes during 1895 – 2006.

ambiguous. In order to solve this problem one can analyze the correlations between event series in comparison with temporal shifts. The earthquake energies on the Earth surface have rather weak, but confident (with probability 95%) positive correlation (r = 0.19) with the length of day (see Table 23.1), which indicates increasing of the earthquake energies during the epochs of the Earth rotation slowdown. However, when the earthquakes outperform the Earth rotation variations, at least, through 7 years the value of r is increasing till 0.49 (Fig. 23.10). Such a high agreement between these event series (r = 0.84) advances again through 67 years (Fig. 23.10), that corresponds to a recurrence step for the Earth rotation rate variations (Fig. 23.2).

The temporal variation of correlation between the values of log E for the land earthquakes and LOD (Fig. 23.10) is close to this correlation that may indicate the dominant effect of dynamical processes in the continental crust on the most significant variations of the Earth rotation rate. Here and for the Earth as whole we observe an opposite close positive correlation (r = 0.79) between the earthquakes energies and the Earth rotation rate within the temporal interval 40 – 50 years (Fig. 23.10). As for oceanic crust (Fig. 23.10), despite the differences in variations of insignificant correlation



Figure 23.8: Autocorrelation for the variations of the mean annual earthquake energies of the ocean earthquakes during 1895 – 2006.



Figure 23.9: Autocorrelation for the variations of the mean annual earthquake energies for the Earth as whole during 1895 – 2006.

coefficients within the middle of this time series, there are some agreements in its begin and end for the Earth as whole and continental crust.

Rather strong negative correlation between the Earth axis inclination (Fig. 23.11) for the coordinate Y and the earthquakes energy is observed during the first 8 years when the earthquakes outperform the nutation of the Earth axis. Especially strong effect to the axis shift is due to the land earthquakes (Fig. 23.11), i.e. within the continental crust. The temporal variations of the earthquake energies within the oceanic crust are weaker agreed with the Earth axis nutation. It is important to note that increasing the earthquake energies corresponds to decreasing the axis inclination. A recurrence of this regularity takes place within a wider time interval of the next 40 - 70 years, where there are the recurring steps for other global processes considered here. Within this interval we fix also the fluctuations connected with the Chandler cycle of the Earth axis nutation. As we can see from Fig. 23.11, the Chandler component of the Earth axis nutation provides lower fluctuations of the correlation coefficient with respect to the component defining more long-term variations of the Earth axis positions.

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Figure 23.10: The variations of the correlation coefficient between the time series of $\log E$ for the earthquakes at the land surface (diamonds), ocean bottom (squares), the Earth as whole (triangles), and LOD.

The negative correlation between temperatures of the land air and sea surface being in intense heat exchange with $\log E$ for the earthquakes is especially appreciable for the continental crust and less for the Earth surface as whole (Table 23.2, Fig. 23.12). Possibly, such difference is a result of reaction of continental crust movable blocks on a higher pressure from dense cold air to the land surface due to high gradient of atmospheric air local load. The oceanic crust does not show such a strong correlation (Table 23.2, Fig. 23.12) due to redistribution of this load in the upper water column. The recurrence of such situation is observed during the temporal interval of 35 - 55 years, where the Chandler cycle component is fixed.

The solar activity variations expressed by the Wolf numbers have predominantly negative correlations with the values $\log E$ for the earthquakes in different regions and the Earth as whole (Table 23.2). Especially significant by the module is the value r for the oceanic crust. This conserves the periodicity of 11-year solar activity cycle within a wide range of shift of the time series for the Wolf numbers with respect to mean annual values of the ocean earthquake energies (Fig. 23.13). Starting from approximately 45 years, for shift of the temporal series of the Wolf numbers respectly to earthquakes, the positive correlation of the Wolf numbers and ocean earthquake energies is especially high that indicates the switch in time of some mechanism for transfer of the delayed active Sun impulse to increasing the earthquake energies.

The large magnitude earthquake events in different Earth regions are shifted relatively to each other in time. The consideration of time series for correlation coefficients between mean annual earthquake energies allows one to establish a sequence of such events in comparison of different regions. We show in Fig. 23.14 the variations of correlation coefficient between the earthquake energies for separate members of the object pairs: in the East and West, North and South hemispheres, as well as in the land and ocean, in dependence of temporal shift. The left plot of the Fig. 23.14 contains the values of r for outrunning earthquakes in the East and North hemispheres, as well as in the land; the right plot of the figure contains the cases of outrunning earthquakes in the West and South hemispheres, as well as in the ocean relative to the second member of the pair correspondingly.

A comparison of two variants for the sequence under study indicates the outrunning role of the earthquakes in the East and North hemispheres, as well as in the land relative to their partners in the regions pairs under consideration. The closest temporal agreements of the earthquake energy variations for these regions are fixed five years before than at adjacent pair regions. The subsequent recurrences of correlation increasing for temporal shifts of 44 - 46 years



Figure 23.11: The variations of the correlation coefficient between the time series of $\log E$ for the earthquakes at the Earth surface (triangles), land (circles), ocean (squares), and the shifts of the Earth axis along the coordinate Y.



Figure 23.12: The variations of the correlation coefficient between the time series of the mean annual temperature of the land air and $\log E$ for the earthquakes at the Earth surface as whole (triangles), as well as for land (squares) and ocean (circles).



Figure 23.13: The variations of the correlation coefficient between the time series of the Wolf numbers and $\log E$ for the earthquakes at the ocean.



Figure 23.14: The variations of the correlation coefficient between the time series of the $\log E$ for the earthquakes at the East and West (squares), North and South (circles) hemispheres, as well as the land and ocean (triangles).

and 61 years (only for the pair: East - West hemispheres) reflect the temporal ranges of this impulse recurrence in the earthquakes of adjacent pair member. Thus an initial impulse of the powerful earthquakes is connected with a region of continental crust position and is placed in the region covered simultaneously by the territories of the East and North hemispheres. This is the Asian continent.

23.4 Discussion

Our statistical analysis evidences the ordering role of the outer cosmic factors in the distributions of the mean annual energies for catastrophic earthquakes. A participation of endogenous factors in statistics of the earthquake energies is

23.4 Discussion

reflected in agreed components of the variations of the Earth rotation rate and geographic pole shifts. The most Earth rotation slowdowns are preceded by the catastrophic earthquakes, which mostly take place within the continental crust. This result may be caused by the crust level oscillations which are larger within the continental block. The $LOD(\Delta t)$ variation does depend on the Earth radius variation ΔR approximately as linear function

$$\Delta t \approx \frac{3}{2} P \frac{\Delta R}{R} , \qquad (23.2)$$

where P is the axial Earth rotation period, R is the effective Earth radius. The small (within a few centimeters) raising and lowering the Earth surface may cause the observed variations of the Earth rotation rate. For example, the crust lifting of 1 cm leads to increasing the Earth rotation period by $\sim 2 \cdot 10^{-4}$ s. The increasing of length-of-day by 10^{-3} seconds may be caused by raising the crust level by 5 cm. We are interested in search for possible mechanisms of the Earth pulsations. Possibly, they are connected with the inner solid core oscillations.



Figure 23.15: Mean annual coordinates of the geographic pole during 1893 - 2009. The axis X is directed along the Greenwich meridian, axis Y – the meridian $90^{\circ}W$.

The earthquakes within the continental crust relative to the ones in the oceanic crust are closely correlated with the Earth axis inclination decreasing. The Earth axis has a precession on elliptic trajectory with the period of 6-7 years due to the solar and lunar tides. In addition, it drifts along the meridian $66^{\circ} \pm 3^{\circ}W$ towards North America (Fig. 23.15). The axis shifts along this direction have a strong positive correlation with the land air and sea surface temperatures. An absence of interconnection between annual quantities of the filling with water inland reservoirs and the Earth axis drifts [20] does not allow one to explain this correlation by the water transfer from polar regions due to the glacier ablation at the global warming. The Earth axis drift in this direction may be caused by the air zonal flows which are more active at increasing the mean annual temperature of ground atmosphere [15], which correlates with the Earth axis inclination (Table 23.1). It is well-known [18, 19] that the impulse momentum is several times larger at the latitudinal movement of air masses due to western winds (which blow from the West to East) by comparison with eastern winds.

However, the data on average coordinates of the catastrophic earthquakes (Table 23.1), which have a good agreement of modal longitudes in the continental parts of the East and West hemispheres ($70^{\circ}E$ and $71^{\circ}W$ correspondingly) with the drift direction of the Earth axis ($66^{\circ} \pm 3^{\circ}W$) indicate other more probable explanations of this drift. It may be caused by convection of sub-crustal mantle material, which defines the places of localization of stress in the continental crust. The action of this mantle flow in the West hemisphere is also reflected in the oceanic crust where the modal coordinates of the oceanic catastrophic earthquakes is agreed with the ones for continental crust. The primary Earth axis drift to the American continent during the whole time interval under study may be the result of a more significant shift of the mantle material towards the West hemisphere, which may compensate for the imbalance between the continental masses of the West and East hemispheres. Possibly, this flow relieves stress in the lithosphere and, primarily, in the continental crust where the earthquake energies have a negative correlation with the Earth axis drift towards the American continent. The Earth axis drift towards the opposite direction aside the Asian continent ($\sim 70^{\circ}E$) is accompanied

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by increasing of the earthquake energies in the continental crust. Global warming during the last century is agreed with this convection mantle flow. This may be a consequence of endogenous heat inflow accumulated by the ocean.

It is interesting that the modal coordinates of the catastrophic earthquakes (Table 23.1) agree with the ones for coupling of three or more different plates, where the earthquakes take place more often. In the East hemisphere, the modal coordinates for the land earthquakes are close to the coupling of the Eurasian, Indian, and Arabian plates, as well as in the ocean there is the connection of the Pacific, Philippines, North American, and Eurasian plates near the East shore of Honshu Island. In the West hemisphere, the modal coordinates of the land and ocean earthquakes agree with each other and correspond to the region of connection of five plates: Cocos, Nazca, Caribian, North- and South American.

In order to establish the causal connections we may compare the energies realized in different global processes. The energy of the Earth rotation is $2.6 \cdot 10^{36}$ ergs and may be found from the relationship:

$$W = I\omega^2 = \frac{1}{5}MR^2\omega^2 , \qquad (23.3)$$

where W is the rotation energy, I is the moment of inertia, M and R are the Earth mass and radius, ω is its angular velocity. The change of the rotation energy due to variation of the period may be approximately estimated by the following formula $\Delta W = 2\Delta PW/P$, where P is the axial rotation period (the length-of-day), ΔP is its variation. Therefore, the length-of-day variation within 10^{-3} s gives a shift in the rotation energy $0, 6 \cdot 10^{29}$ ergs, within $4 \cdot 10^{-3}$ s is $2.4 \cdot 10^{29}$ ergs. Such order of the LOD variation is the most significant within this temporal series and has the recurrence step of 68 years (Fig. 23.2). The shifts of the mean annual LOD's variations are within 0.05 - 0.76 milliseconds that corresponds to shifts in the Earth rotation energy from $0.3 \cdot 10^{28}$ to $4.6 \cdot 10^{28}$ ergs.

The estimate of the energy shift connected with the Earth inclination may be found by the formula

$$\Delta W = \left(\frac{J\omega}{2}\right)\alpha = W\alpha , \qquad (23.4)$$

where J is the Earth torque, α is the Earth axis inclination. Therefore, the inclination of 0", 1 corresponds to the energy of $1.3 \cdot 10^{30}$ ergs. The mean annual shift of the axis along the meridian $\sim 70^{\circ}W$ during the time under consideration is estimated as 0", 003 that corresponds to the energy $3.8 \cdot 10^{28}$ ergs.

The mean annual variations of the catastrophic earthquake energies at the Earth surface within our data base are within $5 \cdot 10^{23} - 2 \cdot 10^{25}$ ergs. The energy of external tidal action from the Sun and Moon is about 10^{29} ergs [16]. The global heat capacity of the atmosphere during the period 1948 – 2006 years within the layer 1000 - 10 gPa is within $(12.74 - 12.78) \cdot 10^{30}$ ergs, and the mean annual variations of this quantity are usually within 10^{27} ergs [17].

The comparison of the mean annual energy variations connected with different global processes indicates that the energy of the surface elastic wave of the earthquakes is a small part of them in many cases. Therefore the catastrophic earthquake events may cluster due to the variations of many more energetic endogenous and cosmic processes. Amongst them, probably, the flows of sub-crustal plastic mantle material and lithospheric plates gliding over the surface of the astenosphere are leading, as well as the movement of air and water masses due to solar activity and endogenous Earth heating. The Earth axial rate variations are essentially more energetic relative to elastic earthquake wave and might influence on them. However, the earthquakes fixed at the Earth surface are the results of more power endogenous processes which could not have precisely energy estimates so far, although they may effect on the mean annual Earth rotation variations. The negative correlation between the Earth rotation rate and earthquake energies evidences the crust lifting at the earthquakes in the modern era, because the lowering of crustal blocks initiates the acceleration of the Earth axial rotation.

The natural component of global warming is possibly the main cause of increasing the mean annual atmosphere temperature fixed from the end of the nineteenth century. This is supported by close correlation between the land air and sea surface temperature, on one side, and the drifts of the Earth axis coordinates initiated by mantle material and lithospheric plates movement, on the other side. In this case, the cause of global warming is increasing of the endogenous heat flow intensity. This is more essential for the ocean, because the continental plates shield this flow stronger than the oceanic ones. An approximate calculation shows that to provide increasing the annual heat capacity of air by the above mentioned value of 10^{27} ergs (when the heat loss is absent) it is enough to heat the ocean only by $\sim 10^{-4}$ °C. If we take into account the heat loss then this value is larger but not so essential that it would be measured using the field measurements of the water temperature for ocean as whole.

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23.4 Discussion

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24 On the Dependence of the Properties of Glasses on Cooling and Heating Rates: What is the Right Deborah Number?

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Heraclitus' "everything flows" was not entirely satisfactory. Were we to disregard the solid and deal with fluids only?

The way out of this difficulty had been shown by the Prophetess Deborah even before Heraclitus. In her famous song after the victory over the Philistines, she sang, "The mountains flowed before the Lord".

When, over 360 years ago, the Bible was translated into English, the translators, who had never heard of Heraclitus, translated the passage as "The mountains

melted before the Lord" - and so it stands in the authorized version. But Deborah knew two things. First, that the mountains flow, as everything flows. But, secondly, that they flowed before the Lord, and not before the man, for the simple reason that man in his short lifetime cannot see them flowing, while the time of observation of God is infinite. We may therefore well define as a non-dimensional

number the Deborah number

 $Dh = \frac{\text{Time of relaxation}}{\text{Time of observation}}$.

The difference between solids and fluids is then defined by the magnitude of *Dh*.

There is a story they tell about two students of theology. They were Praising the Almighty God.

Said one: "For God, one thousand years are like a minute. And as He is the Creator of all, a thousand dollars are for him like a cent."

Said the other: "Wonderful, next time I pray to God, I shall pray "God, give me a cent". Said the first: "What will it help you? He will say "Wait a minute""...

In every problem of rheology make sure that you use the right Deborah number.

Marcus Reiner

Abstract

A short overview on the definition and basic properties of glasses and the glass transition and different methods of their description is given. The analysis starts with a brief description of some experimental findings being of essential importance for the understanding of the glass transition and the vitreous state. The treatment of glasses is then briefly discussed following Simon's model, i.e., treating the glass transition e.g. in cooling as proceeding at some sharp values of temperature, the glass transition temperature, T_g . Advantages and limitations of this method are discussed. Particular attention is here devoted to the relation of glass transition and second order equilibrium phase transitions, the origin of similarities and differences of the behavior of thermodynamic coefficients at such transitions, reflected in different values of the Ehrenfest, respectively, the Prigogine-Defay ratios.

In a next step, the glass transition is described more adequately as proceeding in a certain interval of temperature. The glass transition is hereby theoretically described in terms of a generic approach employing De Donder's structural order parameter method, appropriate expressions for the relaxation behavior of glass-forming systems and a simplified but qualitative correct model of glass-forming melts with one order parameter related to the free volume of the system. Employing this approach the behavior of a variety of thermodynamic quantities describing glass-forming systems in vitrification and devitrification processes is interpreted theoretically. Particular attention is devoted here to the estimation of these quantities in dependence on the cooling & heating rates, varying latter parameter in a broad interval (c.f. also T. V. Tropin, J. W. P. Schmelzer, C. Schick, J. Non-Crystalline Solids **357**, 1291-1302 (2011); **357**, 1303-1309 (2011)).

We start the investigation with the analysis of the equilibrium properties of the system under consideration. In view of current intensive discussions of entropy and the Kauzmann problem, we show here in particular that not employing unfounded extrapolations Kauzmann-type paradoxes do not occur at all. In addition, it is shown that for the configurational contributions of the metastable glass-forming liquid under investigation, the 3rd law of thermodynamics in the formulation of Max Planck is obeyed. As a next step, an overview on different attempts of formulation of kinetic criteria of glass formation is developed. Here in particular the problem is discussed which characteristic times - time of observation, time of relaxation, time of change of external parameters - have to be employed to appropriately develop such criteria. Extending earlier findings. in particular, a general model-independent kinetic criterion for glass formation is formulated as the result of such analysis. In addition, it is shown that it is not - as often claimed - the Deborah number which governs glass-formation.

Employing these results and De Donder's method of description of non-equilibrium processes, the dependence of the structural order parameter on temperature is established for a wide spectrum of cooling and heating rates. Having at our disposal the dependence of the structural order parameter on temperature, entropy and entropy production due to irreversible relaxation in the glass transition region are computed extending previously obtained results (J. Möller, I. Gutzow, J. W. P. Schmelzer, J. Chem. Phys. **125**, 094505/1-13 (2006)). The formulated in latter paper analytical prediction that the entropy production gains in importance with an increase of the rate of change of temperature is verified by the numerical computations and the behavior of entropy in glass transition is discussed. In particular it is shown that - employing the thermodynamics of irreversible processes, the discussed already generalized equation of state and appropriate dependencies for the relaxation behavior - configurational entropy is frozen-in in the glass transition and its value increases with increasing cooling rate. This result already taken alone leaves no room for doubt about the correctness of the conventional point of view of the existence of residual entropy of glasses frozen-in at the glass transition and retained down to absolute zero.

Further-on, based on the kinetic criteria of vitrification, analytical expressions for the dependence of the glass transition temperature on the rate of change of external parameters are derived. In particular, limits of validity of the Bartenev-Ritland equation, predicting a linear dependence of glass transition temperature, T_g , on the logarithm of the cooling rate, $q = (dT/dt) ((1/T_g) \propto A - B \log |q|)$ are analyzed and possible reasons for the deviations from such a linear dependence are discussed. It is shown further that, varying the cooling rates in wide intervals, the traditional definition of the glass transition temperature, T_g , as corresponding to a viscosity of about 10^{13} Poise is not applicable any more. The dependence of the viscosity at the glass transition temperature, $\eta(T_g)$, on cooling rate, q, is established by numerical computations verifying this statement.

In previous own analysis (J. W. P. Schmelzer, I. Gutzow, J. Chem. Phys. **125**, 184511/1-11 (2006)) it was shown that - in contrast to earlier believe - a satisfactory theoretical interpretation of the values of the so-called Prigogine-Defay ratio Π , being a combination of jumps of thermodynamic coefficients at glass transition, can be given employing only one structural order parameter. According to this analysis, the value of this ratio has to be, in accordance with experimental findings, larger than one ($\Pi > 1$). Its particular value depends both on the thermodynamic properties of the system under consideration and on cooling and heating rates. This analysis is extended here and, in particular, the dependence of the value of Π on cooling and heating rates is studied. In addition, an alternative method of determination

24.1 Introduction

of the Prigogine-Defay ratio is outlined, allowing one to determine this ratio having at ones disposal the generalized equation of state of the glass-forming melts. Employing, again, the particular model, theoretical estimates are given for this ratio being in good agreement with experimental data.

Extending this analysis, a comprehensive discussion of the so-called Ehrenfest's relations in second-order phase transitions and their applicability to the glass transition is performed. Based on the kinetic criterion for vitrification general relations for the dependence of the glass transition temperature on pressure (and vice versa) are obtained being essentially ratios of the partial derivatives of the appropriate relaxation times with respect to pressure respectively temperature. Employing further two free volume and entropy based models for the description of viscous flow, relations similar but not fully identical to the classical Ehrenfest relations can be obtained. In this way, it can be explained why one of the Ehrenfest's relations is usually fulfilled in glass transition and the other not.

In a next step, employing the general model-independent definition of internal (fictive) pressure and fictive temperature developed by us recently (J. W. P. Schmelzer, I. Gutzow, J. Non-Crystalline Solids **355**, 653 (2009)), it is shown how these parameters behave in dependence on temperature for different sets of cooling and heating rates. A comparison with experimental results is anticipated. In particular it is shown what kind of effects can be expected if cooling and heating schedules are varied and not performed always with the same constant rate. Finally, an overview on recent discussions on different partly contradicting approaches to the analysis of glasses and the glass transition is outlined and some further consequences and possible extensions of the analysis performed here are discussed briefly.

24.1 Introduction

Following the classical concepts developed by Simon [1, 2], vitrification in the cooling of melts is commonly interpreted as the transformation of a thermodynamically (meta)stable equilibrium system into a frozen-in, thermodynamically non-equilibrium system, the glass. Hereby it is assumed in a first approximation that the transformation proceeds at some well-defined sharp temperature, the glass transition temperature, T_g . However, a more detailed experimental and theoretical analysis shows [3, 4, 5] - as stated explicitly already by Tammann [6] - that the transition to a glass via the cooling of a glass-forming liquid proceeds in a more or less broad temperature range, where the characteristic times of change of temperature, τ_T , and relaxation times of the system to the respective equilibrium states, τ , are of similar magnitude. In this transition interval, irreversible processes take place, resulting both in an irreversible increase of entropy of the whole system as well as finally with a further decrease of temperature in an entropy freezing-in in the glass as well as in significant changes of the temperature dependencies of all other thermodynamic parameters of the vitrifying systems. As we have shown recently (c.f. [7] and also the subsequent more extended analysis of this problem in the present chapter), this vitrification interval and the glass transition temperature, T_g , can be defined - according to these considerations - generally via the relation $\tau_T \cong \tau$ or, employing the definition of the characteristic time of change of the control parameter $\tau_T = (T/|\dot{T}|)$, by

$$\left(\frac{1}{T} \left| \frac{dT}{dt} \right| \right) \tau \cong \text{constant} \quad \text{at} \quad T \cong T_g , \qquad (24.1)$$

where the positive constant is of the order of unity and depends in its value on the chosen precise definition of T_g (see also the subsequent discussion).

The effect of entropy production on glass transition and on the properties of glasses has been analyzed in detail in preceding papers [7, 10]. In this analysis, the structural order-parameter concept as developed by De Donder [11, 12] is employed as well (for a detailed discussion of these concepts see also [2, 5]). In the framework of this approach general expressions for the thermodynamic properties of vitrifying systems like heat capacity, enthalpy, and Gibbs' free energy, and for the entropy and entropy production have been obtained. As one of the general conclusions we could show that entropy production always has a single maximum upon cooling and two maxima upon heating in the glass transition interval. Applying the same concepts, it was shown in subsequent papers [13, 14] that - in contrast to the previous general believe - the experimental data on the so-called Prigogine-Defay ratio, Π ,

$$\Pi = \left. \frac{1}{VT} \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \right|_{T=T_q} \,, \tag{24.2}$$

can be given a theoretical interpretation by introducing only one structural order parameter into the description. Here V is the volume, T the absolute temperature, ΔC_p , $\Delta \kappa$, and $\Delta \alpha$ are the jumps of isobaric heat capacity, isothermal compressibility, and thermal expansion coefficient, respectively. A detailed discussion of this circle of problems including the analysis of alternative approaches is given also in [15]. This discussion will be continued and extended in the present analysis.



Figure 24.1: Left: The first experiment, showing the real course of the specific heats in the glass transition region: (1) Cooling curve, (2) slow heating, (3) rapid heating (schematically after the measurements of Parks and Thomas (1931) [8] with B_2O_3). Note the smooth *s*-shaped change of the specific heat in the cooling run, the two overshoot "noses" in the heating experiments and the change in the position of the inflexion point determining the glass transition temperature, T_g ; Right: $C_p(T)$ -curves obtained in the process of heating of a glass-forming organic polymer melt (polyvinyl acetate) for different heating rates according to the measurements of Zhurkov and Levin (1950) [9]. Curve (1) corresponds to a heating rate of 0.1 K min⁻¹, curve (2) to 0.4 K min⁻¹ and curve (3) to 1.5 K min⁻¹ (for further details see also Figs. 2.22 and 2.42 in [5]).

Above formulated statement - that one structural order parameter is sufficient for the theoretical interpretation of the Prigogine-Defay ratio - does not imply necessarily that always one and only one and not more structural order parameters may be required for an appropriate description of a vitrifying or devitrifying system under investigation (for a detailed discussion of the problem of how many structural order parameters may be required in order to appropriately describe a glass-forming system, see e.g. [2, 5, 15]). In this latter more general case of seven structural order parameters, the classical definition of fictive temperature as introduced by Tool [16] (and the similar definition of fictive pressure) becomes ambiguous (see also [17]) as far as no general definition of these parameters is available. These circumstances are one of the reasons why we searched for and introduced in [14, 15] a new model-independent thermodynamic definition of fictive pressure and temperature. This definition is valid generally independent on the particular features of the systems considered and in particular valid for any arbitrary numbers of structural order parameters required for their description. The analysis of consequences of this new definition is one of the topics of the present analysis.

In more detail, the computations performed in [7, 10, 14] were based on the following premises: We assumed that the cooling process starts at a sufficiently high temperature above T_g at a well-defined stable or meta-stable equilibrium state. The process is then terminated at a sufficiently low temperature, when the system is completely frozen-in for the experimental time scales considered. Then the system is reheated at the same constant rate until the initial meta-stable or stable state is reestablished (i.e., it is supposed that the characteristic relaxation times at this state are considerably smaller as compared with the characteristic times of variation of the external parameter). The analysis of the thermodynamic properties of the glass-forming melts and glasses were performed for such cooling and heating conditions at one given constant rate. Consequently, at such conditions, the dependence of the glass properties on prehistory enters the description via the dependence of its properties on the value of the cooling and heating rates, i.e., the effect of variations of heating and cooling rates in wide ranges on the properties of the glass-forming melts and the glasses will be investigated. In addition, the specific effects will be studied resulting from changes of the cooling and heating conditions i.e. if the cooling and heating schedule is varied. Further, a comparison of the results of different approaches to glass transition will be performed.

The chapter is structured as follows: In Section 24.2, we review briefly some essential features by which glasses are distinguished from conventional systems in equilibrium liquid, crystal or vapor states. For this purpose, first some notations of classical equilibrium thermodynamics are briefly summarized like the notation phases, phase transitions and the Ehrenfest relations. It is shown then which new ingredients have to be introduced into the description in order to allow one a thermodynamic description of glasses and glass-forming melts. Hereby two models are discussed, the so-called Simon's model of glass transition and the generic approach treating the glass transition and glasses via a



Figure 24.2: Left: Temperature dependence of the viscosity of selenium (Nemilov (1964) [18]). Note the break-point in the viscosity curve near $T = T_g$; Right: Temperature dependence of the viscosity of a classical glass-forming melt: the change of the slope of the $\log \eta(T)$ -curve upon vitrification for a soda-lime silicate glass in a very broad viscosity interval based on experimental data of several authors as compiled by Gutzow et al. (for the details see Figs. 2.16 and 3.21 in [5]). Bottom: Temperature dependence of the viscosity of five technologically relevant silicate glass-forming melts of different compositions as obtained by Mazurin et al. (for the details see [19]).

set of structural order parameters. After a brief outline of the model assumptions of the order parameter approach employed, we start with (i.) an analysis of the equilibrium properties of the considered here model liquid in dependence on temperature and a comparison with some previous model investigations. Then, the temperature dependence of the properties of glass-forming melts will be analyzed in detail in dependence on cooling and heating rates. The following properties will be studied: (ii.) structural order parameter; (iii.) entropy production; (iv.) definition of glass transition temperature and limits of validity of the Bartenev-Ritland equation over the considered large range of cooling rates; (v.) value of the viscosity at glass transition; (vi.) configurational specific heat capacity; (vii.) Prigogine-Defay ratio; (viii.) validity of Ehrenfest's relations in glass transition; (ix.) fictive pressure and temperature; (x.) effects of change of cooling and heating conditions. The theoretical results will be compared with experimental data. A summary of the results and discussion of future possible developments completes the chapter.

From a more general point of view, the present chapter is aimed to give some overview on the work carried out in this field in the last 3-5 years. It gives an account of some basic results, but mainly in order to further substantiate and advance the obtained results and to specify future possible developments. In particular, such topics could be (i.) alternative derivation of the Prigogine-Defay ratio from data on metastable equilibrium liquids, (ii.) Reformulation of kinetic criteria of glass-formation, (iii.) 2nd order phase transitions and the glass transition: Are Landau-like concepts applicable to glass transition? (iv.) Are Ehrenfest type relations applicable to glass transition? (v.) Comparison of experimental and theoretical results on heat capacity and related quantities for different cooling & heating regimes. These topics are already reflected partly in the present version of the manuscript but further extensions are anticipated. (vi.) In addition, some summary on the discussion concerning the nature and the typical features of glass transition will be given summarizing to some extent the intensive discussion in this field since the meeting in Trencin in 2008. By mentioned above reasons, the present chapter does not have the aim to be finally polished, for some problems only possible directions of search for solutions will be specified and not the finally hopefully to be obtained results.

24.2 Glasses and the Glass Transition: Some Basic Experimental Facts

An experimental analysis of glass-forming melts and glasses shows several features which are usually not observed and treated in the thermodynamics of equilibrium systems (for a comprehensive overview see [2, 5]). The first of this set of peculiarities is illustrated in Figs. 24.1. As shown in these figures, the thermodynamic properties of glass-forming systems - here the specific heat C_p - depend significantly on prehistory, they are not determined uniquely only by the current values of the external control parameters like pressure, p, and temperature, T.



Figure 24.3: Frequency distribution of the values of the Prigogine-Defay ratio as obtained experimentally. Most frequently Π -values are found in the range $\Pi = (2 - 5)$ in agreement with theoretical estimates (for the details see Figs. 3.17 in [5]) and [13].

A similar behavior is found with respect to kinetic parameters of glass-forming melts like the viscosity, η . Provided the "equilibrium" viscosity of the liquid is described by the Vogel-Fulcher-Tammann equation

$$\eta = \eta_0 \exp\left(\frac{U_0}{k_B(T-T_0)}\right) , \qquad (24.3)$$

then the measured value deviates near and, in particular, below T_g from the respective analytical dependence, i.e., the kinetic coefficients may change at the glass-transition. Examples of such kind of behavior are illustrated in Fig. 24.2.

Jumps in the thermodynamic coefficients - as shown for the specific heat in Fig. 24.1 - are found also for the thermal expansion coefficient, α , and the compressibility, κ . Their combination, the so-called Prigogine-Defay ratio Π , defined by

$$\Pi = \left. \frac{1}{VT} \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \right|_{T=T_q} \cong 1 - 5 , \qquad (24.4)$$

has values larger than one. Normally, values in the range $\Pi \cong 1 - 5$ are observed. A more detailed overview is given in Fig. 24.3.

A similar relationship is found to be of importance for second-order equilibrium phase transitions, where it is denoted as Ehrenfest ratio and the respective parameter Π_E defined similarly has a value equal to one. It is found in this way that the behavior of glass-forming systems is similar but not identical to 2nd order equilibrium phase transitions. So, the question arises what is the origin of this similarity and what makes the difference?! In order to answer this question, we have briefly to review some basic ideas of classical equilibrium thermodynamics.

24.3 Classical Equilibrium Thermodynamics. Phases and Phase Transitions

24.3.1 Phases and Phase Transitions

Classical equilibrium thermodynamics is devoted to the analysis of macroscopic systems in thermodynamic equilibrium states and reversible processes in between them. "Reversible" means that the initial state of a given system can be reestablished without any changes in surrounding systems. For such cases, the properties of the system are independent of prehistory. In order to realize such processes, quasi-stationary processes have to be performed, i.e., the systems has to be transferred to other states via a sequence of equilibrium states. This condition implies that the characteristic relaxation times to the respective equilibrium states are small as compared with the characteristic times of change of the external control parameters.

The notation "Phase" was introduced by J. W. Gibbs [20], it is related to a particular form of (equilibrium) appearance of a given body. In detail, Gibbs wrote: In considering the different homogeneous bodies which can be formed out of any set of component substances, it will be convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its quantity or form. We may call such bodies which differ only in quantity and form as different examples of the same phase. Phases which can exist together, the dividing surfaces being plane, in an equilibrium which does not depend upon passive resistances to change we shall call coexistent ...

It is evident from this definition that Gibbs restricted the meaning of the word phase to equilibrium states (passive resistances to change - or in other words, a kinetic inhibition of the approach to equilibrium - do not exist by assumption). This interpretation follows also from Gibbs phase rule, giving the number of thermodynamic degrees of freedom in dependence on the number of coexisting phases and the number of components in the system (k: number of thermodynamic degrees of freedom)

$$f=2+k-r\geq 0\;,\qquad r\leq k+2\;.$$

This relation holds exclusively for equilibrium states.

The notation phase is treated today in a more general way:

- Equilibrium drops (or other aggregates) in a finite volume of vapor are considered as a well-defined phase although its properties depend on volume (system size).
- Second-order phase transitions are defined following Ehrenfest, where a coexistence of different phases is excluded.
- The notation "kinetic phase transition" has been introduced denoting by such term bifurcations of systems of e.g. differential equations describing the behavior of (in general) open systems.

In application to glass science, the question then is: Is it reasonable to use the term phase eventually in such extended meaning for a glass? The following arguments can be given to arrive at a negative answer to this question:

• The notation *a system is in a glassy state does not define its state*, the state depends on cooling rate or, more generally, on prehistory.

(24.5)

- Provided one would use such notation, then a glass could exist in an infinite number of different phases, which would considerable reduce the use of such notation.
- A glass cannot realize states where a equilibrium coexistence with other phases is found being an essential ingredient of Gibbs's original definition.
- Glasses are systems where "passive resistances to change" are of major significance.

By above given considerations, it is not useful to denote glass as a phase.

24.3.2 Ehrenfests Classification: First and Second-Order Equilibrium Phase Transitions

First-Order Equilibrium Phase Transitions

For the description of processes proceeding by varying the pressure, p, and temperature T, the Gibbs free energy, G, is the thermodynamic potential. Its change is given by [21, 22]

$$dG = -SdT + Vdp , \qquad S = -\left(\frac{\partial G}{\partial T}\right)_p , \qquad V = \left(\frac{\partial G}{\partial p}\right)_T , \qquad (24.6)$$

where S is the entropy and V is the volume.

According to Ehrenfest, first-order equilibrium phase transitions are characterized by equality of the Gibbs free energy of the coexisting different phases

$$G^{(1)}(p,T) = G^{(2)}(p,T) , \qquad (24.7)$$

while the first-order derivatives of G with respect to pressure and temperature

$$\left(\frac{\partial G^{(1)}}{\partial p}\right)_T \neq \left(\frac{\partial G^{(2)}}{\partial p}\right)_T , \qquad \left(\frac{\partial G^{(1)}}{\partial T}\right)_p \neq \left(\frac{\partial G^{(2)}}{\partial T}\right)_p$$
(24.8)

are different. With Eq. (24.6), Eq. (24.8) yields

$$v^{(1)} \neq v^{(2)}, \qquad s^{(1)} \neq s^{(2)},$$
(24.9)

i.e., specific volume, v, and specific entropy, s, have different values in both phases specified by the superscripts (1) and (2), respectively. It follows that first-order phase transitions are characterized by a **qualitative change of the state**, of the structure of the system.

Second-Order Equilibrium Phase Transitions

Following, again, Ehrenfest, second-order equilibrium phase transitions are characterized by equality of Gibbs' free energies of the different phases,

$$G^{(1)}(p,T) = G^{(2)}(p,T) , \qquad (24.10)$$

again, and, in addition, by equality of the first-order derivatives,

$$\left(\frac{\partial G^{(1)}}{\partial p}\right)_T = \left(\frac{\partial G^{(2)}}{\partial p}\right)_T, \qquad \left(\frac{\partial G^{(1)}}{\partial T}\right)_p = \left(\frac{\partial G^{(2)}}{\partial T}\right)_p \implies p = p(T)$$
(24.11)

or

$$v^{(1)} = v^{(2)}, \qquad s^{(1)} = s^{(2)},$$
(24.12)

but inequality of the second-order derivatives,

$$\left(\frac{\partial^2 G^{(2)}}{\partial p^2}\right)_T \neq \left(\frac{\partial^2 G^{(1)}}{\partial p^2}\right)_T , \qquad \left(\frac{\partial^2 G^{(1)}}{\partial T^2}\right)_p \neq \left(\frac{\partial^2 G^{(2)}}{\partial T^2}\right)_p , \tag{24.13}$$

24.3 Classical Equilibrium Thermodynamics. Phases and Phase Transitions

With (c.f. Eq. (24.6))

$$S = -\left(\frac{\partial G}{\partial T}\right)_p, \qquad V = \left(\frac{\partial G}{\partial p}\right)_T, \qquad (24.14)$$

and the definitions of the specific heat at constant pressure, C_p , the isothermal expansion coefficient, α , and the compressibility, κ ,

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p, \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \qquad (24.15)$$

we obtain, consequently,

$$C_p^{(1)} \neq C_p^{(2)}, \qquad \alpha^{(1)} \neq \alpha^{(2)}, \qquad \kappa^{(1)} \neq \kappa^{(2)}.$$
 (24.16)

Latter relations imply that second-order equilibrium phase transitions can be interpreted as **qualitative changes of the reaction of the system** with respect to changes of the external control parameters.

Ehrenfest's Relations and Ehrenfest's Ratio

As indicated in Eq. (24.11), each of the considered identities defines the dependence of pressure on temperature (or vice versa) for the states where a second-order equilibrium phase transition may occur. These two relations can be expressed in the form

$$\frac{dp}{dT} = \frac{1}{VT} \left(\frac{C_p^{(1)} - C_p^{(2)}}{\alpha^{(1)} - \alpha^{(2)}} \right) , \qquad \frac{dp}{dT} = \frac{\alpha^{(1)} - \alpha^{(2)}}{\kappa^{(1)} - \kappa^{(2)}} .$$
(24.17)

They are denoted as Ehrenfest's relations. Since both relations have to be equivalent, we arrive from them at a relation denoted as Ehrenfest's ratio, Π_E , i.e.,

$$\Pi_E = \frac{1}{VT} \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} , \qquad \Pi_E = 1 .$$
(24.18)

For second-order equilibrium phase transitions, the combination of jumps of the thermodynamic coefficients as expressed via Ehrenfest's ratio, Eq. (24.18), has to be equal to one.

Landau Theory of 2nd-Order Phase Transitions: The Case of Two Order-Parameters

¹Second-order equilibrium phase transitions are frequently described in terms of the Landau theory (for the basic treatment, c.f. [21]). In the present section, we outline some essential ingredients of this approach taking into consideration that there exists a variety of attempts to apply it to the description of the glass transition [23, 24, 25, 26]. In addition, we extend this theory to the case of several (here first two) order parameters, however, retaining the approach as simple as possible in order to easily arrive at the basic for our purposes general results.

In order to develop the Landau theory of second-order phase transitions to the case of two order parameters, we write first the Gibbs free energy in the form

$$G = G_0(p,T) + G_{sing}(p,T,x,y),$$
(24.19)

where x and y are considered as two scalar order parameters. In the further discussion, we consider only the singular part of the Gibbs free energy ($G = G_{sing}$) as being dependent on the order parameters. Following the Landau approach, we may write then

$$G = ax^{2} + ay^{2} + bx^{4} + by^{4} + cx^{2}y^{2} \quad \text{with} \quad b > 0 , \quad c > 0 .$$
(24.20)

¹The present subsection has been prepared following a suggestion by Alexander L. Tseskis. The discussions with him on this and related topics are gratefully acknowledged.

The parameter a has to be of the form

 $a = \alpha t$

with

$$t = T - T_c , \qquad \alpha = \text{constant} > 0 . \tag{24.21}$$

For simplicity we assumed here that the expansion coefficients are the same both with respect to x and y. The equilibrium conditions are given then by

$$\left(\frac{\partial G}{\partial x}\right)_{p,T} = \left(\frac{\partial G}{\partial y}\right)_{p,T} = 0 \tag{24.22}$$

or by

$$2bx^{3} + cxy^{2} + \alpha tx = 0, \qquad (24.23)$$

$$2by^\circ + cx^2y + \alpha ty = 0 \; .$$

For $t \ge 0$, the solutions x = y = 0 correspond to the minimum of G. At $t \le 0$, the minimum is determined by

$$2bx^2 + cy^2 + \alpha t = 0 , \qquad (24.24)$$

$$2by^2 + cx^2 + \alpha t = 0 \; ,$$

or by

$$x^{2} - y^{2} = 0$$
, $x^{2} + y^{2} = -\frac{2\alpha t}{2b + c}$, (24.25)

resulting in

$$x^2 = y^2 = -\frac{\alpha t}{2b+c} \,. \tag{24.26}$$

In such approach, we get

$$G = \begin{cases} 0 & \text{for } t \ge 0 \\ \\ -\frac{\alpha^2 t^2}{2b+c} & \text{for } t \le 0 \end{cases}$$
(24.27)

With

$$dG = -SdT + Vdp , \qquad S = -\left(\frac{\partial G}{\partial T}\right)_p \tag{24.28}$$

and

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p \tag{24.29}$$

we arrive at

$$S = \begin{cases} 0 & \text{for } t \ge 0 \\ \frac{2\alpha^2 t}{2b+c} & \text{for } t \le 0 \end{cases}$$

$$C_p = \begin{cases} 0 & \text{for } t \ge 0 \\ \frac{2\alpha^2 T}{2b+c} & \text{for } t \le 0 \end{cases}$$
(24.30)
$$(24.31)$$

24.4 Glasses and the Transition: The Classical Approach

The jump in C_p at T_c is consequently given by $\Delta C_p = 2\alpha^2 T_c/(2b+c)$. It has a different value as compared with the case of only one order parameter as treated by Landau and Lifshitz in [21]. Indeed, for the one-parameter case, one gets instead [21]

$$G = \begin{cases} 0 & \text{for } t \ge 0 \\ -\frac{\alpha^2 t^2}{4b} & \text{for } t \le 0 \end{cases}, \qquad S = \begin{cases} 0 & \text{for } t \ge 0 \\ \frac{\alpha^2 t}{2b} & \text{for } t \le 0 \end{cases}$$

$$C_p = \begin{cases} 0 & \text{for } t \ge 0 \\ \frac{\alpha^2 T}{2b} & \text{for } t \le 0 \end{cases}$$

$$(24.32)$$

$$(24.33)$$

Looking at the results of this simplified treatment of the case of several order parameters, we observe:

- 1. The Landau theory does not supply us with the value of the Ehrenfest ratio but allows us merely to specify the jump of the heat capacity at constant pressure.
- 2. The jumps of the specific heat depends on the model employed and, in particular, on the number of scalar order parameters.
- 3. Once the Landau theory does not allow us to specify the value of the Ehrenfest ratio, it cannot be used to discuss the dependence of this value on the number of order parameters as this is performed with respect to the Prigogine-Defay ratio by Davies and Jones ([27] and subsequent analysis) in application to glass transition. On the other hand, such dependence cannot exist in the framework of equilibrium thermodynamics since otherwise we would come in conflict with the results of the thermodynamic derivation of the Ehrenfest leading always to the result $\Pi_E = 1$ independent on any number of eventually appropriate order parameters (c.f. the analysis performed here earlier).

In the two-parameter model, the second order parameter y can be considered as uniquely defined by the first one, i.e., by x and that x can be considered then as a function of pressure and temperature. Such behavior can be expected to occur always in terms of the Landau theory. Indeed, assuming we have a set of scalar order parameters, $\{x, y_i\}$, then the Gibbs free energy has to be considered as a function of this set of parameters. From the equilibrium conditions,

$$\left(\frac{\partial G}{\partial y_i}\right)_{p,T} = 0, \qquad i = 1, 2, \dots$$
(24.34)

we can express y_i via x. Consequently, the theory is reduced to the quasi-one-dimensional situation again. The final step is then the determination of x in dependence on pressure and temperature via

$$\left(\frac{\partial G}{\partial x}\right)_{p,T} = 0 , \qquad (24.35)$$

Consequently, under the considered conditions, the Landau theory with several scalar order parameters leads qualitatively always to a result identical to the case of assumption of only one order parameter, however, as demonstrated for the considered simplified case, the quantitative results may be different.

24.4 Glasses and the Transition: The Classical Approach

24.4.1 Simon's Model

In Fig. (24.4), typical curves for the density or specific volume of glass-forming systems in glass transition are presented. The density changes in some interval of temperatures until it reaches some saturation. As evident, the density does not depend only on pressure and temperature but also on some structural order parameter indicated on the right part of the figure and denoted here by ξ . According to Simon, the system passes along the metastable equilibrium liquid curve (curve 1 in the schematic interpretation given on the right hand side) until the glass transition point is reached. At this point, by assumption, the system becomes suddenly frozen-in and the value of the order parameter does not change any more (curve 3 in the schematic interpretation given on the right hand side). So, in Simon's model of the glass transition, the real behavior in the glass transition interval (curve 2 in the schematic interpretation given on the right hand side) is reduced to some point.

In such approach,



Figure 24.4: Temperature dependence of the density of a borosilicate glass measured at three different cooling rates. (1): 1 K min⁻¹; (2): 2 K min⁻¹; (3): 10 K min⁻¹; (4): annealing curve. It can be seen that T_g increases with increasing cooling rates (Ritland (1954) [28]); for the details see Figs. 2.33 in [5]).

- classical thermodynamics (1. & 2. laws) is fully applicable;
- the system passes always the same states in cooling and heating, no hysteresis effects have to occur or can be theoretically treated;
- relaxation remains outside consideration!



Figure 24.5: First proof of the kinetic dependence of T_g on cooling or heating rate q (for an alkali-silicate glass, after Bartenev (1951) [29]; for the details see Fig. 5.10 in [5]). By q, here and in Eq. (24.36) the absolute value of the cooling rate is denoted.

In addition, in Simon's approach, the value of the glass transition temperature has to be considered as an experimental parameter. In this way, the question arises, how it can be determined theoretically? Even more, the glass transition temperature is found in a number of cases to be described by a logarithmic function of the cooling rate as shown in Fig. 24.5. The curve can be well-approximated, at least in a number of cases including the data shown in this figure, by a dependence of the form

$$\frac{1}{T_g} = C_1 - C_2 \log q \qquad \text{Bartenev-Ritland} \quad \text{. equation}$$
(24.36)

It follows as a consequence of this and a huge number of similar results that glass transition is a kinetic phenomenon. Consequently, in order to describe it theoretically one has to formulate kinetic criteria for glass-formation. This task will be performed in the next sections.

24.4.2 Kinetic Criteria of Glass-Formation

Kinetic Criteria of Glass-Formation: An Overview on Different Approaches

² Kinetic criteria for glass formation in a mathematical form have been derived in 1949 by Bartenev [30]. The necessity of the dependence of the glass transition temperature on cooling rate was discussed in detail by G. O. Jones in the same year [31], however, without arriving at a mathematical description of such dependence. The analysis of Bartenev was directed to dynamic glass transitions caused by changing the frequency, ω , of periodic deformations. Utilizing some specific model of viscoelastic behavior, he arrived at the following condition for glass-formation

$$\omega \tau|_{T=T_a} \cong \text{constant.}$$
 (24.37)

Employing further an expression for the relaxation time of the form

$$\tau \cong \tau_0 \exp\left(\frac{U}{k_B T}\right) , \qquad (24.38)$$

Bartenev obtained the relation

$$\frac{1}{T_g} = C_1 - C_2 \log \omega . (24.39)$$

In 1951, similar ideas were applied by Bartenev to cooling processes of glass-forming melts, in particular, to silicate glasses [29]. By very qualitative arguments (as his approach was described later by Volkenstein and Ptizyn [32, 33]) or from general considerations (as stated by Sanditov et al. [34] in 2007), he arrived at the relation

$$\left|\frac{dT}{dt}\tau\right|_{T_q} = \text{constant.}$$
(24.40)

Employing for the relaxation time, again, Eq. (24.38), he derived the relation

$$\frac{1}{T_g} = C_1 - C_2 \log \left| \frac{dT}{dt} \right|$$
(24.41)

Lateron, Bartenev denoted Eq. (24.37) as Frenkel-Kobeko equation [35] acknowledging a similar analysis performed by Frenkel [36] and Kobeko [37] earlier as compared with his own one.

Indeed, Frenkel in his well-known monograph [36] (written in the period 1942-43 and citing there much earlier performed own work and the similar to the work of Bartenev [30] analysis by Kobeko [37]) employs in the description additional order parameters (he denotes them also by ξ) which may or may not be functions of pressure and temperature. For latter case, he introduces relations determining their relaxation into equilibrium. He introduces them assuming the principal possibility of a continuous transition from the liquid to the crystalline state (accounting for a principal possibility of a continuous change of the degree of order) and states that such continuous transition is connected with the passage of a set of unstable transient states.

Bartenev's [29, 30] results were extended by him in cooperation with Lukyanov in 1955 [38]. They repeat the derivations of Bartenev from 1949 and 1951 and demonstrate the validity of the Bartenev relation for 9 different substances as well as a similar dependence for oscillatory changes of the systems properties. Similar work was performed by Ritland [28] in 1954, by this reason the respective dependence given by Eq. (24.41) was denoted later commonly as the Bartenev-Ritland equation.

Volkenstein and Ptizyn (1955/56) [32, 33] performed a similar analysis based on a chemical reaction model. In the mentioned two different papers, they arrived at two slightly different expressions

$$|q(T_g)| \left| \frac{d\tau}{dT} \right|_{T_g} \cong 1 , \qquad \left| \frac{d(q\tau)}{dT} \right|_{T_g} \cong 1 .$$
(24.42)

 $^{^{2}}$ The present section originated from a suggestion by Gyan Johari. The discussions with him on this and related topics are gratefully acknowledged.

Employing certain additional conditions, they re-derived the relations formulated by Bartenev

$$\left|\frac{dT}{dt}\tau\right|_{T_g} = \text{constant} . \tag{24.43}$$

They note in their papers as well that in Bartenev's equation, the constant has to be a weak function of T_g .

Moynihan, Easteal, Wilder, and Tucker [40] performed in 1974 a similar detailed analysis and verified the validity of the Bartenev-Ritland equation for a variety of systems considering it as a generally valid relation (c.f. also [41]). A similar point of view was expressed recently in 2007 by Mazurin [42]. So, the question arises, is this point of view correct and/or under which conditions it has eventually to be modified. To the analysis of this problem, we will return shortly.

In the monograph of Gutzow and Schmelzer ([2], Section 3.6), kinetic criteria for glass-formation have been treated in the following way: A fundamental kinetic criterion for glass-formation can be formulated in the form that at the temperature of vitrification the time of molecular relaxation τ_R has to be of the same order as the characteristic observation or stay time Δt for the process considered, i.e.,

$$\tau_R \approx \Delta t \quad \text{for} \quad T = T_q \,. \tag{24.44}$$

For a glass the ratio $\tau_R/(\Delta t)$ is a very large number, while for the liquid in the vicinity of the melting temperature T_m

$$\tau_R \approx (10^{-12} - 10^{-13})s \tag{24.45}$$

is to be expected, resulting in very small values of the ratio

$$Dh = \frac{\tau_R}{\Delta t} . \tag{24.46}$$

This ratio was introduced by Reiner (1964) [43], a well-known specialist in the field of rheology, and is denoted by him as Deborah's number (see also Stevels (1971) [44]).

According to Reiner, the notation Deborah's number stems from a Biblical text where the Judge Deborah (a prophetess, the wife of Lepidoth, who judged Israel in those ancient times) says "The earth trembled ... and the mountains melted from before the Lord" (The Bible; Old Testament; King James Version; Judges 5:5). This statement implies that for the long observation times possible only for God the mountains, having a permanent shape for a human being with his very restricted observation times, are rapidly changing.

A derivation of Eq. (24.44) with respect to temperature results in (see also Cooper, Gupta (1982) $[45]^3$)

$$\frac{d\tau_R}{dT} = -\frac{1}{q} , \qquad (24.47)$$

where the cooling rate q is introduced as

$$q = -\frac{dT}{dt} . (24.48)$$

Applying this definition q is a positive quantity for cooling experiments.

If the already discussed expression

$$\tau_R = \tau_{R0} \exp\left(\frac{U(T)}{k_B T}\right) \tag{24.49}$$

is used for the description of the temperature dependence of the relaxation time ... we have

$$\frac{d\tau_R}{dT} = \tau_R \frac{d}{dT} \left(\frac{U(T)}{k_B T} \right) . \tag{24.50}$$

³In this paper, it was shown that the glass transition range is characterized by $dt \cong d\tau$. This condition goes beyond Eq. (24.44) or, at least, can be deduced from it only in qualitative terms. In the reproduced here derivation, actually the definition of the cooling rate is employed (q = -(dT/dt)) and dt is replaced then - following [45] - by $d\tau_R$. It follows first that the Deborah number concept is not strictly related to the derivation of the criteria for glass transition but only a qualitative correspondence exists. Second, it would be highly interesting to obtain kinetic criteria for glass formation leading directly to the desired results.

24.4 Glasses and the Transition: The Classical Approach

When the activation energy U is considered, approximately, as a constant ($U = U_0$) this expression is simplified to

$$\frac{d\tau_R}{dT} = -\tau_R \frac{U_0}{k_B T^2} \,. \tag{24.51}$$

Eqs. (24.47) and (24.51) yield

$$q\tau_R = \frac{k_B T^2}{U_0} \tag{24.52}$$

The starting equation, Eq. (24.44), on which the derivation is based, holds for $T \approx T_g$. Consequently, in Eq. (24.52) we have to replace T by T_g resulting, finally, in

$$q\tau_R(T_g) = \frac{k_B T_g^2}{U_0} = C_0 . (24.53)$$

In this way, the Frenkel-Kobeko relation is reestablished.

In the mentioned section of [2] and also in [46, 47], the reduced glass transition temperature was then computed as a function of the cooling rate from the Bartenev-Ritland equation resulting from Eq. (24.53) and consequences with respect to the thermodynamic properties of glasses in dependence on cooling rate have been discussed.

In reconsidering in 2006 the kinetic definition of the glass transition temperature [7], we reanalyzed the problem whether indeed from the discussions of the Deborah number a kinetic criterion for glass formation can be derived strictly or whether the derivation is merely of qualitative nature with plausible results but, anyway, not strictly derived. Some first doubts concerning the applicability of such ratio like the Deborah number result already from a detailed study of the paper by Reiner given here at part in the epigraph. As evident, Reiner is not concerned with the possible differences between liquids and glasses but between liquids and solids, in general.

Instead of the approach followed in [2], we developed in [7] a model-independent formulation of the glass transition criterion. In this general model-independent approach, we introduced similar to the characteristic relaxation time, τ_R , defined via

$$\frac{d\xi}{dt} = -\frac{1}{\tau_R(p, T, \xi)} (\xi - \xi_e) , \qquad q = \frac{dT}{dt} , \qquad (24.54)$$

a characteristic time scale of change of temperature, τ_T , as

$$\frac{dT}{dt} = -\frac{1}{\tau_T}T, \qquad \tau_T = \left\{\frac{1}{T} \left|\frac{dT}{dt}\right|\right\}^{-1}.$$
(24.55)

So, provided change of temperature and change of the order parameter would proceed by the same laws, the respective characteristic time scales could be then compared directly. The criterion for glass-formation is given then by the condition that both time scales are of the same order of magnitude, i.e.,

$$\tau_R \cong \tau_T \qquad \Longrightarrow \qquad \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right\} \Big|_{T=T_g} \cong C , \qquad C \cong 1 .$$
(24.56)

This general criterion, Eq. (24.56), contains above mentioned particular criteria as special cases. Indeed, it is equivalent to the Frenkel-Kobeko relation as formulated or derived for some particular model by Bartenev, Volkenstein and Ptizyn (Eqs. (24.42)). In addition, multiplying Eq. (24.56) by temperature T and taking the derivative with respect to T, one obtains immediately Eq. (24.47).

In application to dynamic glass transitions - glass-like transitions at periodic external perturbations as discussed here in connection with the respective analysis of Bartenev - Eq. (24.56) can be employed similarly and directly. Indeed, denoting by $\tau_E = 2\pi/\omega$ the characteristic time of oscillatory changes of the appropriate external control parameter, the criterion for a dynamic glass transition gets the form

$$\tau_R \cong \tau_E = \frac{2\pi}{\omega} , \qquad (24.57)$$

resulting directly in a relation equivalent to Eq. (24.37) without introducing any particular models of the systems behavior.

Employing the general model-independent criterion of glass-formation, Eqs. (24.56) and (24.57), as discussed above, glass-transition can be defined in terms of only two characteristic time scales, the time of change of external

factors and the response time of the system. In this definition, the Deborah number does not occur, there is no need to introduce any observation time. Moreover, the introduction of the observation time or, equivalently, the Deborah number into the discussion of glass transition, seems to be also not suitable from another point of view: Deborah's number - as discussed by Reiner [43] and earlier by Frenkel [36] and Kobeko [37] without employing this notation - specifies some difference or some relativity of the concepts of solids and fluids, but it does not give some specific definition of the glassy state. The reason, why anyway the concept of observation times is till now widely employed can be traced already as well in the work by Frenkel [36]. Frenkel discusses related problems in the following way: In order to investigate a given system, we have to perform some external changes of pressure, temperature or other control parameters. Simultaneously, we measure the response of the system with respect to these external perturbations. In such somewhat artificial interpretation, indeed, the time of change of external control parameters can be treated as observation time. However, such interpretation seems to be artificial and not appropriate introducing some subjective moment into the description which in reality does not exist.

24.4.3 Classical Approaches in the Theoretical Determination of the Prigogine-Defay Ratio

The assumptions underlying Simon's model of the glass transition have been employed by both Prigogine & Defay and Davies & Jones in their theoretical analysis of the value of the Prigogine-Defay ratio in glass transition. Both groups of authors came - as will be shown here - to the result that, provided only one structural order parameter governs the behavior of the system, the Prigogine-Defay ratio has to be equal to one. Their methods and results are reproduced in the next sections in order to show that it is really the mentioned additional assumption - application of Simon's model - leading to their result.

Approach of Prigogine and Defay (1950)

In order to derive a theoretical expression allowing us to determine theoretically the value of the Prigogine-Defay ratio utilizing only one structural order parameter, we summarize first some of basic dependencies giving us the possibility to describe glass-forming systems and the process of vitrification (for the details see [2, 5, 7, 13]). The change of the Gibbs free energy, G, in dependence on temperature, T, pressure, p, and structural order parameter, ξ , can be expressed as

$$dG = -SdT + Vdp - Ad\xi , \qquad (24.58)$$

where S is the entropy, V is the volume and A is the affinity. The following relations hold:

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \cong -G_e^{(2)}(\xi - \xi_e) , \qquad G_e^{(2)} = \left(\frac{\partial^2 G}{\partial \xi^2}\right)\Big|_{p,T,\xi = \xi_e} > 0 .$$
(24.59)

According to Prigogine and Defay [12], changes of the affinity as a function of temperature, T, pressure, p, and structural order parameter, ξ , can be expressed as

$$dA = \frac{(A+h_{p,T})}{T} dT - v_{p,T} dp + a_{p,T} d\xi , \qquad (24.60)$$

$$a_{p,T} = \left(\frac{\partial A}{\partial \xi}\right)_{p,T}, \qquad v_{p,T} = \left(\frac{\partial V}{\partial \xi}\right)_{p,T}, \qquad h_{p,T} = \left(\frac{\partial H}{\partial \xi}\right)_{p,T}.$$
 (24.61)

Taking into account the definition of the Gibbs free energy, G = H - TS, we arrive with Eq. (24.59) at

$$h_{p,T} = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} + T\left(\frac{\partial S}{\partial \xi}\right)_{p,T} = -A + T\left(\frac{\partial S}{\partial \xi}\right)_{p,T}.$$
(24.62)

If one considers not A but ξ as the dependent and T, p and A as the independent variables, Eq. (24.60) may be rewritten as

$$d\xi = \frac{1}{a_{p,T}} dA - \frac{A + h_{p,T}}{T a_{p,T}} dT + \frac{v_{p,T}}{a_{p,T}} dp .$$
(24.63)

24.4 Glasses and the Transition: The Classical Approach

By assumption, ξ is, in general, a function of A, T and p. Its total differential has then the form

$$d\xi = \left(\frac{\partial\xi}{\partial A}\right)_{p,T} dA + \left(\frac{\partial\xi}{\partial T}\right)_{p,A} dT + \left(\frac{\partial\xi}{\partial p}\right)_{A,T} dp.$$
(24.64)

A comparison between Eqs. (24.63) and (24.64) yields

$$\left(\frac{\partial\xi}{\partial A}\right)_{p,T} = \frac{1}{a_{p,T}}, \qquad \left(\frac{\partial\xi}{\partial T}\right)_{A,p} = -\frac{A+h_{p,T}}{Ta_{p,T}}, \qquad \left(\frac{\partial\xi}{\partial p}\right)_{A,T} = \frac{v_{p,T}}{a_{p,T}}.$$
(24.65)

For closed systems in thermodynamic equilibrium, only two of the three thermodynamic state parameters (pressure, p, volume, V, and temperature, T) are independent variables and the structural order-parameter is an unambiguous function of these parameters independent on the prehistory of the system. For such equilibrium states, the thermodynamic coefficients (like thermal expansion coefficient, α , isothermal compressibility, κ , and isobaric molar heat capacity, C_p)

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p, \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p, \qquad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$
(24.66)

can be expressed, consequently, as functions of pressure, p, and temperature, T, exclusively.

Above definitions retain their validity also in the more general case, when the system is in a thermodynamically non-equilibrium state characterized by one (or several) additional structural order-parameter(s), ξ , being not uniquely defined by pressure and temperature alone but depending also on the prehistory. Provided, as an example, we cool down the system with a given rate, q = (dT/dt) < 0. Then, we transfer the system into a glass along one of the possible trajectories of cooling giving rise to different dependencies, $\xi = \xi(p, T; q)$, and A = A(p, T; q). Here q = q(t)specifies the chosen cooling law.

For any of above defined trajectories, $\xi = \xi(p, T; q)$, of vitrification, the thermodynamic coefficients can be expressed as a sum of two terms [12, 13]. For example, the change of the volume in dependence on pressure at constant temperature can be written in the form

$$\left(\frac{\partial V}{\partial p}\right)_{T} = \left(\frac{\partial V}{\partial p}\right)_{T,\xi} + \left(\frac{\partial V}{\partial \xi}\right)_{p,T} \left(\frac{\partial \xi}{\partial p}\right)_{T} . \tag{24.67}$$

With the definition of the compressibility κ (Eq. (24.66)), this equation can be transformed to (c.f. [2, 12])

$$\kappa = \kappa_{\xi} - \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{p,T} \left(\frac{\partial \xi}{\partial p} \right)_{T}$$
(24.68)

The step-like change in the compressibility in glass transition can be expressed therefore as

$$\Delta \kappa = \kappa - \kappa_{\xi} = -\frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{p,T} \left(\frac{\partial \xi}{\partial p} \right)_{T} . \tag{24.69}$$

Similarly to Eq. (24.67), we can express the isobaric heat capacity of the undercooled metastable melt as

$$C_{p} = \left(\frac{\partial H}{\partial T}\right)_{p} = C_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \left(\frac{\partial \xi}{\partial T}\right)_{p}$$
(24.70)

or

$$\Delta C_p = C_p - C_{p,\xi} = \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \left(\frac{\partial \xi}{\partial T}\right)_p \,. \tag{24.71}$$

For the thermal expansion coefficient (defined by Eq. (24.66)), analogous relations

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left\{ \left(\frac{\partial V}{\partial T} \right)_{p,\xi} + \left(\frac{\partial V}{\partial \xi} \right)_{p,T} \left(\frac{\partial \xi}{\partial T} \right)_p \right\} = \alpha_{\xi} + \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{p,T} \left(\frac{\partial \xi}{\partial T} \right)_p , \quad (24.72)$$

$$\Delta \alpha = \alpha - \alpha_{\xi} = \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{p,T} \left(\frac{\partial \xi}{\partial T} \right)_{p}$$
(24.73)

can be derived easily. By a combination of Eqs. (24.69), (24.71) and (24.73), we obtain the following expression for the Prigogine-Defay ratio

$$\Pi(T_g) = \frac{1}{VT} \left\{ \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \right\} \Big|_{T=T_g} = - \left. \frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{T\left(\frac{\partial V}{\partial \xi}\right)_{p,T}} \frac{\left(\frac{\partial \xi}{\partial p}\right)_T}{\left(\frac{\partial \xi}{\partial T}\right)_p} \right|_{T=T_g} = - \left. \frac{h_{p,T}}{Tv_{p,T}} \frac{\left(\frac{\partial \xi}{\partial p}\right)_T}{\left(\frac{\partial \xi}{\partial T}\right)_p} \right|_{T=T_g} .$$
(24.74)

Note that the differences in the thermodynamic coefficients or the partial derivatives in Eq. (24.74) have to determined according to the approach employed for the glass transition temperature $T = T_g$.

Based upon the considerations given above, we have now to express the derivatives $(\partial \xi / \partial p)_T$ and $(\partial \xi / \partial T)_p$ taking into account that the affinity along the chosen path is defined uniquely via pressure and temperature similarly to the order parameter, ξ . Eq. (24.63) yields then

$$d\xi = \frac{1}{a_{p,T}} dA - \frac{A + h_{p,T}}{T a_{p,T}} dT + \frac{v_{p,T}}{a_{p,T}} dp , \qquad (24.75)$$

$$d\xi = \frac{1}{a_{p,T}} \left[\left(\frac{\partial A}{\partial T} \right)_p - \frac{A + h_{p,T}}{T} \right] dT + \frac{1}{a_{p,T}} \left[\left(\frac{\partial A}{\partial p} \right)_T + v_{p,T} \right] dp .$$
(24.76)

According to Eq. (24.60), the affinity A is in general a function of ξ , T and p. Along the given path of cooling, the structural order parameter becomes a function of pressure and temperature. By this reason, the derivative of affinity with respect to pressure and temperature has to be computed similarly like the thermodynamic coefficients as given via Eqs. (24.67), (24.70) and (24.72).

The ratio $((\partial \xi / \partial p)_T / (\partial \xi / \partial T)_p)$, entering Eq. (24.74), can be expressed, consequently, as

$$\frac{\left(\frac{\partial\xi}{\partial p}\right)_{T}}{\left(\frac{\partial\xi}{\partial T}\right)_{p}} = \frac{\left(\frac{\partial A}{\partial p}\right)_{T} + v_{p,T}}{\left(\frac{\partial A}{\partial T}\right)_{p} - \frac{A+h_{p,T}}{T}} = -\frac{Tv_{p,T}}{A+h_{p,T}} \frac{\left[1 + \frac{1}{v_{p,T}} \left(\frac{\partial A}{\partial p}\right)_{T}\right]}{\left[1 - \frac{T}{A+h_{p,T}} \left(\frac{\partial A}{\partial T}\right)_{p}\right]}$$
(24.77)

and Eq. (24.74) yields

$$\Pi(T_g) = \frac{h_{p,T}}{A + h_{p,T}} \frac{\left[1 + \frac{1}{v_{p,T}} \left(\frac{\partial A}{\partial p}\right)_T\right]}{\left[1 - \frac{T}{A + h_{p,T}} \left(\frac{\partial A}{\partial T}\right)_p\right]}\Big|_{T=T_g}$$
(24.78)

Following Simon's model, we have to follow the equilibrium curve up to the glass transition temperature. This assumption implies that both the affinity and the derivative of affinity with respect to pressure and temperature have to be set equal to zero. In such model approach, Eq. (24.78) yields $\Pi = 1$ independent on any additional assumptions concerning the system under consideration. These results were first derived by Prigogine and Defay in 1950 in their first edition of their book [12] (c.f. Chapter 19 there).

1

Approach of Davies and Jones (1953)

In their approach to the determination of the Prigogine-Defay ratio (and a variety of other relationships describing the glass transition), Davies and Jones [27] went the following way. They introduced a differentiable function $\varphi(x, y, \xi)$ of three independent variables x. y, and ξ . In addition, they consider a set of surfaces $u(x, y, \xi) = \text{constant or in}$ other words, a surface $\xi = \xi(x, y)$. One can then determine the derivatives of φ at constant ξ and constant u or for $\xi = \xi(x, y)$. The condition $u(x, y, \xi) = \text{constant}$ is then connected with the equilibrium condition realized for the metastable liquid and constancy of the structural order parameter with the glassy state of the system under consideration. So, it is assumed that - at the glass transition temperature - the equilibrium liquid and glass are immediately located nearby or can be directly transformed into each other, i.e., Simon's model is employed. As the result of such derivations, one obtains

$$\frac{\partial\varphi(x,y,\xi)}{\partial x}\Big|_{u} = \left.\frac{\partial\varphi(x,y,\xi)}{\partial x}\right|_{y,\xi} + \left.\frac{\partial\varphi(x,y,\xi)}{\partial\xi}\right|_{x,y}\left.\frac{\partial\xi}{\partial x}\right|_{y} \,. \tag{24.79}$$

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For any fixed value of y, we have further

$$du = \left. \frac{\partial u(x, y, \xi)}{\partial x} \right|_{y,\xi} dx + \left. \frac{\partial u(x, y, \xi)}{\partial \xi} \right|_{x,y} d\xi = 0.$$
(24.80)

It follows

$$\frac{\partial \xi}{\partial x}\Big|_{y} = -\frac{\frac{\partial u(x,y,\xi)}{\partial x}\Big|_{y,\xi}}{\frac{\partial u(x,y,\xi)}{\partial \xi}\Big|_{x,y}}.$$
(24.81)

Eq. (24.79) reads then

$$\Delta\left(\frac{\partial\varphi}{\partial x}\right) = \left.\frac{\partial\varphi(x,y,\xi)}{\partial x}\right|_{u} - \left.\frac{\partial\varphi(x,y,\xi)}{\partial x}\right|_{y,\xi} = -\varphi_{\xi}\frac{u_{x}}{u_{\xi}}$$
(24.82)

with

$$\varphi_{\xi} = \left. \frac{\partial \varphi(x, y, \xi)}{\partial \xi} \right|_{x, y}, \qquad u_x = \left. \frac{\partial u(x, y, \xi)}{\partial x} \right|_{y, \xi}, \tag{24.83}$$

$$u_{\xi} = \left. \frac{\partial u(x, y, \xi)}{\partial \xi} \right|_{x, y} \,. \tag{24.84}$$

These are the normal partial derivatives.

Equivalently to Eq. (24.82), we get

$$\Delta\left(\frac{\partial\varphi}{\partial y}\right) = \left.\frac{\partial\varphi(x,y,\xi)}{\partial y}\right|_{u} - \left.\frac{\partial\varphi(x,y,\xi)}{\partial y}\right|_{x,\xi} = -\varphi_{\xi}\frac{u_{y}}{u_{\xi}}$$
(24.85)

with

$$u_y = \left. \frac{\partial u(x, y, \xi)}{\partial y} \right|_{x,\xi} \,. \tag{24.86}$$

The equilibrium conditions at appropriate boundary conditions are given by the relation

$$u = f_{\xi}(x, y, \xi) = \left. \frac{\partial f(x, y, \xi)}{\partial \xi} \right|_{x, y} = 0.$$
(24.87)

Then we obtain from Eqs. (24.82) and (24.85)

$$u = f_{\xi}, \qquad \varphi = f_x, \qquad \Delta\left(\frac{\partial f_x}{\partial x}\right) = -\frac{f_{x\xi}^2}{f_{\xi\xi}},$$
(24.88)

$$u = f_{\xi}, \qquad \varphi = f_x, \qquad \Delta\left(\frac{\partial f_x}{\partial y}\right) = -\frac{f_{x\xi}f_{y\xi}}{f_{\xi\xi}},$$
(24.89)

$$u = f_{\xi} , \qquad \varphi = f_y , \qquad \Delta \left(\frac{\partial f_y}{\partial y}\right) = -\frac{f_{y\xi}^2}{f_{\xi\xi}} , \qquad (24.90)$$

$$u = f_{\xi}, \qquad \varphi = f_y, \qquad \Delta\left(\frac{\partial f_y}{\partial x}\right) = -\frac{f_{y\xi}f_{x\xi}}{f_{\xi\xi}}.$$
 (24.91)

From Eqs. (24.88) and (24.90), we obtain

$$\Delta\left(\frac{\partial f_x}{\partial x}\right)\Delta\left(\frac{\partial f_y}{\partial y}\right) = \left[\Delta\left(\frac{\partial f_x}{\partial y}\right)\right]^2 = \left[\Delta\left(\frac{\partial f_y}{\partial x}\right)\right]^2 . \tag{24.92}$$

Now, let us consider the situation that the system is considered at some given pressure, p(x = p), and some given temperature, T(y = T). In such case, the potential function, f, is the Gibbs free energy, G(f = G). Eqs. (24.92) yield then

$$\Delta G_{pp} \Delta G_{TT} = \left(\Delta G_{pT}\right)^2 = \left(\Delta G_{Tp}\right)^2 \,. \tag{24.93}$$

With

$$dG = -SdT + Vdp \tag{24.94}$$

we obtain

$$\frac{\partial G}{\partial p} = V , \qquad \frac{\partial^2 G}{\partial p^2} = \frac{\partial V}{\partial p} , \qquad \frac{\partial^2 G}{\partial p \partial T} = \frac{\partial V}{\partial T} , \qquad (24.95)$$

$$\frac{\partial G}{\partial T} = -S , \qquad \frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T} , \qquad (24.96)$$

and from Eq. (24.93)

$$\Delta\left(\frac{\partial V}{\partial p}\right)\Delta\left(-\frac{\partial S}{\partial T}\right) = \left(\Delta\frac{\partial V}{\partial T}\right)^2 \,. \tag{24.97}$$

With the definitions of thermal expansion coefficient, α , heat capacity at constant pressure, C_p , and compressibility, κ via

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) , \qquad C_p = T \left(\frac{\partial S}{\partial T} \right) , \qquad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right) , \qquad (24.98)$$

we obtain finally

$$\frac{1}{VT} \frac{\Delta\kappa\Delta C_p}{(\Delta\alpha)^2} \Big|_{T=T_g} = 1.$$
(24.99)

As evident and underlined by the authors, the way of derivation of Eq. (24.99) as employed by Davies and Jones and described here briefly does not employ the application of the De Donder method, however, the underlying the respective derivations assumptions are equivalent to the basic assumptions employed by Prigogine and Defay: by both groups of authors, the Simon model of the glass transition is basically utilized.

Davies and Jones: Vitrification in the Case of Several Structural Order Parameters

Davies and Jones [27] showed further already in 1953 that for the case that more than one structural order parameter is required to appropriately describe the state of the glass-forming melt, then the value of the Prigogine-Defay ratio becomes larger than one. In the respective analysis again Simon's model is employed.

For this more general case, Davies and Jones arrive at the following expressions

$$\Delta C_p = \frac{1}{T} \sum_{i,j} \beta_{ij} \left(\frac{\partial H}{\partial \xi_i} \right)_{p,T} \left(\frac{\partial H}{\partial \xi_j} \right)_{p,T} , \qquad (24.100)$$

$$\Delta \alpha = \frac{1}{TV} \sum_{i,j} \beta_{ij} \left(\frac{\partial H}{\partial \xi_i} \right)_{p,T} \left(\frac{\partial V}{\partial \xi_j} \right)_{p,T} , \qquad (24.101)$$

$$\Delta \kappa = \frac{1}{V} \sum_{i,j} \beta_{ij} \left(\frac{\partial V}{\partial \xi_i} \right)_{p,T} \left(\frac{\partial V}{\partial \xi_j} \right)_{p,T}$$
(24.102)

with

$$\Delta \kappa \Delta C_p \ge T V (\Delta \alpha)^2 . \tag{24.103}$$

It is noted then that for the case that the number of structural order parameters is equal to one, Eq. (24.99) is reestablished, again. However, it is further mentioned that this relation, Eq. (24.99), is also fulfilled, if for all structural order parameters, the relations

$$\left(\frac{\partial H}{\partial \xi_i}\right)_{p,T} = k \left(\frac{\partial V}{\partial \xi_j}\right)_{p,T} , \qquad i = 1, 2, \dots, n$$
(24.104)

hold. So, the existence of more than one structural order parameters does not imply necessarily that the Prigogine-Defay ratio will be larger than one. Even more, DiMarzio stated later [48] that even in the case of several structural order

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parameters, the Prigogine-Defay ratio has to be equal to one provided the Simon model is employed in the description of the glass transition. This conclusion was, however, later refuted by Goldstein [49] and Gupta & Moynihan [50] (c.f. also [51]).

We will show furtheron that an alternative resolution of the deviations between theoretical predictions and experimental data on the Prigogine-Defay ratio is possible. This resolution works already in the case when only one structural order parameter is employed but not Simon's but a more realistic model of the glass transition is utilized.

Do There Exist Ehrenfest-type Relations in the Description of the Glass Transition: Formulation of the Problem

The classical thermodynamic derivation of the Ehrenfest ratio was here sketched earlier. Since for 2^{nd} order equilibrium phase transitions pressure and temperature of the transition point are connected via the Ehrenfest relations Eqs. (24.17)

$$\frac{dp}{dT} = \frac{1}{VT} \left(\frac{C_p^{(1)} - C_p^{(2)}}{\alpha^{(1)} - \alpha^{(2)}} \right) , \qquad \frac{dp}{dT} = \frac{\alpha^{(1)} - \alpha^{(2)}}{\kappa^{(1)} - \kappa^{(2)}} , \qquad (24.105)$$

the Ehrenfest ratio Eq. (24.18) follows immediately by setting equal both right hand sides of above relations. As a consequence, only two of the three equations, Eqs. (24.17) and (24.18), are independent.

One can pose now the question, whether, in treating the glass transition, the Prigogine-Defay ratio Eq. (24.99) can be supplemented by relations of the form of Eq. (24.105) or not. Extending their analysis performed in [27] Davies and Jones in [52] really derived such kind of relations. They, again, based their derivation on Simon's model assuming that at glass transition the relations $\Delta V = 0$ and $\Delta S = 0$ hold similar to 2nd order equilibrium phase transitions (c.f. Eqs. (24.12)). In such approach, they arrived for the case of one order parameter at

$$\frac{dT_g}{dp} = \frac{\Delta\beta}{\Delta\alpha} \,, \tag{24.106}$$

$$\frac{\Delta\beta}{\Delta\alpha} = TV \frac{\Delta\alpha}{\Delta C_p} \,. \tag{24.107}$$

Such relations and the corresponding value of the Prigogine-Defay ratio are widely discussed and employed later by different authors [50, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65] and sometimes modifications are introduced in order to reconcile theory and experiment.

Summarizing the experimental data by various authors [66, 67, 68, 69, 70] including own ones, Goldstein [53] outlined that generally the result

$$\frac{dT_g}{dp} = TV \frac{\Delta\alpha}{\Delta C_p} < \frac{\Delta\beta}{\Delta\alpha}$$
(24.108)

is found, i.e., not both of Eqs. (24.106) and (24.107) are fulfilled but only one. As the result of his analysis he concluded that the failure of the coupled set of Eqs. (24.106) and (24.107) is a consequence of the weakness of the free volume theory. This point of view was supported by Angell and Sichina [71] noting that Eq. (24.106) fails completely in the description of experimental data while Eq. (24.107) has been tested in a number of cases as being successful. This result is at least qualitatively confirmed by molecular dynamics computations performed by Ribeiro et al. [65]. In contrast, Nieuwenhuizen [58, 59] states that Eq. (24.106) is always satisfied and that Eq. (24.107) is principally incorrect and has to be supplemented by additional terms.⁴

However, to repeat the question formulated at the end of the previous section, is such thermodynamically based approach really correct?! As mentioned already by DiMarzio [73] in related discussions with Gupta and Moynihan: In the simplest view of order parameter theory (SOPT) it is imagined that the freezing-in occurs abruptly. Above the transition line, the order parameters ... are free to relax to whatever values which will minimize the free energy, while below the transition line they attain a time independent value ... SOPT can be viewed only as a very crude approximation to the more general time-dependent order parameter theory. In their reply, Gupta and Moynihan [74] noted: We agree with DiMarzio that this (i.e. SOPT) is only a simple view on the glass transition and that deeper understanding will result from a detailed kinetic analysis of relaxation of internal parameters. We will return to this problem shortly realizing such detailed kinetic approach.

⁴A critical analysis demonstrating the inconsistency of the thermodynamic method of Nieuwenhuizen is given in our papers [15, 112].

24.5 Generic Approach to Glass Transition

24.5.1 Structural Order-Parameter Approach: General Characterization

In the preceding sections, we discussed some spectrum of problems and results of the analysis of glass-forming melts and glasses employing Simon's model of the glass transition. This model has some important advantages in treating these phenomena, however, also some severe disadvantages. This point was already clearly expressed by Gustav



Figure 24.6: Left: Sir Francis Simon (born Franz Eugen Simon (2. July 1893 - 31. October 1956)) was a German and later British physical chemist. He received his doctoral degree from the University of Berlin, working in the research group of Walther Nernst on low-temperature physics related to the Nernst Heat Theorem (Third law of thermodynamics). Right: Gustav Heinrich Johann Apollon Tammann (28. May 1861 - 17. December 1938) was a prominent chemist-physicist of Baltic-German descent who made important contributions in the fields of glassy and solid solutions, heterogeneous equilibria, crystallization, and metallurgy [75].

Tammann (1933) in his monograph Der Glaszustand [6]. He wrote there:

- Es ist ... nicht richtig, von einem Transformationspunkt der Gläser zu sprechen, richtiger wäre es ... Transformationsintervall zu sagen ... It is incorrect to talk about a transformation point, instead one has to use transformation interval ...;
- Das innere Gleichgewicht stellt sich im Erweichungsintervall der Gläser nicht sofort ein wie in beweglichen Flüssigkeiten ... The internal equilibrium is established not immediately like in mobile liquids ...;
- Die Geschwindigkeit der Einstellung des inneren Gleichgewichtes wächst mit abnehmender Viskosität also mit wachsender Temperature ... The rate of establishment of the internal equilibrium increases with decreasing viscosity i.e. increasing temperature ...

Going over to such a more detailed description, in thermodynamics one or a set of additional structural order parameters have to be introduced. This approach is illustrated in Fig. 24.7. In this figure, the experimental results and theoretical treatment are sketched once again as shown already in Fig. 24.4 but in a somewhat different form. At least, one additional structural order-parameter (connected in our approach with volume), ξ , has to be introduced into the description like the fictive temperature as employed first by Tool [16]. In stable and metastable equilibrium, the structural order parameter is uniquely defined by pressure and temperature, $\xi = \xi_e(p, T)$. In general, however, its value is not equal to the equilibrium value ($\xi \neq \xi_e(p, T)$), it is determined by cooling and heating rates (or more generally, by the path of evolution).



Figure 24.7: Temperature dependence of the density of a borosilicate glass measured at three different cooling rates. (1): 1 K min⁻¹; (2): 2 K min⁻¹; (3): 10 K min⁻¹; (4): annealing curve. It can be seen that T_g increases with increasing cooling rates (Ritland (1954) [28]); for the details see also Figs. 2.33 in [5]).

24.5.2 De Donder's Order-Parameter Approach: Basic Equations

In De Donder's method of description of such non-equilibrium systems, the basic equation for a closed system and one structural order parameter is given by

$$dU = TdS - pdV - Ad\xi . \tag{24.109}$$

Here A is the affinity of process of structural reorganization. According to the 2^{nd} law of thermodynamics, we have

$$dS = d_e S + d_i S$$
, $d_e S = \frac{dQ}{T}$, $d_i S \ge 0$, (24.110)

and the combined first and second laws yield

$$dU = Td_eS + Td_iS - pdV - Ad\xi.$$
(24.11)

$$dU = dQ - pdV = Td_e S - pdV.$$
(24.112)

As a direct consequence, we get

$$Td_i S = Ad\xi$$
 or $d_i S = \left(\frac{A}{T}\right)d\xi$, (24.113)

$$T\frac{d_iS}{dt} = A\frac{d\xi}{dt}$$
 or $\frac{d_iS}{dt} = \left(\frac{A}{T}\right)\frac{d\xi}{dt}$ (24.114)

giving a relation between entropy production, affinity and change of the order parameter. In equilibrium, the affinity is equal to zero.

In experimental investigations of glasses and glass-forming melts, the systems are considered at given values of pressure and temperature. In such case, the thermodynamic description has to be performed via the Gibbs free energy, G. Employing the definition of G

$$G = U - TS + pV, \qquad dG = -SdT + Vdp - Ad\xi, \qquad (24.115)$$

we get

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \,. \tag{24.116}$$

The equilibrium condition

$$A|_{\xi=\xi_e} = -\left(\frac{\partial G}{\partial \xi}\right)\Big|_{p,T,\xi=\xi_e} = 0 \qquad \Longrightarrow \qquad \xi_e = \xi_e(p,T) \tag{24.117}$$

allows one then to establish the dependence of the structural order parameter on pressure and temperature. In order to express the affinity, we employed the following relations

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \cong G_e^{(2)}(\xi - \xi_e) , \qquad G_e^{(2)}(p,T,\xi_e) = \left(\frac{\partial^2 G}{\partial \xi^2}\right)\Big|_{p,T,\xi=\xi_e} > 0 , \qquad (24.118)$$

arriving at relatively simple expression for the affinity and the entropy production.

$$A = -G_e^{(2)}(\xi - \xi_e) \qquad \Longleftrightarrow \qquad d_i S = \left(\frac{A}{T}\right) d\xi . \tag{24.119}$$

24.5.3 Relaxation of Glass-Forming Melts: General Considerations

The relaxation of the structural order parameter we assume in general to be described by

$$\frac{d\xi}{dt} = -\frac{1}{\tau(p,T,\xi)} (\xi - \xi_e) , \qquad (24.120)$$

$$\tau \simeq \tau_e = \tau_0 \exp\left(\frac{U_a(p,T)}{RT}\right) , \qquad \tau_0 = \frac{k_B T}{h} , \qquad U_a(p,T) = U_a^* \left(\frac{T}{T - T_0}\right) . \tag{24.121}$$

Here the relaxation time depends not only on pressure and temperature but, in general, also on the structural order parameter (see [2, 5, 16] and Fig. 24.8). In the computations, performed here, the dependence on the structural order parameter will be neglected not changing the basic results (computations performed for the more general case are given in [7]; a consideration of the possible spectrum of relaxation laws which can be obtained in the general case if the relaxation time is considered as dependent in the structural order parameter is given in Chapter 3 of the present book in the Appendix).

24.5.4 Generalized Equation of State: Results of a Lattice-Hole Model

In order to theoretically analyze the behavior of glass-forming melts, as one requirement, the essential thermodynamic properties of the respective systems have to be introduced based on some model considerations i.e., we have to connect the conventional thermodynamic parameters of the glass-forming system with the structural order parameter or the appropriate set of structural order parameters. The respective relationship we denote as generalized equation of state.

For the specification of the thermodynamic properties of glass-forming melts, we employ here relations derived from a simple lattice-hole model of liquids discussed in detail in [2, 7, 13, 15] (a similar model has been employed recently by Johari in the analysis of the intensively discussed problem of configurational and residual entropies of defect crystals and the entropy's behavior on glass formation [77] and also by Goldstein [78]). The structural order parameter is connected in the framework of this model with the free volume of the liquid and defined via the number of unoccupied lattice sites (or holes), N_0 , per mole of the liquid each of them having a volume, $v_0(p, T)$, identical to the volume occupied by a structural unit of the liquid at the same values of pressure and temperature. According to this model, the molar volume of the liquid is determined as [2, 5, 7, 13, 15]

$$V(p,T,\xi) \cong N_A v_0(p,T) (1+\xi) , \qquad \xi = \frac{N_0}{N_A + N_0} \cong \frac{N_0}{N_A} .$$
 (24.122)

Here N_A is the Avogadro number. In the framework of this model, the fully ordered or crystalline state corresponds to a value of the structural order parameter equal to $\xi = 0$ [2].

The thermodynamic functions of the system are described in the framework of this model by the sum of contributions resulting from the thermal motion of the molecules of the liquid and, in addition, from the configurational contributions described by the structural order parameter, ξ . The configurational contribution to the molar volume (or the excess molar volume) is given, consequently, by

$$V_{conf} \cong N_A v_0(p, T) \xi . \tag{24.123}$$

The configurational contribution to the enthalpy, H_{conf} , of one mole of the liquid is described in the framework of this lattice-hole model via the molar heat of evaporation, $\Delta H_{ev}(T_m)$, of the liquid at the melting temperature as

$$H_{conf} = \chi_1 \Delta H_{ev}(T_m) \xi \,. \qquad \Delta H_{ev}(T_m) \cong \chi_2 R T_m \quad \text{with} \quad \chi_2 = 20 \,. \tag{24.124}$$



Figure 24.8: Top: Relaxation of the coefficient of refraction n of an optical borosilicate glass according to the measurements of Winter-Klein (1943) [39] for two different values of temperature as indicated in the figure. Note that in this figure the approach to equilibrium from a higher value of the fictive temperature is given by the lower curves, while the upper curves correspond to initially lower values of the fictive temperature. Bottom: Viscosity versus time curves for two samples of a silicate glass with the same composition but different thermal histories heat-treated at 486°C (after Lillie [76]). Curve (1): Glass sample equilibrated at a lower temperature (478°C). Curve (2): Glass sample transferred from temperatures considerably above 486°C to room temperatures and brought to 486°C afterwards. Note that in both cases from different sides the same equilibrium value of the viscosity is approached corresponding to the equilibrium value of the structural order parameter.

The configurational part of the entropy per mole is described in this model via the conventional mixing term

$$S_{conf} = -R\left(\ln(1-\xi) + \frac{\xi}{1-\xi}\ln\xi\right) .$$
(24.125)

With H = U + pV, we obtain for the configurational contribution to the internal energy the relation

$$U_{conf} = [\chi_1 \Delta H_{ev}(T_m) - pv_0(p, T)] \xi .$$
(24.126)

Finally, employing the definition of Gibbs' free energy, G = U - TS + pV, we arrive at

$$G_{conf} = \chi_1 \Delta H_{ev}(T_m)\xi + RT\left(\ln(1-\xi) + \frac{\xi}{1-\xi}\ln\xi\right) .$$
(24.127)

The equilibrium value of the structural order parameter, $\xi = \xi_e$, is determined via the relation

$$(\partial G_{conf}/\partial \xi)_{p,T} = 0.$$
(24.128)

With Eqs. (24.124) and (24.127), we obtain the following result

$$\frac{(1-\xi_e)^2}{\ln\xi_e} = -\frac{1}{\chi} \left(\frac{T}{T_m}\right) \qquad \text{where} \qquad \chi = \chi_1 \chi_2 \ . \tag{24.129}$$

Knowing the value of χ_2 (c.f. Eq. (24.124)), we determine the value of the parameter χ_1 demanding that at $T = T_m$ the value of ξ_e should be approximately equal to 0.05 (corresponding to experimentally observed density differences between liquid and crystal at the melting temperature, T_m [2]). In the computations performed here we set $\chi_2 = 20$ and $\chi_1 = 0.166$ resulting in $\chi = 3.32$.

As it should be the case, in the vicinity of the state of configurational equilibrium, we obtain from Eq. (24.127) after performing a truncated Taylor expansion the result

$$G_{conf}(p,T,\xi) \cong G_{conf}(p,T,\xi_e) + \frac{1}{2} \left(\frac{\partial^2 G_{conf}}{\partial \xi^2} \right) \Big|_{p,T,\xi=\xi_e} (\xi - \xi_e)^2 .$$
(24.130)

The value of $G_e^{(2)} = (\partial^2 G_{conf}/\partial\xi^2)|_{\xi=\xi_e} > 0$ at equilibrium can now be easily calculated based on Eqs. (24.127) and (24.129). For physically reasonable small values of ξ , we get as an estimate [15]

$$G_e^{(2)} \cong \frac{RT}{\xi_e}$$
 (24.131)

24.5.5 Analysis of Equilibrium Properties of the Model System

Knowing the dependence of the structural order parameter and, in particular, its equilibrium value (c.f. Eq. (24.129)) on temperature, one can establish the deviations of all thermodynamic functions discussed above from the respective equilibrium values provided the temperature dependence of the structural order parameter, $\xi = \xi(T)$, is known. For this reason, the determination of the function $\xi = \xi(T)$ is of basic importance for the understanding of the behavior of the thermodynamic properties of vitrifying melts. This task will be performed in Section 24.6. However, first we will analyze some essential equilibrium properties of the model under consideration.

A linear extrapolation of the temperature dependence of the structural order parameter - as indicated by a dashed curve in the left hand side of Fig. 24.9 - to temperatures below the vitrification range would lead to an intersection with the abscissa at some finite temperature. In contrast, the correct (for the considered model) dependence $\xi_e = \xi_e(T)$, given by Eq. (24.129), does not cross the abscissa but approaches it from above in the limit $T \rightarrow 0$. Quite interestingly, the type of temperature dependence of the structural order parameter can be divided into two regions, a high-temperature one, where the structural order parameter changes significantly with the change of temperature and a low-temperature region, where the respective changes are of minor relevance. The behavior of the structural order parameter is reflected also in a similar kind of behavior of the configurational entropy (c.f. Fig. 24.10). In this way, employing not a linear extrapolation but the correct (for the considered model) result, Kauzmann type paradoxes [79] do not occur here et all.

Moreover, we find here a deep analogy in the consequences of above given analysis to the statistical model considerations performed by Gibbs and Di Marzio [80, 81]. The mentioned authors showed based on a statistical analysis of a different model system that the entropy of the liquid approaches the entropy curve of the crystal at some temperature, T_2 . At lower temperatures both quantities coincide more or less. It was supposed first by Gibbs and Di Marzio that there is some sharp change of the behavior at T_2 , this requirement has been later formulated less strictly [82]. As evident from Figs. 24.9 and 24.10, the analog of this particular temperature T_2 is equal in our model to $T_2 \approx 0.4T_m$. Both models show that there exist very specific equilibrium states at low temperatures where changes of temperature (and pressure) lead only to negligible changes of the value of the order parameter so that its effect on the state of the liquid can be widely ignored (c.f. also Mazurin [17]).


Figure 24.9: Left: Typical behavior of the structural order parameter, ξ , in dependence on temperature in the vicinity of the conventionally defined glass transition range. By full curves, the dependencies $\xi(T)$ are shown if the system is cooled down and heated with the same constant absolute value of the heating rate (see further discussion), the dashed curve shows here the equilibrium value of this parameter in the given range of temperature. Right: Dependence of the equilibrium value of the structural order parameter for the whole range of temperature between melting temperature and absolute zero as obtained in the framework of the lattice model employed here.

24.6 Dependence of Properties of Glass-Forming Melts and Glasses on Cooling and Heating Rates: Method of Analysis

24.6.1 Method of Description of the Kinetics of Isothermal Relaxation

A large amount of experimental data shows that the relaxation kinetics of glass-forming melts to the respective stable or meta-stable equilibrium states can be generally expressed in the form [2, 5, 7, 15]

$$\frac{d\xi}{dt} = -\frac{1}{\tau} (\xi - \xi_e) , \qquad (24.132)$$

where the relaxation time τ is a function of pressure, temperature and, in general, of the structural order parameter or the set of structural order parameters. Neglecting here such a dependence of τ on the structural order parameter (i.e., identifying τ with its value for the stable or metastable equilibrium liquid, $\tau \rightarrow \tau_e$), this parameter can be expressed in the form [2, 17]

$$\tau_e = \tau_0 \exp\left(\frac{U_a(p,T)}{RT}\right) , \qquad \tau_0 = \frac{h}{k_B T} , \qquad (24.133)$$

where the activation energy, U_a , of the relaxation processes obeys the inequality [2]

$$\frac{dU_a(p,T)}{dT} \le 0.$$
(24.134)

As a typical example, we will employ here the Vogel-Fulcher-Tammann equation for the description of isothermal relaxation [2, 5, 17], where the activation energy can be written as

$$U_{a}(p,T) = U_{a}^{*} \left(\frac{T}{T - T_{0}}\right) .$$
(24.135)

Here U_a^* and T_0 are empirical constants specific for the substance considered. The parameter T_0 we set equal in the following model computations to $T_0 = T_m/2$, where T_m is the melting or liquidus temperature of the liquid. At the glass transition temperature, T_g (obtained at conventional moderate cooling rates and referring to a viscosity of the order of 10^{13} Poise [2, 17]), the activation energy, U_a , is of the order $(U_a(T_g)/RT_g) \cong 30$. With $(T_g/T_m) \cong 2/3$, we obtain as an estimate $(U_a^*/RT_g) = 7.5$. The pre-exponential term, τ_0 , in Eq. (24.133) is determined basically by



Figure 24.10: Configurational contributions to the entropy of the meta-stable equilibrium glass-forming melt resulting from a combination of Eqs. (24.125) (left figure) and (24.129) (right figure).

the frequency of molecular oscillations. It is practically not affected by deviations of the system from the respective equilibrium state. For an estimate of its value, we employ here the relation $\tau_0 = (h/k_B T)$, where h is Planck's constant.

In order to account for the effect of deviations of the system from equilibrium on its relaxation behavior, the activation energy, U_a , has to be considered, in general, as a function not only of pressure and temperature, but also of the structural order-parameter, ξ [2, 5, 83, 84]. Such effects we do not take into account here since they will lead only to quantitative modifications and not affect the main qualitative results.

24.6.2 Description of the Cyclic Processes under Consideration

In the further analysis, we consider mainly cyclic processes of the following type: At constant pressure, we cool the system with a constant rate,

$$q = \frac{dT}{dt} = \text{constant} . \tag{24.136}$$

Since, according to Eq. (24.136), dT and dt are linearly dependent, we can always go over - as performed first by Bragg and Williams [85] - from a differentiation or integration with respect to time to the respective procedures with respect to temperature (dT = qdt) and vice versa (dt = dT/q) with different signs of the parameter q (q < 0 for cooling and q > 0 for heating processes) [85]. Eq. (24.132) then takes the form [3, 4, 85]

$$\frac{d\xi}{dT} = -\frac{1}{q\tau}(\xi - \xi_e) . \tag{24.137}$$

We denote Eq. (24.137) as the Bragg-Williams equation (c.f. [3, 4, 5, 7]). Note that the transition from Eq. (24.132) to Eq. (24.137) retains its validity if cooling and heating rates depend on time (or temperature).

The cyclic process we start at some well-defined stable or metastable equilibrium state. In the cooling process, the internal structural order-parameter, ξ , cannot follow, in general, the change of temperature of the system. It cannot be represented, consequently, as a function only of pressure and temperature, but depends also on the rate of change, q, of temperature (reflecting the prehistory), i.e.,

$$\xi = \xi(p, T; q) . \tag{24.138}$$

From a mathematical point of view, Eq. (24.138) is a direct consequence of the differential equation, Eq. (24.137). Since the derivative $(d\xi/dT)$ depends on the heating and cooling rates, q, the solution has to depend on these parameters as well.

Reaching temperatures sufficiently below the temperature of vitrification, T_g , the relaxation time becomes extremely large (c.f. Eqs. (24.133) and (24.135)), and the value of ξ becomes frozen-in, i.e. it practically does not change any more in the time scales of the experiment. At and below this temperature, the glass behaves as a solid body. Reversing now the process (again the pressure being fixed) and heating-up the system with the same heating rate (with respect to its absolute value), we arrive after some time at the initial state, again. We assume in this way that the initial state is sufficiently near to or even higher then the melting temperature so that the characteristic times of relaxation become small as compared with the characteristic times of heating of the sample. In the course of the heating process, the structural order-parameter is an unambiguous function of the heating rate, again, similar to the case of cooling. Note, however, that the function will be different for heating and cooling. Mathematically, this difference is expressed in Eq. (24.138) by the differences in the sign of the rate of change of temperature, being negative for cooling (q < 0) and positive for heating (q > 0) processes.

24.7 Dependence of Properties of Glass-Forming Melts and Glasses on Cooling and Heating Rates: Results of Analysis

24.7.1 Structural Order Parameter

In order to determine the values of the configurational contributions to the thermodynamic quantities of the glassforming melt, respectively, the glass, the temperature dependence of the structural order parameter has to be determined. For one moderate value of the rate of change of temperature, this dependence is shown already in Fig. 24.9 (left part).

In Figs. 24.11a, the $\xi = \xi(T)$ -curves are shown in a wider range of rates of change of temperature. The temperature is given here as $\theta = T/T_m$ and the rate of change of temperature as

$$q_{\theta} = \frac{d}{dt} \left(\frac{T}{T_m} \right) = \frac{d\theta}{dt} , \qquad \theta = \frac{T}{T_m} .$$
(24.139)

As seen from the figure, with a decrease of the rate of change of temperature the cooling-heating hysteresis loops become less expressed and the process of glass transition approaches more and more the simplified model as suggested by Simon, i.e., the system goes over to the glass suddenly at a certain temperature, T_g . Two questions arise in this respect: (i.) Will such kind of behavior continue also down to even lower values of cooling-heating rates which can be analyzed within reasonable computer times? (ii.) What will be the behavior if we similarly further increase cooling and heating rates? Or to be more precise, provided we can reach such cooling rates that the characteristic times of relaxation and cooling are comparable already at or even above the melting temperature T_m , will there occur certain peculiarities or not?

The answers to these questions are illustrated in Fig. 24.11b. Here the results are shown for the $\xi(T)$ -dependencies for the cooling and heating rates in the range of q_{θ} -values (in units of s⁻¹) given by $10^{-7} \le q_{\theta} \le 10^8$ and for reduced temperatures in the range $0.5 \le \theta \le 1.3$. It is obvious that the already mentioned tendency - approach of a behavior as reflected by the Simon model - is retained also for the much larger range of cooling & heating rates in the limit of cooling and heating rates tending to zero. And, in the alternative limiting case of very high cooling and heating rates, the curves show no peculiarity when the glass transition temperature approaches the melting temperature, T_m , or even becomes larger than T_m . So, provided such very high rates of change of temperature could be reached, the transition to a glass proceeds in a qualitatively similar way independent on whether we go over to a glass from a metastable or a stable equilibrium state of the liquid.

As a quantitative measure of the degree at which hysteresis effects occur, the area enclosed by the $\xi(T)$ cooling & heating curves can be taken. The results are shown in Fig. 24.12.

24.7.2 Entropy Production and Entropy

Once the dependence of the structural order parameter on time and/or temperature is established, one can immediately compute the structural contributions to the thermodynamic and kinetic parameters of the system, provided the general dependence of these properties on the structural order parameter is known. We will start the respective computations with the determination of the entropy production following the respective advice of Prigogine & Defay ([12], page xviii): *The fundamental problem of the thermodynamics of irreversible processes is the explicit evaluation of the entropy production*.



Figure 24.11: Dependence of the curves $\xi = \xi(\theta)$ (with $\theta = (T/T_m)$) on cooling & heating rates defined by Eq. (24.139) a) in the range $10^{-3}s^{-1} \le q_{\theta} = (d\theta/dt) \le 10^2s^{-1}$ (more or less easily accessible experimentally); b) in the whole range of q_{θ} -values ($10^{-7}s^{-1} \le q_{\theta} \le 10^8s^{-1}$) exceeding partly the ranges of cooling & heating rates accessible, at least, at present (q_{θ} is given here in s^{-1} , see also text).

The hysteresis effects, shown in Figs. 24.11a and b, are deeply connected with entropy production in cooling and heating due to irreversible relaxation processes of the structural order parameter to the respective equilibrium value. This interrelation is illustrated in Fig. 24.13. Here the entropy production terms are shown, again, in dependence on the rate of cooling and heating processes. The curves are computed via Eq. (24.140) [7]

$$\frac{d_i S}{d\theta} = \frac{G_e^{(2)}}{T_m \theta q_\theta \tau} (\xi - \xi_e)^2 .$$
(24.140)



Figure 24.12: Area of the hysteresis loop of the $\xi(T)$ -curves in dependence on the rate of change of temperature: a) Definition of this parameter; b) Area enclosed by the $\xi(T)$ -curves in dependence on cooling-heating rates.

Again, similar to the $\xi(T)$ -curves, with increasing rates of change of temperature the effect of entropy production becomes more expressed reconfirming the theoretical prediction given by us in [7].

From a general point of view, this effect can be interpreted as follows: With an increase of the rate of change of external parameters, the deviations from equilibrium, as a rule, become larger. As a result, the rate of entropy production becomes higher. A more specific theoretical interpretation of the numerical results presented in Fig. 24.13 in the process under consideration can be given in the following way: According to the theoretical concepts employed in the present chapter (c.f. also [2, 5, 7, 13, 15]), the glass transition temperature T_g is defined by the relation, Eq. (24.1), or, equivalently (taking into account that θ varies only slightly), by (c.f. Eq. (24.139))

$$|q_{\theta}| \tau(T_g) \cong \text{constant}$$
 (24.141)

In verbal form, the vitrification temperature is reached, when the characteristic relaxation times are comparable in magnitude with the characteristic times of change of temperature. It follows as one consequence that - describing



Figure 24.13: Entropy production (Eq. (24.140)) in vitrification and devitrification in a cyclic cooling-heating run experiment. Top: The entropy production has one maximum for cooling (full curve) and two maxima in heating processes (dashed curve). Bottom: Similar curves for different cooling and heating rates: The cooling & heating rates are changed in the range $10^{-7} \le q_{\theta} \le 10^7$ (q_{θ} is given here in s⁻¹, see also text). With an increase of the rate of change of temperature, the effect of entropy production increases.

the viscosity via the VFT-equation - the glass transition temperature has to be always located above the Kauzmann temperature T_0 , since the assumption $T_g = T_0$ would lead to a zero cooling rate required in order to reach such state, i.e., to a process which cannot be realized.



Figure 24.14: Total entropy, $\Delta_i S$, produced in the system in the cyclic cooling-heating process. In the cooling run, the entropy production becomes effective in the vitrification range, it drops then to zero due to the large relaxation times. In the subsequent heating, again, entropy is produced in the same temperature range as in the cooling process. Note that the entropy produced in cooling is larger than the entropy generated in heating. This result is due to the difference in the values of $(\xi - \xi_e)$ in the glass transition interval for cooling and heating, respectively.

With Eqs. (24.131) and (24.140) (as shown in detail in [7]), the entropy production due to relaxation can be written in the form

$$\frac{d_i S}{d\theta} \cong \frac{R}{q_{\theta} \tau} \frac{(\xi - \xi_e)^2}{\xi_e} . \tag{24.142}$$

It follows that, in the vicinity of the glass transition temperature, T_g , independent of the substance considered and the rate of change of temperature (or, more generally, the external control parameter), the relation $|q_\theta|\tau \cong$ constant holds (c.f. Eq. (24.141), again). Consequently, the magnitude of the entropy production is determined in the glass transition interval, in general, basically by the ratio $(\xi - \xi_e)^2/\xi_e$.

On the other hand, Eq. (24.137) may be rewritten also in the form

$$\frac{d\xi}{d\theta} = -\frac{1}{q_{\theta}\tau}(\xi - \xi_e) . \tag{24.143}$$

Supplemented by the definition of the glass temperature, Eqs. (24.1) and (24.141), this relation shows that the rate of approach of the structural order-parameter temperature, ξ , to its equilibrium value, ξ_e , is, near to the glass transition temperature, independent of the cooling rate and determined exclusively by the difference $(\xi - \xi_e)$. For this reason, with increasing cooling rates higher values of the difference $(\xi - \xi_e)$ are expected to be found, in general, near T_g : the rate of approach of ξ to ξ_e is proportional to $(\xi - \xi_e)$ near T_g but the rate of change of ξ_e increases with increasing cooling rates (similar considerations can be made also with respect to the heating runs). As the result, an increased entropy production has to be expected, in general, with increasing rates of change of the control parameters. Vice versa, with a decrease of the cooling rate the entropy production term should loose its importance.

In Fig. 24.14, the total entropy produced in a cooling & heating cycle is shown for an intermediate cooling rate (c.f. [7]). Having at one's disposal the dependencies of the structural order parameter on temperature for different cooling and heating rates, one can immediately reproduce the respective dependencies for the configurational entropy, S_{conf}/R , employing Eq. (24.125). They coincide in its qualitative shape with the curves of the temperature dependence of the structural order parameter (c.f. [5, 7]) and by this reason are not given here separately. For any given value of cooling and heating rate, a definite non-zero value of the configurational entropy is frozen-in, the respective value increases



Figure 24.15: Dependence of the frozen-in values of the configurational entropy, S_{conf} , of the given model system on cooling rates.

with increasing absolute value of the cooling rate. The dependence of this frozen-in value of entropy on cooling rates is shown in Fig. 24.15.

A comparison of the total entropy production, being in the order of magnitude equal to

$$\frac{\Delta_i S}{R} \cong 10^{-4} - 10^{-5} , \qquad (24.144)$$

with the configurational contributions, being in the order of magnitude equal to

$$\frac{S_{conf}}{R} \cong 10^{-2}$$
, (24.145)

shows that entropy production terms are negligible as compared with the configurational contributions to the entropy. This fact is established also by a more detailed analysis [5, 86, 83] reconfirming previous investigations e.g. by Davies and Jones [52]. Davies and Jones noted as a result of their analysis of this problem: ... we conclude that the neglect of the irreversible production of entropy leads to no significant error in determining the residual entropy ... and, at another place, to glasses the Nernst heat theorem is not applicable. Consequently, the thermodynamic determination of the zero-point entropy of glasses - as discussed in detail in [2, 5] - leading to non-zero values at $T \rightarrow 0$ is fully correct. In general and as it follows also from the analysis of the model system employed here (c.f. Fig. (24.10)), while the metastable liquid fulfils the third law of thermodynamics in the formulation assigned commonly to Planck [5], the frozen-in glass does not obey this formulation.

At another place in their papers, Davies and Jones especially analyzed the applicability of thermodynamics to glass transition. Accounting for that the effect of entropy production is small, they concluded that thermodynamics in its classical form is applicable to glass formation. Even more, as evident from the analysis performed here and outlined in previous sections, the results for the model system as derived here are obtained by non-equilibrium thermodynamic methods fully accounting for the non-equilibrium character of the glass transition. They give as well - and in contrast to alternative statements as summarized recently in [129] - an additional proof of the validity of the "conventional point of view" that glasses have a non-zero residual entropy depending on cooling rates. A detailed discussion of a variety of additional arguments in favor of this point of view can be found in [2, 5, 86, 88, 89]. In a more general context, the validity of the "conventional point of view" on the behavior of entropy at glass transition we consider to be proven by Szilard's principle. According to Szilard's principle [90], first formulated by him in 1925, the results of existing or possible model approaches, formulated in the framework of statistical mechanics, have to correspond - and never to contradict - the basic principles of thermodynamics being a generalization of knowledge, accumulated in the whole

development of science. A more detailed analysis of this and related topics will be given in the final part of the present chapter.

24.7.3 Glass Transition Temperature and the Bartenev-Ritland Equation

The problem of the definition and experimental determination of the glass transition temperature, T_g , has been reviewed recently in detail by Mazurin [42]. Enclosed we cite - as a starting point of our analysis of the dependence of the glass transition temperature on cooling and heating rates - some of his comments in this respect.

Mazurin stated in his analysis that "the glass transition temperature is a specific temperature in the glass transition range, i.e., in the range in which a cooled meta-stable melt transforms gradually into a vitreous material, whose structure remains unchanged during further cooling (or the corresponding temperature for the reverse transition during heating of this material). In principle, the choice of a particular standard point in the glass transition range is immaterial", however, it has to be defined precisely when different measurements of this quantity are performed and compared. It is noted then further by him that "the percentage of works in which the authors determined the glass transition temperatures T_g by using either the dilatometric method or the DTA and DSC techniques is equal to 99%" (the method of determination of T_g via these methods - as described by Mazurin [42] - is illustrated in Fig. 24.16). Further he pointed out that both methods may lead, however, to significant deviations of the determined values of T_g .

Discussing in his analysis [42] the Bartenev-Ritland equation [2, 5], i.e., the dependence connecting cooling rate q and glass transformation temperature, T_g

$$\frac{1}{T_g} = A - B \log|q| \tag{24.146}$$

(where A and B are constants), and in particular the work of Moynihan et al. [40] in this respect, Mazurin concludes that the dependence $1/T_g$ vs. $\log |q|$ has to be represented by a straight line. "It is especially important", he continues "that, within the limits of experimental error, the slope of this straight line coincides with the slope of the temperature dependence of the viscosity in the 1/T vs. $\log \eta$ coordinates, where η is the viscosity of the glass under investigation and the temperature T is expressed in degrees Kelvin".

However, for example, experimental analyzes on 8 different organic and inorganic glass-forming systems have shown [91] that at part considerable deviations from such simple linear dependence are found (c.f., for example, Fig. 24.17). Thus, the problem arises how these deviations can be reconciled with the summarizing statement on a very large number of systems as made by Mazurin.

Finally, he notes "the glass transition temperature T_g is often taken to be equal to the temperature corresponding to a specific viscosity (as a rule, it is 10^{13} Poise)". Continuing his argumentation, Mazurin outlines further that, once the glass-transition temperature is a function of cooling rate, also the viscosity at T_g has to depend on cooling rate. Experimental examples in this respect are given then by him and it is stated that "the widespread opinion that the glass transition temperatures for glasses of any compositions are close to temperatures corresponding to a viscosities of 10^{13} Poise does not hold true. However, the glass transition temperatures determined under conditions similar to the standard conditions for the majority of the glasses studied up to now correspond to temperatures at which the viscosities vary in the range from 10^{12} to 10^{14} Poise". Departing from these statements, the second topic of our analysis in this section is, whether the Bartenev-Ritland equation holds true also for a wider range of cooling rates for the model system considered and under which conditions deviations from such dependence can be expected. Further, we would like to check in which interval the value of the viscosity at T_g may vary and how the dependence η vs. $\log |q|$ will look like for the considered system.

Mazurin concludes the analysis of this problem with the following statement: "*Here, it should be noted that these deviations for all the glasses studied up to now even at very high cooling rates begin at temperatures lying below the liquidus temperature*". So the final problem we would like to address in this section is whether it is possible, at least, in principle, to go over to a vitreous state starting from thermodynamically stable states of the liquid. That such possibility may indeed exist is highly probable taking into account that there are several glass-forming substances, which for steric reasons cannot crystallize at all and therefore have also no melting temperature.

In the present analysis, we will employ the following definition of the glass transition temperature, T_g : In Fig. 24.9, the structural order parameter is shown in dependence on temperature for cooling and heating. By a dashed curve, the meta-stable equilibrium state is reflected. Provided, we employ Simon's model, then we may ask at which temperature the glass-forming melt has to become suddenly a glass to reach at low temperatures the same state as approached



Figure 24.16: Most common methods of experimental determination of T_g as described by Mazurin [42]: Top: Temperature dependencies of the change in the length of the sample measured by a dilatometer under a very low measuring pressure in the glass transition range during (1) uniform cooling and (2) heating at the same rate. Straight lines (3) reflect linear extrapolations of the respective curves. Bottom: Illustration of the determination of the glass transition temperature dependence of the thermal expansion coefficient. Here (1) refers to cooling, (2) to heating while (3a) and (3b) reflect linear extrapolations of the respective curves, again. The temperature dependence of the heat capacity has a similar shape.

via the real process shown in the figure by full curves. The respective temperature we will denote here as T_g . Its definition is illustrated in Fig. 24.18, it is similar to the definition as employed in experimental investigations illustrated in Fig. 24.16a. This definition is deeply connected with the concept of fictive temperature and the traditional method of its determination. It leads also to values of T_g which are near to the one's resulting from an alternative definition



Figure 24.17: Activation diagram for an amorphous polymer (PEK) from TMDSC (solid symbols; left axis) and conventional DSC (open symbols; right axis) measurements. The right axis corresponds to the upper curve. These points were shifted downwards in the case of PEK for log (Y) = 1.1 to bring both data-sets in accordance as indicated in the figure. The triangles are from Perkin Elmer DSC 7 and the squares from Setaram DSC 121 (the figure is taken from [91]).

of this quantity as proposed by Gutzow et al. [3, 5, 92] and illustrated in Fig. 24.19. Indeed, knowing the temperature dependence of the structural order parameter ξ , the derivatives of $\xi(T)$ with respect to temperature may be computed. The results are shown in Fig. 24.19. In the framework of the lattice-hole model discussed briefly earlier and employed here for the analysis, a definition of the glass transition temperature can be given identifying it with the inflexion point of the configurational specific heat or equivalently of the $(d\xi(T)/dT)$ -curve. As a consequence, the glass transition temperature T_g may be defined in terms of the structural order parameter via

$$\frac{d^{3}\xi(T)}{dT^{3}}\Big|_{T=T_{q}} \cong 0.$$
(24.147)

This definition identifies T_g with the inflexion point of the temperature dependence of the configurational contributions to the specific heat (for an overview on different attempts of determination of T_g , see [2, 17, 42]).

Employing above formulated definition of T_g , in Fig. 24.20 (for convenience, in this figure by q_θ the absolute value of the cooling rate is denoted) a check of the validity of the Bartenev-Ritland equation is performed. While in the upper figure, for a smaller range of cooling rates, the dependence could be eventually interpreted via a straight line (in agreement with Mazurin's statement), for a wider range of rates of change of temperature significant deviations occur and the results cannot be represented any more by the Bartenev-Ritland equation. As shown in the lower figure, however, the results even in such interval of cooling rates are nicely described by a similar relation, Eq. (24.150), which will be derived here shortly. In this way, the confirmation of the Bartenev-Ritland equation in a large number of experimental measurements can be interpreted, at least, partly as the result of a limited range of cooling and heating rates employed for the analysis. For larger ranges of cooling and heating rates, deviations from such linearity are to be expected. This expectation can be founded as follows.

Employing Eq. (24.1) as the method of determination of T_g with the specification as discussed here above and expressing the relaxation time via

$$\tau \simeq \tau_e = \tau_0 \exp\left(\frac{U_a}{RT}\right), \qquad \tau_0 = \frac{h}{k_B T}$$
(24.148)



Figure 24.18: Illustration of the method of definition of the glass transition temperature as employed in the present analysis. The black curve corresponds here schematically to the dependence of the equilibrium value of the structural order parameter on temperature, i.e., $\xi_e = \xi_e(T)$. In cooling a liquid, the order parameter cannot follow, in general, the change of the external parameter and deviates from the equilibrium value. The possible real course in cooling is reflected via the blue curve while the heating process is reflected by the red curve. According to Simon's classical model of vitrification, the order parameter is identical to ξ_e down to $T = T_g$ and at this temperature, the structure becomes suddenly frozen in (horizontal red curve). Computing the values of the glass transition temperature, we define it in the way as illustrated in this figure.



Figure 24.19: Dependence of the derivatives of the structural order parameter ξ with respect to temperature, T, for the cooling (left) and heating (right) runs. The glass temperature, T_g , can be defined in such a way that at $T \cong T_g$, the third order derivative of $\xi(T)$ is nullified (c.f. [3, 5, 92]).

with a constant value of the activation energy U_a , then an expression of the form of Eq. (24.146) is obtained immedi-



Figure 24.20: Check of the validity of the Bartenev-Ritland equation: While in the upper figure, Fig. 24.20a, for a smaller range of cooling and heating rates, the dependence could be eventually interpreted via a straight line, for wider ranges of rates of change of temperature significant deviations occur (Fig. 24.20b). As shown in the lower figure (Fig. 24.20c), however, the results even in such huge interval of cooling rates are nicely described by a straightforward modification of the Bartenev-Ritland equation, Eq. (24.150), being a direct consequence of the definition of the glass transition range, Eq. (24.1), if the temperature dependence of the relaxation time is described by the Vogel-Fulcher-Tammann–equation (see text).

ately, where A and B are parameters depending weakly on temperature, only. This is the Bartenev-Ritland equation [28, 29]. It is thus a direct consequence of the basic definition of the glass transition range, Eq. (24.1), provided the relaxation behavior can be expressed in the simple form as given with Eq. (24.148) involving the additional approximation of constant activation energy of relaxation processes.

Utilizing the more correct VFT-equation [2, 5, 17] for the description of the relaxation behavior

$$\tau \cong \tau_e = \tau_0 \exp\left(\frac{U_a^*}{R(T - T_0)}\right) , \qquad \tau_0 = \frac{h}{k_B T}$$
(24.149)

with a constant value of the activation energy U_a^* , then an expression of the form

$$\frac{1}{(T_g - T_0)} \cong A_1 - B_1 \log|q|$$
(24.150)

is found instead giving an excellent theoretical interpretation of the results shown in in Figs. 24.20, in general, and in Fig. 24.20c, in particular. In an even more correct approach, taking into account a dependence of the relaxation time on the structural order parameter [5, 7], these dependencies will be further modified, in general.

24.7.4 Value of the Viscosity at Glass Transition

Proceeding with the analysis, we can compute now other thermodynamic parameters in dependence on cooling and heating rates. One of them, the dependence of the frozen-in value of the structural order parameter (we denote this parameter here as ξ_{Simon}) on cooling rates is shown on Fig. 24.21. Combining this result with the dependence of the glass transition temperature on cooling rate, we arrive at a curve connecting glass transition temperature and structural order parameter. It is given in the right side of Fig. 24.21. Further, identifying the viscosity at $T \cong (2/3)T_m$ with the conventionally assumed for T_g value equal to 10^{13} Poise, we can determine the viscosity at the glass transition temperature in dependence on cooling rate. The results are shown in Fig. 24.22. It is evident that - at least - in terms of the model analysis where the cooling rates may be changed in a very large interval the viscosity at T_g may considerably deviate from the standard value and by far exceed even the commonly found experimentally range as reported by Mazurin (10^{12} to 10^{14} Poise [42]).



Figure 24.21: Dependence of the frozen-in value of the structural order parameter, ξ_{Simon} , on the value of the cooling rate (a) and on the glass transition temperature, θ_q (b).

Finally, we have to mention that even such large cooling rates may be chosen that the transition to a glass proceeds not from the metastable continuation of the equation of state of the liquid but directly by freezing-in the equilibrium liquid. It is interesting to note here that the possibility of glass transition above the normal melting or freezing point was realized already very early e.g. by Jones [31] with reference to experimental work performed by Smekal [93]. However, in some contradiction to such insight the viscosity at glass transition was identified by them also [27, 31] - following Tammann [6] - to be equal to 10^{13} Poise. Jones [31] already stated as well that such melting temperature may even have no meaning since many organic substances form glasses on cooling because no crystalline structure can form on account of the length or complicated nature of the molecules.

24.7.5 Thermodynamic Coefficients and Prigogine-Defay Ratio: Analysis in Terms of the Generic Approach

Configurational Specific Heat

Going over to the analysis of methods of theoretical determination of the value of the Prigogine-Defay ratio, in a first step we will analyze the behavior of the thermodynamic coefficients in vitrification in dependence on cooling rate. As an example, we consider here the configurational specific heat.

The specific heat along the path, given by $\xi = \xi(p, T; q)$, is a function of pressure, temperature and the structural order-parameter, i.e., $C = C(p, T, \xi)$. Assuming the pressure to be kept constant, we have, by definition,

$$C_p(p,T,\xi) = \frac{dQ}{dT} . \tag{24.151}$$

From the first law of thermodynamics (dU = dQ - pdV) and the definition of the enthalpy, H = U + pV, we obtain

$$dH = dQ + Vdp \tag{24.152}$$



Figure 24.22: Dependence of the viscosity at glass transition temperature on cooling rates. Since according to Eq. (24.150), the ratio $(1/(T_g - T_0))$ is a linear function of the logarithm of the cooling rate, according to $\eta = \eta_0 \exp(U_a^*/(R(T - T_0)))$ a linear dependence of $\log \eta$ on $\log q_\theta$ has to be expected. This result is confirmed by the numerical computations.

resulting, with the condition p = constant, in

$$dH = C_p(p, T, \xi) dT . (24.153)$$

In a more extended form, Eq. (24.153) can be written as the sum of two terms (c.f. [2, 5, 7])

$$C_p(p,T,\xi) = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \frac{d\xi}{dT} \,. \tag{24.154}$$

The first term on the right hand side of above equation reflects the contribution to the specific heat due to thermal motion of the molecules (e.g. the phonon part), while the second term refers to configurational contributions.

Employing the model of glass-forming melts discussed above, the configurational contribution to the specific heat, $C_{p,conf}$, is given with Eq. (24.124) by

$$C_{p,conf} = \left(\frac{\partial H_{conf}}{\partial \xi}\right)_{p,T} \frac{d\xi}{dT} = \chi_1 \Delta H_{ev}(T_m) \frac{d\xi}{dT} .$$
(24.155)

In the model of vitrification, developed by Simon, the glass-forming system remains in a metastable state until a certain temperature, T_g , is reached in the cooling process (i.e., $\xi = \xi_e$ for $T \ge T_g$). At this temperature, the system becomes frozen-in and the structural order-parameter does not change any more in the further cooling process (i.e., $(d\xi/dT) = 0$ for $T \le T_g$ or $\theta \le \theta_g$). The configurational contribution, $C_{p,conf}$, to the specific heat resulting from processes of structural reorganization, has then, consequently, the form

$$C_{p,conf}^{(Simon)} = \begin{cases} \chi_1 \Delta H_{ev}(T_m) \left(\frac{d\xi_e}{dT}\right) & \text{for } T_g \le T \le T_m \\ 0 & \text{for } 0 \le T < T_g \end{cases}$$
(24.156)



Figure 24.23: Top: Configurational contribution, $C_{p,conf}(p, T, \xi)$, to the specific heat, $C_p = C_p(p, T, \xi)$, as obtained via Simon's model approach (black curve) and the model of a continuous transition as employed here (blue and red curves). Note that, in describing vitrification more appropriately in terms of a continuous transition, the specific heats turn out to be different for cooling and heating runs. Bottom: Configurational contributions to the specific heats are shown for different values of the cooling & heating rates.

with (c.f. Eq. (24.129))

$$\frac{d\xi_e}{dT} = \chi \left(\frac{T_m}{T^2}\right) \frac{\xi_e (1 - \xi_e)^3}{1 - \xi_e + 2\xi_e \ln \xi_e}$$
(24.157)

or

$$\frac{d\xi_e}{d\theta} = \frac{1}{\chi} \frac{\xi_e (\ln \xi_e)^2}{(1 - \xi_e + 2\xi_e \ln \xi_e)(1 - \xi_e)} .$$
(24.158)

In contrast, considering vitrification as a continuous transition from a metastable to a frozen-in state, we have generally

$$C_{p,conf} = \chi_1 \Delta H_{ev}(T_m) \frac{d\xi}{dT} \cong \chi R T_m \frac{d\xi}{dT} , \qquad T_0 \le T \le T_m .$$
(24.159)

In addition, the configurational contribution to the specific heat becomes also different in dependence on whether we consider cooling or heating processes. Results of the theoretical computations of the configurational contributions to the specific heats are shown in Fig. 24.23.

A comparison of experimental and theoretical results is given in Fig. 24.24. It is evident that the respective curves are widely, at least, qualitatively identical taking into account that in the experiments not only the configurational but the full specific heat is shown in dependence on temperature.



Figure 24.24: Left: $C_p(T)$ -curves obtained in the process of heating of a glass-forming organic polymer melt (polyvinyl acetate) for different heating rates according to the measurements of Zhurkov and Levin (1950) [9]. Curve (1) corresponds to a heating rate of 0.1 K min⁻¹, curve (2) to 0.4 K min⁻¹ and curve (3) to 1.5 K min⁻¹ (for further details see also Figs. 2.22 and 2.42 in [5]). Right: Configurational contributions to the specific heat as determined theoretically.

Similarly to the specific heat,

$$C_p(p,T,\xi) = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{p,T} \frac{d\xi}{dT} , \qquad C_{p,conf} = \left(\frac{\partial H_{\xi}}{\partial \xi}\right)_{p,T} \frac{d\xi}{dT}$$
(24.160)

one can define the configurational contributions to the thermal expansion coefficient, α

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p, \qquad \alpha_{conf} = \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{p,T} \left. \frac{d\xi}{dT} \right|_p$$
(24.161)

and the compressibility, κ

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T , \qquad \kappa_{conf} = -\frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_T \left. \frac{d\xi}{dp} \right|_T$$
(24.162)

All these configurational contributions are determined essentially by the derivatives of the structural order parameter with respect to pressure, p, and temperature, T. Consequently, in the glass transition we are encountered, again, with qualitative change of the reaction of the system but this time going over from the response characteristic for a metastable equilibrium system to the response of the respective frozen-in non-equilibrium system, the glass, i.e.,

$$\left(\frac{d\xi}{dT}\right) \neq 0 \quad \text{and} \quad \left(\frac{d\xi}{dp}\right) \neq 0 \quad \iff \quad \left(\frac{d\xi}{dT}\right) = 0 \quad \text{and} \quad \left(\frac{d\xi}{dp}\right) = 0 \ .$$
 (24.163)

These characteristic features of the glass transition determine both the similarity and the difference of the glass transition as compared to second order equilibrium phase transitions and determine the specific value of the Prigogine-Defay ratio. To the theoretical determination of this ratio we return in the next sections.

Application of De Donder's Method

One of the basic characteristics of the glass transition is the so-called Prigogine-Defay ratio, Π [2, 13]. It gives a general correlation between the jumps of compressibility, $\Delta \kappa$ (Eq. (24.69)), thermal expansion coefficient, $\Delta \alpha$ (Eq. (24.73)), and isobaric heat capacity, ΔC_p (Eq. (24.71)), near to the glass transition temperature, $T = T_q$, and is defined as

$$\frac{1}{VT} \left\{ \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \right\} \bigg|_{T=T_g} = \Pi .$$
(24.164)

Here V is the volume of the system under consideration. A similar relation is of significance in the description of second-order equilibrium phase transitions, where it is denoted as Ehrenfest's ratio, here this parameter is equal to one (see [21, 22] and the earlier performed here analysis).

Experimental analyzes show that the value of the Prigogine-Defay ratio is larger than one [2, 13]. For a long time it was assumed that from a theoretical point of view such result can be explained only if it is assumed that several order parameters determine the state of a glass. However, in a recent reconsideration of this problem Schmelzer and Gutzow [5, 13, 15] could show that one structural order parameter is sufficient for an explanation of the mentioned experimental data provided one goes in the interpretation of vitrification beyond the classical model of Simon. Indeed, as shown here earlier, the value of the Prigogine-Defay ratio can be estimated in terms of De Donder's approach (c.f. also [10, 14] and Eq. (24.78)) as

$$\Pi(T_g) = \frac{h_{p,T}}{A + h_{p,T}} \frac{\left[1 + \frac{1}{v_{p,T}} \left(\frac{\partial A}{\partial p}\right)_T\right]}{\left[1 - \frac{T}{A + h_{p,T}} \left(\frac{\partial A}{\partial T}\right)_p\right]}\right|_{T = T_g}$$
(24.165)

Employing the model of glass-forming melts, estimates can be easily made of the derivatives $(\partial A/\partial p)$ and $(\partial A/\partial T)$. As it turns out the terms with the derivatives of the affinity with respect to pressure and temperature in the square brackets in Eq. (24.165) are small in comparison with one. By this reason, we can neglect them in a good approximation reconfirming⁵ the result obtained in [13, 15], i.e.,

$$\Pi(T_g) \cong \left. \frac{h_{p,T}}{A + h_{p,T}} \right|_{T=T_g} \,. \tag{24.166}$$

Employing Simon's model for the estimation of the Prigogine-Defay ratio

.

$$\xi = \xi_e \quad \text{for} \quad T \ge T_g , \quad \xi = \xi_e(T_g) \quad \text{for} \quad T < T_g , \qquad (24.167)$$

we arrive at

$$A = -G_e^{(2)}(\xi - \xi_e) , \qquad A(T_g) = -G_e^{(2)}(T_g) \left(\xi(T_g) - \xi_e(T_g)\right) = 0 \implies \Pi = 1 .$$
 (24.168)

In addition, no hysteresis effects occur, i.e., the value of the Prigogine-Defay ratio is the same for cooling and heating. In terms of the generic model of vitrification and relaxation, we have generally

$$A = -G_e^{(2)}(\xi - \xi_e) , \qquad G_e^{(2)} > 0 , \qquad h_{p,T} > 0 , \qquad A + h_{p,T} > 0 .$$
(24.169)

For cooling, $\Pi > 1$, is obtained and for heating, $\Pi < 1$. Treating vitrification in the way presented, one structural order parameter is sufficient to explain a value of $\Pi \neq 1$! The results of the analysis are illustrated on Fig. 24.25.

Having arrived at these results, the question arises now which value has to be taken to interpret experiments? In experiment, not the current values of the ratio of the thermodynamic coefficients in cooling and/or heating are compared but the jumps in the extrapolations of the equilibrium values. Having a look at the configurational contributions to the specific heat as shown in Fig. 24.25, it is evident that from the knowledge of the cooling curves one can make estimates of the experimentally determined values of the jumps of the thermodynamic coefficients in vitrification. Indeed, it can be assumed that the cooling curve intersects the dashed Simon's model curve at nearly half of its jump at T_q ($\varphi \cong 2$).

$$\Delta C_p^{(exp)} = \varphi C_{p,conf}(T_q) \tag{24.170}$$

⁵The discussions with Drs. Jean-Luc Garden and Herve Guillou, Grenoble, France, at the 11th Lähnwitzseminar on Calorimetry in June 2010 in Rostock on this topic are appreciated stimulating us to present here a more detailed derivation of these results as compared to our first papers [13, 15] on this topic.



Figure 24.25: Treating vitrification in terms of Simon's model (curve 3), we get $\Pi = 1$. In contrast, considering cooling processes, then we arrive at $\Pi > 1$ (A < 0) while for heating, $\Pi < 1$ (A > 0) is obtained.

Assuming in agreement with experiment that similar dependencies hold also for thermal expansion coefficient and compressibility

$$\Delta \alpha^{(exp)} = \varphi \alpha_{conf}(T_g) , \qquad \Delta \kappa^{(exp)} = \varphi \kappa_{conf}(T_g)$$
(24.171)

we get the following relation for the of the Prigogine-Defay ratio, $\Pi^{(exp)}$, as it is determined experimentally.



Figure 24.26: Dependence of the Prigogine-Defay ratio of the given model system on cooling rates.

$$\Pi^{(exp)} = \frac{1}{VT} \left\{ \frac{\Delta C_p^{(exp)} \Delta \kappa^{(exp)}}{(\Delta \alpha^{(exp)})^2} \right\} \bigg|_{T=T_g} = \Pi(T_g)^{\text{cooling}} = \left. \frac{h_{p,T}}{A + h_{p,T}} \right|_{T=T_g}^{\text{Cooling}} > 1 .$$
(24.172)

As already shown in [13] employing, again, the same model, we arrive at

$$\Pi = \frac{1}{1 - \left(\frac{G_e^{(2)}}{\chi R T_m}\right) \left(\xi - \xi_e\right)\Big|_{T = T_g}} \cong \frac{1}{1 - \frac{\theta}{\chi} \left(\frac{\xi - \xi_e}{\xi_e}\right)\Big|_{T = T_g}}.$$
(24.173)

Thermodynamic properties of the system under consideration affect in this model the value of the Prigogine-Defay ratio via the parameter χ and the function $\xi_e = \xi_e(T)$ while the dynamics of the glass transition and the dependence on cooling rate is determined via the values of θ and ξ all of them taken at the appropriate for the cooling rate value of glass transition temperature. The results of computations of this dependence are shown on Fig. 24.26.

24.7.6 Thermodynamic Coefficients and Prigogine-Defay Ratio: Determination via the Analysis of the Equilibrium Properties of Glass-forming Melts

A First Alternative Approach

In the determination of the experimentally measured values of the Prigogine-Defay ratio as performed in the previous section, the additional assumption as given by Eqs. (24.170) and (24.171) was employed supplementing the general results obtained via the application of the De Donder thermodynamic method. It has been shown that the Prigogine-Defay ratios have to be larger than one (qualitatively in full agreement with experiment) but quantitatively the mentioned approximations may introduce some error. By this reason, the analysis of alternative approaches is of interest.

Eqs. (24.69), (24.71) and (24.73) supply us with the configurational contributions to the thermodynamic coefficients both for the real course of vitrification and devitrification but also for the changes of the state of the metastable equilibrium melt. In latter case, the affinity A is equal to zero and earlier employed equations (Eqs. (24.58)-(24.65)) cannot be used. However, the configurational contributions to the equilibrium thermodynamic coefficients can be determined directly knowing the configurational contributions to the enthalpy, the volume and the partial derivatives $(\partial \xi_e / \partial T)_p$ and $(\partial \xi_e / \partial p)_T$ for the respective metastable equilibrium states. Similarly to Eq. (24.74), we get

(0.77)

$$\Pi(T_g) = \frac{1}{VT} \left\{ \frac{\Delta C_p \Delta \kappa}{(\Delta \alpha)^2} \right\} \Big|_{T=T_g} = -\frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{T\left(\frac{\partial V}{\partial \xi}\right)_{p,T}} \left(\frac{\partial \xi_e}{\partial T}\right)_p} \left|_{T=T_g;\xi=\xi_e}$$
(24.174)

this time directly for the experimentally measured values of the Prigogine-Defay ratio.

In order to compute these quantities, we utilize here again a mean-field model discussed in the present chapter already earlier. According to this model, the molar volume of the liquid is determined via the relation Eq. (24.122). The configurational contribution to the molar volume (or the excess molar volume) is given, consequently, by Eq. (24.123). The configurational contribution to the enthalpy, H_{conf} , of one mole of the liquid is described in the framework of this lattice-hole model via the molar heat of evaporation, $\Delta H_{ev}(T_m)$, of the liquid at the melting temperature via Eq. (24.124). The configurational part of the entropy per mole is described in this model via the conventional mixing term Eq. (24.125), the configurational contribution to the internal energy via Eq. (24.126), the Gibbs' free energy via Eq. (24.127). The equilibrium value of the structural order parameter, $\xi = \xi_e$, is determined via the relation $(\partial G_{conf}/\partial \xi)_{p,T} = 0$. With

$$\frac{\partial G}{\partial \xi} = \chi_1 \Delta H_{ev}(T_m) + RT \frac{\ln \xi}{(1-\xi)^2}$$
(24.175)

and Eqs. (24.124) and (24.127), we obtain Eq. (24.129), again.

In the vicinity of the state of configurational equilibrium, we obtain from Eq. (24.127) after performing a truncated Taylor expansion the result

$$G_{conf}(p,T,\xi) \cong G_{conf}(p,T,\xi_e) + \frac{1}{2} \left(\frac{\partial^2 G_{conf}}{\partial \xi^2} \right) \Big|_{p,T,\xi=\xi_e} \left(\xi - \xi_e \right)^2.$$
(24.176)

The value of

$$\frac{\partial^2 G}{\partial \xi^2}\Big|_{\xi=\xi_e} = RT \frac{\partial}{\partial \xi} \left[\frac{\ln \xi}{(1-\xi)^2}\right]_{\xi=\xi_e} > 0$$
(24.177)

at equilibrium can now be easily calculated based on Eqs. (24.127) and (24.129). For physically reasonable small values of ξ , we get as an estimate [15]

$$G_e^{(2)} \cong \frac{RT}{\xi_e}$$
 (24.178)

Table 24.1:	Data employed	and results	of computat	ions via Eq.	(24.184) c	of the 1	Prigogine-	Defay r	atio for	different
systems.										

Glass	T_g, \mathbf{K}	T_m, \mathbf{K}	$\Delta H(T_m)$	ρ_{solid}	ρ_{liquid}	$\Delta \rho(T_m)$	$\rho(T_g)$	Π_{calc}	Π_{exp}
			kJ/mol	g/cm ³	g/cm ³	g/cm ³	g/cm ³		
SiO ₂		1900-2100	9.58	2.648 [94, 95]	2.2	0.448	2.2	28.16	$10^{3}-$
		1873-1998 [94]	8.51						10^{5}
		1983	7.7 [95]						
		846 [95]							
B_2O_3	550	723 [94]	24.56 [95]	2.55 [94, 95]	2.46	0.09	2.46	23.7	4.7
	525	783 [94]			[94]				
	[96]	750 [95]							
Rubber	320	371 - 448	4.761 [97]	1.43	1.2	0.23	1.2	13.4	8.3
	284								[27]
	[97]								
Glycerol	183	290 ± 4 [97]	18.28 [94, 95]	1.375	1.126	0.115	1.325	5.0	9.4
		291 [94, 95]							
Glucose	300	414 [97]	31.42	1.54 [94]	1.36	0.18	1.36	2.75	3.7
		420 [97]	34.2 [98]						[27]
		423 [97]							
		419 [94]							
Se	300	490 [95]	6.69 [94, 95]	4.81 (gray)	3.99	0.82,	4.79	11.8	2.4
		494 [94]	4.485 [99]	4.39 (alpha)	[94]	~ 0.72	[100]		[27]
				[94, 95]		[100]			
Polystyrene	350	513 [94]	11	1.05 [94]	0.9534	0.0966	0.9534	12.7	16
	368		2.14 [101]						[27]
	[94]		5.9 [102]						

With above relations, we get with Eqs. (24.123) and (24.124)

$$\left(\frac{\partial V}{\partial \xi}\right)_{p,T} = N_A v_0(p,T) , \qquad \left(\frac{\partial H}{\partial \xi}\right)_{p,T} = \chi R T_m , \qquad (24.179)$$

and, with Eq. (24.129) and assuming $\chi={\rm constant},$

$$\left(\frac{\partial\xi_e}{\partial T}\right)_p = -\frac{1}{\chi T_m} \frac{1}{\frac{\partial}{\partial\xi} \left[\frac{(1-\xi)^2}{\ln\xi}\right]_{\xi=\xi_e}}, \qquad \left(\frac{\partial\xi_e}{\partial p}\right)_T = \frac{T}{\chi T_m^2} \frac{1}{\frac{\partial}{\partial\xi} \left[\frac{(1-\xi)^2}{\ln\xi}\right]_{\xi=\xi_e}} \frac{dT_m}{dp}.$$
 (24.180)

According to Eq. (24.177), here the inequality

$$\frac{\partial}{\partial\xi} \left[\frac{(1-\xi)^2}{\ln\xi} \right]_{\xi=\xi_e} < 0 \tag{24.181}$$

has to be fulfilled.

A substitution of Eqs. (24.179) and (24.180) into Eq. (24.174) yields

$$\Pi = \frac{\chi R}{N_A v_0(p_g, T_g)} \frac{dT_m}{dp} .$$
(24.182)

Employing the Clausius-Clapeyron equation [21, 22] for the description of the change of the melting temperature with pressure

$$\frac{dT_m}{dp} = T_m \frac{\Delta V(T_m)}{\Delta H(T_m)} , \qquad (24.183)$$

where ΔV and ΔH are the change of molar volume and of molar enthalpy in the liquid-solid phase transformation, we arrive finally at

$$\Pi = \frac{\chi RT_m}{N_A v_0(p_g, T_g)} \frac{\Delta V(T_m)}{\Delta H(T_m)} .$$
(24.184)

Results of computations of the Prigogine-Defay ratio according to this equation are presented in Table 24.1. Accounting for possible errors in the determination of the respective experimental values, the theoretical results are considered as quite satirsfactory.

Possible Generalizations

In a more general approach, we omit so far the specification of H_{conf} according to Eq. (24.124). Then we arrive instead of Eq. (24.175) at the more general relation

$$\left. \frac{\partial G}{\partial \xi} \right|_{p,T} = \left. \frac{\partial H}{\partial \xi} \right|_{p,T} + RT \frac{\ln \xi}{(1-\xi)^2} \tag{24.185}$$

resulting in

$$\left. \frac{\partial H}{\partial \xi} \right|_{p,T,\xi=\xi_e} = -RT \frac{\ln \xi_e}{(1-\xi_e)^2} \ . \tag{24.186}$$

For the partial derivatives $(\partial \xi_e / \partial T)_p$ and $(\partial \xi_e / \partial p)_T$, we obtain then instead of Eqs. (24.180)

$$\left(\frac{\partial\xi_e}{\partial T}\right)_p = -\frac{1}{RT\frac{\partial}{\partial\xi}\left[\frac{\ln\xi}{(1-\xi)^2}\right]_{\xi=\xi_e}} \left\{ \left.\frac{\partial^2 H}{\partial T\partial\xi}\right|_{\xi=\xi_e} + R\frac{\ln\xi_e}{(1-\xi_e)^2} \right\} , \qquad (24.187)$$

$$\left(\frac{\partial\xi_e}{\partial p}\right)_T = -\frac{1}{RT\frac{\partial}{\partial\xi} \left[\frac{\ln\xi}{(1-\xi)^2}\right]_{\xi=\xi_e}} \frac{\partial^2 H}{\partial p\partial\xi}\Big|_{\xi=\xi_e} .$$
(24.188)

The expression for the Prigogine-Defay ratio, Eq. (24.174), reads then

$$\Pi(T_g) = -\frac{\left(\frac{\partial H}{\partial \xi}\right)_{p,T}}{T\left(\frac{\partial V}{\partial \xi}\right)_{p,T}} \left\{ \frac{\frac{\partial^2 H}{\partial p \partial \xi}\Big|_{\xi=\xi_e}}{\left.\frac{\partial^2 H}{\partial T \partial \xi}\Big|_{\xi=\xi_e} + R\frac{\ln \xi_e}{(1-\xi_e)^2}} \right\} \right|_{T=T_g,\xi=\xi_e} .$$
(24.189)

So, having at one's disposal the generalized equation of state of the systems under consideration, one can immediately determine the value of the Prigogine-Defay ratio. Since T_g depends on the cooling rate (or, more generally, on prehistory) the Prigogine-Defay ratio has to depend, in general, both on the thermodynamic properties of the systems and on the way the system is transferred to a glass.

24.7.7 Do There Exist Ehrenfest-type Relations in the Description of the Glass Transition: The Answer

Introductory Comments

Somewhat earlier, we already posed the question whether Ehrenfest-type relations,

$$\frac{dp}{dT} = \frac{1}{VT} \left(\frac{C_p^{(1)} - C_p^{(2)}}{\alpha^{(1)} - \alpha^{(2)}} \right) = \frac{1}{VT} \frac{\Delta C_p}{\Delta \alpha} , \qquad \frac{dp}{dT} = \frac{\alpha^{(1)} - \alpha^{(2)}}{\kappa^{(1)} - \kappa^{(2)}} = \frac{\Delta \alpha}{\Delta \kappa} , \qquad (24.190)$$

valid for 2^{nd} order equilibrium phase transitions, can be employed and/or derived also for the description of vitrification, i.e., relations describing the change of the glass temperature with change of pressure. Now, we are able and going over to definitely answer this question.

In accordance with the generic approach to the glass transition, treating this process adequately as a kinetic phenomenon proceeding in a given temperature interval, glass transition is a freezing-in process, when the characteristic times of change of the external control parameters become equal to the characteristic relaxation times of the glassforming melt. As it was already discussed in detail, in general, the state of the glass depends on the prehistory, i.e., on the heating-cooling rates, q(t), on the rates of change of pressure, (dp/dt), or of any other appropriate control

parameters. So, in the general case, the value of the glass transition temperature, T_g , and/or the corresponding value of the pressure, p_g , can be considered as a certain type of functional of the functions describing the change in time of the control parameters. Consequently, in treating the problem how the glass transition temperature in cooling depends eventually on pressure, we have to specify the process conditions in order to give a definite answer. However, from this summary of considerations it is evident in advance that a straightforward extension of the classical Ehrenfest relations to glass transition is obviously not correct.

The dependence of the glass transition temperature on pressure, we will discuss here for two situations: (i.) First, for the most frequently occurring or analyzed situation, when the temperature of the glass-forming melt is changed at constant pressure and (ii.) second, when the pressure is changed at constant temperature.

Pressure Dependence of the Glass Transition Temperature at Isobaric Cooling: General Results

For the present case, we have derived as a condition for glass formation the following general condition: Introducing the characteristic time of change of temperature as

$$\frac{dT}{dt} = -\frac{1}{\tau_T}T, \qquad \tau_T = \left\{\frac{1}{T} \left|\frac{dT}{dt}\right|\right\}^{-1}, \qquad (24.191)$$

we arrived at Eq. (24.56) or

$$\tau_R \cong \tau_T \implies \left\{ \frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right\} \Big|_{T=T_g} \cong C(p,T) , \quad C \cong 1$$
(24.192)

as the definition of the glass transition temperature, T_g . Here it is assumed that in the course of cooling the pressure is kept constant. The change of the glass transition temperature with a change of pressure can be determined then via the relation

$$dC(p,T) = \left(\frac{\partial C}{\partial T}\right)_{p} dT + \left(\frac{\partial C}{\partial p}\right)_{T} dp \qquad (24.193)$$
$$= \left(\frac{\partial}{\partial T} \left(\frac{1}{T} \left|\frac{dT}{dt}\right| \tau_{R}\right)\right)_{p} dT + \left(\frac{\partial}{\partial p} \left(\frac{1}{T} \left|\frac{dT}{dt}\right| \tau_{R}\right)\right)_{T} dp = 0,$$

since Eq. (24.56) (or Eq. (24.192)) has to be fulfilled for both considered values of pressure. Assuming that the cooling rate in the glass transition range has the same value in both considered cases, we arrive at

$$\left\{-\frac{1}{T^2}\left|\frac{dT}{dt}\right|\tau_R + \frac{1}{T}\left|\frac{dT}{dt}\right|\left(\frac{\partial\tau_R}{\partial T}\right)_p\right\}dT + \left\{\left(\frac{1}{T}\left|\frac{dT}{dt}\right|\right)\left(\frac{\partial\tau_R}{\partial p}\right)_T\right\}dp = 0$$
(24.194)

or

$$\frac{dT_g}{dp} = -\frac{\left(\frac{\partial \tau_R}{\partial p}\right)_T}{\left(\frac{\partial \tau_R}{\partial T}\right)_p - \frac{\tau_R}{T}}$$
(24.195)

or, in a commonly good approximation,

$$\frac{dT_g}{dp} \simeq -\frac{\left(\frac{\partial \tau_R}{\partial p}\right)_T}{\left(\frac{\partial \tau_R}{\partial T}\right)_p} \quad \text{at} \quad \left| \left(\frac{\partial \tau_R}{\partial T}\right)_p \right| \gg \frac{\tau_R}{T} .$$
(24.196)

In this way, we have obtained general relations for the dependence of the glass transition temperature on pressure at otherwise unchanged cooling conditions. In a next step, we are going to derive some more detailed consequences. For this purpose, we have to discuss the relation between pressure and temperature dependence of the relaxation time. Here we follow first an approach derived earlier for the analysis of the pressure dependence of viscosity [103].

Incorporation of the Dependence of Characteristic Relaxation Times on Pressure: Free Volume Approach

We outline here our earlier performed derivations for the description of the pressure dependence of the viscosity [103] assuming, in addition, that viscosity and relaxation time behave similarly.

We consider liquids of constant composition in (stable or metastable) thermodynamic equilibrium states. According to the Gibbs phase rule, the number of degrees of freedom of the system is equal to two, and thus one can choose temperature and pressure as the independent variables determining the properties of the system. In such cases, the viscosity, η , can be considered as a function of pressure and temperature, i.e.

$$\eta = \eta(p,T)$$
 . (24.197)

In their extended investigation of similarities and differences of liquid-vapor and liquid-solid phase transitions, Skripov and Faizullin [104, 105] analyzed the dependence of viscosity, η , on temperature, T, and pressure, p, for several classes of liquids. They restricted their analysis to the cases where the thermal expansion coefficient of the liquid is positive (this property is fulfilled at atmospheric pressure for most but not all liquids). The analysis of both literature data and their own results led those authors to conclude that the following relations must be fulfilled

$$\left(\frac{\partial \eta}{\partial T}\right)_p < 0 , \qquad (24.198)$$

$$\left(\frac{\partial\eta}{\partial p}\right)_T > 0.$$
(24.199)

These relations imply that the viscosity must decrease with increasing temperature (for isobaric processes), and must increase with increasing pressure (at isothermal conditions). Moreover, considering the viscosity as a function of pressure and temperature, i.e. $\eta = \eta(p, T)$, they wrote down the following identity

$$\left(\frac{\partial\eta}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_\eta \left(\frac{\partial p}{\partial \eta}\right)_T = -1.$$
(24.200)

Eq. (24.200) follows from purely mathematical considerations and does not involve originally any physics.

Taking into account the viscosity dependencies given by Eqs. (24.198) and (24.199), they concluded that the inequality

$$\left(\frac{\partial p}{\partial T}\right)_n > 0 \tag{24.201}$$

must be fulfilled. This equation - appearing here first as a purely mathematical relation - has, of course, a quite definite physical meaning. As mentioned earlier, the viscosity of liquids of constant composition in (stable and metastable) thermodynamic equilibrium states can be considered as a function of two state variables, pressure and temperature, i.e., $\eta = \eta(p, T)$. However, if one considers viscosity as constant (i.e., $\eta = \eta(p, T) = \text{constant}$), then this relation gives a dependence between pressure and temperature (at constant viscosity). So Eq. (24.201) implies that - in order for the viscosity to remain constant - an increase of temperature leads to effects which can be compensated by an increase of pressure.

It should be stressed that Eqs. (24.198) and (24.199) are corroborated by a variety of experimental results and lead to the theoretical consequence given by Eq. (24.201). However, one can easily reverse above argumentation. Indeed, taking into account general concepts connecting viscosity with the "free volume" in the liquid [2, 36, 104, 105] we can analyze theoretically how the partial derivative $(\partial p/\partial T)_{\eta}$ should behave. Taking into account, in addition, Eq. (24.198), one can arrive then at the desired theoretical prediction concerning the pressure dependence of the viscosity.

Indeed, following the classical work of Frenkel [36], the essence of "free volume" concepts can be expressed as follows: (i.) "free volume" uniquely determines the value of the viscosity, η ; (ii.) "free volume" is uniquely determined by the total volume, V(p, T), of the liquid and not by pressure, p, and temperature, T, separately. Frenkel mentioned Batchinskij's equation as one example for such type of dependence. The respective ideas have been developed later on by different authors advancing particular models of free volume theories for the dependence of the viscosity on the thermodynamic state parameters. In contrast to such earlier attempts, here we employ only above given essence of free volume concepts without specifying any particular models for viscous flow.

In order to proceed we realize that the free volume of liquids, as a rule, decreases with pressure. This way, in order to reestablish the value of the free volume (and the resulting value of viscosity), one has to vary the temperature

to such extent as to compensate the changes of free volume due to the effect of pressure. Consequently, from such general theoretical considerations, one arrives directly at the inequality Eq. (24.201), but now independently of the knowledge of experimental data. Taking exclusively the dependence given by Eq. (24.198) from experiment, we then arrive, utilizing Eq. (24.200), at Eq. (24.199). In this way, employing only general concepts connecting viscosity with free volume of the liquid (and assuming the absence of any other structural changes in addition to densification) we can conclude that, in isothermal conditions, the viscosity has to increase, as a rule, with increasing pressure. However, exceptions from this general rule are possible, as will become evident from the following quantitative analysis.

In addition to the qualitative conclusions given above, one can easily formulate a method to quantitatively estimate the pressure dependence of viscosity (in isothermal conditions) provided the temperature dependence of viscosity (at constant pressure) and some other purely thermodynamic characteristics of the liquid are known. Indeed, according to above analysis, we may connect variations in viscosity with variations of "free volume" and suppose that the free volume is uniquely connected with the total volume of the system. Then, in order to secure constancy of viscosity, one has to demand that the total volume of the system is kept constant if both pressure and temperature are varied slightly by dT and dp, respectively. From Eq. (24.202),

$$dV(p,T) = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp = 0, \qquad (24.202)$$

we then get the following result

$$\left(\frac{\partial T}{\partial p}\right)_{\eta} \cong \left(\frac{\partial T}{\partial p}\right)_{V} = -\frac{\left(\frac{\partial V}{\partial p}\right)_{T}}{\left(\frac{\partial V}{\partial T}\right)_{p}}.$$
(24.203)

With Eq. (24.200), we finally obtain

$$\left(\frac{\partial\eta}{\partial p}\right)_{T} = \left(\frac{\partial\eta}{\partial T}\right)_{p} \frac{\left(\frac{\partial V}{\partial p}\right)_{T}}{\left(\frac{\partial V}{\partial T}\right)_{p}} = -\frac{\kappa(p,T)}{\alpha(p,T)} \left(\frac{\partial\eta}{\partial T}\right)_{p}, \qquad (24.204)$$

where κ is the isothermal compressibility and α the isobaric thermal expansion coefficient, i.e.,

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T , \qquad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) . \tag{24.205}$$

Assuming, as mentioned, that the relaxation behavior is governed by viscosity (which is valid in a large variety of cases [2, 17]), we arrive with above given considerations at

$$\left(\frac{\partial \tau_R}{\partial p}\right)_T = -\frac{\kappa(p,T)}{\alpha(p,T)} \left(\frac{\partial \tau_R}{\partial T}\right)_p , \qquad (24.206)$$

and with Eq. (24.196) at

$$\frac{dT_g}{dp} \cong \frac{\kappa(p,T)}{\alpha(p,T)} \quad \text{at} \quad \left| \left(\frac{\partial \tau_R}{\partial T} \right)_p \right| \gg \frac{\tau_R}{T} . \tag{24.207}$$

It follows that at "normal" situations, when the thermal expansion coefficient is positive, the glass transition temperature increases with increasing pressure at otherwise identical process conditions. In addition, the relation obtained - at least in the considered approximative limit - is similar to one of the Ehrenfest relations but not identical since here only thermal expansion coefficient and compressibility of the equilibrium liquid enter the equation and not differences between glass and melt.

Pressure Dependence of the Glass Transition Temperature at Isobaric Cooling: Application to Other **Mechanisms of Relaxation**

The characteristic relaxation time can be generally expressed in the form [2, 106, 107]

$$\tau = \tau_0 \exp\left(\frac{A(p,T)}{k_B T}\right) . \tag{24.208}$$

It is a consequence of the fact that relaxation is governed by local fluctuations, and the magnitude of the fluctuations depends in general on pressure and temperature (and for $T \leq T_q$ also on the appropriate set of structural order parameters). Employing the general relations Eq. (24.196), we arrive with Eq. (24.208) at

$$\frac{dT_g}{dp} \cong -\frac{\left(\frac{\partial \tau_R}{\partial p}\right)_T}{\left(\frac{\partial \tau_R}{\partial T}\right)_p} \cong -\frac{\left(\frac{\partial A(p,T)}{\partial p}\right)_T}{\left(\frac{\partial A(p,T)}{\partial T}\right)_p}.$$
(24.209)

Terms considered to be small are neglected here again.

Different models of viscous flow result in different values of the activation energy term A(p,T) [2, 106, 107]. In particular, employing the Adam-Gibbs entropy model [108], characterized by

$$\frac{A(p,T)}{k_B T} = \frac{B}{TS_c} , \qquad B = \text{constant} , \qquad (24.210)$$

where S_c is the molar configurational entropy, we arrive at

(- -)

$$\frac{dT_g}{dp} \cong -\frac{\left(\frac{\partial S_c}{\partial p}\right)_T}{\left(\frac{\partial S_c}{\partial T}\right)_p} \cong \frac{\left(\frac{\partial V_c}{\partial T}\right)_T}{\left(\frac{\partial S_c}{\partial T}\right)_p} \cong TV \frac{\Delta \alpha}{\Delta C_p}\Big|_{(p_g, T_g)} .$$
(24.211)

In this way, we arrive at the second of Ehrenfest's equations but in a purely kinetic treatment.

Conclusions

The following conclusions can be drawn from the above given analysis:

- The kinetic criteria for glass formation do allow one to derive relations which are identical or similar to Ehrenfest's relations.
- Provided viscous flow and/or relaxation can be described by free volume concepts, then we arrive at a relation similar but not identical to one of the Ehrenfest relations. Instead of

$$\frac{dT_g}{dp} = \frac{\kappa^{(1)} - \kappa^{(2)}}{\alpha^{(1)} - \alpha^{(2)}},$$
(24.212)

we obtain (c.f. Eq. (24.207))

$$\frac{dT_g}{dp} = \frac{\kappa}{\alpha} . \tag{24.213}$$

Eq. (24.212) is consequently not automatically fulfilled (as stated by Nieuwenhuizen [58, 58]) and, in addition, its general failure in comparison with experiment [53] becomes understandable, it does not hold even in the case that free volume governs viscous flow.

- Provided entropy differences govern the relaxation behavior in the form as described by the Adam-Gibbs equation, then the kinetic approach leads directly to the second of the Ehrenfest relations. Consequently, the origin of the fulfillment of the second Ehrenfest relation can be connected with the ability of the Adam-Gibbs equation to describe the viscosity of glass-forming melts [107].
- A detailed analysis of the validity of the derived here equations in comparison with experiment like those performed e.g. in [62, 63, 109] is considered to be of large interest.

Temperature Dependence of the Glass Transition Pressure at Isothermal Change of Pressure

For the analyzed now case, we may proceed in a similar way as discussed for cooling and heating processes before. Introducing the characteristic time of change of pressure as

$$\frac{dp}{dt} = -\frac{1}{\tau_p}p , \qquad \tau_p = \left\{\frac{1}{p} \left|\frac{dp}{dt}\right|\right\}^{-1}$$
(24.214)

we arrive at

$$\tau_R \cong \tau_p \qquad \Longrightarrow \qquad \left\{ \frac{1}{p} \left| \frac{dp}{dt} \right| \tau_R \right\} \Big|_{p=p_g} \cong C(p,T) , \qquad C \cong 1$$
(24.215)

as the definition of the glass transition pressure, p_g . Here it is assumed that in the course of change of pressure the temperature is kept constant. The change of the glass transition pressure with a change of temperature can be determined then via the relation

$$dC(p,T) = \left(\frac{\partial C}{\partial T}\right)_{p} dT + \left(\frac{\partial C}{\partial p}\right)_{T} dp \qquad (24.216)$$
$$= \left(\frac{\partial}{\partial T} \left(\frac{1}{p} \left|\frac{dp}{dt}\right| \tau_{R}\right)\right)_{p} dT + \left(\frac{\partial}{\partial p} \left(\frac{1}{p} \left|\frac{dp}{dt}\right| \tau_{R}\right)\right)_{T} dp = 0.$$

Assuming that the rate of change of pressure in the glass transition range has the same value in both considered cases, we arrive at

$$\left\{\frac{1}{p}\left|\frac{dp}{dt}\right|\left(\frac{\partial\tau_R}{\partial T}\right)_p\right\}dT + \left\{-\frac{1}{p^2}\left|\frac{dp}{dt}\right|\tau_R + \left(\frac{1}{p}\left|\frac{dp}{dt}\right|\right)\left(\frac{\partial\tau_R}{\partial p}\right)_T\right\}dp = 0$$
(24.217)

or

$$\frac{dp_g}{dT} = -\frac{\left(\frac{\partial \tau_R}{\partial T}\right)_p}{\left(\frac{\partial \tau_R}{\partial p}\right)_T - \frac{\tau_R}{p}}$$
(24.218)

and, finally, in a commonly good approximation,

$$\frac{dp_g}{dT} \cong -\frac{\left(\frac{\partial \tau_R}{\partial T}\right)_p}{\left(\frac{\partial \tau_R}{\partial p}\right)_T} \quad \text{at} \quad \left| \left(\frac{\partial \tau_R}{\partial p}\right)_T \right| \gg \frac{\tau_R}{p} .$$
(24.219)

In this way, we have obtained general relations for the dependence of the glass transition pressure on temperature at otherwise unchanged conditions. Obviously, in the considered approximative case, we get the earlier obtained result,

$$\frac{dp_g}{dT} \simeq \frac{\alpha(p,T)}{\kappa(p,T)} \quad \text{at} \quad \left| \left(\frac{\partial \tau_R}{\partial p} \right)_T \right| \gg \frac{\tau_R}{p} , \qquad (24.220)$$

again.

24.7.8 Fictive Temperature and Fictive Pressure

For the first time, the concept of a structural order parameter was introduced into glass science by Tool [16] in terms of fictive temperature. Already Davies and Jones [27] noted that instead of fictive temperature one can employ equivalently the concept of fictive pressure as the determining structural order parameter. This concept was further advanced in recent years by Landa et al. [110, 111] who developed an interpretation of the glass transition and accompanying effects employing the concept of negative internal pressure as the structural order parameter (for a discussion of their concept, see [112]). Gupta [113] developed a theoretical approach treating both fictive temperature and fictive pressure as independent parameters. There exist a variety of further attempts to employ these concepts in the treatment of glass-forming systems, some of them are discussed in detail also in [15].

24 On the Dependence of the Properties of Glasses on Cooling and Heating Rates

The introduction of the concept of fictive temperature has been very fruitful being a particular realization of the thermodynamic requirement that for the thermodynamic description of glasses as non-equilibrium systems additional state parameters, the structural order parameters, have to be introduced. Hereby the fictive temperature is one of the possible candidates. In case that one structural order parameter is sufficient for the description of the glasses, then the fictive temperature can be determined by extrapolating glass properties linearly up to the respective metastable equilibrium curves. Then, a fictive temperature may be uniquely determined. In the present paper, T_g is taken practically identical to the fictive temperature in the classical Tool's interpretation. The value of the fictive temperature determines then uniquely the state of a glass similar to the order parameter ξ employed here. However, the situation may become much more complex, if several order parameters are required for the determination of the glass-forming melt and the glass. In such case, the definition of a fictive temperature becomes ambiguous without developing a proper way of its determination.



Figure 24.27: Fictive pressure and fictive temperature, defined via the general thermodynamic approach (Eqs. (24.223), (24.224), (24.226), and (24.227)), as a function of temperature for different cooling rates.

As shown by us recently [5, 15], a general model-independent definition of fictive temperature and fictive pressure can be advanced not only for the case that one structural order parameter describes the system under consideration but even for the general case of an arbitrary number of f structural order parameters. In latter general case, the combined

24.7 Dependence of Properties of Glass-Forming Melts and Glasses on Cooling and Heating Rates

first and second laws of thermodynamics can be written as [2, 5, 15]

$$dU = TdS - pdV - \sum_{i=1}^{f} A_i d\xi_i .$$
(24.221)

Along a given path of evolution of the system, the different order parameters are functions of the external control parameters taken here to be entropy and volume. We get then

$$dU = \left\{ T - \sum_{i=1}^{f} A_i \left(\frac{\partial \xi_i}{\partial S} \right)_{V, \{\xi_j; j \neq i\}} \right\} dS - \left\{ p + \sum_{i=1}^{f} A_i \left(\frac{\partial \xi_i}{\partial V} \right)_{S, \{\xi_j; j \neq i\}} \right\} dV .$$
(24.222)

As a consequence, the fictive pressure and the fictive temperature can be determined similarly to the definition of the respective parameters in classical equilibrium thermodynamics via

$$T_{fictive} = \left(\frac{\partial U}{\partial S}\right)_{V} = T - \sum_{i=1}^{J} A_{i} \left(\frac{\partial \xi_{i}}{\partial S}\right)_{V, \{\xi_{j}; j \neq i\}}, \qquad (24.223)$$

$$p_{fictive} = -\left(\frac{\partial U}{\partial V}\right)_{S} = p + \sum_{i=1}^{f} A_{i} \left(\frac{\partial \xi_{i}}{\partial V}\right)_{S, \{\xi_{j}; j \neq i\}} .$$
(24.224)

Eqs. (24.223) and (24.224) represent - as we believe - the most general and appropriate definition of these internal parameters. Such believe is due to the following considerations: (i.) It is a straightforward generalization of the basic thermodynamic definitions of temperature and pressure as known from classical equilibrium thermodynamics (e.g. [21, 22]). For stable and metastable thermodynamic equilibrium states, the so-defined parameters are again equal to normal pressure and temperature (since for these states $A_i = 0$ for i = 1, 2, ..., f holds). In general, these parameters depend on the path the system is transferred into the respective state reflecting in this way the non-equilibrium nature of the system. (ii.) Having at one's disposal the generalized caloric equation of state $U = U(S, V, \xi_1, \xi_2, ..., \xi_f)$ (i.e. the dependence of the internal energy on the external control parameters S and V and the chosen set of structural order parameters $\{\xi_i\}$ to be obtained from experiment or statistical mechanical model computations), fictive temperature and fictive pressure can be determined uniquely via Eqs. (24.223) and (24.224) independent of the number of structural order parameters required for the description of the system under consideration. (iii.) Employing the definition of fictive pressure and fictive temperature as developed by us (Eqs. (24.223) and (24.224)), the fundamental law of thermodynamics for closed systems and arbitrary numbers of structural order parameters can be written as

$$dU = T_{fictive} dS - p_{fictive} dV . \tag{24.225}$$

In such definition, fictive temperature and fictive pressure have a much broader meaning as to represent structural order parameters, they represent the generalizations of the external control parameters (external pressure, p, and external temperature, T) governing the thermodynamic behavior of closed systems for equilibrium states and reversible processes proceeding in between them.

The property listed above as (ii.) - general validity of the definition of fictive pressure and temperature Eqs. (24.223) and (24.224) independent of the number of structural order parameters - is not fulfilled, for example, for the definition of these parameters given by Gupta [110]. In particular, latter approach does not allow one uniquely to determine $p_{fictive}$ and $T_{fictive}$ for the case that only one structural order parameter is required. The extension of Gupta's approach to f independent structural order parameters is as a rule also impossible since f sets of equations of the form as given by Gupta will not have, in general, a solution. Note as well that even in the case that only one structural order parameter is required for the description of the system, both $T_{fictive}$ and $p_{fictive}$ are different, in general, from T and p.

For the case that only one structural order parameter is required and this order parameter is expressed in terms of the utilized here lattice-hole model, the expressions for fictive pressure and temperature are of the form [15]

$$T_{fictive} = T\left\{1 - \left(\frac{\xi - \xi_e}{\xi_e}\right)\frac{(1 - \xi)^2}{\ln\xi}\right\} \cong T\left(\frac{\xi}{\xi_e}\right) , \qquad (24.226)$$

$$p_{fictive} = p - \frac{RT}{N_A v_0(p,T)} \left(\frac{\xi - \xi_e}{\xi_e}\right) . \tag{24.227}$$

The dependence of fictive pressure and fictive temperature according to above given general definition is illustrated for the model system in Figs. 24.27.

Note that fictive pressure and temperature are thus uniquely determined via the knowledge of the value of ξ . Such general definition fulfils the usually assumed limiting condition that in stable and metastable equilibrium fictive pressure and temperature are equal to external pressure and temperature. For temperatures tending to zero (since for $T \to 0$, we have $\xi_e \to 0$ and $(T/\xi_e) \to \infty$), the relations

$$\frac{T_{fictive}}{T} \to \infty, \qquad \frac{p_{fictive}}{p} \to -\infty \quad \text{for} \quad T \to 0$$
(24.228)

hold.

24.7.9 Effect of Variation of Cooling and Heating Rates: First Tentative Studies Introduction

In the previous analysis, we have studied the thermodynamic properties of glass-forming melts and glasses varying the heating and cooling rates over 10 decades. However, it was always assumed that both in heating and cooling, the absolute values of the rates of change of temperature are the same. In the present section, we use the developed approach to obtain temperature dependencies of heat capacity and several other properties of atactic polystyrene for different cooling rates, but assuming a constant heating rate. The values of cooling and heating rates are chosen in order to correspond to planned fast scanning calorimetry experiments on polystyrene.



Figure 24.28: Temperature dependence of the order parameter, ξ , employed for modeling of polystyrene glass transition at constant heating rate and different cooling rates.

Model System and Process Conditions

As mentioned, in the present work, we consider the glass transition of atactic polystyrene. Modeling of the experimental conditions is performed for the fast scanning calorimetry setup, described, for example, in [114]. Here, we consider series of cooling-heating cycles in the temperature range $t = (20 - 220)^{\circ}$ C (T = 293 - 493 K) with a constant heating rate of $(dT/dt) = 10^{4}$ K/s and cooling rates changing in the interval $(dT/dt) = (10^{-3} \div 10^{6})$ K/s. We employ

the notations of reduced temperature $\theta = (T/T_m)$ and $d\theta = q_\theta dt$, again, where q_θ is the cooling/heating rate in the reduced values of temperature. Then, we may write

$$\frac{d\xi}{d\theta} = -\frac{1}{q_{\theta}\tau} \left(\xi - \xi_e\right) \ . \tag{24.229}$$

Melting temperature for polystyrene is: $T_m = 512$ K, the additional model parameters [2, 7] are the same as chosen earlier: $(U_a^*/RT_m) = 6.52$, $\chi = \chi_1\chi_2 = 3.32$. The set of defined above parameters and equations is sufficient for the description of glass transition of polystyrene in the present model approach.

Results and Discussion

The obtained temperature dependencies of the order parameter ξ for different cooling rates are presented in Fig. 24.28. The cooling slope and the frozen-in values of ξ for each value of q_{θ} repeat the dependencies as obtained earlier here and in [10]. The modified Bartenev-Ritland equation [10]

$$\frac{1}{T_g - T_0} \cong A_1 - B_1 \log|q| \tag{24.230}$$

is therefore satisfied in the whole range of q_{θ} (Fig. 24.29). The obtained values for Eq. (24.230) parameters are $A_1 \approx 9.4 \cdot 10^{-6} \text{ K}^{-1}$, $B_1 \approx -6.4 \cdot 10^{-6} \text{ K}^{-1}$. However, when compared to the respective $\xi(\theta)$ -curves, obtained here earlier and in previous work [10] when cooling and heating rates where equal in each cycle, a qualitative difference can be observed.



Figure 24.29: Dependence of inverse temperature of glass transition on logarithm of cooling rate for polystyrene. This plot allows one to obtain the parameters of modified Bartenev-Ritland equation.

The heating run is always performed at 10^4 K/s in the modeled experiment. It can be noticed that the final adjustment of ξ towards its equilibrium value occurs at a narrow interval of temperatures ($\theta \approx 0.75 - 0.85$) as compared to the situation shown here earlier and discussed in detail also in [7 - 10]. We can conclude then that this θ -interval is defined by the value of $q_{\theta}^{heating}$ and not by the frozen-in, initial for the heating cycle, value of ξ .

Another conclusion from Fig. 24.28 concerns the non-monotonous character of the ξ -slope at heating. This character is well pronounced for $q_{\theta}^{cooling} \ge q_{\theta}^{heating}$ with a decrease at lower θ and a rapid increase at higher θ . As $q_{\theta}^{cooling}$ becomes lower than $q_{\theta}^{heating}$ (slow cooling with comparatively fast heating) the decrease in the ξ -slope towards ξ_e is



Figure 24.30: Temperature dependence of produced entropy during cooling-heating run at three different cooling rates: 10^{-4} K/s, 10^{4} K/s, 10^{6} K/s.

very small and, finally, at $q_{\theta}^{cooling} = 10^2$ K/s can be neglected. For $q_{\theta}^{cooling}$ in the interval from 10^2 K/s down to 10^{-3} K/s and $q_{\theta}^{heating} = 10^4$ K/s both cooling and heating dependencies can be considered as monotonous.



Figure 24.31: The dependence of total entropy produced during a heating run on the logarithm of initial cooling rate in the modeled experiment on polystyrene.



Figure 24.32: Configurational part of heat capacity of polystyrene at glass transition for constant heating rates and different cooling rates.

In Fig. 24.30 the temperature dependence for the produced entropy for three different modeled cycles are shown. The calculations were performed by the following equation:

$$\frac{d_i S}{d\theta} = \left. \frac{\partial^2 G}{\partial \xi^2} \right|_{\xi = \xi_e} \frac{\left(\xi - \xi_e\right)^2}{T_m \theta q_\theta \tau} \,. \tag{24.231}$$

A typical heating slope with two maximums, in agreement with above discussion on monotony of the ξ slopes, is strongly pronounced for $q_{\theta}^{cooling} = q_{\theta}^{heating}$ and eventually transfers to a curve with one maximum as the difference $\left|\log\left(\frac{q_{\theta}^{cooling}}{q_{\theta}^{heating}}\right)\right|$ grows. This statement is demonstrated in Fig. 24.31, where the total entropy produced during a heating run in the considered experiment is shown with respect to $q_{\theta}^{cooling}$. From Fig. 24.31 it seems likely that the total entropy produced grows faster with increase of the order of cooling rate, than with its decrease.

Finally, the temperature dependence of configurational part of isobaric heat capacity for the modeled experiments on atactic polystyrene has been calculated by equation [7]

$$C_{p,conf} \cong \chi R \frac{d\xi}{d\theta}$$
 (24.232)

In Fig. 24.32 cooling and heating slopes for $C_{p,conf}$ are presented for the whole range of q_{θ} . For an explicit comparison with experiment another part of specific heat capacity, connected with thermal motion of molecules, must be calculated and added to Eq. (24.232). Yet, qualitatively, one can compare already the configurational part, obtained in this work. For example, the C_p slopes on constant heating after cooling at different rates for PCL polymer measured by fast scanning calorimetry instrument [114] are in qualitative agreement with Fig. 24.32.

Conclusions

The previously developed model approach for describing the kinetics of glass transition [5] has been utilized in this section for obtaining the characteristic dependencies for atactic polystyrene material for planned future fast scanning

calorimetry experiments. The results obtained for the specific heat capacity are in qualitative agreement with existing own similar experiments on PCL.

24.7.10 General Results

Completing the analysis, we finally derive some integral characteristics of the cyclic processes analyzed which do not depend on particular properties of the systems under consideration but are consequences from the basic laws of thermodynamics (c.f. also [5, 7]). Since we start at and return to equilibrium states, the thermodynamic state functions like entropy, enthalpy, and Gibbs' free energy recover after the completion of the cyclic process the same values they had at the starting point. In this way, we may write, for example,

$$\oint dS = \oint d_e S + \oint d_i S = 0.$$
(24.233)

Since

$$\oint d_i S \ge 0 \tag{24.234}$$

holds, we get

$$\oint d_e S = \oint \frac{dQ}{T} = \oint \frac{C_p(p, T, \xi)}{T} dT \le 0.$$
(24.235)

Note that the specific heat depends here not only on (the constant) pressure and (the changing in time) temperature but also on the structural order-parameter, ξ . Only for reversible cyclic processes, the equality sign in Eq. (24.235) holds, but this is not the case in vitrification, where cooling and heating is accompanied, in general, by non-equilibrium relaxation and entropy production processes. Similarly, Eq. (24.151) yields (at assumed constancy of pressure)

$$\oint dH = \oint dQ = \oint C_p(p, T, \xi) dT = 0.$$
(24.236)

Note that all relations derived in this section are valid independent on any particular assumptions about cooling or heating rates employed in the realization of the cyclic processes discussed.

Experimental examples are shown in Figs. 24.33. In Fig. 24.33a [115], the full specific heat capacity in vitrifying and devitrifying polystyrene is shown for a cooling and subsequent heating process (standard DSC measurement with Setaram DSC 121 at a cooling & heating rate of q = 1 K/min, the mass of the sample is 230 mg). Integration leads here to

$$\oint dH = \int_{340K}^{400K} \left(c_p^{heating} - c_p^{cooling} \right) dT = 0.008 \,\mathrm{J/g} \,, \tag{24.237}$$

$$\oint d_e S = \int_{340K}^{400K} \left(\frac{c_p^{heating} - c_p^{cooling}}{T}\right) dT = (-7 \pm 2) \cdot 10^{-5} \,\mathrm{J/(gK)} \,. \tag{24.238}$$

In Fig. 24.33b [116], the heat capacity of a 20 ng PCL sample is shown heated with a rate of 1000 K/s after preliminary cooling at 300 K/s and 50000 K/s in both cases showing cold crystallization and melting. The cooling curve is approximated by a straight line. The respective enthalpy and entropy values are obtained here as

$$\oint dH = \int_{220K}^{350K} \left(c_p^{heating} - c_p^{cooling} \right) dT = 0.006 \,\mathrm{J/g} \,, \tag{24.239}$$

$$\oint d_e S = \int_{220K}^{350K} \left(\frac{c_p^{heating} - c_p^{cooling}}{T} \right) dT = (-4 \pm 1) \cdot 10^{-4} \,\mathrm{J/(gK)}$$
(24.240)



Figure 24.33: Top: Full specific heat capacity in vitrifying and devitrifying polystyrene [115] is shown for a cooling (full curve) and subsequent heating (dashed curve) process (standard DSC measurement with Setaram DSC 121 at a cooling & heating rate of q = 1 K/min, the mass of the sample is 230 mg). Bottom: Heat capacity of a 20 ng PCL sample [116] is shown heated with a rate of 1000 K/s after preliminary cooling at 300 K/s (heating curve is given by a full curve) and 50 000 K/s (heating curve is given by a dashed curve). The cooling curve is approximated by a straight line.

for the sample cooled with a rate 300 K/s. For the sample, cooled with a rate of 50000 K/s, we get instead

$$\oint dH = \int_{220K}^{350K} \left(c_p^{heating} - c_p^{cooling} \right) dT = 0.01 \,\mathrm{J/g} \,, \tag{24.241}$$

$$\oint d_e S = \int_{220K}^{350K} \left(\frac{c_p^{heating} - c_p^{cooling}}{T} \right) dT = (-1.5 \pm 1) \cdot 10^{-4} \,\mathrm{J/(gK)} \,. \tag{24.242}$$

Eqs. (24.237), (24.239), and (24.241) give for the experimental analyzes the values of the uncertainties in the measurements of the specific heats for closed loops in temperature and, as a consequence, the uncertainty in the enthalpy. As evident from Eq. (24.236), from a theoretical point of view, the respective integrals should be equal to zero. Knowing

the uncertainty in the measurement of the enthalpy, we can estimate the uncertainty in the measurement of the entropy as $\Delta S \cong \Delta H/T_g$. For the uncertainties in these cases of glass transition (Eq. (24.237)), we obtain as an estimate $\Delta S \cong 2 \cdot 10^{-5}$ J/(g K). The error in the determination of the entropy is consequently by one order of magnitude lower than the estimates obtained via Eq. (24.238), for the cold crystallization - melting process (Eqs. (24.239) and (24.241)) the uncertainty is $1 \cdot 10^{-4}$ J/gK. As evident, Eq. (24.235) is fulfilled, however, entropy production effects are small (c.f. also [86, 127, 128]).

24.8 Statistical-Mechanical versus Thermodynamical Description of Vitrification: Some Brief Comments on a Current Debate

With thermodynamics, you can calculate almost everything, but crudely with kinetic theory, less things, but more accurately, and with statistical physics almost nothing exactly.

Eugene Wigner

Nobody knows what entropy really is, and if you use the word 'entropy' in an argument, you will win every time.

John von Neumann

The central problem is to explain in molecular terms the way in which the glass differs from the liquid and the nature of the change from the glass to the equilibrium liquid. In view of the complexity of glass-forming substances we cannot hope for a detailed microscopic theory.

R. O. Davies and G. O. Jones

Very often attempts to find a better solution are an enemy of finding a good one. So, let us be engaged in the may be less prestigious but more useful task to improve the relaxation theory of glass transition. Here a huge amount of things has to be and can be done.

Oleg V. Mazurin

In view of the ongoing current discussion on the correct theoretical description of the glass transition and the nature of the vitreous state, it seems to be useful to make some overview on the actual state of affairs and, if possible, to come to some tentative conclusion. The problem under discussion was formulated in papers by Kivelson and Reiss [117, 118] and later employed by Gupta and Mauro, it can be formulated as follows:

• D. Kivelson and H. Reiss, *Metastable Systems in Thermodynamics: Consequences, Role of Constraints*, J. Phys. Chem. **B 103**, 8337 (1999) [117].

Metastable states are not in true equilibrium and so cannot be directly treated by thermodynamics and statistical thermodynamics. To circumvent this difficulty one can specify an equivalent equilibrated state, equivalent in the sense that the observed macroscopic features are indistinguishable from those of the metastable state, and equilibrated because of the imposition of auxiliary constraints which totally block the very slow relaxations that cannot be completed during the time of the experiment. This procedure permits one to treat metastable systems consistently within a completely time independent and causal thermodynamic framework. It also gives a consistent description of the entropy of glassy and similar random metastable systems in which the entropy vanishes as $T \rightarrow 0$ K, and it explains the apparent residual entropy at 0 K obtained in most conventional analyses based upon experiments carried out over irreversible paths (but not always recognized as such).

• H. Reiss, Apparent entropy, residual entropy, causality, metastability, constraints, and the glass transition, J. Non-Crystalline Solids **355**, 617-623 (2009) [118].

A thermodynamic framework for the investigation of 'residual entropy' and related phenomena is developed, expanding and clarifying the work of Kivelson and Reiss and the important work of several other investigators. The main difficulties encountered in the development of such a framework are the need to deal with constrained equilibrium as well as to include irreversible processes in the overall study. These challenges are met by using the device of auxiliary constraints and the equivalent equilibrated states that they produce. The importance of
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a thermodynamic framework is tied to the fact that evolving molecular theories of residual entropy, which also impact the glass transition, no matter how sophisticated, invariably contain approximations whose effects are hard to assess. Thus a thermodynamic framework provides a vehicle within which the internal consistency of a theory can be tested. Phenomena that are treated in such a framework, along with others, are those mentioned in the title of this paper. The concept of residual entropy, its reality or unreality, is often considered to be an unimportant issue. The findings of this paper, besides emphasizing the unreality of residual entropy, show that the question of its existence is a significant one. Among other things, the fundamental principle of causality is involved and we should not be so cavalier as to dispense with it. Among other rigorous analysis we present an argument involving an ideal binary solution whose behavior as the limiting behavior of a real solution provides access, in principle, to experiment. The argument does make the generally accepted assumption that, at equilibrium at 0 K, pure crystals of the binary system's components have zero entropy. It strongly suggests that residual entropy, in general, is an impression that stems from the inclusion of an irreversible step in an experimental thermodynamic cycle.

• P. K. Gupta and J. C. Mauro, *The configurational entropy of glass*, J. Non-Crystalline Solids **355**, 595-599 (2009) [119].

Configurational entropy is of fundamental importance to understanding the universal nature of the glassy state. According to the conventional view, the configurational entropy of a liquid is 'frozen' below the glass transition temperature (T_g) all the way to absolute zero. Contrary to this, we claim that: (i) there is an entropy loss associated with the liquid to glass transition, and (ii) the configurational entropy in the glassy state vanishes at absolute zero. This paper contrasts our arguments (called the 'entropy loss' view) and the conventional view.

J. C. Mauro, P. K. Gupta, R.J. Loucks, and A. K. Varshneya, *Non-equilibrium entropy of glasses formed by continuous cooling*, J. Non-Crystalline Solids **355**, 600-606 (2009) [120].
 We propose a generalized definition of entropy accounting for the continuous breakdown of ergodicity at the laboratory glass transition. Our approach is applicable through all regimes of glass forming, from the equilibrium liquid state through the glass transition range and into the glassy state at low temperatures. The continuous loss of ergodicity during the laboratory glass transition is accompanied by a loss of entropy as the system gradually becomes trapped in a subset of the configurational phase space. Using a hierarchical master equation approach, we compute the configurational entropy of selenium, a simple but realistic glass-former, for cooling rates covering 25 orders of magnitude, viz., 10⁻¹² to 10¹² K/s. In all cases, the entropy of glass is zero in the limit of absolute

This point of view has been intensively discussed in the literature and at different conferences. Some papers in this respect are summarized below:

zero temperature, since here the system is necessarily confined to a single microstate.

• M. Goldstein, On the reality of residual entropies of glasses and disordered crystals, J. Chem. Phys. **128**, 154510 (2008) [121].

We show that the hypothesis that the configurational entropy of a liquid disappears when it is kinetically frozen into a single glass state implies a spontaneous decrease of entropy. We show further that this is not an innocuous exception to the second law that requires a slight modification of that law, but rather implies directly the possibility of an uncompensated conversion of heat to work. We also note that the number of microstates visited in the course of a measurement does not determine the entropy, but rather that this number is always an inconceivably small fraction of the accessible microstates. Various experimental and computational tests of the possible vanishing of configurational entropy on kinetic arrest (e.g., from studies of glass vapor pressure and solubilities, and the coexistence curve between a disordered crystal and the liquid), with the exception of one questionable case, are consistent with the view that it does not vanish. We then show that this result is actually required by the second law. These considerations apply equally to the residual entropy of disordered crystals.

• M. Goldstein, On the reality of the residual entropy of glasses and disordered crystals: The entropy of mixing, J. Non-Crystalline Solids **357**, 463 (2011) [78].

We have previously shown that the assumption that the configurational entropy of a supercooled liquid vanishes at T_g leads to a non-trivial violation of the second law. Here we consider the example of the entropy of mixing. We use as a model system two similar chemical substances which form an ideal solution in a mixed phase. We apply the reasoning of our earlier paper to show that this vanishing would lead to a dilemma; either it violates the second law of thermodynamics, or else it cannot be demonstrated by any conceivable experiment. We show further that the vanishing of the entropy of mixing on kinetic arrest leads to the counter-intuitive result that the chemical potential of each component in an infinitely dilute kinetically arrested (or glassy) solution can equal or the chemical potential of the pure component. The most parsimonious conclusion from these results is that residual entropies are real.

24 On the Dependence of the Properties of Glasses on Cooling and Heating Rates

• M. Goldstein, On the reality of the residual entropies of glasses and disordered crystals: Counting microstates, calculating fluctuations, and comparing averages, J. Chem. Phys. **134**, 124502 (2011) [122].

In the course of an on-going debate on whether glasses or disordered crystals should have zero entropy at 0 K, i.e., whether the residual entropy assigned to them by calorimetric measurements is real, the view has been expressed by some who hold the zero entropy view that to measure entropy, all or an appreciable number of the microstates that contribute to the entropy must be visited. We show here that the entropy calculated on the basis of the number of microstates visited during any conceivable time of measurement would be underestimated by at least 20 orders of magnitude. We also examine and refute the claim that an ensemble average for glassy systems, which predicts a finite residual entropy, also predicts physically impossible properties. We conclude that calorimetrically measured residual entropies are real.

• S. V. Nemilov, Zero-point entropy of glasses as physical reality, J. Non-Crystalline Solids 355, 607-616 (2009) [123].

The paper presents an analysis of the physical nature of the author's results obtained since 1995 in the field of thermodynamics of the vitreous state (classic approximation). Excess entropy and free energy at 0 K are considered as the measures of non-equilibrium extent of glass with respect to crystal. Experimental data for melts and glasses of various chemical natures are generalized. A general form of the relations between reversible changes in free energy, enthalpy and entropy and their frozen values at the formation of any glass is shown. The problem of functional dissimilarity of the heat capacity of glass and that of crystal has been solved within the framework of the principle of free energy minimization as a result of self-organization of the vibration spectrum according to the frozen structure. The complete stabilization of glass structure at Kauzmann's temperature or below it is forbidden by topological reasons and (or) by thermodynamics. The effects of pressure on the thermodynamic properties of glasses are shown. Possible particular applications of the analysis of self-organization in chaotic systems are exemplified by the modeling of the abilities of neural systems.

• P. Richet, *Residual and configurational entropy: Quantitative checks through applications of Adam - Gibbs theory to the viscosity of silicate melts*, J. Non-Crystalline Solids **355**, 628-635 (2009) [107].

In this paper the traditional view that glasses possess residual entropy, which can be determined by calorimetric means, is quantitatively supported by applications of Adam and Gibbs configurational entropy theory to the temperature, composition and pressure dependencies of the viscosity of silicate melts. This theory is also in harmony with the mechanisms of viscous flow, as understood from NMR experiments, according to which viscosity is controlled by the rate of bond rearrangements between network-forming cations and oxygens. As a matter of fact, Adam and Gibbs basic expression relating structural relaxation times to the reciprocal of the product of temperature and configurational entropy can be derived from a phenomenological analysis of the temperature dependence of the activation energy for viscous flow. Adam-Gibbs theory thus works well for silicate melts because network-modifying cations also play a role in bond rearrangements such that, as a bulk property, configurational entropy is actually relevant to structural relaxation and flow.

• R. Conradt, *On the entropy difference between the vitreous and the crystalline state*, J. Non-Crystalline Solids **355**, 636-641 (2009) [124].

The paper deals with the entropy difference between frozen-in phases and their equilibrium counterparts. First, the nature of data compiled in thermochemical data collections are briefly reviewed, comprising data for non-equilibrium phases. Then, experimental evidence from earlier literature is compiled showing that the conventional entropy of a frozen-in phase at zero Kelvin assumes a non-zero residual value S(0). Based on calorimetric data from multiple sources, the same evidence is elaborated for diopside glass, yielding $S_{glass}(0) = 24.8 \pm 3$ J/(mol K), a value reproducing a result published earlier. The zero Kelvin enthalpy of this glass is $H_{glass}(0) = 81 \pm 8$ kJ/mol. For $S_{glass}(0)$, a structural interpretation in terms of silicate chain mixing is proposed, yielding a lower threshold for $S_{glass}(0)$. From the point of view of statistical mechanics, non-zero residual entropies of frozen-in phases can be derived from ensemble averages, however, not from time averages.

• U. Fotheringham, A. Baltes, R. Müller, and R. Conradt, *The residual configurational entropy below the glass transition: Determination for two commercial optical glasses*, J. Non-Crystalline Solids **355**, 642-652 (2009) [125].

Essentially from differential scanning calorimetry and viscosimetry, the residual configurational entropy below the glass transition is determined for two linearly cooled commercial optical glasses, K7 and NLaK12 from SCHOTT. The procedure is according to the conventional understanding of glass entropy and the conventional description of the configurational state by a distribution of fictive temperatures. For a cooling rate of 10 K/min, the residual

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entropy values found below the glass transition are 0.146 J/ (g K) for K7 and 0.148 J/(g K) for N-LaK12. The result is discussed comparing with both the lower limit for the residual entropy resulting from the reversibly exchanged heat ($\int dq/T$, 'Clausius limit') and the upper limit given by the configurational entropy of an equilibrium liquid with the same fictive temperature. The difference between the residual entropy and its lower limit is equal to the entropy generation due to the fall-out from equilibrium during linear cooling. The difference between the residual entropy and its upper limit is the driving force of the crossover- (or Kovacs-) effect. It turns out that the difference between the residual entropy and the Clausius limit is very small. The values found amount to less than 0.0001 J/(g K) for both glasses. Therefore, this difference can be neglected concerning the extrapolation of the Adam-Gibbs relation to low temperatures.

• G. P. Johari, *Configurational and residual entropies of non-ergodic crystals and the entropy's behavior on glass formation*, J. Chem. Phys. **132**, 124509 (2010) [77].

We use thermodynamics of lattice vacancies to test the merits of the view that (i) statistical entropy, $k_B \ln \Omega$, vanishes on vitrification of a liquid and hence there is no residual entropy and (ii) $k_B \ln \Omega$ of a nonergodic state would increase with time t as its structure relaxes. We argue that this view conflicts with the precepts of the configurational entropy of a crystal, $-R[x \ln x + (1 - x) \ln(1 - x)]$, where x is the fractional population of vacancies, and with the observed decrease in x with t on structural relaxation. The issue of whether the entropy of a kinetically arrested crystal state is equal to $k_B \ln \Omega$ or equal to $-R[x \ln x + (1 - x) \ln(1 - x)]$ can be resolved by measuring the vapor pressure, the emf of an electrolytic cell, and by scanning calorimetry. We also consider how the energy landscapes of a crystal and liquid differ, and point out that since crystals are in a non-equilibrium state, their thermodynamic data are inappropriate for testing the validity of the third law.

• D. P. B. Aji and G. P. Johari, *Fictive Temperature, Structural Relaxation, and Reality of Residual Entropy*, J. Phys. Chem. **B 114**, 9578-9585 (2010) [126].

By determining the fictive temperature, T_f , in two ways from the same C_p -data, we investigate whether the residual entropy, S_{res} , of a glass could be an artifact of using the $C_p d \ln(T)$ -integral in the glass-liquid temperature range. Although the integral gives only the upper and lower limits of the real entropy change, it is still useful and is distinguished as $\Delta \sigma$. We determine T_f^{σ} from $\Delta \sigma$ and the usual T_f^H from the $C_p dT$ integral for two metal alloy glasses, a basalt composition glass and a spray-quenched propylene glycol glass from the available data, and find that T_f^{σ} is about the same as T_f^H within errors. To substantiate it, we report a differential scanning calorimetry study performed during cooling of the Mg65Cu₂₅Tb₁₀ and Pd₄₀Ni₁₀Cu₃₀P₂₀ melts and on heating their glassy states at the same rates. In addition, we simulate $C_p - T$ plots from a known model for non-exponential, nonlinear relaxation and analyze the data. The quantity $\Delta \sigma$ on cooling the liquid and heating the glass differs negligibly; that is, net change in a temperature cycle between glass and its melt is close to zero, a characteristic of a nearly reversible change. We conclude that spontaneous enthalpy release has little effect on the entropy change determined from the $C_p d \ln(T)$ integral and, contrary to recent suggestions, S_{res} is real.

• G. P. Johari, On resolving the statistical and calorimetric entropies of glass and non-crystalline solids, and the residual entropy problem, Thermochimica Acta 500, 111-118 (2010) [127].

In statistical terms, the configurational entropy, S_{conf} , of a structure of fixed configuration is zero, i.e., its $\Omega = 1$ in the Boltzmann equation, $S_{conf} = k_B \ln \Omega$. On that basis, a recent discussion has drawn two inferences: (a) S_{conf} is lost when a liquid vitrifies and thus a glass has no residual entropy, S_{res} , and (b) structural relaxation of a glass would first increase its S_{conf} with time from its zero value and then decrease S_{conf} to the equilibrium value, thus causing the slope of its free energy against time plot to abruptly decrease after a certain time period. Both conclusions conflict with the classical, textbook analysis of the calorimetric data, and with the experimental findings. To evaluate the merits of these conclusions, we use the difference between the free energy of glass (and of supercooled liquid) and its crystal phase. If the inferences based on the statistical view are valid, (i) this difference would show a gap between the glass and supercooled liquid in the T_g range, (ii) the slope of the plot of this difference against T would be much less at $T < T_g$ than at $T > T_g$, and (iii) annealing would decrease this difference by a relatively large amount. After constructing such plots from the known C_p data, we propose that measurement of the vapor pressure, sublimation rate, solubility, chemical reaction rate, and emf of a cell made from glassy-metal electrodes may be useful for testing whether or not S_{conf} is lost on vitrification. The data available provide no support for the entropy-loss view.

 G. P. Johari, D. P. B. Aji, L. Gunawan, Clausius limits on cooling and heating through the liquid-glass range of three pharmaceuticals and one metal alloy - Annealing effects and residual entropy, Thermochimica Acta 522, 173-181 (2011) [128].

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The time-dependent, irreversible value of the heat capacity, C_p , measured in the glass-formation range, forbids one from estimating the entropy. To find out how much can the estimate differ from the real change in entropy, we determine the change in the $C_p dT$ and $C_p d \ln T$ integrals before and after isothermal annealings by DSC studies of three pharmaceuticals, acetaminophen, carbamazepine and griseofulvin and one metal alloy, $Mg_{65}Cu_{25}Tb_{10}$. The $C_p d \ln T$ integrals for the cooling and the heating paths approach the same value when annealing is minimized, or else when the effect of annealing is taken into account. The Clausius limits determined using the Bestul and Chang method show that irreversibility has lesser effect on the estimate of residual entropy than found earlier, and its value can be reasonably estimated from the C_p -data. We also discuss the relevant features of dynamic C_p , and conclude that entropy is an ensemble-averaged value.

• G. P. Johari and J. Khouri, *Entropy change on the cooling and heating paths between liquid and glass and the residual entropy*, J. Chem. Phys. **134**, 034515 (2011) [83].

We analyze the $C_p - T$ data for the glassy state of eight materials of varied molecular interactions and structures to investigate how the use of the $C_p d \ln T$ integral in the time-dependent (nonreversible) thermodynamic path between a liquid and glass affects our estimates of the entropy. Since the change in entropy on such a path cannot be determined, we estimate the upper and lower values of the change, $\Delta\sigma$, from the $C_p d \ln T$ integral. For the same rates of cooling and heating and without annealing, $\Delta\sigma$ on the cooling path is negligibly different from that on the heating path. The difference is 1/60th - 1/25th of the lowest known value of the residual entropy and even less than the configurational entropy of the supercooled liquid at its kinetic freezing temperature. Thus use of the $C_p d \ln T$ integral in the nonreversible path does not introduce significant errors in estimating the residual entropy. Dynamic C_p data cannot be used to infer that configurational entropy decreases on glass formation. Time dependence of the $C_p - T$ path has little consequence for reality of the residual entropy.

The point of view of the present authors on this topic is described in detail in the monographs [2, 5] and a variety of papers on this and related topics ([7, 10, 14, 86] and references cited therein). We will not repeat them here in detail. We would like only to mention that we fully retain with the conventional point of view and that there exists a variety of glass properties (solubility, vapor pressure, reactivity, etc.) which can not be understood appropriately in terms of the entropy loss assumption. In addition, also own analysis have shown that the classical approach to the determination of entropy remains valid since entropy production terms are small in comparison with the configurational or frozen-in values. This latter effect is discussed also in detail in the present chapter.

Having in view above given quotations, we have would like also to express our general opinion in this respect:

- Any real advancement in statistical modeling, in general, and, in particular, of glass forming systems is highly desirable but a very complicated task.
- However, statistical models have not the right to contradict thermodynamics (both equilibrium and thermodynamics of irreversible processes) latter being "condensates" of experimental knowledge and a description of the average phenomenological behavior of the respective systems (Szilard's principle).

In particular, the computations of the residual or configurational entropy performed in the present chapter as well show - in a fully straightforward way without any arbitrary assumptions - that entropy becomes frozen-in in cooling and depends on cooling rates.

This formulated point of view concerning the relationship between thermodynamic and statistical physics is also underlined as an essential requirement of any theory by Howard Reiss [118] in above reprinted abstract (even if he arrives then at a different to our point of view results): *The importance of a thermodynamic framework is tied to the fact that evolving molecular theories of residual entropy, which also impact the glass transition, no matter how sophisticated, invariably contain approximations whose effects are hard to assess. Thus a thermodynamic framework provides a vehicle within which the internal consistency of a theory can be tested.*

Despite the overwhelming majority of arguments in favor of the conventional point of view and against the "entropyloss-view", the authors of latter approach retain so far with their opinion. This fact can be traced e.g. in the paper

• J. C. Mauro, R. J. Loucks, and S. Sabyasachi, *Heat capacity, enthalpy fluctuations, and configurational entropy in broken ergodic systems*, J. Chem. Phys. **133**, 164503 (2010) [129].

A common assumption in the glass science community is that the entropy of a glass can be calculated by integration of measured heat capacity curves through the glass transition. Such integration assumes that glass is an equilibrium material and that the glass transition is a reversible process. However, as a non-equilibrium and non-ergodic material, the equations from equilibrium thermodynamics are not directly applicable to the glassy state. Here we investigate the connection between heat capacity and configurational entropy in broken ergodic

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systems such as glass. We show that it is not possible, in general, to calculate the entropy of a glass from heat capacity curves alone, since additional information must be known related to the details of microscopic fluctuations. Our analysis demonstrates that a time-average formalism is essential to account correctly for the experimentally observed dependence of thermodynamic properties on observation time, e.g., in specific heat spectroscopy. This result serves as experimental and theoretical proof for the nonexistence of residual glass entropy at absolute zero temperature. Example measurements are shown for Corning code 7059 glass.

Even more, the paper is announced by the authors as *the long-awaited experimental and theoretical proof for the nonexistence of residual glass entropy at absolute zero temperature...*

In this respect, one has to note that

- till that paper there have been obviously no experimental data available to the authors supporting their 'entropy loss view' approach;
- the respective claims are not correct as analyzed in detail by Johari in the subsequently cited papers:
 - G. P. Johari, *Mechanical relaxation and the notion of time-dependent extent of ergodicity during glass transition*, Physical Review E, accepted for publication [130].

A postulate that ergodicity and entropy continuously decrease to zero on cooling a liquid to glassy state was used to support the view that glass has no residual entropy, and the features of mechanical relaxation spectra were cited as proof for the decrease. We investigate whether such spectra and the relaxation isochrones can serve as the proof. We find that increase in the real component of elastic moduli with increase in spectral frequency does not indicate continuous loss of ergodicity and entropy, and the spectra do not confirm isothermal glass transition or loss of entropy. Variation of ergodicity and entropy with the spectral frequency has untenable consequences for both thermodynamics and molecular dynamics, and implies that despite a broad distribution of its relaxation times, an equilibrium liquid be considered always ergodic. Perturbation from equilibrium used to obtain a spectra do not have the effect of dynamic freezing and unfreezing, and Maxwell-Voigt models for mechanical response function have neither the characteristic irreversibility of liquid-glass transition, nor are commutable to ergodicity or entropy.

- G. P. Johari, Specific heat relaxation-based critique of isothermal glass transition, zero residual entropy and time-average formalism for ergodicity loss, Thermochimica Acta **523**, 97-104 (2011) [131].

In support of the view that entropy is lost on glass formation, the C'_p relaxation spectra were regarded as experimental proof of time- and temperature-dependent loss of both ergodicity and entropy, and confirmation of isothermal glass transition. Also, both $C_p \to 0$ and $S \to 0$ in the limits of $t_{obs} \to 0$ s, and $T \to 0$ K were cited as further proof. We found no experimental evidence in support of the view. A critical examination shows that the C'_p and C''_p spectra used to reach these conclusions indicate phase-lag between the response and perturbation, not loss of ergodicity or loss of configurational degrees of freedom, and $C_p \to 0$ as $T \to 0$ K is not evidence for $S \to 0$ as $T \to 0$ K. The notions of partial ergodicity and entropy and their dependence on t_{obs} are inconsistent with the properties measured during cooling, heating and isothermal annealing, and thermodynamic consequences of the apparent proof are untenable. The premise that glass formation is a process of continuously breaking ergodicity with entropy loss does not merit serious consideration.

Consequently, one has to conclude that the "entropy loss view" does not give an appropriate description of the glass transition and the properties of glasses. As far as the basic gap of the theory - the incorrect description of the behavior of the entropy in vitrification - cannot be removed, also all other eventual predictions should be considered as questionable.

24.9 Discussion

In the present paper, the behavior of a variety of thermodynamic properties of glass-forming melts and glasses is analyzed in dependence on cooling and heating rates varying its absolute value in a wide range. This renewed interest is partly caused by the fact that such experiments are feasible, now, analyzing glass-forming melts in the range of cooling and heating rates in the range between 10^{-4} K/s up to 10^5 K/s [132, 133]. Here we concentrated the attention on the computation of some spectrum of quantities which are of particular interest in a variety of applications and for the general understanding of the nature of the glass transition. Of course, this spectrum of characteristics could be enlarged treating similarly, for example, not only the configurational but also the full specific heat capacities, the configurational contributions to the volume and the volume as a function of cooling and heating rates. In addition, we have computed here the Prigogine-Defay ratio as a function of the cooling rate. Similarly, one could also compute the jumps in the

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thermodynamic coefficients separately and check some relations derived in our previous papers, in particular, in [7, 13]. As an additional example, one could check also some experimental rules like, e.g., the rule proposed by Simha and Boyer [134] connecting the jump of the expansion coefficient with T_q

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p, \qquad T_g \Delta \alpha \cong \text{constant} .$$
(24.243)

The authors derive this relation based on the concept of the glass temperature as an iso-free volume state. Since obviously this condition is not fulfilled, also the result is expected to be not correct.

In the present analysis, we assumed moreover that cooling and heating proceed with the same absolute value of the rate of change of temperature. Here also modifications can be introduced reflecting peculiarities of experiments performed and giving thus the possibility of a theoretical interpretation. In addition, we considered cyclic processes, where the initial state is always reestablished after the completion of the process of cooling and subsequent heating. Provided one starts the cycle at temperatures inside the vitrification interval, then the behavior of the system should depend on the number of the cycle in a series of cyclic heating and cooling processes. It would be of interest to perform also experiments in this respect and to compare them with the theoretical predictions obtained in the framework of the theory presented here. Finally, similar studies can be performed also with a similar approach for the case that vitrification and devitrification is due not to change of temperature but, for example, of pressure or other appropriate external control parameters. The mentioned spectrum of tasks will be addressed in future analyzes.

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25 Review on the Phenomenology and Mechanism of Atmospheric Ice Formation: Selected Questions of Interest

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One might ask: Why mathematical models are needed at all – especially when the people who build these models are the first to admit that models are *not* 'realistic'?

In fact, the paradoxical answer to this question is that models are successful not *despite* but *because* they are not realistic: The basic idea of a mathematical model is to explain a certain phenomenon with simplifying assumptions. Thus, reality can never be represented perfectly, but if an assumption matches reality partially, it is very interesting to see how far this assumption can go.

Taken from Siekmann, 2009

Abstract

The physical description of clouds inclusive all forms of their constituent hydrometeors is one of the most uncertain parts of present numerical weather prediction (NWP) and climate modelling. One of the key prerequisites for a more sophisticated cloud treatment is a better understanding of aerosol and hydrosol formation via multi-component vapour \rightleftharpoons liquid \rightleftharpoons solid phase transitions. Salt segregation and ice crystallisation in multi-component solutions is of special importance here, since the hydro-thermodynamic and physico-chemical conditions in Earth's atmosphere are to force phase transitions proceeding via different liquid and solid states of electrolyte particles and water. In this study, we give an overview on the phenomenology and genesis of ice nucleation in Earth's atmosphere. In the supplementary material

we present the thermodynamic and kinetic foundation of state-of-the-art modelling of atmospheric ice nucleation according to [64, 92], and [60, 61, 62, 63], the thermodynamic theory of deliquescence/efflorescence developed by [100, 101, 102, 103], as well as a theoretical approach to efflorescence employing classical nucleation theory [88, 90, 91]. Based on a literature study, we identified some so far unsolved problems of ice nucleation: (i) determination of key thermodynamic properties of supercooled water and hexagonal ice¹, (ii) determination of physico-chemical, morphological, topographical, and structural properties of catalytic surfaces, (iii) consideration of deliquescence-, efflorescence-, and thermal-induced hysteresis effects, and (iv) consideration of droplet deformation in an external gravitational field. Furthermore, we discuss the possibilities of non-classical methods for parameter fixing, such as state-of-the-art *ab initio* Molecular Dynamics (MD) simulations.

25.1 Introduction

The molecule of water is a complex object, forming the matrix of life, being the most common solvent for chemical processes, playing a major role in the determination of the Earth's climate, and appearing on planets, moons, and comets [69, 116]. The scientific motivation to deal with², the basic notions of³, and the current needs for⁴ investigating

²More than 50% of mid-latitude precipitation is produced via cold-cloud (involving ice) processes, whereas in the tropical region the proportion reaches 30% ([16] and references therein). Ice clouds impact both the latent and radiative heating processes, and in turn the circulation and the energy of water cycles in the atmosphere. Principal mechanisms for the generation of upper tropospheric ice clouds include detrainment from deep convective clouds and *in situ* ice nucleation driven by synoptic motions, mainly in mid-latitudes. For both ice water path and ice water content, "ice" represents all frozen hydrometeors, which can include cloud ice (typically suspended or "floating"), and ice mass precipitating forms such as snow and graupel. When modelling ice clouds, several processes must be considered in cloud schemes: the formation (e.g., ice nucleation, water vapour deposition) and possible sedimentation of cloud condensates, the growth and interactions (e.g., deposition and riming, aggregation) and falling out of precipitation, the evaporation/sublimation of both clouds and precipitation, and possibly advection of the cloud condensates. The importance of obtaining a more comprehensive understanding and improved capability for modelling upper tropospheric ice clouds cannot be underestimated as "cloud feedbacks remain the largest source of uncertainty" in determining Earth's equilibrium climate sensitivity, specifically to a doubling of carbon dioxide [122]. Present-day shortcomings in the representation of upper tropospheric ice clouds in general circulation models (GCMs) lead to errors in weather and climate forecasts as well as account for a source of uncertainty in climate change projections. From an intercomparison of cloud ice model representations of the simulations assessed in the Intergovernmental Panel on Climate Change Fourth Assessment Report, [122] reported that the globally averaged cloud ice water path differs by a factor of 20 between the largest and smallest values. Even when the two largest outliers have been removed, there was still a factor of about 6 between the largest and smallest values. On a regional scale differences of up to nearly 2 orders of magnitude have been recognized. For the cloud ice mass (having significant importance within the context of climate change and its associated model projection uncertainties) it is critical that this level of model uncertainty will be reduced.

³The initiation of ice crystallisation and cloud glaciations at temperatures above about -35°C is performed heterogeneously, i. e., it requires the presence of a catalysing surface in form of ice nuclei (IN). The latter are known to lower the thermodynamic energy barrier to form a critical embryo of the new phase. In the presence of IN, ice can crystallise in relatively warm environments. IN relevant to atmospheric ice formation include: black carbon soot (aircraft exhaust, fossil fuel combustion, biomass burning), organic carbon, mineral dust (crustal material from surface sources, kaolinite, montmorillonite) coated with or immersed in aqueous sulphuric acid and/or organic droplets, partially deliquesced ammoniated sulphates and sea salt etc. [58]. Crystallised salts in ammoniated aerosols above ice saturation may serve as active sites for heterogeneous ice nucleation (e. g., solid inclusions of crystalline (NH₄)₂SO₄ (mmersed in supercooled (NH₄)₂SO₄/H₂O solutions, solid inclusions of crystalline letovicite immersed in supercooled (NH₄)₁SO₄/H₂O solutions, solid inclusions of crystalline letovicite immersed in supercooled (NH₄)₁SO₄/H₂O solutions, solid inclusions of cliquescing aerosols (c.f. [58] and references cited therein). Sea-salt aerosols from accumulation mode are a complex mixture of many different ionic species dissolved in water. In the polar marine boundary layer (MBL) sea salt is mostly present in the liquid state. Sea-salt aerosols may be transported into the upper troposphere over oceans, whereas their aggregate state there is widely unknown.

 4 [12] identified, among others, the following open questions regarding ice nucleation: (a) Homogeneous nucleation: What is the structure of the ice embryo and does it form in the bulk liquid, at the liquid surface, or in a liquid subsurface? Has the new ice embryo already the structure of the bulk phase? Is freezing only a function of the water activity as suggested by semi-empirical models? What is the underlying mechanism, that explains laboratory measurements? (b) Heterogeneous nucleation: What are the most important properties of the heterogeneous nucleator? Lattice mismatch between ice and substrate were found to be sometimes a good indicator of how effectively a substance will promote ice nucleation. Unfortunately, it is not a predictive property. The presence of defects in the substrate, the type of bond, that the adsorbing water molecules form with the substrate, and the type of atoms exposed

¹Hexagonal ice Ih is one of the 13 different known H_2O -ice polymorphs. It is a very anisotropic crystal, consisting of a stack of basal planes of molecules arranged in hexagons. Perpendicular to the basal planes are the prismatic planes (primary and secondary). The binding energy is weaker among the basal planes than among prismatic planes. Consequently, the growth and melting kinetics may depend on which plane is the liquid/ice interface. Cubic ice Ic has very similar properties (structure, density, heat capacity, etc.) to the most common hexagonal ice Ih, of which it is a metastable form. Water, confined in nanopores, was found to freeze to cubic ice. Cubic ice is also present in the upper atmosphere. Very recently, a new pentagonal H_2O -ice polymorph was found.

25.1 Introduction

atmospheric ice formation have been reinforced, e. g., by the comprehensive reviews and compilation studies of [12, 16, 76, 115, 122]. Heterogeneous ice nucleation has been studied for many years, yet it remains poorly understood, especially on a molecular level [22, 77]. Consequently, it remains on the agenda for research, as exemplarily seen from the following studies:

- heterogeneous freezing of aqueous particles induced by crystallised ammonium sulphate, ice, and letovicite by [133, 134] using optical microscopy (OM) and differential scanning calorimetry (DSC), by [1], and by [132], who focused on the role of water activity in heterogeneous nucleation using OM/DSC;
- heterogeneous ice nucleation ability and properties of mineral dust and soot particles by [54] and [70] in sample chambers, by [128] employing environmental scanning electron microscopy (ESEM), and by [27] employing an optical microscope coupled to a flow cell;
- heterogeneous ice nucleation ability of oxalic acid in the immersion mode by [129] and [121] in cloud chamber experiments;
- efficiency of immersion mode ice nucleation on surrogates of mineral dust by [80] using DSC;
- variability and chemical composition of atmospheric heterogeneous ice nuclei (IN) by [94] using mass spectrometry;
- investigation of the crystallographic misfit or disregistry between hexagonal ice and kaolinite from grand canonical Monte Carlo calculations [22] etc.

[58] (and references cited therein) emphasised, that in striking contrast to homogeneous nucleation, any theoretical description of heterogeneous freezing must face the following problems:

- Surface morphology: Surface roughness may be caused by steps, dislocations, cracks, or other morphological irregularities. These defects (active sites) are hypothesized to promote nucleation through an inverse Kelvin effect. Hereby, the supersaturation in concave features (nano-cavities) increases compared to a flat surface. Such effects may be relevant for solid micro-crystals and fractal soot particles. Fast crystal growth rates at high supersaturations favor the generation of surface defects, which influence rates of adsorption and surface diffusion of molecules.
- Chemical composition: Soot particles contain organic matter and sulphate. Pure hydrocarbons or pure hydrogenated graphites are not able to serve as ice nucleators, but the chemical treatment with sulphuric acid or with oxidising agents (e. g., OH radicals) may increase the number of hydrogen-bonding groups (active sites) and enhance the wettability as a necessary condition for a particle to act as an efficient IN. In the presence of sufficient co-adsorption of H₂O molecules at the surface, a supercooled liquid layer can be formed, producing a mixed particle containing a solid core surrounded by a liquid shell. Coating may also take place at the surface of mineral dust or other solid airborne particles.
- Memory effects of particle evolution: This process is related to pre-activation or pre-conditioning and hydration dehydration induced hysteresis. It may occur, when a particle once formed ice and then experiences subsaturated conditions. The H₂O molecules bounded at the surface may not fully evaporate, leaving behind active sites, which belong to the same crystal system as ice. Some active sites may survive under subsaturated conditions. If a pre-activated particle experiences supersaturation again, it may nucleate ice earlier than the previously unactivated particle under otherwise similar conditions. However, when the pre-activated particle is exposed to very dry conditions for a sufficiently long time, the active sites may vanish, and with them the ability to nucleate ice efficiently may also vanish.

In order to consider freezing processes in meso- and large scale models, different parameterisation approaches have been developed (e. g., [5, 6, 18, 21, 55, 56, 57, 59, 74, 75, 84, 108]).

on the substrate all affect heterogeneous nucleation. However, the relative importance of these factors is unknown. What is the mechanism underlying evaporation nucleation? Observations revealed ice nucleation in solution droplets as they evaporated. Does this happen at a critical solute concentration? It is more important for some solutes than others? Under which atmospheric conditions does it occur? In their conclusions, [12] emphasised that the parameterisation of heterogeneous freezing is much more difficult than that of homogeneous freezing because the factors controlling heterogeneous processes are not well known, both experimentally and theoretically. Theoretically frameworks are necessary to separate important factors for the ice-nucleation activity from the unimportant ones, to distinguish effects altering the degree of nucleation ability etc.

25.2 State-of-the-Art Ice Nucleation Modeling

25.2.1 Microscopic Perspective on Crystal Nucleation

According to [89], crystallisation of a fluid is a complex process, during which different process parameters will change simultaneously:

- Crystals have periodic positional order and can be distinguished from a liquid by its density. According to the author, the crystal density has finite Fourier coefficients at wave vectors, that correspond to reciprocal lattice vectors of a solid.
- During crystallisation, the density of the fluid changes. In molecular-scale crystals both orientational and translational order appears.
- In an alloy, the composition changes during crystallisation.

The crystallisation process can be characterised in terms of specific order parameters, allowing the differentiation of the crystalline from the liquid phase. [89] emphasised, that a first-time appearing small crystallite may differ sharply from the eventual bulk equilibrium phase with respect to its density, its composition, and even its structure⁵. Crystallisation is a first-order phase transition, which requires the overcoming of an energy barrier to occur: (i) In order to eliminate their surface free energies, small crystallites tend to disappear even in supercooled fluids or supersaturated solutions. (ii) The newly emerging crystal can only further grow when a critical size is reached. In this case, crystal growth by the driving force becomes energetically favourable over crystal disappearance. The determination of the properties of the critical nucleus, such as size, free energy, and kinetics of formation are the subject of nucleation theory [89].

- Classical nucleation theory (CNT) is based on the following assumptions:
- Even very small crystallites have all the properties at the centre of their bulk crystal.
- These crystallites differ from their bulk phases only in their relatively large surface-to-volume ratio [89].

According to [89], CNT is limited because it cannot identify or be used to study the different pathways to crystallisation when the various order parameters do not all change at the same time. However, while CNT assumes bulk behaviour and sharp interfaces between crystal and melt or crystal and solution, the opposite extreme is true for computer simulation via molecular dynamics or Monte Carlo techniques [89]. The latter were argued to provide atom-level details, but sometimes at the cost of lengthy calculations or limited physical insight. In the subsequent sections, we will discuss both aspects in detail and will take up the cudgels on behalf of classical thermodynamics and CNT owing to their rich yield and predictive power for atmospheric applications.

25.2.2 Basic Concepts of Ice Nucleation

Pruppacher et al. ([92], Section 9.2.5; see also [16]) distinguished between two conceptually different hypotheses to explain the heterogeneous freezing behaviour of a population of supercooled water drops:

• Stochastic hypothesis: This hypothesis is based on the assumption, that at a given temperature all equal-sized ice embryos, which are formed within equal-sized supercooled water drops, have the same probability to reach the size of a critical embryo or germ as a result of random fluctuations in rates of attachment and detachment of water molecules. The formation of ice germs by such fluctuations is considered to proceed more effectively in the presence of foreign particles (e. g., cloud condensation nuclei). Even if the presence of such particles in water will enhance the efficiency of random nucleation, the particles will not affect the freezing process by their singular freezing characteristics (thus, freezing remains a stochastic process). Under these conditions, the freezing behaviour of a population of water drops can be described as follows. Let N_0 denote the total number of isolated water drops with equal drop volume V_d , N_u the number of unfrozen, and N_f the number of frozen drops. The number of ice germs, $dN_{i,g}$, formed during the time interval dt in the volume N_uV_d reads ([92], see p. 211 therein)⁶:

$$dN_{i,g} = N_{i,g}(t+dt) - N_{i,g}(t) = N_u V_d J(T) dt .$$
(25.1)

⁵For example, ([89] and references therein) referred to an entirely different symmetry of a small crystallite in comparison to the bulk crystal (e. g., body-centred cubic instead of face-centred cubic). Furthermore, the author noted, that the subsequent change to the new structure may take place only during later stages of growth.

⁶In Eq. (25.1), $V_d J(T)$ plays the role of a rate of freezing. The time interval dt is considered to be so small, that $V_d J(T) dt = dN_{i,g}/N_u$ is a probability of formation of one critical ice embryo per drop time dt, which will be less than unity.

25.2 State-of-the-Art Ice Nucleation Modeling

Here, J(T) denotes the ice nucleation rate, given in units of $[m^{-3}s^{-1}]$. Assuming the total number of drops being constant, one obtains:

$$N_0 = N_{\rm u} + N_{\rm f} = \text{const.} \quad \rightsquigarrow \quad \mathrm{d}N_{\rm u} = -\mathrm{d}N_{\rm f} \;. \tag{25.2}$$

The freezing of a drop is considered to be a result of only one nucleation event per $drop^7$. Therewith, one obtains the following differential equation for the number of unfrozen drops:

$$dN_{i,g} = dN_f = -dN_u \quad \rightsquigarrow \quad -\frac{1}{N_u} \frac{dN_u}{dt} = V_d J(T) .$$
(25.3)

Using the initial condition $N_{\rm u}(t=0)=N_0$ one arrives at the following time-dependence of the number of unfrozen drops:

$$\ln \frac{N_{\rm u}(t)}{N_0} = -V_{\rm d} J(T)t .$$
(25.4)

It appears, that according to the latter equation, the number of unfrozen drops decreases with time. The stochastic nature of this concept is reflected by the employment of the nucleation rate, which is predicted by the classical nucleation theory (CNT). This equation is valid for both the homogeneous and heterogeneous ice nucleation rates (the latter requiring the knowledge of specific IN parameters such as activation energies and contact angles).

• Singular or "deterministic" hypothesis: Here, nucleation is considered to be fully controlled by the singular freezing characteristics of aerosol particles incorporated in drops, such as impurities or active sites on the surface of ice nuclei, where each site has a characteristic temperature (for freezing nucleation) or saturation ratio (for deposition nucleation). Both "threshold temperature" and "threshold saturation ratio" (or degree of supersaturation with respect to ice) are basic notions of this nucleation hypothesis. According to ([92], see p. 350-351 therein), the singular hypothesis implies, that the number of ice germs formed in a drop volume at a certain temperature (or supercooling) is given by the number of aerosol particles $n_p(T)$ inside the drop, which become active as IN between $T_0=273.15$ K and T:

$$\mathrm{d}n_{\mathrm{p}}(T) = J(T)\,\mathrm{d}t \qquad \rightsquigarrow \qquad n_{\mathrm{p}}(T) = \int_{t_0}^t J(T)\,\mathrm{d}t \;.$$

For $N_{\rm u}(T_0) = N_0$ and $n_{\rm p}(T_0) = 0$ one obtains:

$$-\frac{\mathrm{d}N_{\mathrm{u}}}{N_{\mathrm{u}}} = V_{\mathrm{d}} \,\mathrm{d}n_{\mathrm{p}}(T) \qquad \rightsquigarrow \qquad \ln \frac{N_{\mathrm{u}}(T)}{N_{0}} = -V_{\mathrm{d}}n_{\mathrm{p}}(T) \,. \tag{25.5}$$

It appears, that the number of unfrozen drops will not change with time for a given supercooling, i. e., new nucleation events will not occur if the environmental conditions remain the same. IN, which nucleate at different temperatures (or supersaturation) are assumed to possess different surface characteristics or sizes. Identical IN must nucleate all together at the same ambient conditions.

For more detailed discussion of both stochastic and singular hypotheses, the reader is referred to [92].

According to [16], the singular hypothesis or singular-like "threshold parameterisation concepts" are widely adopted in many meteorological cloud models. Such approaches are formulated in terms of the number of ice particles, generated through deposition or condensation-freezing nucleation, as a function of either temperature or ice supersaturation, or a combination of the two variables ([16] and references therein). Although easy to use, [16] identified the following deficiencies of such threshold approaches:

- 1. The underlying formulas are mostly empirical and do not consider the temporal and spatial variations of atmospheric IN.
- 2. By treating the nucleation process in a diagnostic way, such schemes cannot describe the situations, when IN actually have been consumed earlier even in the same cloud, thus they tend to over-predict the number of ice particles. It is impossible to recount the IN, when ice particles formed on them evaporate.

 $^{^{7}}$ ([92], see p. 211 therein) argued, that ice formation is the result of only one nucleation event per drop, since the growth velocity of ice is very large at the supercooling where ice nucleation takes place. The authors further argued, that the first emerging germ can grow quickly enough to convert the drop into ice before any other, secondary germ is formed. Furthermore, during germ growth, latent heat is released, which will immediately lead to an increase of the drop water temperature. This temperature enhancement will drastically reduce the nucleation rate of other germs, and thus protect the primary germ from secondary ones.

3. These empirical formula obviously lose track of individual IN, thus are not suitable for evaluating IN of different origins or physical properties such as size.

Employing the stochastic concept (based on CNT), [16] proposed a parameterisation of the heterogeneous ice nucleation rate using contact angle and activation energy derived from laboratory data⁸.

25.2.3 History

In the literature many empirical parameterisations of ice nucleation have been published, and several theoretical derivations were described in the textbooks. The empirical parameterisations suggested number concentrations of ice crystals, $N_i(T)$, either as a function of temperature T [19, 20, 36, 92], or as a function of ice supersaturation S_i , $N_i(S_i)$ [48, 84]. The theory based on Thomson's equation [111] for the critical radius $R_c(T)$ and critical formation energy $\Delta F_c(T)$ provided only the T-dependence. There were attempts to use the "old CNT" (restricted to the T-dependence) in cloud models, but it did not give realistic N_i values. Especially, CNT was found to overestimate N_i at low temperatures in the upper troposphere by several orders of magnitude [92]. Therefore, CNT was rejected as a tool for cloud and climate modelling, and the models used for many years various empirical parameterisations despite of their deficiencies.

When investigations of cirrus in the upper troposphere and of polar stratospheric clouds (PSCs) were intensified at the end of 1980's, empirical methods were rejected as well, because predicted N_i values were found to be by many orders of magnitude higher than observed ones [96, 97]. The situation appeared to be in a dead-end street, especially as no methods were available to describe heterogeneous freezing at all. Therefore, the hypothesis of homogeneous freezing of haze particles was adopted and promoted in the literature [45, 96, 97]. The papers of [60, 61, 62], hereafter called KC theory, opened a loophole from this situation. To the best of our knowledge, the stochastic KC approach is the physically most sophisticated model for the prediction of nucleation rate coefficients of both homogeneous and heterogeneous freezing, that is currently available for atmospheric applications.

The KC theory is based on CNT, but with essential extensions. Until the end of 1990's, CNT applications to freezing (at least as known in cloud and climate physics) did not provide simultaneous dependencies on T and S_i . While [64, 65] promoted CNT for application to homogeneous ice nucleation, [60, 61, 62] promoted CNT for application to heterogeneous ice nucleation by advancing an important step forward. The authors derived equations for both the critical radius and the critical cluster formation energy as functions of five parameters: temperature T, water saturation ratio $S_{\rm w}$, finite radius of a freezing drop, misfit strain, and external pressure. The nucleation rate expression is used in the classical form, but became also a function of all these five variables [61, 62]. The most essential and practical extension of CNT by Khvorostyanov and Curry for modelling applications was the consideration of $S_{\rm w}$ along with T. Droplet activation on aerosols (CCN) is regulated by a negative feedback mechanism involving the water supersaturation: activated drops absorb water vapour, thus decreasing the water supersaturation, and subsequently stop drop activation at some limits of the droplet concentration $N_{\rm d}$. Prior to the KC theory, no similar negative feedback mechanism was considered in ice nucleation by freezing. The empirical parameterisations proposed by [48] and [84] described the dependence on humidity, but without theoretical foundation. Apart from that, the approaches of [48] and [84] did not describe the strong T-dependence observed in ice nucleation. The KC theory provided both T- and $S_{\rm w}$ -dependencies simultaneously for heterogeneous nucleation, as was previously realised for homogeneous freezing nucleation in [64]. This enhancement introduced a strong negative feedback in ice nucleation, which is much stronger than for drop nucleation (exponential dependence in ice nucleation vs power law in drop nucleation), thereby decreasing the number concentration of nucleated ice crystals, N_i, by several orders of magnitude as compared to the analysis without consideration of $S_{\rm w}$. Therewith, predicted $N_{\rm i}$ values became comparable to measured ones.

The droplet concentration in clouds is typically a few hundred per cubic centimeter, comparable to CCN concentrations, while ice crystal concentrations are several orders of magnitude smaller (typically from a few to a few tens in moderately cold clouds and to a few hundred per liter in colder cirrus clouds, which is only a tiny fraction of IN). The KC theory allowed the explanation of this phenomenon by the prediction of a much stronger exponential negative

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⁸However, the data obtained in the approach of [16] seem to be somewhat uncertain because the authors solved a system of equations with the number of unknown parameters (activation energy, contact parameter, surface tension, etc.) being greater than the number of equations (ln J). In mathematical terms, this leads to an "incorrectly formulated or underdefined problem" (sometimes arising, e. g., in remote sensing and reverse problems). ([16], see p. 7445 therein) correspondingly emphasised, "that the contact angle and the activation energy derived in this study should not be interpreted as true physical terms, when one knows so little about the mechanism of ice nucleation and acknowledges, that the classical theory is tentative." According to the authors, contact angle and activation energy derived in their study should be regarded as "apparent" thermodynamic parameters. Furthermore, [16] described their fitting for the immersion freezing mode, using equations which are valid only at a relative humidity of RH_w=100% (S_w=1), but not at small subsaturations as in the deliquescence-heterogeneous-freezing (DHF) mode. Thus, their data cannot be used to describe freezing at water vapour subsaturation.

feedback in ice nucleation than the one provided by the power law in drop nucleation. Thus, KC theory represents an important step forward within the framework of CNT: the KC formulation of CNT provided a practical tool for multiscale modelling of clouds, weather, and climate, allowing one the simulation of ice crystal concentrations in realistic orders of magnitude [18, 63, 65, 66, 67].

25.2.4 Khvorostyanov–Curry Theory of Heterogeneous Freezing

The KC theory considers steady-state nucleation and is based on the employment of the capillarity approximation (CPA). The catalysing substrate is a deliquescent mixed CCN⁹. Equations for the critical radius and activation energy show, that nucleation becomes possible due to the catalysing effect of insoluble substrate within the CCN. This catalysing effect counteracts the freezing point depression by the solution effect. Surface catalysis significantly lowers the energy barrier for freezing and permits freezing at a smaller supercooling than that for homogeneous freezing. The KC theory predicts, that ice nucleation may occur with noticeable and significant rate on the surface of the insoluble substrate embedded in a solution drop, which has formed on a dry CCN.

The KC theory is based on the following premises:

- The same deliquescent hygroscopic aerosol (haze particles) that serves as CCN may serve also as IN under freezing conditions.
- In contrast to the homogeneous nucleation case, these haze particles contain an insoluble substrate.
- In contrast to drop activation, where the soluble fraction determines the activity of a nucleus, heterogeneous ice nucleation is determined also by the insoluble fraction of CCN, which is a nucleation catalyser.
- Heterogeneous ice nucleation may occur on these CCN-IN (this process may take place both at water supersaturations and subsaturations, but above the deliquescent threshold of the soluble fraction).

The KC theory permits ice nucleation under conditions of subsaturation with respect to liquid water, whereby deliquescence of mixed CCN can form an ice particle at supercooled temperatures. The authors called their mechanism "deliquescent-heterogeneous freezing" (DHF) of mixed CCN, which contains homogeneous nucleation as a special case. The nucleating system is approximated by a spherical four-phases system consisting of (a) an ambient vapour serving as the primordial phase (I), (b) a supercooled solution serving as the maternal phase (II) for nucleation, (c) an ice germ representing the embryonic phase (III), and (d) a foreign substrate (CCN-IN) serving as the nucleation catalyser (IV).

The ice germ of radius $R_c^{(III)}$ (critical radius) forms on the surface of a curved insoluble substrate with radius $R_N = R^{(IV)}$ inside an aqueous solution drop with radius $R^{(II)}$. At the beginning, before deliquescence sets in, the original CCN is dry and has the radius $R_{N,0}$. The ice germ is in thermodynamic equilibrium with the parent supercooled solution (internal equilibrium), and the supercooled solution is in equilibrium with the environmental moist air (external equilibrium). Both conditions define the critical ice germ radius $R_c^{(III)}$. For such a system CNT delivers expressions for the determination of the rate coefficient of heterogeneous germ formation in a supercooled droplet of water or an aqueous solution.

The rate of heterogeneous germ formation in a supercooled droplet of water or solution, $J_{\rm fr}$ (per second and particle), reads ([61, Eq. (2.1) therein)

$$J_{\rm fr}(T, R_{\rm N}) = rC_{\rm het} \exp\left(-\frac{\Delta F_{\rm act}}{k_{\rm B}T} - \frac{\Delta F_{\rm c}}{k_{\rm B}T}\right) ,$$

$$C_{\rm het} \approx \frac{k_{\rm B}T}{h} c_{\rm 1s} \cdot 4\pi R_{\rm N}^2 , \qquad c_{\rm 1s} \approx 10^{15} \,{\rm cm}^{-2} .$$
(25.6)

Here, $k_{\rm B}$ and h are the Boltzmann and Planck constants, T is the temperature in units of [K], $\Delta F_{\rm act}$ is the activation energy at the solution/ice interface, $\Delta F_{\rm c}$ is the critical energy of germ formation, $C_{\rm het}$ is the normalisation function, $R_{\rm N}$ the radius of an insoluble fraction of an aerosol particle (ice nuclei, IN), and $c_{\rm 1s}$ is the concentration of water molecules adsorbed on the unit area of a surface.

⁹The authors generalised the concept of homogeneous freezing of fully dissolved CCN to the case of mixed CCN freezing, extending the concept to temperatures as high as a few degrees below 0° C.

Based on the entropy equation for the system at equilibrium, the KC theory predicts an expression for the critical radius of the ice germ, $R_c^{(III)}$ ([61], Eqs. (2.2)-(2.5) therein):

$$\begin{aligned} R_{c}^{(\text{III})} &= \frac{2\sigma^{(\text{IIII})}}{\rho_{1,0}^{(\text{III})} \left(\frac{\overline{\mathcal{L}}_{1,0}^{(\text{III}\to\text{III})}}{M_{1}}\right) \ln\left(\frac{T_{0}}{T}\right) + \frac{R_{u}T\rho_{1,0}^{(\text{III})}}{M_{1}}H_{cs} - C_{\varepsilon}\varepsilon^{2} - \frac{2\sigma^{(\text{I/III})}}{R^{(\text{III})}} ,\\ H_{cs} &= \frac{A_{K}}{R^{(\text{III})}} - \frac{B_{R}}{(R^{(\text{III})})^{3} - R_{N,0}^{3}} ,\\ A_{K} &= \frac{2\sigma^{(\text{I/III})}M_{1}}{\rho_{1,0}^{(\text{III})}R_{u}T} , \quad B_{R} = \frac{n_{\text{ion}}\Phi_{\text{osm}}\chi_{\text{m},2}^{(\text{IV})}M_{1}\rho_{N,0}R_{N,0}^{3}}{M_{2}\rho_{1,0}^{(\text{III})}} ,\\ \overline{\mathcal{L}}_{1,0}^{(\text{III}\to\text{III})} &= \int_{T}^{T_{0}} \frac{\mathcal{L}_{1,0}^{(\text{III}\to\text{III})}(T)/T}{\ln(T_{0}/T)} \, \mathrm{d}T . \end{aligned}$$

In Eq. (25.7), R_u denotes the universal gas constant, $T_0=273.15$ K the triple point, $\mathcal{L}_{1,0}^{(\text{III}\to\text{II})}$ is the molar latent heat of melting (in units of $[\text{J}\,\text{mol}^{-1}]$), $\sigma^{(\text{I/II})}$ and $\sigma^{(\text{II/III})}$ are the surface tensions at the vapour/liquid and liquid/solid interfaces, $\varrho_{1,0}^{(\text{III})}$, $\varrho_{1,0}^{(\text{III})}$, and $\varrho_{\text{N},0}$ are the mass densities of water, ice, and of the original dry CCN before deliquescence, M_1 and M_2 are the molar masses of water (solvent) and of the soluble material of the nucleus (solute), n_{ion} is the total number of ions, into which a solute molecule dissociates in the pure solvent, Φ_{osm} is the osmotic coefficient of the solute in solution, and $\chi_{m,2}^{(\text{IV})}$ is the mass fraction of the solute in the original dry CCN. The overbar of $\mathcal{L}_{1,0}^{(\text{IIII}\to\text{III})}$ denotes the effective average molar latent heat of melting. In the denominator of the $R_c^{(\text{III})}$ expression there appears an additional term (not considered in previous approaches), which is associated with the elastic strain ε produced in the ice embryo by the insoluble substrate. The authors considered $\varepsilon \approx 1\% -5\%$. The parameter C_{ε} has the dimension of pressure and amounts $C_{\varepsilon} \approx 1.7 \cdot 10^{16}$ J m⁻³ (for a detailed discussion see the online supplementary material). Equation (25.7) is valid for an ice germ, that may form inside both non-activated CCN and a cloud drop.

Depending on the vapour saturation ratio with respect to liquid water, $S^{(I/II)}$, the following three cases can occur:

- 1. freezing of deliquescent CCN at subsaturated conditions relative to water at $S^{(I/II)} < 1$;
- 2. activation of cloud drops at the condensation stage (at supersaturated conditions relative to water) at $S^{(I/II)} \ge 1$;
- 3. freezing at $S^{(I/II)} > 1$ of residual interstitial CCN that are left after drop formation (mostly at cloud temperatures -10° C to -20° C).

Processes 1 and 3 correspond to the deliquescence-freezing (or condensation freezing) mode, and process 2 corresponds to the immersion-freezing mode. For the deliquescence-freezing mode, [61] employed the Köhler equation and derived a simplified expression of Eq. (25.7) for the critical ice germ radius:

$$R_{c}^{(\text{III})} = \frac{2\sigma^{(\text{II}/\text{III})}}{\rho_{1,0}^{(\text{III})} \left(\frac{\overline{\mathcal{L}}_{1,0}^{(\text{III}\to\text{III})}}{M_{1}}\right) \left[\ln\left(\frac{T_{0}}{T}\left(S^{(\text{I}/\text{II})}\right)^{G(T)}\right) - \frac{R_{0}}{R^{(\text{III})}}\right] - C_{\varepsilon}\varepsilon^{2} ,$$

$$H_{sc} = \frac{A_{K}}{R^{(\text{III})}} - \frac{B_{R}}{(R^{(\text{III})})^{3} - R_{N,0}^{3}} = \ln S^{(\text{I}/\text{II})} ,$$

$$G(T) = \frac{R_{u}T}{\mathcal{L}_{1,0}^{(\text{III}\to\text{III})}} , \qquad R_{0} = \frac{2\sigma^{(\text{I}/\text{II})}M_{1}}{\rho_{1,0}^{(\text{III}\to\text{III})}} .$$
(25.8)

Here, G(T) is a dimensionless parameter, and R_0 a scaling radius. Given the critical radius from Eq. (25.8), the critical

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energy ΔF_c of germ formation can be determined as follows ([61], Eqs. (2.9)-(2.10) therein)

$$\Delta F_{\rm c} = \frac{4}{3} \pi \sigma^{(\rm II/III)} \left(R_{\rm c}^{(\rm II/III)} \right)^2 \Omega_F(m, x) - \alpha_{\rm AS} R_{\rm N}^2 (1 - m)$$

$$\Omega_F(m, x) = \frac{1}{2} \left[1 + \alpha^3 + x^3 \left(2 - 3\beta + \beta^3 \right) + 3m \, x^2 \left(\beta - 1 \right) \right] ,$$

$$\alpha = \frac{1 - m \, x}{\varphi(m, x)} , \qquad \beta = \frac{x - m}{\varphi(m, x)} , \qquad \varphi = (1 + x^2 - 2m \, x)^{1/2} ,$$

$$m = \cos \theta = \frac{\sigma^{(\rm II/IV)} - \sigma^{(\rm III/IV)}}{\sigma^{(\rm II/III)}} , \qquad x = \frac{R_{\rm N}}{R^{(\rm III)}} .$$
(25.9)

In Eq. (25.9), $\Omega_F(m, x)$ is a geometric shape factor describing the catalysing effect of the CCN geometry as a function of the contact or wettability parameter m at the liquid/solid interface (with θ denoting the contact angle) and the dimensionless length x. The parameter m is a function of the surface tensions at the solution/substrate, germ/substrate, and solution/germ interfaces $\sigma^{(II/IV)}$, $\sigma^{(III/IV)}$, and $\sigma^{(II/III)}$, respectively. The term containing the parameter $\alpha_{AS}=0-4\pi$ arises from the consideration of "active sites" at the CCN-IN surface. In the area of active sites, $A_{AS} = \alpha_{AS}R_N^2$, the contact parameters amounts m=1.

To close their model equations, several crucial nucleation parameters have to be estimated (see Table 25.1).



Figure 25.1: $T-S^{(I/II)}$ diagram of the critical radius $R_c^{(III)}/[10^{-7} \text{ cm}]$ (in the plot denoted as r_{cr}) for the freezing mode. The critical radius is displayed as a function of supercooling $\Delta T = T - T_0$ and saturation ratio over water $S^{(I/II)}$ (here denoted as S_w). The $R_c^{(III)}$ values are the same as for homogeneous nucleation (taken from [61], Fig. 1 therein).

For illustration of the deliveries of the KC theory, here we want to restrict our review to some selected results. Figure 25.1 shows the critical radius $R_c^{(\text{III})}$ (isolines) for the DHF mode as a 2-D function of temperature T and saturation ratio over water $S^{(I/\text{III})}$ (hereafter plots like this are called $T-S^{(I/\text{II})}$ diagrams). Since $R_c^{(\text{III})}$ does not depend on $\Omega_F(m, x)$, $R_c^{(\text{III})}$ is identical to the values for homogeneous nucleation. The isolines of $R_c^{(\text{III})}$ run from the lower right-hand corner to the upper left-hand corner, since the associated temperature increase of $\Delta T=50 \text{ K}$ is approximately compensated by the humidity increase of $\Delta \text{RH}_w=50 \%$. Values of the critical radius range from $R_c^{(\text{III})} \approx 10^{-7} \text{ cm}$ at $\vartheta \approx -55^{\circ}\text{C}$ and $S^{(\text{I/II})} \approx 1.3$ to $R_c^{(\text{III})} \approx 10^{-6} \text{ cm}$ at higher T or lower $S^{(\text{I/II})}$. The denominator in the $R_c^{(\text{III})}$ expression given by Eq. (25.8) controls the domain of definition of $R_c^{(\text{III})}$. If the denominator is positive

$\begin{array}{l} \mathrm{d} \ \mathrm{Klett} \ (1997), \mathrm{Khvorostyanov} \ \mathrm{and} \ \mathrm{Curry} \ (2004b): \\ \hline 1 \\ = c_{\mathrm{L}} \left(\frac{T}{[\mathrm{K}]} \right) \left[\mathrm{tanh} \left(\frac{T/[\mathrm{K}] - T_{1}}{T_{2}} \right) + 1.6 \right] \\ \frac{1}{c_{2}} = 40 \mathrm{K}, c_{\mathrm{L}} = 8.82, T \geq 160 \mathrm{K} \\ \mathrm{d} \ \mathrm{Klett} \ (1977) \\ - \sigma(\mathrm{m/rV}) \\ \overline{\mathrm{m/rV}} \ , \ m = 0.5 \\ \overline{\mathrm{m/rV}} \ , \ m = 0.5 \\ 0.1 \ \mathrm{effery} \ \mathrm{and} \ \mathrm{Austin} \ (1997): \\ M_{\mathrm{A}} = 0.5 \\ 0.1 \ \mathrm{effery} \ \mathrm{and} \ \mathrm{Austin} \ (1997) \\ M_{\mathrm{A}} = 0.5 \\ 0.1 \ \mathrm{effery} \ \mathrm{and} \ \mathrm{Austin} \ (1997): \\ M_{\mathrm{A}} = 0.5 \\ M_{\mathrm{A}} = $
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D); leftery and Austin (1997): $L_{M}^{(III) \to (II)} \left(\rho_{110}^{(III)} / M_{1} \right)^{2/3} N_{A}^{-1/3} - k_{\sigma} T$ $L_{M}^{(III) \to (II)} \left(\rho_{100}^{(III)} / M_{1} \right)^{2/3} N_{A}^{-1/3} - k_{\sigma} T$ $I = 18 \text{ geol}(-1, k_{\sigma} = 9 \times 10^{-5} \text{ J} \text{ m}^{-2} \text{ K}^{-1}$ $e^{(a),(b); \sigma^{(II)(II)}} = \left \sigma^{(II)} - \sigma^{(I)(II)} \right $ $e^{(a),(b); \sigma^{(II)(II)}} = \left \sigma^{(I)(II)} - \sigma^{(I)(II)} \right $ d Klett (1977), Khvorstyanov and Curry (2004b): f = f = f = f = f = f = f = f = f = f =
$\begin{split} L_{\mathrm{M}}^{\mathrm{(III)}\rightarrow(\mathrm{III)}}\left(\varrho_{1,0}^{\mathrm{(III)}}/M_{\mathrm{I}}\right)^{2/3}N_{\mathrm{A}}^{-1/3}-k_{\sigma}T\\ 1=\mathrm{B}\mathrm{genol}^{-1},k_{\sigma}=9\times10^{-5}\mathrm{Jm}^{-2}\mathrm{K}^{-1}\\ e^{(a)}(b);\rho^{(IIIII)}=\left \sigma^{(III)}_{\mathrm{(III)}}-\sigma^{(IIII)}_{\mathrm{(III)}}\right \\ \mathrm{d}\mathrm{Klet}(197),\mathrm{Khvorstyanov}\mathrm{and}\mathrm{Curry}(2004b);\\ \mathrm{d}\mathrm{Klet}(197),\mathrm{Khvorstyanov}\mathrm{and}\mathrm{Curry}(2004b);\\ \mathrm{d}\mathrm{Klet}(197),\mathrm{Khvorstyanov}\mathrm{and}\mathrm{Curry}(2004b); \end{split}$
$\begin{split} & 1 = 18 \text{ gmol}^{-1}, k_{\sigma} = 9 \times 10^{-5} \mathrm{Jm}^{-2} \mathrm{K}^{-1} \\ e^{(\alpha),(b)}; \sigma^{(11/11)} = \left \sigma^{(1/11)} - \sigma^{(1/11)} \right \\ & \text{v and Curry (2004b)}; \sigma^{(11/11)} \approx \sigma^{(1/111)}/4 \\ & \text{d Klett (1977), Khvorostyanov and Curry (2004b)}; \end{split}$
$\rho^{(m)}(x)$; $\sigma^{(m)}(x) = \left[\sigma^{(m)} - \sigma^{(m)}\right]$ v and Curry (2004b); $\sigma^{(II/III)} \approx \sigma^{(I/III)}/4$ d Klett (1997), Khvorostyanov and Curry (2004b): $\langle T \rangle = \langle m \rangle = \langle m \rangle^{-3}$
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$u_1 + u_2 \left([\mathbf{K}] \right) + u_3 \left([\mathbf{N}] \right) + u_4 \left([\mathbf{K}] \right) \left([\mathbf{N}] \right) + u_3 \left([\mathbf{N}] \right) + u_6 \left([\mathbf{N}] \right) $
ge source concentration by weight
$a_{2} = -0.249, a_{3} = -0.97, a_{4} = 3.4 \cdot 10^{-2}, a_{5} = 0, a_{6} = -3.5 \cdot 10^{-5}$
nuric-acid solution:
$a_2 = -0.225, a_3 = -0.98, a_4 = 3.395 \cdot 10^{-2}, a_5 = -5.1 \cdot 10^{-5}, a_6 = -1.24 \cdot 10^{-4}$
al. (1997): $\sigma^{(I/III)} = 0.105 \text{J} \text{m}^{-2}$
): $\alpha_{AS} = 0 - 4\pi$
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 Table 25.1: Closure parameters in the deliquescent-heterogeneous freezing model of [61].

definite (corresponding to positive critical radii), nucleation is allowed to occur, vice versa, the region of vanishing or negative definiteness of the denominator (corresponding to infinite and negative critical radii) defines the region

⁽⁶⁾ Alternatively, one might employ the semi-empirical *Girifalco-Good-Fowkes-Young equation* for two mutually entirely immiscible phase, (β) and (γ), interacting only through additive dispersion forces, whose constants obey a geometric mean law (Adamson and Gast 1997, Eq. (X-45) and references therein):

 $\sigma^{(\beta/\gamma)} = \sigma^{(\alpha/\beta)} + \sigma^{(\alpha/\gamma)} - 2 \Phi \sqrt{\sigma^{(\alpha/\beta)} \sigma^{(\alpha/\gamma)}} \, .$

The parameter Φ should be unity if molecular diameters obey a geometric mean law and is often omitted.



Figure 25.2: Logarithm of the critical energy $\Delta F_c/[erg]$ (in the plot denoted as $\log_{10} F_{cr}$) for the freezing mode as a function of supercooling $\Delta T = T - T_0$ and saturation ratio over water $S^{(I/II)}$ (here denoted as S_w), calculated with a contact parameter of m=0.5 and a substrate radius of $R_N=0.26 \,\mu\text{m}$. The unlabeled (uneven) isoline denotes the boundary of the region of prohibited nucleation according to Fig. 25.1 (taken from [61], Fig. 3 therein).

of prohibited nucleation in the $T-S^{(I/II)}$ diagram. Figure 25.2 displays the 2-D field of the critical energy ΔF_c on the $T-S^{(I/II)}$ diagram, corresponding to $R_c^{(III)} \left(T, S^{(I/II)}\right)$. The regime, where nucleation is prohibited to occur, is located in the lower left-hand part of the diagram. This region corresponds to the region with $R_c^{(III)} \rightarrow \infty$ and $R_c^{(III)} < 0$ depicted in Fig. 25.1. Figure 25.3 shows the logarithm of the freezing nucleation rate per particle $J_{\rm fr}/[{\rm s}^{-1}]$ according to Eq. (25.6), displayed in the $T-S^{(I/II)}$ diagram for a contact parameter of m=0.5 and a substrate radius of $R_{\rm N}=0.26 \,\mu{\rm m}$. The freezing rate is a highly non-linear function of both temperature and water vapour saturation ratio. The figure reveals very high gradients of the freezing rate, which varies by 10–15 orders of magnitude over the temperature range of 5 K or a relative humidity range of 5 %. The bold isoline "0" corresponds to a freezing rate of $J_{\rm fr}=1 \,{\rm s}^{-1}$. It indicates the T and $S^{(I/II)}$ values, at which the freezing becomes significant. Figure 25.4 illustrates the temperature dependence of $J_{\rm fr}/[{\rm s}^{-1}]$ for various relative humidities. This plot demonstrates, that even relatively small variations in humidity and its variation with temperature results in a significant change of the freezing rate.

For a detailed discussion of the predictive power of the KC theory the reader is referred to

- Ref. [61, 63] for deliquescent-heterogeneous freezing,
- to [62] for volume heterogeneous vs. surface quasi-heterogeneous freezing, for surface melting, and for freezing and melting point depressions, and
- to [18, 63, 65, 66, 67] for atmospheric multiscale modelling applications.

For the details of the KC theory the reader is referred to the supplementary material.



Figure 25.3: Logarithm of the freezing nucleation rate $J_{\rm fr}/[{\rm s}^{-1}]$ as a function of two variables: supercooling $\Delta T = T - T_0$ and saturation ratio over water $S_{\rm w} = S^{(1/11)}$ for a contact parameter of m = 0.5 and a substrate radius of $R_{\rm N} = 0.26 \,\mu{\rm m}$. The bold isoline "0" corresponds to a freezing rate of $J_{\rm fr} = 1 \,{\rm s}^{-1}$ (taken from [61], Fig. 5 therein).

25.3 Starting Points for Further Studies

25.3.1 General Remarks

The KC theory is a powerful tool for the interpretation of both laboratory and field experiments on water freezing as well as for application in sophisticated models of cloud microphysics (moment-based and sectional models) within the framework of weather and climate prediction. Starting point for refinements may concern (i) the determination of the required input parameters as well as different thermodynamic and kinetic functions used in the theory, and (ii) details of the mechanism of heterogeneous freezing.

More information is needed on the CCN-IN properties (with respect to both zeroth- and higher-order statistical
moments) such as number concentration, particle size distribution, insoluble aerosol fraction, contact parameter,
elastic strain parameter, and active site parameter. Several of these properties may strongly depend on the specific
aerosol fraction. A characterisation of ambient CCN-IN with respect to nucleation-relevant physical parameters
is required¹⁰.

¹⁰Refined experimental data are a real problem, including surface tensions and melting heat for solutions, measurements of crystal concentrations under various conditions along with simultaneous measurements of the aerosol parameters: size spectra, chemical composition. There are still great uncertainties in measurements of the number concentration of ice crystals, N_i . As reviewed in [84], the earlier measurements of nucleated crystals or IN with static filter techniques prior to the 1980's-1990's gave the values of N_i by 1–2 orders of magnitude smaller than subsequent experiments with the Continuous Flow Diffusion Chambers (CFDC). The old measurements (still before CFDC) yielded IN concentrations much lower than ice crystal concentrations in clouds. This experience caused the development of several hypotheses of crystal multiplications in clouds. Newer measurements with CFDC in 1980's-1990's gave higher IN concentrations and allowed to decrease partially the need in hypotheses on ice multiplication. Yet, the measured in the chambers IN concentrations are lower than crystal concentrations in clouds. The reason is that CFDC also may severely underestimate N_i because the time of aerosol processing in a CFDC is 7–15 s only (supported by a few experiment references), but crystal nucleation usually takes much longer times, from a few tens seconds to a few tens minutes, as cloud models show [61, 73]. Therefore, the current experimental techniques do not allow yet to perform a full reliable verification of the theories, and development



Figure 25.4: Freezing nucleation rate $J_{\rm fr}/[{\rm s}^{-1}]$ for the CCN freezing mode as a function of temperature with the contact parameter of m=0.5 for different saturation ratios over water $S_{\rm w}=S^{(\rm I/II)}$: 1.05 (crosses), 1.001 (circles), 0.95 (diamonds), 0.90 (triangles). The threshold of homogeneous freezing of drops with $R^{(\rm II)}=0.2-5\,\mu m$ at $\vartheta=-42^{\circ}C\ldots-38^{\circ}C$ is denoted by an ellipse (taken from [61, Fig. 6 therein).

- Refined measurements and/or the evaluation of non-classical methods are required to derive enhanced parameterisations of the fundamental thermodynamic parameters like the mass densities of ice and water, latent heat of melting, and interfacial energies. For example, molecular dynamic (MD) simulations or density functional theory (DFT) should be tested with respect to their capability to provide such parameters. How can these methods help to achieve significant refinements of freezing rate models? Can they help to estimate the latent heat of melting and/or other properties?
- Perhaps some additional mechanisms can be considered in the theory, for example surface effects (line tension concept, contact angle hysteresis).

25.3.2 Aspects of Substrate Formation

Shchekin–Shabaev–Rusanov Theory on Deliquescence/Efflorescence of Hygroscopic Aerosol Particles

Soluble substances (mostly salts) have a strong affinity for moisture, i. e., they are able to absorb water molecules from the ambient air. When the ambient relative humidity (RH) is sufficiently high, the water uptake continues until the hygroscopic particle completely dissolves in the absorbed water, in this way forming a pure solution droplet. The

of more sophisticated methods is necessary. One possibility would be to make the chambers much larger in order to capture the entire cycle of ice nucleation. Another problem in measurements concerns the determination of the chemical composition of IN, which is not always or rarely available. The study of [17] is an example of a good experiment. The authors measured chemical composition, but could detect insoluble fraction only if greater than 10%. However, even IN with smaller insoluble fractions can be efficient IN. Thus, improvements of measurements of chemical composition, especially of insoluble fraction are needed.

transition from partial to complete dissolution is called deliquescence, and the RH threshold at which a soluble particle completely dissolves is called deliquescence humidity (DRH). For highly soluble salts such as NaCl and small condensation nuclei, deliquescence occurs at subsaturation of the ambient partial water vapour with respect to a flat surface of pure bulk water (RH<100%), but at water vapour supersaturation with respect to the equilibrium vapour pressure over a curved surface of the solution droplet. In the case of low soluble and larger nuclei, deliquescence can also occur in supersaturated vapour.

The reverse process, called efflorescence (or crystallisation), leads to hydrosol formation by precipitation of solid crystals from the solution within existing droplets. Crystallisation proceeds via two steps: (i) nucleation and (ii) crystal growth. In the nucleation step, solute molecules, dispersed in the solvent, start to form clusters on the nanometer scale. To become stable nuclei, clusters need to reach a critical size, which depends on temperature, supersaturation, and the droplet size. The crystallisation is driven by the supersaturation of the solution, which depends on both ambient relative humidity and temperature. The relative humidity at which efflorescence sets in, is called efflorescence humidity (ERH). The difference between DRH and ERH results in a hysteresis effect. Owing to the high variability of the relative humidity and temperature, hysteresis effects effectively impact the partitioning between solid and aqueous phases of tropospheric NaCl and $(NH_4)_2SO_4$ particles.

The practical relevance of the consideration of memory effects results from both anthropogenic and natural emissions of aerosols and their subsequent evolution in the atmosphere. Hygroscopic aerosol particles may experience deliquescence/efflorescence-induced hysteresis effects during hydration/dehydration caused by micro-turbulence (see, e. g., [11])¹¹. This implies thermodynamically stable configurations, in which a core substrate (originating from primary emissions), coated by a soluble shell substrate of certain thickness (an inorganic salt from secondary aerosol formation), may coexist in thermodynamic equilibrium with an aqueous solution, whereas the thickness of the inorganic salt mantle and the concentration of the solution depends on external (vapour \rightleftharpoons liquid) and internal (liquid \rightleftharpoons soluble substrate) thermodynamic equilibrium conditions.

The formulation of a deliquescence/efflorescence model requires the determination of the aggregate state of an aqueous solution droplet in dependence on the ambient temperature, relative humidity, initial sizes of both soluble core and droplet etc. The DRH and ERH have to be determined from both kinetic and thermodynamic theories. In the initial state, the system consists of a soluble solid core (phase (IV)) with radius R_N , embedded in a solvent vapor (phase (I)) within fixed volume V at absolute temperature T. In the final state, a liquid droplet (phase (II)) of radius $R^{(II)}$ is formed, either including a partially dissolved residual core of radius R'_N , enveloped by a liquid film of thickness $h=R^{(II)}-R'_N$ (phase (II)), or the residual core completely dissolves, $R'_N=0$. The equilibrium droplet must satisfy two thermodynamic conditions: (a) external equilibrium between the liquid phase (II) and the ambient vapour phase (I); (b) internal equilibrium between the liquid phase (IV).

Employing the mechanical and thermodynamic concept of the disjoining pressure, the authors of [100, 101, 103] formulated a generalised Gibbs–Kelvin–Köhler equation for the external equilibrium and a generalised Ostwald–Freundlich equation for the internal equilibrium in the theory of nucleation on soluble particles (hereafter called SSR theory). These equilibrium conditions allow the DRH determination. The ERH cannot be obtained from the pure thermodynamic approach alone, but requires a kinetic consideration (e. g., [88, 90, 91, 102]). As the size-dependent DRH and ERH are, in principle, safely measurable quantities, their knowledge can be used to derive the otherwise difficult to measure interfacial energy of the liquid/solid interface, $\sigma^{(II/IV)}$, which is key input parameter of a heterogeneous nucleation model.

¹¹The aggregate state of hygroscopic particles has a strong impact on atmospheric radiation and chemistry [123, 124]. Solid particles may serve as ice nuclei, as considered here, and influence cirrus formation. Aqueous particles have a larger mass extinction efficiency but a smaller backscattered fraction than their solid counterparts. Furthermore, they may act as chemical microreactors for hydrolysis, secondary organic aerosol formation, micellisation, heterogeneous surface reactions etc. Owing to the high variability of the relative humidity in the planetary boundary layer, hysteresis effects were found to effectively impact the partitioning between solid and aqueous phases of tropospheric sulphate-ammonium particles on a global scale [123]. Moreover, such effects were reported to have a significant impact on the sulphate direct climate forcing (SDFC). Depending on how these effects were parameterised in a global 3-D chemical transport model, an uncertainty in the SDFC of 23 % on the global scale, but of much higher values on regional scales have been found from sensitivity studies [124]. However, state-of-the-art aerosol dynamics models (such as implemented in the French chemistrytransport model CHIMERE) include many more processes, than simply deliquescence and efflorescence, such as the formation of aerosol particles (AP) by several mechanisms, gas absorption, hygroscopic growth, particle coagulation and breakup, several tens or a few hundred chemical reactions, sedimentation and uplift, washout by rain and snow, etc. Deliquescence and efflorescence (if any in a given air mass) are only a tiny part of all these processes. The KC theory describes some elementary process, and can be considered as some "freezing" analog of Twomey's theory of drop activation [92], or of Maxwell's theory of particle growth. All three theories need the supersaturation. KC theory can be included as a freezing/melting module in some local, regional or global dynamic cloud-aerosol model, as modules of drop activation or growth are included. Similarly, the deliquescence/efflorescence theory of Shchekin et al. (see below in the main text) can be included in such models as well.

25.3 Starting Points for Further Studies

For the details of the SSR theory the reader is referred to the supplementary material.

Predictions from the Khvorostyanov–Curry Theory

Figure 25.5 displays the temperature–saturation ratio $(T-S_w)$ phase diagram of the melting temperature ([62], Fig. 2b therein) and the deliquescence temperature, calculated with the KC model and compared with experimental data. These two curves form a typical, asymmetric "mustache". The melting temperature and the deliquescence temperature meet at the eutectic point (here, at T=255 K, $S_w=0.83$). There also exists a complementary curve pair, given by the freezing temperature curve and the efflorescence temperature curve, lying below the melting/deliquescence temperature curve pair and also occurring at very different humidities (not shown here). Deliquescence typically occurs at deliquescence humidities of DRH=70-80 %, and freezing at freezing humidities of FRH=95-100 %, i. e., both humidities being far from each other. Efflorescence occurs at even lower relative humidities of ERH=20 - 40%. Between the deliquescence stage of an aerosol particle and its freezing, there may be a multitude of acts of aerosol coagulation or gas absorption, chemical reactions, etc. Thus, deliquescence and freezing are fairly decoupled processes. On the other hand, deliquescence (as well as other aerosol–gas interactions) can be considered as predecessors of freezing by controlling the size of residual aerosol radii. For further discussions of $T-S_w$ phase diagrams, the reader is referred to [23] and [17].



Figure 25.5: Temperature–saturation ratio $(T-S_w)$ phase diagram of the melting temperature ("T_m") and the deliquescence temperature ("T_{deliq}"). The melting temperature curve is taken from ([62], Fig. 2b therein).

Complementarity of Both Theories

The KC and SSR theories are two complimentary theories, that describe two branches in the $T-S_w$ phase diagram: While the KC theory describes the melting and freezing temperatures, the SSR theory the deliquescence and efflorescence temperatures. Both theories can be included as two modules into some dynamical numerical model to simulate aerosol-cloud interactions.

25.3.3 Surface-Stimulated Crystallisation

In the limiting case of homogeneous freezing of an aqueous solution, the KC theory provides expressions for both ice embryo formation within the bulk volume of the droplet as well as formation of an embryo at the interface of its own melt and gas (vapour or humid air) (formation of "tiny pancake ice" at the vapour/liquid interface by surface quasi-heterogeneous freezing) [62].

There is an ongoing controversy on the atmospheric preference of volume-based or surface-stimulated nucleation¹². For example, [107] examined data from electrodynamic levitation of charged particles very critically with respect to surface-stimulated nucleation, but could not find any hint for this mechanism being involved. In contrast to this, other laboratory studies [99, 109], thermodynamic arguments [24, 25, 26, 110], molecular dynamics simulations [8, 71, 114, 120], and high-speed VIS and IR monitoring of the freezing process of freely suspended aqueous solution droplets in an ultrasonic levitator [8] revealed pro's for surface-stimulated crystallisation and an inevitable need for its theoretical description. Non-classical methods, such as density-functional theory, can help to elucidate and to understand the phenomenon of surface freezing at the microscopic level, as demonstrated, e. g., by [93]¹³.

25.3.4 Liquid–Solid Interface Parameters

The determination of the critical formation work in nucleation theory is based on the thermodynamic theory of heterogeneous systems developed by Gibbs. In his approach, a real inhomogeneous system is replaced by a model system consisting of two homogeneous phases divided by a mathematical surface of zero thickness. While the properties of the ambient phase are known, the bulk properties of the critical cluster are determined via Gibbs' equilibrium conditions. The cluster bulk properties determined in this way are widely identical to the properties of the newly evolving macroscopic phase coexisting in stable equilibrium with the ambient phase at a planar interface. This assumption, called capillarity approximation, is the most basic premise of CNT. For example, in liquid \rightleftharpoons crystal phase transitions (by segregation in multi-component solutions or ice crystallisation) the liquid/solid interfacial energy (of the crystalline embryo embedded in its melt mother phase), $\sigma^{(L/S)}$, is considered as a macroscopic property having a value equal to that of a planar interface, $\sigma^{(L/S,\infty)}$ (bulk property). If one assumes, that CNT holds, then it is possible to extract interfacial energy and contact angle, respectively, from experimentally determined nucleation rates.

The determination of the interfacial energy (as well as of the more complex contact angle or wettability parameter, and lattice disregistry between single crystals of ice and the pure substrate) is a cumbersome and challenging endeavor $[16]^{14}$. To date, there has been no reliable method to measure the liquid/crystal interfacial energy (e. g., [3]). A review of previous methods to estimate the liquid/crystal interfacial energy has been performed by [43]. While the interfacial energy of the water/hexagonal ice (Ih) interface, $\sigma^{(II/III)}$, has been determined in the vicinity of the melting point by various methods (including crystal growth, shape of grain boundary groove, contact angle, morphological instability, dendritic growth), its temperature dependence is highly uncertain. By fitting nucleation rate data to the theory, one can obtain the interfacial energy of critical size nuclei as a function of temperature. It is commonly believed that the bulk

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¹²We can point out to the following interesting paradox: On one hand, cloud drops generally begin freezing only below $\vartheta = -10...-12^{\circ}$ C. Therefore, many clouds are supercooled but liquid [92]. This is the basis for weather modification by cloud seeding with dry ice, AgI, and similar agents, many hundreds huge projects still continuing around the world for 60 years. On the other hand, it can be observed in autumn and spring, that thin ice films form at night on the water surface in the barrels or on the ground, although temperature did not fall below $\vartheta = -2...-3^{\circ}$ C, only. This looks like surface freezing, but we can raise the question, why then cloud drops do not freeze in this way? Vice versa, if the surface mechanism suggested by Tabazadeh, Djikaev, and others acted as it should (or expected), would cloud seeding not be impossible?

¹³[93] studied freezing and re-entrant melting of colloidal particles in two dimensions at exposition to a one-dimensional periodic potential by means of density-functional theory employing Rosenfeld's "fundamental measure functional" for the description of hard-particle fluids. According to the first-time exploration of these phenomena by lasers, they have been named laser-induced freezing (LIF) and laser-induced melting (LIM) in the literature. The authors predicted density profiles of the perturbed liquid phases which were found to be consistent with prevailing perceptions of induced freezing and melting phenomena. According to that, particle fluctuations play an important role in the phase transition, because the re-entrant liquid phase can be seen as stripes of particles confined by the external potential, where the correlations between stripes are lost. In the region of the phase diagram where re-entrant melting was observed, the authors found that the density profile of the perturbed liquid resembled stripes of liquid separated by stripes with nearly zero density of a specific width.

¹⁴Owing to its impact on the critical cluster formation energy, both the interface energy of the interface between the new embryo and the mother phase and the contact angle act as "butterfly-effect" parameters in nucleation rate predictions. Small changes in the interface energy or the contact angle may lead to large changes of the nucleation rate coefficient by many orders of magnitude. Earlier, [7] argued, that the interface free energy, derivable from the nucleation rate, plays a role somewhat analogous to that of the activation energy in the kinetics of chemical reactions. Although its name is suggestive of a thermodynamic variable, it is a kinetic parameter. Its most important role is to facilitate the estimation of nucleation rates at greater or smaller degrees of supercooling from a given measured rate. Such an undertaking has been found to be helpful in forecasting whether or not transitions, seen to occur on the microsecond time scale of electron diffraction experiments, might be reproduced at greater supercooling on the picoseconds time scale of MD simulations. To what extent the interface energy reflects the true thermodynamic variable has not been determined very precisely. As CNT has only qualitative validity, the interface energy as a kinetic parameter must, to some extent, be a bit of a fiction. However, [7] and [47] interpreted their laboratory measurements in terms of conventional capillarity theory because it does provide a means of comparing results of enormously disparate nucleation rates on a common and intuitive basis.

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properties of the critical cluster of the newly evolving phase, derived from Gibbs' thermodynamic equilibrium approach, represent a correct description of the critical cluster. However, Gibbs himself noted that, in general, the properties of the critical cluster may differ from the predictions obtained in his approach ([40], see p. 2697 therein). [38] commented, that the nucleus of the critical size is less ordered than the corresponding bulk phase, and added, that in consequence any fitted $\sigma^{(II/III)}$ dependence arises from two physically different factors: the temperature dependence of $\sigma^{(II/III)}$ for a planar interface and its size dependence. Frequently, when CNT is employed to analyse experimental data, the size dependence of the interfacial energy is not considered. In determining the liquid/solid interfacial energy from nucleation experiments, $\sigma^{(L/S)}$ loses its meaning of a physical quantity and becomes a fit parameter, that compensates the inappropriate choice of the bulk reference states for the description of the critical clusters. In this way, CNT loses its predictive power [38, 39, 40]. Despite of these known shortcomings, CNT is frequently employed to estimate interfacial energies (e. g., [16, 53, 78]), and the contact parameter or lattice disregistry (e. g., [27, 105, 130]). For example, ([53], Eqs. (7) and (8) therein) estimated the bulk water/ice interfacial energy employing the semi-empirical Turnbull ansatz [112, 113] for bulk liquid/solid interfacial energies of metals and metalloids. To achieve agreement with laboratory measurements, [53] modified this ansatz by addition of a temperature-dependent empirical term and parameter fitting to the measurements of nucleation rate coefficients. Similarly, [27] calculated heterogeneous nucleation rate coefficients from measurements of the onset conditions required for ice nucleation and used these values to infer contact angles between the mineral substrates and an ice embryo employing CNT/CPA.

For systems with multiple interfaces, like heterogeneously nucleating systems, there are more degrees of freedom than for homogeneously nucleating ones. Therefore, a fitting procedure may easily result in "right predictions for the wrong reason". For heterogeneous nucleation this problem was recently addressed by [16]. Adopting the validity of CNT/CPA, the authors performed a multidimensional fitting procedure to jointly estimate the contact angle and the activation energy (energy of vapour desorption for deposition nucleation, activation energy for the transfer of a water molecule across the water/ice interface for freezing nucleation) for different IN¹⁵ from a compilation of all available nucleation datasets. However, [16] emphasised, that the contact angles and the activation energies derived in their study should not be interpreted as true physical terms. Apart from that one should consider, that laboratory measurements itself give reason for severe difficulties in identifying even the nucleation mechanism itself (homogeneous vs. heterogeneous nucleation) (e. g., [10, 17, 49, 50, 51]).

Improved estimations of the liquid/solid interface energy and the contact angle as functions of both temperature and cluster size can be obtained by the following attempts:

1. The starting point for the estimation of the bulk water/ice interfacial energy, $\sigma^{(II/III,\infty)}$, is the classical Turnbull ansatz:

$$\sigma^{(\text{II/III},\infty)} \approx k_T L_{\text{M}}^{(\text{III}) \to (\text{III})} \left(\varrho_{1,0}^{(\text{III})} / M_1 \right)^{2/3} N_{\text{A}}^{-1/3} , \qquad k_T = 0.32 , \qquad M_1 = 18 \,\text{g mol}^{-1} .$$

Here, $L_{\rm M}^{(\rm III)\to(\rm II)}$ is the molar latent heat of melting (derived from specific entropies of water and ice), $\varrho_{1,0}^{(\rm III)}$ is the mass density of the ice phase, M_1 the molar mass of water, and $N_{\rm A}$ the Avogadro constant. The molar latent heat of melting can be derived from both the specific water and ice entropies, which are obtained from both a new equation of state and a comprehensive Gibbs potential of water ice Ih. These new relations are based on a significantly enlarged experimental data set compared to their predecessors [28, 29, 30, 31, 32, 33, 34, 83]. In conjunction with the IAPWS-95 formulation for the fluid phase of water, the new chemical potential of ice allow one the computation of the melting and sublimation curves from the triple point down to 130 K sublimation temperature^{16,17}.

2. The predictive power of density-functional theory from statistical mechanics in studying crystal nucleation in simple and complex fluids and in determining melt/crystal interface energies for planar interfaces has been demon-

¹⁵The authors considered soot, bacteria (*Erwinia herbicola, Pseudomonas syringae, Pseudomonas aeruginosa*), pollen (grass, oak, pine, birch, eucalyptus, China rose), and mineral dust (hematite/corundum, Asian dust, Saharan dust, Arizona test dust).

¹⁶Available from the webpage of the International Association for the Properties of Water and Steam (IAPWS), http://www.iapws.org/.

¹⁷It would be nearby to alternatively employ MD simulations for the determination of thermodynamic bulk properties of water and its ice polymorphs. However, even the most sophisticated water potential models in MD simulations are not able to meet the accuracy required for such purposes. The reverse is true, the experimental data, such as those of Feistel and Wagner, are used to benchmark MD models. In the literature, the parameters of the most popular water potential models were fitted to reproduce water properties at room temperature and pressure (temperature of maximum density of water, vapourisation enthalpy, melting temperature of ice, phase equilibria of water) (e. g., [35, 69, 116, 117, 125]).

strated by [89]¹⁸. The bulk water/ice interfacial energy, $\sigma^{(II/III,\infty)}$, can be *a posteriori* corrected for curvature effects employing Diffuse Interface Theory (DIT) of [41, 42] and the Cahn–Hilliard-type Density Functional Theory (DFT) of [43]. The relevance to explicitly consider a CPA correction was recently demonstrated by [127] for the thermodynamics of homogeneous nucleation of ice particles in the polar summer mesosphere.

3. Molecular Dynamics (MD) simulations¹⁹ of electrolyte solutions can provide useful information about the liq-

 18 [89] compared crystallisation in simple fluids such as metals (atoms interacting through the Lennard–Jones 6–12 potential) with crystallisation in complex fluids (more complex interaction potential) such as colloidal suspensions and proteins dissolved in solution. For simple fluids [89] showed, that the physical assumption underlying CNT (all the order parameters changing together through the interface, so that the critical nucleus has all the properties of the bulk crystalline phase at its centre) is not true in the non-classical density-functional approach. In the liquid phase the density was predicted to be low and the structural order parameter being zero. Moving toward the crystalline phase, the structural parameter changes at first, only later does the fluid density change as well. Thus the crystal/melt interface was characterised by a crystalline structure but a liquid-like density. It was described as an ordered liquid or as an expanded solid. For a simple argon-like liquid, the author also determined the planar interfacial free energy in terms of LJ well depth and range parameters, which was found to be in good agreement with molecular dynamic studies from the literature. The critical nucleus free energy were too high by tens of $k_{\rm B}T$. Therefore, the CNT rates were too low by many orders of magnitude.

Studying crystallisation from solutions [89] addressed following question: when particles from solution join a growing small cluster, are they ordered in periodic structures resembling the crystalline solid? In terms of the solute concentration and a crystalline structure parameter (used as order parameters), the author reformulated this question as follows: do the solute concentration and the crystalline structure parameter change together, in this way ensuring that at each stage the tiny clusters are well-defined crystallites, or does the concentration change first and the structure afterwards? If the latter would be true, then small clusters would be disordered and would only start to look like crystals when they grew past a given size [89]. The author did not explicitly include the solvent (water), but instead, considered implicitly the effect of the solvent by using an effective interaction potential between solute particles in the presence of a background of water. In this way the complex fluid was modelled by treating an one-component fluid of solute particles in a uniform water background, and instead of the solute concentration once again a solute density variable could be used along with a structural parameter. By using an interaction potential differing from that for the simple fluid, the author demonstrated, that during the fluid-to-crystal transition the solute density changed at first (giving amorphous clusters), followed by the appearance of crystalline order. The author especially focussed on the crystallisation of large particles (colloids, proteins) from aqueous solution. In this case, the interaction potential was modelled by a hard sphere plus a very short-ranged but deep attractive tail (short-ranged on the scale of the particle size). Previous computer simulations of such large molecules revealed, that the fluid-fluid critical point in the phase diagram moves below the fluid-solid coexistence curve, transferring the liquid phase in a metastable state. Most importantly, these simulations demonstrated a different mechanism of crystal nucleation and growth in solutions: small clusters were disordered and only become crystalline when they grew large enough. By the choice of a special form of the interaction potential, [89] confirmed these simulation results by his density-functional approach. From calculations of cluster free energies and barriers to nucleation, the author found a lowering of the free energy at a temperature close to the metastable critical point, because of the ease of changing the density at this point. This result confirmed previous density-functional calculations of crystal nucleation in proteins from solution showing a decrease of the critical nucleus free energy by $100k_{\rm B}T$ over a 20% temperature range centred on the metastable critical point, for a given thermodynamic driving force arising from supersaturation. From this result [89] concluded, that nucleation of protein crystals may be most favourable in a narrow window, where the nucleation rate is especially low for a given growth rate. This finding supports the experimental evidence on the existence of a "nucleation window" in protein crystallisation.

¹⁹MD simulation is a computational method by which the time evolution of all molecules in a model system is calculated by solving Newton's equation of motion. The starting point is an initial configuration for the system, i. e., the initial coordinates for all the atoms in the system. The initial velocities are randomly assigned following the Maxwell distribution for the desired temperature. An interaction model potential has to be provided, from which the forces acting on every particle can be calculated. Then, considering that these forces are constant during a very small time interval, the new positions and velocities can be calculated. The size of this time interval, or time-step, is usually of the order of $\Delta t=10^{-15}$ s (femtoseconds). Typical total simulation times are of the order of 10^{-8} s (tens of nanoseconds). MD is a very successful technique commonly used in many different classes of systems, from biological solutions to metallic alloy.

MD simulations applied to the ice growth problem are still in their infancy for the following reasons: (a) Water models were developed for the treatment of systems at room temperature, and thus were not adequate for simulations at low temperature. Only recently (beginning 2002) more attention has been paid to the problem of a good model for ice simulations. (b) Until very recently computers were not fast enough to be able to simulate a system with a sufficient number of molecules to display the freezing process [13]. At present, the majority of MD simulations are performed by using non-polarisable force fields such as AMBER, CHARMM, GROMOS, GROMACS, OPLS, PMEMD, in lucem Molecular Mechanics (ilmm) software packages. Only a few models account for electronic polarisation explicitly (e.g., molecular dynamics electronic continuum (MDEC) model, Niesar–Corongiu–Clementi (NCC) model). There exist different **water** (non-polarisable and polarisable) potential models, suggesting that none is completely satisfactory (e.g., Simple Point Charge potentials SPC, SPC/E (extended), SPC/FQ (four point fluctuating charge); Transferable Intermolecular Potentials TIP3P, TIP4P, TIP4P/Ew, TIP4P/ice, TIP4P/2005, TIP4P/FQ, TIP5P, TIP5P/E; TTM2.1/F; F3C; "six-site" H₂O potential; POL5; Gaussian Charge Polarisable (GCP) model; AMOEBA water model). Some of them are more popular than others, indicating that they are not all equivalent. For **ions** there also exist both non-polarisable and dipole-polarisable potential models (e.g., AH/SWM4-DP ion models).

The difficulty in simulating ice nucleation arises from the fact, that hydrogen bonding between individual water molecules yields a

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uid/solid interface energy. Such simulations can be used to estimate the temperature dependence of the solution/ice interface energy and to examine the validity range of Turnbull's ansatz and Antonoff's rule. The practicability of MD simulations to estimate interface energies at the liquid/solid interface has been demonstrated by [71] and $[3]^{20}$. However, these studies did not consider ion-induced effects, such as

- the influence of dissolved ions on the bulk properties of water, such as viscosity and entropy of solvation²¹,
- the electric charge separation at the interface between single crystals of ice Ih and a dilute electrolyte solution during the freezing process (formation of Workman–Reynolds Freezing Potential (WRFP) between the solid and liquid phases)²²,
- the negative adsorption of inorganic ions at any interface, leading to an increase of the interface energy²³, brine rejection from freezing aqueous solutions²⁴,

disordered 3-D hydrogen-bond network, whose rugged and complex global potential energy surface permits a large number of possible network configurations. Therefore it is very challenging to reproduce the freezing of real water into a solid with unique crystalline structure. For pure and spatially unconfined water, MD simulations of freezing are severely hampered by the large number of possible network configurations that exist.

The first successful MD simulation of ice nucleation and the growth process leading to water freezing was performed by [82] for 512 water molecules. To simulate the initiation of homogeneous freezing of water in the subsurface, [120] used the GROMACS 3.3 program package. The simulation of ≈ 600 water molecules in a unit cell of $\approx 15 \times 15 \times 100$ Å³ for ≈ 500 ns took an equivalent of ≈ 1000 CPU days on an Intel Xeon processor machine (parallel run on eight processors).

²⁰MD simulations to estimate interface energies at the vapour/liquid interface have been performed, e. g., by [4, 15, 52, 95]. [44] employed both Monte Carlo (MC) simulations and density functional theory (DFT) for such purposes.

 21 The influence of dissolved ions on the bulk properties of water, such as viscosity and entropy of solvation, is hypothesised to be related to the effect of ions on the hydrogen-bond network of water molecules. Some ions exhibit stronger interactions with water molecules and are known as structure makers, whereas some others show weaker interactions with water molecules than water itself and are known as structure breakers (considerable destruction of tetrahedral network by highly concentrated ions). This ion effect on the molecular structure is approximately equivalent to the application of high pressure. Contrarily, some studies do not support these conclusions and indicate that the structure breaking is only caused by the formation of the first hydration shell, outside which the influence can be neglected. Generally, hydrated ions decrease the equilibrium melting point of ice, whereas the degree varies with the solute concentration. When increasing the concentration, the homogeneous nucleation of a glass). It is also suggested, that homogeneous nucleation in aqueous solutions is determined by the water activity and is independent of the nature of solutions. Compared with homogeneous nucleation, heterogeneous nucleation in aqueous solutions is less investigated due to the complexity of various heterogeneous nuclea as well as the interaction with dissolved ions, although it is the dominant mechanism of ice nucleation in both laboratory and nature ([77], see also references therein).

²²The WRFP effect across the interface between single crystals of ice Ih and dilute electrolyte solutions has been measured the first time by [126]. Measured WRFP is dependent on the concentration of the ionic solution, forming a parabolic graph when plotting WRFP as a function of concentration. WRFP depends slightly on the type of cation, but markedly on the type of anion. The dependence relies mostly on electro-negativity of the solute, which itself depends on the ion size and solute structure. Large electro-negativity of the ionic atom or molecules is required to replace the largely electro-negative oxygen atom of a water molecule in the ice lattice. If the ionic solute in the solution is an atom and is adequately electro-negative (e. g., F^-), it usually replaces the oxygen atom of a water molecule in the lattice. However, if the ionic solute in the solution is a molecule (e. g., F^-), it usually replaces the oxygen atom of a water molecule, so that it will be able to take the place of a water molecule in the lattice. When a solution of NH_4Cl or $(NH_4)_2SO_4$ is frozen, the ammonium ion is preferentially incorporated into the ice and produces a WRFP with a negative sign ([126], see references therein).

²³The surface tension of water increases with addition of inorganic electrolytes having relatively small ions. Some organic ions are also known to increase the surface tension. The surface tension of solutions increases almost linearly with increasing concentration of salts. A critical review and advanced theory of this phenomenon was proposed by ([81], see references therein). The major players determining the surface tension of the aqueous electrolyte are the electrostatic effect of image forces at the interface and negative adsorption of small ions. According to classical Gibbs theory, the air/liquid interface of an electrolyte solution is essentially devoid of ions. This is a consequence of the Gibbs adsorption equation, which relates the increase in surface tension observed for all inorganic salts to a negative surface excess of ions. Onsager and Samaras proposed a theory, according to which image charge repulsion of the ions repels them from the interface. This model predicts the outermost liquid layer to be essentially devoid of ions. However, observations revealed a dramatically different behaviour for highly polarisable ions (like large anions). The concentrations of some anions were found to actually be enhanced at the vapour/liquid interface. It is suggested, that this phenomenon is attributed to the preference of highly polarisable ions for the surface. This is a consequence of this ion disrupting the hydrogen bond network of water due to its preference to act as a donor of hydrogen bonds, but not as an acceptor. Some salts do not produce the monotonic increase in surface tension of the Onsager–Samaras model (Jones–Ray effect).

²⁴The insolubility of inorganic salts in ice is known as brine rejection from freezing salt solutions. For temperatures below the melting and above the eutectic point (point of equilibrium between the three phases crystalline, solution, ice) of a given salt, the

- the effect of ion force field polarisability on the interfacial electrostatic potential of aqueous solutions of inorganic salts²⁵,
- the adsorption of "anti-freezing" molecules on the ice surface, resulting in a freezing temperature depression without an appreciable change in the melting temperature²⁶.

Guiding modelling studies for the elucidation of freezing (with respect to, e. g., model setup, initial configuration, boundary conditions, molecule potentials, equilibration method, thermostat/barostat) were performed by

• Ref. [119] on brine rejection from freezing salt solutions²⁷,

²⁵X-ray photo-electron spectroscopy and MD simulations revealed a density enhancement of large, polarisable anions in the outermost interfacial layer (in the vicinity of the Gibbs dividing surface (GDS)) of aqueous salt droplets. Here, strong anion-water induced dipole interactions accompanying asymmetric surface salvation easily offset the energetic penalty associated with partial anion desolvation at the surface. The polarisability of the anionic species and the solvent play a major role in this phenomenon. Further significant contributors are: ion size, entropic effects arising from solvent structure and reorganisation, ion surface charge density, magnitude of the water dipole moment (and its variation in the asymmetric interfacial region, the particular nature of the salvation shell surrounding the ion). Large, softer anions (e. g., Br⁻, I⁻) exhibit significant surface effects, whereas small, hard anions (e. g., F⁻) show negligible surface density enhancement. Recently, [125] studied the impact of the ion polarisability (employing state-of-the-art polarisable molecular models incorporating dipole induction effect) on the interfacial electrostatic potential of several monovalent aqueous salt solutions. The electrostatic potential provides complementary information on the orientational order at the interface. The system of interest was a two-phase system consisting of a solution in equilibrium with its vapour. Such a system requires the use of polarisable water models, since fixed-charged models parameterised according to the average electrostatic environment of the isotropic bulk phase cannot optimally model the low-density vapour side of the interface. The authors decomposed the electrostatic potential into contributions from dipole and higher-order moments, i. e., the quadrupole moment in the case of water. In the interfacial region, the dipole moments of the individual solvent molecules monotonically undergo a transition from a large condensed phase value to a much weaker gas-phase value. The orientations and induced dipoles of water molecules were found to be more strongly perturbed in the presence of polarisable ions via a stronger ionic double layer effect arising from greater charge separation. Both anions and cations exhibit enhanced induced dipole moments and strong z-alignment in the vicinity of the GDS with the magnitude of the anion induced dipoles being nearly an order of magnitude larger than those of the cations and directed into the vapour.

²⁶The Gibbs–Kelvin theory predicts, that the freezing point of a tiny spherical particle is proportional to the interfacial energy and inversely proportional to its radius. The accumulation of certain molecules (anti-freezing agents, e. g., inorganic salts like NaCl, KCl, CaCl₂; organic molecules such as glucose, sucrose, raffinose; anti-freeze proteins (AFPs) such bovine serum albumin (BSA), size-mutated beetle *Tenebrio molitor* (Tm) and winter flounder AFPs; anti-freeze glycoproteins (AFGPs)) onto the growing surfaces of ice crystals results in the creation of numbers of convex ice surfaces at the limited open spaces of ice between the bound molecules. The free energy of the convex ice surfaces becomes larger with the increase of the surface curvature. Therefore, further binding of water molecules onto the convex ice surfaces becomes energetically unfavourable, leading to the suppression of the ice crystal growth by increasing the number of bound anti-freezing molecules. In this way, the increasing curvature subsequently leads to a lowered temperature for the growth of the ice crystal ([72, 79], see references therein).

The depression of the homogeneous freezing point, $\Delta T_{\rm hf}$, scales in proportion with the melting point depression, $\Delta T_{\rm m}$:

$$\Delta T_{\rm hf} = \lambda \Delta T_{\rm m}$$

Here, $\Delta T_{\rm hf}$ is the change in freezing temperature of a solution particle, relative to the freezing point of a pure water droplet of the same size, which in turn is depressed below the freezing point of bulk water. The term $\Delta T_{\rm m}$ assumes a positive value, that increases with the solute concentration in solution droplets. The parameter λ is a proportionality constant. Classical theory does not readily explain values $\lambda \neq 1$. For $\lambda = 1$, the temperature at which a given fraction of solution drops freezes is depressed from the temperature required to freeze the same fraction of pure water drops (of the same size) by the interval $\Delta T_{\rm m}$. If $\lambda > 1$, then additional supercooling of solution drops, over that due to the presence of solute, is required for freezing. Values of $\lambda < 1$ suggest that some solution or surface effects cause freezing to occur more readily in the solute drops, since the temperature required for freezing a certain fraction is higher than the temperature expected from the melting point depression. Values of λ range from 1.4 to 2.3 for various solutes [17]. The difference between the melting and freezing temperatures is called thermal hysteresis (TH). [68] pointed out, that the change in the freezing point of an aqueous solution, the solute of which can dissolve in freezing ice. The KC theory predicted λ values varying mostly in the range $\lambda = 1.9-2.2$ for aqueous ammonium-sulphate and sulphuric-acid solutions ([62], Figs. 3b, c therein).

 27 In the MD simulations of [119], periodic boundary conditions were employed with a unit cell with approximate dimensions of $^{22}\times^{23}\times^{43}$ Å³, consisting of 720 H₂O molecules and a variable number of salt ions. One fourth of the volume was constructed as a proton disordered cubic ice, while the rest was initially in the liquid phase. The system consisted of an infinite patch of cubic ice in the *xy*-plane surrounded by liquid water, with two (111) ice/water interfaces perpendicular to the *z*-axis per unit cell. Salt was introduced

solution freezes as neat ice with salt ions being rejected into the unfrozen part of the system. As the freezing process progresses a salt concentration gradient, as well as a temperature gradient (due to latent heat release) is established across the freezing front. This leads to macroscopic instabilities due to which an originally planar freezing front becomes corrugated. Brine rejection occurs during impact freezing of supercooled cloud water droplets, which contain salt ions originating from the soluble CCN. This process is hypothesised to be involved in thundercloud electrification via transfer of salt ions during collisions of ice crystals with the brine covered surface of graupel [119].

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- Ref. [77] on the supercooling capability of aqueous NaCl and KCl solutions²⁸,
- Ref. [14] on ice growth from a supercooled ionic water solution with explicit vapour water and vapour ice interfaces²⁹,
- Ref. [72, 79, 87] on thermal hysteresis activity of several anti-freeze proteins,
- Ref. [125] on the impact of ion force field polarisability on the interfacial electrostatic potential of aqueous monovalent salt solutions³⁰.

With respect to theoretical treatment we want to refer to the study of [81], who proposed a quantitative theory of the surface tension and surface potential of aqueous solutions of electrolytes, which includes image forces at liquid interfaces, ions of finite radii, the hydrophobic effect, and the Parsons–Zobel effect. For aqueous NaCl³¹ and KCl solutions, the authors found good correlation between theory and experimental data both qualitatively and quantitatively over a wide range of concentrations.

Challenges in MD simulations of the freezing process are

• the consideration of charge separation at the interface between single crystals of ice Ih and dilute electrolyte solutions³², and

 28 [77] used the four-site TIP4P potential function. The potential energy in the system involves the 6–12 Lennard–Jones and Coulomb interactions between all molecules and ion pairs of sites.

²⁹The simulated system of [14] consisted of 1524 water molecules, 6 Na⁺ and 6 Cl⁻ ions. The initial configuration was prepared by bringing together a pure ice (half) system with 768 molecules, with a pure water (half) system with the same number of molecules. The basal plane of the ice was selected to form the water/ice interface. After equilibration the heterogeneous system consisted of an ice layer in contact with a liquid layer on one side and vacuum on the other side. The other liquid surface was also facing vacuum. Six ion pairs were incorporated to the system, and 12 water molecules were removed. On the liquid side the molecules exchange was done within the bulk of the system, and the ions were placed forming a staggered pattern. On the ice side, the ions were placed just outside. The dimension of the simulation box was approximately $3 \times 3 \times 12 \text{ nm}^3$ (Parrinello–Rahman barostat, Nose–Hoover thermostat). Full periodic boundary conditions were applied. The simulations were carried out using the GROMACS v3.2 programm. The water model used was a six-site model (rigid water molecule with three Lennard–Jones (oxygen and hydrogens) sites and five charged sites (hydrogens, one point charge on the bisector of the HOH angle and two point charges in the region of the oxygen lone pair orbitals)). The interaction parameters for the non-polarizable Na⁺ and Cl⁻ were taken from the computer code AMBER 7. The equations of motion were integrated using a leap-frog algorithm with a time step of $\Delta t = 1$ fs. Two trajectories of 50 ns were simulated.

 30 [125] employed the polarisable TIP4P-FQ (transferable intermolecular potential four point fluctuating charge) water model to describe the water component of the vapour/solution interface. It is a rigid water model, characterised by a single Lennard–Jones interaction site placed on the oxygen atom and a massless, off-atom M-site, which carries the instantaneous oxygen partial charge. The TIP4P-FQ model allows for quadrupole moment induction through the redistribution of molecular partial charge, which is not permitted in many other commonly used rigid dipole polarisable water models. To model the ion potentials two sets derived from the AH/SWM4-DP ion model were employed: (a) non-polarisable models, in which electrostatic interactions are described by fixed, unit point charges; (b) dipole-polarisable Drude models. Both ion models share the same Lennard–Jones parameters and differ only in the inclusion of Drude polarisability. The MD simulations were performed using the Chemistry at HARvard Molecular Mechanics (CHARMM) package version 34a1. The aqueous salt solutions (with prescribed molality) were assembled from 988 TIP4P-FQ water 24×24×100 Å³, that is approximately half-occupied by solution. This yields a periodic replication of a rectangular unit cell with size 24×24×100 Å³, that is approximately half-occupied by solution. All interfacial systems were sampled under conditions of constant temperature and volume (*NVT*) for a total of 80 ns following 500 ps of initial equilibration from a previously equilibrated geometry [125].

 31 Hydrated NaCl particles play an important role in Earth's atmosphere. Such particles, emerging from the ocean and also from some volcanos, may become part of the atmosphere or deposited on the ocean shore. In both situations they play an important role as providers for chloride species and/or catalysts for pollution reactions as f. i. those involving (N–O)-compounds.

 32 Due to the low solubilities of salt ions in ice, large unit cells would be required for obtaining statistically significant data.

into the system by replacing randomly chosen liquid-phase water molecules by the appropriate number of sodium and chloride ions. All simulations were carried out using the PMEMD program employing standard non-polarisable rigid-monomer force field for water (SPC/E potential) and ions. Classical equations of motion were propagated numerically with a time step of $\Delta t=1$ fs. Production runs were performed over hundreds of nanoseconds. The resulting trajectories were analysed in terms of density profiles (oxygen atoms, Na⁺, Cl⁻ ions). The authors demonstrated, that both sodium and chloride ions are rejected by the advancing freezing front into the remainder of the liquid phase. Eventually, the system freezes as neat ice almost completely, the ions being expelled into a small volume of concentrated brine. This region with high salt concentration has a glassy character showing slow tendency for incorporation of further water molecules into the ice lattice. At higher salt concentrations, an ion can be sometimes trapped inside the ice crystal. A chloride anion (but not a sodium cation) was observed to be deposited in the top layer of ice, which suggests charge separation at the interface [119].

• the direct estimation of the contact angle³³ at the solution/ice/substrate interface.

We are not aware of direct MD simulations of the contact angle at the solution/ice/substrate interface. However, in the literature there are a few studies addressing the estimation of the contact angle at the vapour/liquid/solid interface by means of non-classical methods. Methodical guidance for contact angle simulations are provided by the MD studies of [46] to determine the contact angles of water droplets on the surface of crystalline and amorphous plastic materials³⁴, of [104] to determine the temperature dependence of the contact angle of vapour/liquid/solid interface³⁵, and of [9]

³⁴[46] performed MD simulations to determine the contact angles of water droplets on frozen crystalline and two amorphous polyethylene (PE) and polyvinyl chloride (PVC) surfaces. For both PE and PVC, the simulation systems consisted of eight molecules, with each molecule composed of about 100 monomers: (a) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_2 - CH_2)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (b) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99} - CH_3$; (c) composition of the PE chain: $CH_3 - (CH_3 - CH_3)_{99}$ sition of atactic PVC chain: CH₃-(CHCl-CH₂)₉₉-CHCl-CH₃ with equal fractions of meso- and racemic diacids distributed randomly along the chain. The force field parameters for PE and PVC were given in ([46], Tables 1 and 2 therein). Amorphous surfaces of two different densities were produced for each polymer (PE and PVC) by pressing the amorphous bulk polymer step by step at elevated temperature between two repulsive grid surfaces until a density equivalent to the target density at room temperature was reached. Different-sized water droplets and two water models (simple point charge and extended simple point charge (SPC and SPC/E)) were used to study the magnitude of the line tension and the effect of model bulk energy on water contact angles. The simulations were performed with the GROMACS molecular dynamics simulation package. Bulk simulations of polymers were carried out using a constant pressure and temperature (NPT) ensemble at 1 bar pressure with periodic boundary conditions; all other simulations used a constant volume and temperature (NVT) ensemble with periodic boundary conditions. The Berendsen algorithm was used for temperature and anisotropic pressure couplings. Short-range intermolecular interactions of full atomistic models were presented by Lennard-Jones potentials employing a specified cutoff radius and geometric mean combination rules. Long-range Coulombic interactions of the polymer models were handled with the particle mesh Ewald (PME) method using the slab correction for surface systems. The authors quantified the line tension τ using the modified Young's equation, which relates microscopic contact angle θ to its macroscopic counterpart $\theta^{(\infty)}$ via

$$\cos\theta = \cos\theta^{(\infty)} - \frac{\tau}{R_{\rm B}\sigma^{\rm (V/L)}}$$

Here, $R_{\rm B}$ denotes the base radius of the water droplet and $\sigma^{\rm (V/L)}$ the surface tension at the water vapour/liquid interface. The authors found a positive line tension of $\tau=10^{-12}-10^{-11}$ N on crystalline PE, but no well-defined line tension in the case of crystalline PVC. The SPC/E water model produced typically larger microscopic contact angles than the SPC model. Employing the SPC water model, the authors predicted a macroscopic contact angle of $\theta=113^{\circ}$ C for the water/crystalline PVC interface, which were reported to be in good agreement with experimental data. The results for the amorphous surfaces differed from those on the crystalline surfaces. The differences were more dependent on the amorphicity of the surface than on the density. For the PE surface, the water droplet contact angle was larger on the amorphous than on the crystalline surface, while for the PVC surface the contact angle was smaller on the amorphous than on the crystalline surface [46].

 35 [104] simulated a Lennard–Jones (LJ) liquid (argon) and water droplets adjacent to a solid surface. In this simulation, the particleparticle mesh method was used for long-range force correction: (a) Argon droplet on a virtual solid wall: For this case, the size of the simulation box was $47.04 \times 47.04 \times 70.56$ Å³. The solid wall was assumed to consist of four layers of atoms arranged as a fcc lattice with its $\langle 111 \rangle$ surface in contact with the fluid. The solid wall was taken to be that of platinum with a lattice constant of 2.776 Å and mass density of $g=21.45 \times 10^3$ kg m⁻³. For the solid–solid interaction, the LJ potential was applied with defined energy and length parameter to model the platinum atomic vibrations in the lattice. The LJ potential was also used for the solid–liquid interactions by scaling the LJ energy and length parameters for argon. Initially, 980 atoms were stacked in a simple cubic structure above the center plane. The initial velocities were assigned to the atoms randomly according to the system temperature. Periodic boundary conditions were applied along the *x*- and *y*-directions. In the *z*-direction velocity changed sign. (b) Water droplet on a platinum surface: For this case, the domain size was chosen to be $80 \times 80 \times 80 \times 80 \text{ nm}^3$. Equivalent potential field was applied instead of the five layers of platinum atoms [fcc(111)] at the bottom of simulation domain. Initially, $13 \times 13 \times 10$ water molecules were placed on the platinum surface.

Periodic boundary conditions were specified at the four-side surfaces and a mirror boundary at the top surface. The simple point charge/extended potential (SPC/E) was used for water-water interactions and the Z-P potential for water-platinum interactions, respectively. The time step was $\Delta t=1$ fs. Berendsen's thermostat was used. The center of mass of the system was adjusted in the x-y plane to eliminate numerical momentum errors. The density was sampled by dividing the simulation domain into $200 \times 200 \times 300$ small cubes with cube length of 0.2352 Å.

After the system reached equilibrium, the contact angle θ , or the wettability parameter m,

$$m = \cos \theta = \frac{\sigma^{(V/S)} - \sigma^{(L/S)}}{\sigma^{(V/L)}}$$

³³The contact angle is a result of a balance between the fluid–fluid and fluid–solid interactions. When the fluid–solid interaction is sufficiently large, the liquid wets better the surface and the contact angle tends to become smaller (or even zero). Small contact angles mean, that the surface is difficult to clean. Greater hydrophilicity of the surface would improve removal of, e. g., soil (in the case of polyethylene plastics for housewares and polyvinyl chloride for floor coverings) because of the weaker attraction for the soil than water, when water molecules approach to the surface. Alternatively, on a highly hydrophobic surface, contaminating particles are carried away by water droplets rolling off the surface in what is known as the Lotos effect [46, 9].

employing DFT to determine the dependence of the wetting angle on smooth solid surfaces on the parameters in the Lennard–Jones potentials for fluid–fluid and fluid–solid interactions and on temperature³⁶.

25.3.5 Latent Heat of Melting

Another important input parameter entering the description of ice nucleation is the specific latent heat of melting, $L_{1,0}^{(\text{III} \to \text{III})}(T)$, which varies significantly with temperature: It is about $80 \text{ cal g}^{-1} \approx 335 \text{ kJ kg}^{-1}$ at $\vartheta = 0^{\circ}\text{C}$, decreases about twice to $40 \text{ cal g}^{-1} \approx 167 \text{ kJ kg}^{-1}$ at $\vartheta = -40^{\circ}\text{C}$. The $L_{1,0}^{(\text{III} \to \text{III})}(T)$ behavior at $\vartheta < -40^{\circ}\text{C}$ is uncertain. However, the latent heat of melting of such low temperatures is required for simulations of cirrus, polar stratospheric clouds, mesospheric clouds in Earth's atmosphere, of clouds of Mars, Venus and Jovian (reviews of their atmospheres can be found in ([23], Chapter 14 therein)) as well as of clouds with various ices on the other planets of the solar system. In the literature, several reconstructions and extrapolations of $L_{1,0}^{(\text{III} \to \text{III})}(T)$ to the lower temperatures have been reported (see, e. g., the review study of [85]). According to the "mechanical stability limit conjecture" it is assumed that liquid water cannot be superheated, stretched, or supercooled indefinitely. As a consequence one should expect strong fluctuations at the stability limit. For supercooling of water, a stability limit is assumed to be located at $\vartheta_s = -45^{\circ}\text{C}$ ([92], Chapter 3 therein). However, in view of experimental and numerical studies the mechanical stability conjecture becomes questionable: (a) laboratory studies revealed no changes of the correlation length of density fluctuations for temperatures approaching θ_s , and electron diffraction measurements showed supercooling of H₂O at very low temperatures (below the ϑ_s).

The authors of [31] proposed a new equation of state (EoS) for H₂O ice Ih covering the ranges 0-273.15 K and 0 Pa-210 MPa. It serves as a fundamental equation, from which additional properties, such as the latent heat of melting, are obtained as partial derivatives by thermodynamic rules. The authors emphasised, that in conjunction with the IAPWS-95 formulation for the fluid phases of water the new chemical potential of ice allows one an alternative computation of the melting and sublimation curves, being especially improved near the triple point and valid down to 130 K sublimation temperature. Feistel (2011, personal communication) noted, that the EoS of ice is valid down to T=0 K, but the EoS of liquid water is solely an extrapolation below the freezing point, which describes all known measured data well there. Thus, the EoS of water is considered to be valid down to $\vartheta \approx -20^{\circ}$ C³⁷. The author noted, that at very low temperatures ice should undergo sublimation rather than melting. Sublimation heats have been calculated down to just above the absolute zero point [32].

25.3.6 Sample-Size Effects in Nucleation

Cloud droplets represent effective chemical micro-reactors for multi-component reactions and phase transitions, whereat the initial concentrations of the chemical compounds may vary over wide ranges, depending on the specific atmospheric

with $\sigma^{(V/S)}$, $\sigma^{(L/S)}$, and $\sigma^{(V/L)}$ denoting the interface energies of the vapour/solid, liquid/solid, and vapour/liquid interfaces, respectively, was directly derived from liquid and vapour density plots in the x-z and y-z planes. The boundary of the liquid droplet was defined by the contour line corresponding to the average of liquid and vapour densities. The droplet boundary showed statistical fluctuations and had a curved interface. The contact angle was calculated by drawing a tangent line near the contact line. This procedure was applied for both planes, and the contact angle was calculated as an average from the measured values in the x-z and y-z planes, respectively. In this way, the dependence of the contact angle on the Lennard–Jones energy parameter and the temperature was obtained, $\theta=\theta(\varepsilon_{LJ}, T)$. It was demonstrated, that the contact angle decreases with increasing system temperature dependence of the water–platinum contact angle was fitted to a second-order polynomial:

$$\theta / [\circ] = -31.61 + 245.33T^{\star} - 265.44T^{\star 2}$$
, $T^{\star} = T/T_{\rm c} < 0.75$.

Here, T_c denotes the critical temperature of water [104].

³⁶Firstly, [9] determined the fluid density distribution (FDD) by minimising the Helmholtz free energy of the system. Secondly, the profile of the drop was extracted from the obtained FDD by assuming an equimolar dividing surface. Finally, the contact angle which this profile makes with the solid surface was determined for various values of the parameters involved in the interaction potentials and various temperatures. For argon as a reference fluid and solid carbon dioxide as the reference solid, the authors proposed scaling laws for the dependence of the contact angle on a dimensionless energy parameter, characterising the substrate and the fluid, on further dimensionless parameter, characterising the temperature effect, and on the average fluid densities. Assuming that the obtained result can be extrapolated to macroscopic drops, this result can qualitatively explain the different temperature behaviors of the contact angle observed in experiments.

³⁷([31], Table 19 therein) provided corresponding values of the specific latent heat of melting in the temperature range $250 \text{ K} \le T \le 273.15 \text{ K}$: $L_{1,0}^{(\text{III} \to \text{II})}(T=273.15 \text{ K}) = 333.446 \text{ kJ kg}^{-1}$, $L_{1,0}^{(\text{III} \to \text{II})}(T=250 \text{ K}) = 268.915 \text{ kJ kg}^{-1}$.

conditions. Chemical aqueous-phase reactions may have far reaching consequences for atmospheric phase transitions. Immersion freezing is stimulated by initial germ formation in the embedding mother phase (the solution droplet). The formation of such initial germs can be induced by preceding hydrosol formation in aqueous solution droplets, followed by turbulence induced dehydration/evaporation of the droplets. Due to atmospheric turbulence such droplets can be captured by up- and downdrafts or by lateral entrainment and detrainment processes, bringing the cloud droplets in rapidly changing hydro-thermodynamical and physico-chemical ambient conditions. Near cloud edges cloud droplets can more effectively evaporate than in the interior of clouds. Evaporation leads to rapid decrease of the reactor size, accompanied by extremely high supersaturations near to the spinodal.

As a consequence of aqueous-phase chemical reactions and "phase transformation processes in confined space" stable aggregates can be formed in the droplet. These aggregates can either stimulate subsequent freezing of the liquid phase, or after evaporation, can become a part of the atmospheric aerosol ("cloud droplet residuals"). Cyclic cloud processing of such residuals can cause hysteresis and memory effects. Thus, the analysis of size effects of the mother phase volume on nucleation and growth is of high practical importance. Methodical guidance on the treatment of nucleation in confined space on the base of a generalisation of Gibbs thermodynamic theory is provided by [98].

25.3.7 Non-Sphericity of Droplet Morphology

When describing freezing of submicron solution particles or small drops, which is the most relevant case in the atmosphere, the assumption of sphericity is fully satisfied. However, as can be seen from levitation experiments, e. g., the high-speed monitoring study of the freezing process of levitating aqueous solution droplets (equatorial diameters D = 1.5-4.5 mm) of [8], large droplets can assume a non-spherical shape. In principle, non-sphericity impacts the external mechanical equilibrium between the droplet and the ambient vapour. Employing Gibbs' classical thermodynamic theory, [118] generalised the Laplace equation for the mechanical equilibrium of an isolated vapour/liquid/solid system in a gravitational field (sessile drop on a planar solid substrate). In order to study the impact of the drop shape on ice nucleation in a millimeter-sized levitating droplet the Laplace equation (employed in the nucleation thermodynamics) must be modified correspondingly.

25.3.8 CCN Active Site Statistics

Ref. [37] and references therein demonstrated the freezing-enhancing effect of re-entrant cavities ("active sites"), located on the surface of a catalysing substrate. A sophisticated theoretical treatment of active-site effects in freezing requires a comprehensive characterisation of small-scale topographical variations of CCN surfaces. State-of-the-art optical and electron microscopy of ambient CCN-IN provide a suitable database for a geometrical surface characterisation. By application of methods of geomorphometry and image processing different proxies for the characterisation of particle surfaces can be obtained: relief energy and drainage density of the CCN topography, texture measures, frequency distributions of concave and convex deviations from the mean height, length scale statistics, auto-correlation function etc. A great challenge would be the derivation of a classification of natural occurring CCN in groups with characteristic topographic features, quantified by robust metrics employing a minimum number of parameters. On this base, active-site statistics can be obtained as an input for freezing modelling.

25.3.9 Glass Transition

In a comprehensive review of homogeneous crystal nucleation in silicate glasses, [40] gave a profound notional orientation on glass transition. According to the authors, glasses can be defined as non-crystalline solids, undergoing a glass transition during their preparation. One method to vitrify a liquid is its supercooling down at sufficiently high rates. In this case, crystallisation can be decreased to very low rates or completely arrested down to temperatures corresponding to very high viscosities ($\eta \ge 10^{12} - 10^{13} \text{ Pa s} \approx \eta(T_g)$, with T_g denoting the glass transition temperature) [40]. At $T < T_g$ the very high viscosity will prevent large-scale atomic rearrangements, leading to a freezing-in of the molecular structure. According to [40], structural freezing-in means, that the structural rearrangements required to keep the liquid in the appropriate metastable equilibrium state cannot follow any more the change of temperature. The process of freezing-in the structure of a supercooled liquid transforming it into a glass is denoted as glass transition. Characteristic features of glass-forming liquids are typically (i) relatively high viscosities at the melting point or liquidus, and (ii) a steep increase of the viscosity with decreasing temperature, both favouring vitrification. The authors concluded, that the glass structure must be similar to that of the parent supercooled liquid at temperatures near T_g . [40] characterised the thermodynamics of glass transition as follows:
25.3 Starting Points for Further Studies

- Glass is thermodynamically unstable with respect to the supercooled liquid. There exists no energy barrier between the glass and its corresponding supercooled (metastable) liquid³⁸.
- Apparently, the high stability of the glassy state reflects a decreased relaxation capability, originating from the impossibility of the system to evolve to a metastable state (caused by the kinetic inhibition of this process at low temperatures). Upon heating the system, the capability of structural relaxation increases and may lead to the adoption of a metastable liquid state corresponding to the given temperature.
- This metastable state can go over into the crystalline state, which requires overcoming of a thermodynamic potential barrier.
- Therefrom it follows, that glass formation and crystallisation are competitive processes.

The characteristic time of the glass state is highly temperature dependent³⁹. Depending on the nature and the location of crystallisation from metastable liquids, [40] distinguished different mechanisms⁴⁰. The authors listed a number of arguments to use glass-forming melts as interesting models for the investigation of nucleation, growth, and overall crystallisation phenomena (e. g., serving as "Drosophila" of nucleation theory).

Here, we want to emphasise the atmospheric relevance of glass transition, which was recently addressed, e. g., by [131] and [86]. [131] identified the formation of glassy aerosol particles as a new process, by which water soluble organics might influence ice nucleation, ice growth, chemical reactions and water uptake of aerosols in the upper troposphere. The authors characterised glassy aerosol particles as disordered amorphous (non-crystalline) solids, formed when a liquid is cooled without crystallisation until the viscosity increases exponentially and molecular diffusion practically ceases. Employing differential scanning calorimeter, the glass transition temperatures, homogeneous ice nucleation temperatures, and ice melting temperatures of various aqueous inorganic, organic and multi-component solutions were investigated for different solutes (polyols, glucose, raffinose, levoglucosan, an aromatic compound, sulfuric acid, ammonium bisulfate and mixtures of dicarboxylic acids (M5), of dicarboxylic acids and ammonium sulfate (M5AS), of two polyols, of glucose, and ammonium nitrate, and of raffinose and M5AS. The authors found, that the glass transition temperatures of the aqueous solutions from the investigated inorganic solutes are too low to be of atmospheric importance $(T_{\sigma} \approx 180 \,\mathrm{K})$. In contrast to this, aqueous organic and multi-component solutions were found to readily form glasses at low but atmospherically relevant temperatures ($T_{\rm g} \leq 230$ K). The authors derived state diagrams (in terms of temperature and water activity), revealing that the higher the molar mass of the aqueous organic or multi-component solutes, the higher the glass transition temperature of their respective solutions at a given water activity. To a less extent, the glass transitions temperature was found to depend also on the hydrophilicity of the organic solutes. The authors concluded, that aerosol particles containing larger ($\geq 150 \text{ g mol}^{-1}$)) and more hydrophobic organic molecules are more likely to form glasses at intermediate to high relative humidities in the upper troposphere. Finally, their results suggested, that the water uptake of aerosols, heterogeneous chemical reactions in aerosol particles, as well as ice nucleation and ice crystal growth can be significantly impeded or even completely inhibited in organic-enriched aerosols at upper tropospheric temperatures. This has implications for cirrus cloud formation and upper tropospheric relative humidity. In order to fully assess the influence of glassy aerosols on the direct and indirect aerosol effect on the characteristic scale of single clouds as well as on regional to global scales, [131] demanded microphysical and/or large scale modelling studies to incorporate glass formation processes. Furthermore, a better knowledge of the chemical composition of the upper tropospheric aerosol is required to improve our understanding of ice cloud formation and upper tropospheric humidity.

[86] performed laboratory studies on the formation of the metastable cubic phase of ice Ic via glass formation. Cubic ice can form when inorganic solution droplets freeze below about 200 K. However, owing to the large and sometimes dominant proportions of oxygenated organic material in tropospheric aerosols in addition to inorganic substances, the author investigated the influence of a characteristic proxy for these organics on the cubic ice formation. [86] demonstrated, that the threshold freezing temperature below which cubic ice forms and persists will be shifted to considerably

³⁸[131] noted, that during the glass transition neither a release of latent enthalpy nor a discontinuous change in the ordering of the molecules occurs, making glass formation not easily observable by many experimental techniques.

³⁹According to [40], at room temperature glasses can exist for extremely long periods. This is caused by their high viscosity, inhibiting structural rearrangements required for crystal nucleation and growth. Though, when a glass is heat-treated for a sufficiently long time at temperatures within or above the glass transition range, devitrification readily starts (starting usually from the surface, and sometimes starting in the bulk via heterogeneous or homogeneous nucleation).

 $^{^{40}}$ [40] distinguished the following mechanisms of nucleation (i. e., the process of formation of the precursors of the crystalline phases): (i) homogeneous nucleation (stochastic process occurring with the same probability in any given volume (or surface) element), (ii) heterogeneous nucleation (occurring on preferred nucleation sites, e. g., such as pre-existing interfaces, previously nucleated phases, and surface defects). Furthermore, according to the nucleation location, volume (bulk) and surface crystallisation can be distinguished.

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higher temperatures in solution droplets containing a carboxylic acid (2-hydroxypropane-1,2,3-tricarboxylic acid, citric acid, $C_6H_8O_7$ used as proxy) ($\approx 219\pm 6$ K). Cubic and the stable hexagonal ice are the only phases to crystallise in micrometre sized citric acid droplets and therefore always exist in contact with aqueous citric acid solution. Considering the ubiquity of oxygenated organic material with similar functionality to citric acid in the atmosphere, the author argued, that cubic ice may be stabilised in solution droplets under a much wider temperature range than previously thought. Furthermore, the extremely high viscosity of aqueous citric acid solutions at low temperatures is considered to play an important role in the stabilisation of cubic ice. The point in the state diagram (temperature–composition (= citric acid mass fraction) plot), where the glass transition temperature crosses the liquid/ice Ic equilibrium line defines that temperature, below which ice crystallisation will most likely be incomplete and the solvent mediated phase transformation will not be active even at much lower cooling rates ([86], see Fig. 3 therein). Cubic ice embedded within a highly viscous (or glassy) solution will form below this threshold, even at the lowest atmospheric cooling rates (assuming, that T_g is independent of the cooling rate). From the positions of the liquid/ice Ic line and the T_g line in the state diagram, the author reported this threshold (i. e., the line-crossing point) amounting ≈ 208 K. The stabilisation of ice Ic within solution droplets and the subsequent formation of clouds composed of ice Ic would have important consequences for the relative humidities with respect to flat surfaces of hexagonal and cubic ice read:

$${\rm RH}_{\rm Ih} = \frac{p_{\rm H_2O}}{p_{\rm Ih}^0} \;, \qquad {\rm RH}_{\rm Ic} = \frac{p_{\rm H_2O}}{p_{\rm Ic}^0}$$

Here, $p_{\rm H_2O}$ denotes the vapour pressure of water, and $p_{\rm Ih}^0$ and $p_{\rm Ic}^0$ the equilibrium vapour pressures of water over flat surfaces of hexagonal and cubic ice, respectively. The equilibrium vapour pressure of ice Ic was reported to be $\approx 11\%$ higher than that of ice Ih, i. e., $p_{\rm Ih}^0 < p_{\rm Ic}^0$. Therewith, one has:

$$\frac{\mathrm{RH}_{\mathrm{Ih}}}{\mathrm{RH}_{\mathrm{Ic}}} = \frac{p_{\mathrm{Ic}}^{0}}{p_{\mathrm{Ih}}^{0}} > 1$$

Assuming clouds being composed of ice Ic, than $RH_{Ih} > 100 \%$ within ice clouds might be expected, which would explain observed large RH_{Ih} values within ice clouds ([86], see references therein).

25.4 Supplementary Material

The supplementary material included into the website-version of the present chapter and available as pdf-file from the authors contains a description of the theory of atmospheric water freezing and of deliquescene/efflorescence within the framework of classical thermodynamics and classical nucleation theory. The description is based on the theoretical approaches of ([92], Chapters 4-7, and 9 therein), of [60, 61, 62, 63, 64], of [100, 101, 102, 103], and of [88, 90, 91]. Additional sources for the elaboration of the details of the calculus are cited in the text. The description includes

- the thermodynamic and kinetic foundation of the theory of phase transitions,
- the theory of ice nucleation by heterogeneous freezing of deliquescent mixed CCN as proposed by [61],
- the theory of
 - volume freezing via homogeneous and heterogeneous processes, and
 - surface freezing and surface melting regimes via pseudo-heterogeneous processes

including the determination of freezing and melting temperatures, freezing and melting point depressions, and freezing and melting temperature lapse rates as proposed by [62],

- the theory of surface-diffusion mediated heterogeneous freezing according to ([92], Section 9.1.3.1 Nucleation on a planar substrate),
- the thermodynamic theory of deliquescence/efflorescence of soluble particles as proposed by [100, 101, 102, 103], including
 - the derivation of the generalised Gibbs-Kelvin-Köhler equation of the theory of nucleation on soluble particles, and
 - the generalised Ostwald–Freundlich equation of the theory of solutions (both equations employing the mechanical and thermodynamic concept of disjoining pressure),
- a theoretical approach to efflorescence employing classical nucleation theory [88, 90, 91].

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26 Vom Sechseckigen Schnee: Strena seu de Nive sexangula (Some Excerpts)

Johannes Kepler

¹Wirklich, ohne echtes Wissen ist das Leben tot. Hätte doch die Ehebrecherin jener netten Aesopschen Fabel² etwas von dem Formvermögen, das im Schnee wirkt, gewusst, dann hätte sie ihren Gatten überreden können, sie hätte vom Schnee empfangen, und es wäre ihr das Kind ihrer Liebe nicht so leicht durch die List des Gatten geraubt worden...

Nach einer Beschreibung von Bad Boll ragt bei einem Mineral der oberste Teil eines Ikosaeders hervor. Daraus ergibt sich, dass dieses Formvermögen wahrscheinlich bei verschiedenen Flüssigkeiten unterschiedlich ist.
Beim Vitriol kommt häufig die kubisch-rhombische Figur vor. Beim Salpeter ist dieselbe Figur zu finden
Daher mögen die Chemiker sagen, ob im Schnee ein Salz stecke und welcher Art dieses Salz ist und wie es die Figur hervorbringt.
Aber ich - da ich jetzt an das Tor der Chemie geklopft habe und sehe, wieviel noch zu sagen wäre bis man in dieser Sache die Ursachen kennengelernt hat - ich will lieber von Dir ... hören, was Du denkst, als dass ich Dich weiter mit gelehrten Reden ermüde.

Nichts folgt.

Ende

¹Johannes Kepler (27. 12. 1571 - 15. 11. 1630), Vom sechseckigen Schnee. Akademische Verlagsgesellschaft Geest & Portig, Leipzig, 1987; Ostwalds Klassiker der Exakten Wissenschaften, Bd. 273.

²Ein Kaufmann, der über zwei Jahre in der Fremde weilte, fand seine Frau zu Hause mit einem neugeborenen Kind. Er war verwundert und fragte seine Frau, wie das wohl möglich sei. Sie antwortete ihm, sie habe aus Schnee ein kleines Kind geformt und es aufgegessen. Daher habe sie das Kind bekommen. Der Kaufmann liess es geschehen. Als der Knabe sieben Jahre alt war, nahm ihn der Kaufmann mit auf eine längere Reise, damit er Gesellschaft habe. So sagte er seiner Frau. Doch gab er den Knaben einem anderen Kaufmann in dem fremden Land, damit er dort leben möge.

27 Appendices

In dem von mir vertretenen Fache der theoretischen Physik ist diese Frage gegenwärtig noch nicht so weit akut geworden, um mich zu einer speziellen Stellungnahme zu veranlassen. Ich will aber gerne im allgemeinen meine Erfahrungen und Ansichten zu dem Punkt in aller Kürze zur Kenntnis bringen.

Wenn eine Frau, was nicht häufig ist, aber doch bisweilen vorkommt, für die Aufgaben der theoretischen Physik besondere Begabung besitzt und ausserdem den Trieb in sich fühlt, ihr Talent zur Entfaltung zu bringen, so halte ich es, in persönlicher wie auch in fachlicher Hinsicht, für unrecht, ihr aus prinzipiellen Rücksichten die Mittel zum Studium von vornherein zu versagen,

ich werde ihr gerne, soweit es überhaupt mit der akademischen Ordnung verträglich ist,

den probeweisen und stets widerruflichen Zutritt zu meinen Vorlesungen und Übungen gestatten

und habe in dieser Beziehung auch bis jetzt nur gute Erfahrungen gemacht.

Andererseits muss ich aber daran festhalten, dass ein solcher Fall immer nur als Ausnahme betrachtet werden kann, und dass es insbesondere höchst verfehlt wäre, durch Gründung besonderer Anstalten die Frauen zum akademischen Studium heranzuziehen, wenigstens insofern es sich um die rein wissenschaftliche Forschung handelt.

Amazonen sind auch auf geistigem Gebiet naturwidrig.

Bei einzelnen praktischen Aufgaben, z.B. in der Frauenheilkunde, mögen vielleicht die Verhältnisse anders liegen, im allgemeinen kann man aber nicht stark genug betonen, dass die Natur selbst der Frau ihren Beruf als Mutter und als Hausfrau vorgeschrieben hat und dass Naturgesetze unter keinen Umständen ohne schwere Schädigungen, welche sich im vorliegenden Fall besonders an dem nachwachsenden Geschlecht zeigen werden, ignoriert werden können.

Max Planck

Im Leben geht es nicht darum, gute Karten zu haben, sondern auch mit einem schlechten Blatt gut zu spielen.

Robert Louis Stevenson

27.1 Programs of the Research Workshops 2009, 2010 and 2011

27.1.1 Research Workshop 2009

Sunday, April 12: 9.30

1. Vladimir S. Balitsky (Chernogolovka, Russia): Visualization "in situ" of the Behavior and Phase Transformations of Oil and other Hydrocarbons in Aqueous Solutions at Temperatures up to 400 °C and Pressures up to 150 MPa

2. Hans-Jürgen Hoffmann (Berlin, Germany): Energy and Entropy of Crystals, Melts and Glasses

3. Vladimir Ya. Shur (Ekaterinburg, Russia): Nano-domain Kinetics in Ferroelectrics: Physical Basis of Nanodomain Engineering & Nanotechnology in the Innovative University

4. Andriy M. Gusak, T. V. Zaporoshets (Cherkasy, Ukraine), K. N. Tu (Los Angeles, USA): Nucleation and Reactive Formation of Nanoshells and Nanowires

5. Irina G. Polyakova (St. Petersburg, Russia): Surface and Volume Crystallization of Sodium Borate Glasses

6. Georgi Th. Guria, M. Herrero, Ksenia E. Zlobina (Moscow, Russia): Nucleation Phenomena in the Fibrin Polymerisation-Fragmentation Kinetics

Monday, April 13: 9.00

7. Nicolay P. Malomuzh (Odessa, Ukraine): Nucleation and Modified Cluster Approach in Application to Glass-Forming Liquids

8. Galina G. Boiko (St. Petersburg, Russia): Modelling of Silicon Dioxide in the Liquid, Crystalline and Vitreous States by Molecular Dynamics Simulations

9. Alexander I. Krivchikov, O. Korolyuk, I. Sharapova, O. Romantsova (Kharkov, Ukraine): Crystallization and Annealing Effect in Thermal Conductivity of Solid Primary Alcohols

10. Oxana A. Korolyuk, A. I. Krivchikov, I. Sharapova, O. Romantsova (Kharkov, Ukraine): Thermal Conductivity of Metastable States of Solid Simple Alcohols

11. Boris Z. Pevzner (Laboratory of Glass Properties, St.-Petersburg, Russia): Sintering of Crystallizing Glass Powders: Simultaneous Consideration of Crystallization, Viscosity and Fusion Diagram of Glass-forming Systems

12. Leonid M. Landa, Sc. Thomsen (Carleton, USA): Negative Pressure and Strength of Glasses before and after Tempering and Application to Silica-Glass

Special lectures: 18. 30

13. Kirill I. Shmulovich (Chernogolovka, Russia), L. Mercury, C. Ramboz, M. El Mekki (Orleans, France): Vapor Phase Nucleation in Micro-volumes (d =3-300 μ m) of Liquids: Density, Negative Pressure, Concentration, Kinetic and Size Effects

14. Naoum M. Kortsensteyn: Some other Spectacular Adventures of N. M. K. and his Wife this time in Bavaria and eventually Poland

Tuesday, April 14: 9.00

15. Vladimir G. Baidakov (Ekaterinburg, Russia): Spinodal and Pseudo-Spinodal Curves: Definitions, Existence and Results of Molecular-Dynamics Computations

16. Attila R. Imre (Budapest, Hungary): Determination of the Location of the Spinodal by MD-Simulations

17. Vitaly B. Rogankov (Odessa, Ukraine): Quasi-binodal at Negative Pressures as a Possible Limit of Actual Metastability

18. Dmitry I. Zhukhovitskii (Moscow, Russia): Surface and Bulk Fluctuations of Lennard-Jones Clusters

19. Dmitry Yu. Ivanov (St. Petersburg, Russia): Theory and Experiment in 2nd Order Phase Transitions and Critical Phenomena (in Application to Pure Liquids)

20. Vladimir E. Vinogradov, P. A. Pavlov (Ekaterinburg, Russia): Experimental Investigation of Superheating of Liquids under Large Negative Pressures

Special lectures: 18. 30

21. Genri E. Norman (Moscow, Russia): a) Nucleation Phenomena at High Strain Rate Loading of Metals b) Spontaneous Dislocation Nucleation at Plastic Deformation; - Alexey Yu. Kuksin (Moscow, Russia): Nucleation

Preceding Fracture of Metals - Vasili V. Pisarev (Moscow, Russia): Large-Scale Cavity Growth in a Lennard-Jones Liquid - Oleg V. Sergeev (Moscow, Russia): Kinetic Spinodal and Spectral Analysis of Fluctuations in a Lennard-Jones Liquids

22. Vladimir V. Stegailov (Moscow, Russia): Nucleation During the Methane Clathrate Hydrate Decay

Wednesday, April 15: 9.00

23. Jürn W. P. Schmelzer (Dubna, Russia & Rostock, Germany): Cluster-Size Distributions in Nucleation-Growth Processes: Some "History" and Motivation for Renewed Interest

24. Mykola O. Pasichnyy, A. S. Shirinyan (Cherkasy, Ukraine), J. W. P. Schmelzer (Dubna, Russia & Rostock, Germany), A. S. Abyzov (Kharkov, Ukraine): Cluster Size Distributions in First-Order Phase Transitions in Binary Solutions: Evolution Along the Optimal Trajectory

25. Andriy A. Kovalchuk, A. S. Shirinyan (Cherkasy, Ukraine), J. W. P. Schmelzer (Dubna, Russia & Rostock, Germany): Cluster Size Distributions in First-Order Phase Transitions in Binary Solutions: General Approach (two models)

26. Dragomir Tatchev (Sofia, Bulgaria & Berlin, Germany): Kinetics of Primary Crystallization of Hypoeutectic Amorphous Ni-P Alloys Studied by in-situ ASAXS and DSC

27. Naoum M. Kortsenshteyn, A. K. Yastrebov (Moscow, Russia): Dynamics of Evolution of the Droplet Size Distribution Function at a Gradual Creation of Supersaturation for Various Modes of Droplet Growth

28. N. M. Kortsenshteyn, Arsenij K. Yastrebov (Moscow, Russia): Influence of Heat Exchange Between Droplets and Vapour in a Vapour-Gas Mixture on the Dynamics of the Droplet Size Distribution Function

Special discussion: 18. 30

a) Andriy A. Kovalchuk, Aram S. Shirinyan (Cherkasy, Ukraine): Evolution of Cluster Size Distributions accounting for Heterogeneous Nucleation

b) Alexander S. Abyzov, A. A. Kovalchuk, J. W. P. Schmelzer, V. V. Slezov: Evolution of Cluster Size Distributions in Phase Formation Processes in Multi-Component Solutions: Nucleation and Spinodal Decomposition

c) A. A. Kovalchuk, Aram S. Shirinyan, A. S. Abyzov, J. W. P. Schmelzer: Evolution of Cluster Size Distributions: Confinement Effects . . .

Thursday, April 16: 9.00

29. Arkady E. Glikin (St. Petersburg, Russia): Homogeneous Nucleation of Mixed Crystals in Solutions: Distribution of Crystals in Isomorphic Compositions and Sizes

30. Timur V. Tropin, M. V. Avdeev, V. B. Priezzhev, V. L. Aksenov (Dubna & Moscow, Russia): Application of Nucleation Theory for describing the Kinetics of Cluster Formation and Growth in Solutions of Fullerene C60

31. Valeri I. Leiman, V. Maksimov, P. Valov (St. Petersburg, Russia): Size Distribution of CuCl-Particles Depending on Temperature and Time of Nucleation

32. Alexander R. Gokhman, F. Bergner (Odessa, Ukaine; Dresden, Germany): Application of Rate Theory to Interpret Positron Annihilation Lifetimes for Neutron Irradiated Pure Iron

33. Yu. S. Bilogorodskyy, Aram S. Shirinyan (Cherkasy, Ukraine), J. W. P. Schmelzer (Dubna, Russia & Rostock, Germany): Influence of Particle Sizes of a Nano-powder on Nucleation and Growth of Different Crystallographic Phases during Temperature Cycling (30 min)

34. Alexander L. Tseskis (Leverkusen, Germany): On BEC in Weakly Interacting Systems (30 min)

35. Oleg A. Osmayev, R. V. Shapovalov (Kharkov, Ukraine): Two-Mass Transport Mechanism of Grain Boundary Segregation (30 min)

Special lectures: 18. 30

36. Alexey A. Lushnikov: The Adventures of a Russian in Finland

37. Alexander L. Tseskis: Other Spectacular Adventures, this time of A. L. T. and his Wife in Europe

Friday, April 17: 9.00

38. Alexey A. Lushnikov (Moscow, Russia): Coalescence of Graphs

39. Werner Ebeling (Berlin, Germany): Novel Theoretical Approaches to Coulomb Explosion of Clusters

40. Alexander P. Chetverikov, W. Ebeling, M. G. Velarde (Saratov, Russia; Berlin, Germany; Madrid, Spain): Thermal Solitons in Nonlinear Lattices

41. Pavel V. Kashtanov (Moscow, Russia): Nucleation Processes in Magnetron Plasma

42. R. S. Berry, Boris M. Smirnov (Moscow, Russia): Phase Transitions in Metal Clusters

43. A. E. Kuchma, Gennady Yu. Gor, F. M. Kuni (St. Petersburg, Russia): Gas Bubble Growth Dynamics after its Nucleation in Supersaturated Solutions

44. Jürn W. P. Schmelzer (Dubna, Russia & Rostock, Germany): On the Concept of Temperature in Application to Small Systems

Saturday, April 18: 9.30

45. Valeri V. Levdansky (Minsk, Belorussia), J. Smolik, V. Zdimal, and P. Moravec (Prague, Czech Republic): Effect of Surface Phenomena in Condensation of Molecules on Small Charged Aerosol Particles

46. Alexander K. Shchekin, T. Podguzova (St. Petersburg, Russia): New Results on the Combined Effects of Disjoining Pressure and Electric Field in Nucleation on Nanosized Charged Solid Nuclei

47. Anatoly Kuchma, F. M. Kuni, A. K. Shchekin (St. Petersburg, Russia): Effect of Excluded Volume on the Nucleation Stage in First-Order Phase Transitions

48. Olaf Hellmuth (Leipzig, Germany), A. K. Shchekin (St. Petersburg, Russia), J.W.P. Schmelzer (Dubna, Russia & Rostock, Germany): On the Contribution of Organic Vapours to Atmospheric New Particle Formation

49. Victor B. Kurasov (St. Petersburg, Russia): Theory of Transversal Transitions in Nucleation

50. Vladimir P. Yefimov, A.S. Abyzov, A.N. Dovbnya, V.V. Slezov A.V. Rybka, V.V. Zakutin, N.G. Reshetnyak, A.A. Blinkin, Y.P. Bereznyak, V.P. Romasko, Yu.E. Gordienko, S.V. Babychenko, G.N. Bendeberya (Kharkov, Ukraine): Formation of Nano-size Amorphous-crystalline Structures in Silicon under Irradiation

27.1.2 Research Workshop 2010

Sunday, April 11: 9.30

1. Christoph Schick, E. A. Zhuravlev, A. Wurm (Rostock, Germany): Fast Scanning Nano-Calorimetry (106 K/s) - Applications to Polymers and Metals

2. Evgeny A. Zhuravlev, C. Schick (Rostock, Germany): Crystal Nuclei Formation and Growth in Poly (ecaprolactone) studied by Fast Scanning Calorimetry

3. Hans-Jürgen Hoffmann (Berlin, Germany): Melting, Glass Transition and Relaxation of Inorganic Glasses: 2 Parts

4. Akira Takada (Tokyo, Japan): Entropy of Glass: Interpretation in Terms of Statistical Mechanics

5. Galina G. Boiko (St. Petersburg, Russia): Some Theoretical Approaches to Glass Transition Process Description

Monday, April 12: 9.00

6. Vladimir G. Baidakov (Ekaterinburg, Russia): Experimental Investigations of Nucleation in Superheated and Super-Cooled Water

7. Azat O. Tipeev, V. G. Baidakov, S. P. Protsenko (Ekaterinburg, Russia): Crystallization of a Super-Cooled Lennard-Jones Liquid: Molecular Dynamics Analysis

8. Vladimir M. Fokin (St. Petersburg, Russia), Alexander S. Abyzov (Kharkov, Ukraine), J. W. P. Schmelzer (Dubna & Rostock), E. D. Zanotto (Sao Carlos, Brazil): Stress Induced Pore Formation and Phase Selection in a Crystallizing Stretched Glass

9. Galina A. Sycheva (St. Petersburg, Russia): Heterogeneous Nucleation of Lithium Meta- and Disilicate Crystals in Photostructurable Glasses

10. Boris Z. Pevzner, V. P. Klyuev, I. G. Polyakova (St. Petersburg, Russia): Thermal Expansion over the Glass Transition Region: Influence of Composition and Structure of Glasses

11. Andriy M. Gusak, A. O. Kovalchuk (Cherkassy, Ukraine), K. N. Tu (Los Angeles, USA): Diffusion and Nucleation Problems in Growth and Reactions of Nanowires

12. Andrii O. Kovalchuk, A. M. Gusak (Cherkassy, Ukraine): Modification and Direct Verification of Classical Nucleation Theory in Point Contact Reactions

Special lectures: 18. 30

13. Akira Takada (Tokyo, Japan): Some Reflections on Japan

14. Naoum M. Kortsenshteyn (Moscow, Russia): Some other Spectacular Adventures of Naoum M., his Wife and their camera this time in Prague and Kamchatka

Tuesday, April 13: 9.00

15. Rafael M. Hovhannisyan, H. Alexanyan (Erevan, Armenia): Phase and Glass Forming Diagrams in the Binary Gallium Borate and Ternary Barium Gallium Borate Systems

16. Martun Hovhannisyan, H. Alexanyan, R. Hovhannisyan (Erevan, Armenia): Phase Diagram and Stoichiometric Glass Ceramic Formation in the BaO-Bi2O3-B2O3 system

17. Georgy N. Gontcharov (St. Petersburg, Russia): Nucleation of Iron Nuclei at Stellar Synthesis of Actinide and Super-Heavy Nuclides

18. Alexander P. Chetverikov (Saratov, Russia), W. Ebeling (Berlin, Germany), M. G. Velarde (Madrid, Spain): Dynamics of Localized Excitations in Heated Nonlinear Two-Dimensional Lattices

19. Ilya A.Valuev, W. Ebeling, M. Yu. Romanovsky (Moscow, Russia & Berlin, Germany): Numerical Simulation of Nanocluster Coulomb Explosion

20. R. S. Berry, Boris M. Smirnov (Chicago, USA, Moscow, Russia): Cluster Catalysis as a Result of Subsequent Transitions between Configuration States of Clusters and Reagents

Wednesday, April 14: 9.00

21. Dragomir Tatchev, A. Hoell, A. Heinemann, S. Haas, D. Tatchev, R. Kranold, M. Müller, G. Goerigk (Sofia, Bulgaria & Berlin, Germany): Nanostructure and Chemical Composition of Precipitates in Silver-free Photo-chromic Glasses

22. Alexander R. Gokhman (Odessa, Ukraine), F. Bergner, R. Küchler (Dresden, Germany): Rate Theory and SANS Study of Phase Separation in a Neutron Irradiated Fe-12.5at

23. Yu. Ts. Oganessian (Dubna, Russia): Synthesis of the new 117 Element

24. Naoum M. Kortsenshteyn, Arseny K.Yastrebov (Moscow, Russia): Heat Exchange between Droplets and Vapour in View of the Dynamics of Evolution of the Droplet Size Distribution Function

25. Naoum M. Kortsenshteyn and E. V. Samuilov (Moscow, Russia): Formation of the Submicron Condensed Phase in the Volume of Combustion Products of Coals

26. Alexander L. Tseskis (Leverkusen, Germany): Path Integral and Thermodynamics

Special lectures: 18. 30

27. Leonid N. Davydov (Kharkov, Ukraine): Thorium Fuel Cycle: Perspectives and Problems

28. Alexander L. Tseskis (Leverkusen, Germany): NRW/Germany-some colourful pictures and even more colourful comments

Thursday, April 15: 9.00

29. Attila R. Imre (Budapest, Hungary): Bubble Nucleation in Geo-Fluids

30. Sergey P. Fisenko (Minsk, Belorussia): Towards to the Statistical Theory of Nucleation Kinetics in a Liquid Solution

31. Dmitri I. Zhukhovitskii (Moscow, Russia): Surface Oscillations of a Charged Cluster

32. Aram S. Shirinyan, Yu. Bilogorodskyy (Kiev & Cherkassy, Ukraine): Effect of a Size-Dependence of the Hetero-Diffusion Coefficient on the Nano-phase Growth in a Binary Diffusion Couple at Initial Stage of Phase Formation

33. Pavel V. Kashtanov (Moscow, Russia): Critical Phenomena in Clusters

34. Vitaly B. Rogankov (Odessa, Ukraine): Concept of Non-Classical Spinodal and Near-Critical Heterophase Fluctuations

35. Vladimir N. Kondratyev (Kiev, Ukraine): Stability of Hot Droplets: Molecular Dynamics Simulations

Friday, April 16: 9.00

36. Stanislav V. Burov, E. N. Brodskaya, A. K. Shchekin (St. Petersburg, Russia): Aggregation Work in Nonionic and Ionic Micellar Solutions: Theory and Molecular Dynamics Simulations

37. Anatoly E. Kuchma (St. Petersburg, Russia): Some New Analytical Results in the Theory of Supercritical Droplet Growth

Alexander K. Shchekin (St. Petersburg, Russia): Slow Relaxation and Aggregation in Ionic Micellar Solutions
 Gennady Yu. Gor, A. E. Kuchma (St. Petersburg, Russia): Bubble Growth in Supersaturated Solutions:

Dissociation of Solute Molecules

40. Valery V. Levdansky, J. Smolik, V. Zdimal, P. Moravec (Minsk, Belorussia & Prague, Czech Republic): Molecule Trapping in Formation of Nanoscale Particles (Clusters) by Deposition from a Gas Phase

41. Valeri I. Leiman, P. Valov, V. Maksimov, O. Derkacheva (St. Petersburg, Russia): Formation and Dissolution of Subcritical Nuclei of CuCl in Glass

42. Olga Yu. Derkacheva, P. Valov, V. Leiman, V. Maksimov (St. Petersburg, Russia): Scattering of Light on Small CuCl Particles in Glass

Saturday, April 17: 9.00

43. Gennady Yu. Gor (St. Petersburg, Russia & USA): Some Reflections on my Work in the USA

44. Genry E. Norman, A. V. Yanilkin (Moscow, Russia): Spontaneous Homogeneous Nucleation of Dislocations: Theory and Molecular Dynamics Modelling and Simulation

45. Grigory S. Smirnov, V. V. Stegailov (Moscow, Russia): Atomistic Simulation of Nucleation Events in Methane Hydrates

46. G. E. Norman, Vasili V. Pisarev (Moscow, Russia): Nucleation Phenomena at Crystallization: Molecular Dynamics Modeling and Simulation

47. Jürn W. P. Schmelzer (Rostock, Germany and Dubna, Russia): On the Determination of the Kinetic Pre-factor in Crystal Nucleation in Multi-Component Systems

27.1.3 Research Workshop 2011

Sunday, April 17: 9.30

1. Vladimir S. Balitsky, L. Balitskaya, M. Novikova, G. Bondarenko (Chernogolovka, Russia), S. Penteley (Nancy, France): In-situ Behaviour and Phase States of Aqueous-Hydrocarbon Fluids at Elevated and High Temperatures and Pressures

2. Alexander G. Simakin (Chernogolovka, Russia): Cluster Size Dynamics of Magmatic Minerals: Records of the Interplay of Multi-scale Processes

3. Maria N. Khotienkova, V. G. Baidakov, V. N. Andbaeva, A. M. Kaverin (Ekaterinburg, Russia): Capillary Constant and Surface Tension of Methane-Nitrogen Solutions: Experiment

4. Vitaly B. Rogankov (Odessa, Ukraine): Asymmetry of Nucleation in Metastable Vapor and Liquid Phases

5. Gerd Röpke (Rostock, Germany): Cluster Formation and Nuclear Liquid-Gas Phase Transition

6. Dmitry N. Voskresensky (Moscow, Russia): Viscosity and Thermal Conductivity in First-Order Phase Transitions

7. Kyrill A. Bugaev, A. I. Ivanytskyi, E. G. Nikonov, A. S. Sorin and G. M. Zinovjev (Kiev, Ukraine): Can we Rigorously Define the Phases in a Finite System?

8. Evgeny Kolomeitsev (Banska Bystrica, Slovakia): Mesonic Condensates in Dense Nuclear Matter

9. Minoru Okamoto (Tsukuba, Japan): Three-Dimensional Calculation of Inhomogeneous Structure in Low-Density Nuclear Matter

Monday, April 18: 9.00

10. Akira Takada (Asahi Glass Company, Japan): Revisit of Entropy Issues in Non-Equilibrium States

11. Mars Z. Faizullin, V. N. Skokov, V. P. Koverda (Ekaterinburg, Russia): Glass Transition and Crystallization of Water and Aqueous Solutions of Organic Liquids

12. Oksana A. Korolyuk (Kharkov, Ukraine): New Effects in the Thermal Conductivity of Molecular Glasses: Mono-Hydroxyl Alcohol

13. Alexander I. Krivchikov, O. A. Korolyuk, I. V. Sharapova, M. Hassaine, R. J. Jimenez-Rioboo, M. A. Ramos (Kharkov, Ukraine): Solid State Transformations and Thermal Properties of Metastable States of Butyl Alcohol at Low Temperatures

14. Irina G. Polyakova, I. E. Apakova, T. S. Markova, Oleg V. Yanush (Saint Petersburg, Russia): Prediction of Crystalline Compounds on the Basis of Vibrational Spectra of Silicate, Borate and Tellurite Glass-forming Systems

15. Galina G. Boiko (St. Petersburg, Russia): Visible Light Scattering by Glasses During Phase Separation Processes

27.1 Programs of the Research Workshops 2009, 2010 and 2011

16. Boriz Z. Pevzner, V. V. Golubkov, O. V. Yanush (St. Petersburg, Russia): Initiation of Defects in Quartz and Vitreous Silica and their Evolution into the Vitreous Coesite Phase under the Influence of Neutron Irradiation *Special lectures:* 18. 30

17. Vladimir S. Balitsky, Lyudmila V. Balitskaya (Chernogolovka, Russia): A Geological Excursion to the North of Russia

18. David Blaschke (Wroclaw, Poland & Dubna, Russia): Exploration of the QCD Phase Diagram with Heavy-Ion Collisions and Stellar Collapse Simulations

Tuesday, April 19: 9.00

19. Donguk Suh and Kenji Yasuoka (Tokyo, Japan): Heterogeneous Nucleation based Nanoparticle Growth Analysis by Molecular Dynamics

20. Vladimir G. Baidakov, V. E. Vinogradov, P. A. Pavlov (Ekaterinburg, Russia): Spontaneous Cavitation in Argon and in Solutions of Helium in Argon

21. Konstantin S. Bobrov, V. G. Baidakov (Ekaterinburg, Russia): Spontaneous Cavitation in a Lennard-Jones Liquid at Temperatures Below the Triple Point

22. Timur V. Tropin, J. W. P. Schmelzer, C. Schick (Dubna, Russia & Rostock, Germany): On the Dependence of the Properties of Glasses on Cooling and Heating Rates

23. A. Yu. Kuksin, G. E. Norman, V. V. Pisarev, Vladimir V. Stegailov (Moscow, Russia): Atomistic and Classical Kinetic Theories of Nucleation

24. G. E. Norman, Vasili V. Pisarev (Moscow, Russia): Crystal-Melt Surface Energy and Crystal Nucleation Kinetics in Liquid Aluminum

25. Lada N. Kolotova, G. E. Norman, V. V. Pisarev (Moscow, Russia): "Thermodynamic" Properties of Glassy Aluminium

Wednesday, April 20: 9.00

26. A. P. Chetverikov, Werner Ebeling, G. Röpke, M. G. Velarde (Saratov, Russia; Berlin, Germany; Rostock, Germany; Madrid, Spain): Nonlinear Excitations and Hopping Transport in Two-dimensional Atomic Layers

27. Alexander P. Chetverikov, W. Ebeling, M. G. Velarde (Saratov, Russia; Berlin, Germany; Madrid, Spain): Properties of Localized Excitations in Multi-layer Two-Dimensional Lattices

28. Boris M. Smirnov (Moscow, Russia): Kinetic and Diffusion Regimes of Cluster Processes in Gases

29. Nikolay P. Mikhin, Ye. Vekhov (Kharkov, Ukraine): On the Mechanism of Destabilization of the HCP-Phase of Solid Helium

30. Valentyn Yu. Rubanskiy, A. Lisunov, V. Maidanov, S. Rubets, E. Rudavskii (Kharkov, Ukraine): Formation of a Glassy Phase in Deformed Solid Helium in the Supersolid Region

31. Nikolay P. Mikhin, A. Birchenko, Ye. Vekhov, E. Rudavskii (Kharkov, Ukraine): BCC-HCP Transition in 4He: Homogeneous and Heterogeneous Nucleation. Effect of 3He Impurities

Special lectures: 18. 30

32. Georgy N. Goncharov, V. V. Orlov (St.-Petersburg, Russia): Clustering of Global Events in Modern History of the Earth

33. Alexander S. Abyzov, A. Kolesnik (Kharkov, Ukraine): A Travel Through Europe

Thursday, April 21: 9.00

34. Andriy M. Gusak (Cherkassy, Ukraine): Flux-Driven Nucleation

35. Andriy O. Kovalchuk, D. V. Butenko (Cherkassy, Ukraine): Strong Limitations in Applicability of Classical Nucleation Theory to Diffusion-Controlled Phase Transitions

36. Aram S. Shirinyan, Yu. S. Bilogorodskyy (Kiev and Cherkassy, Ukraine): The Influence of Thickness of Metallic Solid Nanofilms on the Energy of Interatomic Interaction and Shift of Phase Diagram

37. Yuriy S. Bilogorodskyy (Cherkassy, Ukraine), A. S. Shirinyan (Kiev, Ukraine), J. W. P. Schmelzer (Dubna & Rostock, Germany): Features of Size Dependent Hysteresis and Phase Formation Kinetics during Temperature Cycling of Metal Nanopowders

38. Alexander R. Gokhman, F. Bergner, U. Birkenheuer, A. Ulbricht (Odessa, Ukraine; Dresden, Germany): Cluster Dynamics Study of Defect Evolution in Neutron-Irradiated Dilute and Concentrated Fe-Cr Alloys

39. Roman V. Shapovalov, V. V. Slezov, A. S. Abyzov, L. N. Davydov, (Kharkov, Ukraine): Effect of Variable External Parameters on the Nucleation and Growth of New Phase Clusters

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40. Alexander L. Tseskis, N. M. Kortsensteyn, J. W. P. Schmelzer (Leverkusen, Germany; Moscow, Russia; Dubna & Rostock): On "Smoothing" of First-Order Phase Transition in Small Systems *Special lectures:* 18, 30

41. Georgi T. Guria, O. A. Dudchenko (Moscow, Russia): Nucleation Phenomena in the Human Cardiovascular System

42. NMK and FAR (Moscow, Russia): We have been in Sorrento and we want to return there

Friday, April 22: 9.00

43. P. M. Valov, Valeri I. Leiman, O. Yu. Derkacheva, V. M. Maksimov, E. S. Markov, A. O. Vinogradov (St. Petersburg, Russia): Determination of Critical Nuclei Sizes in a Solid Solution of CuCl in Glass

44. Valery V. Levdansky, J. Smolik, V. Zdimal (Minsk, Belorussia & Prague, Czech Republic): Size Effects in Physicochemical Processes in Heterogeneous Systems with Nanoscale Objects

45. A. E. Kuchma, Alexander K. Shchekin (St. Petersburg, Russia): Self-Similar Regime of Droplet Growth Including the Stefan Flow

46. Dmitry Yu. Ivanov (St. Petersburg, Russia): New Test of the Applicability of the Ising Model to the Description of Real Liquids

47. Alexander K. Shchekin, M. S. Kshevetskyi, O. S. Pelevina (St. Petersburg, Russia): Fusion and Fission in Micellization Processes

48. Dmitry V. Tatyanenko, A. K. Shchekin (St. Petersburg, Russia): Nucleation on a Partially Wettable Solid Substrate: Thermodynamics and an Interface Displacement Model

Saturday, April 23: 9.30

49. Georgy N. Goncharov (St.-Petersburg, Russia): Approach to Cluster Model for Stellar Nucleosynthesis of Superheavy and Actinide Elements

50. Naoum M. Kortsenshteyn, A. K. Yastrebov (Moscow, Russia): Interphase Heat Transfer at Formation of Condensation Aerosol for Different Regimes of Droplet Growth

51. N. M. Kortsenshteyn, Arsenij K. Yastrebov (Moscow, Russia): Bulk Condensation of Supersaturated Vapour during Flow in a Nozzle

52. Roman V. Shapovalov (Kharkov, Ukraine): The Limit Solubility Relationships Derived Based on Frenkel's Heterophase Fluctuations Theory

53. Dmitry I. Zhukhovitskii (Moscow, Russia): The Bare Surface Tension and Fluctuations of Clusters with Long-Range Interaction

27.2 Content of the Proceedings *Nucleation Theory and Applications* 1997-99, 2000-02, 2003-05, 2006-08

Nucleation Theory and Applications

J. W. P. Schmelzer, G. Röpke, V. B. Priezzhev (Eds.) Joint Institute for Nuclear Research Publishing Department Dubna, Russia, 1999

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27.3 Monographs Published or Accepted for Publication by WILEY-VCH and Springer Prepared by Participants of the Workshops

Collections of Overview Lectures

J. Schmelzer, G. Röpke, R. Mahnke (Eds.): Aggregation Phenomena in Complex Systems Wiley-VCH Publishers, Weinheim, 1999.

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Monographs

- I. Gutzow, J. Schmelzer: The Vitreous State. Thermodynamics, Structure, Rheology, and Crystallization, Springer, 1995.
- 2. B. M. Smirnov: Clusters and Small Particles, Springer, 2000.
- 3. B. M. Smirnov: Physics of Atoms and Ions, Springer, 2003.
- 4. B. M. Smirnov: Principles of Statistical Physics, WILEY-VCH, Berlin Weinheim, 2006.
- 5. V. P. Skripov, M. Z. Faizullin: Solid-Liquid-Gas Phase Transitions and Thermodynamic Similarity, WILEY-VCH, Berlin-Weinheim, 2006 (Ed. J. W. P. Schmelzer).
- G. Baidakov: Explosive Boiling of Superheated Cryogenic Liquids, WILEY-VCH, Berlin - Weinheim, 2007 (Ed. J. W. P. Schmelzer).
- 7. B. M. Smirnov: Plasma Processes and Plasma Kinetics, WILEY-VCH, Berlin Weinheim, 2007.
- 8. R. Feistel, G. Nausch, N. Wasmund: State and Evolution of the Baltic Sea, 1952-2005, WILEY, 2008.
- 9. D. Yu. Ivanov: Critical Behavior of Non-Ideal Systems, WILEY-VCH, Berlin Weinheim, 2008 (Ed. J. W. P. Schmelzer).
- 10. V. V. Slezov: On the Kinetics of First-Order Phase Transitions, WILEY-VCH, 2009 (Ed. J. W. P. Schmelzer).
- 11. B. M. Smirnov: Cluster Processes in Gases and Plasmas, WILEY-VCH, Berlin Weinheim, 2006.
- 12. A. M. Gusak et al.: Diffusion-Controlled Solid-State Reactions, WILEY-VCH, 2010 (Ed. J. W. P. Schmelzer).
- 13. J. W. P. Schmelzer, I. Gutzow, Glasses and the Glass Transition, WILEY-VCH, 2011.
- 14. R. Feistel, W. Ebeling: Physics of Self-Organisation and Evolution, WILEY, 2011 (in press).

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