Thermodynamic Limit in Statistical Physics^{*}

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Abstract

The thermodynamic limit in statistical thermodynamics of many-particle systems is an important but often overlooked issue in the various applied studies of condensed matter physics. To settle this issue, we review tersely the past and present disposition of thermodynamic limiting procedure in the structure of the contemporary statistical mechanics and our current understanding of this problem. We pick out the ingenious approach by N. N. Bogoliubov, who developed a general formalism for establishing of the limiting distribution functions in the form of formal series in powers of the density. In that study he outlined the method of justification of the thermodynamic limit when he derived the generalized Boltzmann equations. To enrich and to weave our discussion, we take this opportunity to give a brief survey of the closely related problems, such as the equipartition of energy and the equivalence and nonequivalence of statistical ensembles. The validity of statistical mechanics. The major aim of this work is to provide a better qualitative understanding of the physical significance of the thermodynamic limit in modern statistical physics of the infinite and "small" many-particle systems.

Keywords: Statistical mechanics; thermodynamic equilibrium; equipartition of energy; Gibbs ensembles method; distribution functions; equivalence and nonequivalence of statistical ensembles; thermodynamic properties of many-particle systems; the thermodynamic limit; small systems; nanothermodynamics.

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1 Introduction

Equilibrium statistical mechanics^{1,2,3,4,5,6,7,8,9} is a well explored and relatively well established subject, in spite of some unsettled foundational issues. However, it was claimed about decade ago in an authoritative scientific journal¹⁰ that

The fact that classical equilibrium statistical mechanics works is deeply puzzling.

The purpose of the present paper will be to elucidate certain aspects of the reconciliation between the statistical mechanics and mechanics, i.e. dynamical systems,^{11,12} to emphasize and address a few important reasons for such a workability. Our central interest here will be the thermodynamic limit, equipartition of energy and equivalence and nonequivalence of ensembles.

In classical equilibrium statistical thermodynamics one deals with equilibrium states of a system. It is assumed that each of those states corresponds to a set of indistinguishable microstates, because the temperature, the pressure, and all other the so-called thermodynamic variables have the same value for each microstate of the set. Quantities, such as pressure and temperature are termed the state variables, which characterize the system in the state of statistical equilibrium. The thermodynamic limit is reached when the number of particles (atoms or molecules) in a system tends to infinity.

Hence, in statistical physics, the *thermodynamic limit* denotes the limiting behaviour of a physical system that consists of many particles (or components) as the volume V and the number N of particles tends to infinity. Simultaneously, the density ratio $N/V \sim n$ approaches a constant value. Many characteristic properties of macroscopic physical systems only appear in this limit, namely phase transitions, universality classes and other critical phenomena.

It is worth noting that the problem of the thermodynamic limit at the earlier stage of statistical mechanics was hid behind many technicalities of the new discipline.^{1,2,3,4,5} Some part of modern textbooks do the same. Contrary to this, other modern textbooks (see, e.g., Refs.^{6,7,8}) discuss the thermodynamic limit carefully and with eminently suitable manner. For example, the textbook by Widom⁷ mention the thermodynamic limit by nine times and book by Dorlas⁸ devotes to this question the special chapter. It is remarkable, that the first time when the notion of the thermodynamic limit appears in the Widom's book,⁷ is that when he derives the celebrated Rayleigh-Jeans law.² These authors^{6,7,8} demonstrated explicitly the essential role of the thermodynamic limit (which has already been presented in an implicit form in Jeans book²) for the consistent derivation of that law and other important issues of statistical mechanics.

A significant step in the rigorous treatment of the thermodynamic limit was made by N. N. Bogoliubov, who developed a general formalism for establishing of the limiting distribution functions in the form of formal series in powers of the density. In his famous monograph,^{13,14} Bogoliubov outlined the method of justification of the thermodynamic limit and derived the generalized Boltzmaun equations from his formalism (see also $\operatorname{Refs}^{9,15,16}$). For this purpose, he introduced the concept of stages of the evolution-chaotic, kinetic, and hydrodynamic and the notion of the time scales, namely, interaction time, free path time, and time of macroscopic relaxation, which characterize these stages, respectively. At the chaotic stage, the particles synchronize, and the system passes to local equilibrium. He showed then, that at the kinetic stage, all distribution functions begin to depend on time via the one-particle function. Finally, at the hydrodynamic stage, the distribution functions depend on time via macroscopic variables, and the system approaches equilibrium. Bogoliubov also introduced the important clustering principle. Furthermore, these distribution functions, which are equal to the product of functions, one of which depends only on momenta being indeed the Maxwell distribution, and the second one depends only on coordinates. Bogoliubov conjectured that it is often convenient to separate the dependence on momenta and consider distribution functions, which will depend only on coordinates passing then to the thermodynamic limit. Thus, on the basis of his equations for distribution functions and the cluster property, the Boltzmann equation was first obtained without employing the molecular chaos hypothesis.

Indeed, let us consider^{9,15} the state of a finite system, which consists of N particles distributed with density 1/V in a region Λ with volume V, $|\Lambda| = V$. The system is described by a probability distribution function $F_{N,\Lambda}(t, x_1, x_2 \dots x_N)$ given on the phase space x = (p, q), where p is a momentum, and q is a coordinate. This function is defined as the solution of the corresponding Liouville equation, which satisfies certain initial conditions, described in Refs.^{13,14} The interaction potential $\Phi(q_i - q_j)$ was supposed to be the pairwise.

The average value of an observable $A_N(t, x_1, x_2 \dots x_N)$, where A_N is a real symmetric function, is given by the formula

$$\langle A_N(t)\rangle = \int A_N(t, x_1, x_2 \dots x_N) F_{N,\Lambda}(t, x_1, x_2 \dots x_N) dx_1 dx_2 \dots dx_N.$$
(1)

The state of an infinite system is obtained as a result of the thermodynamic limit procedure under which the number of particles N and the volume V of the region Λ tend to infinity while the density remains constant:

$$N \to \infty$$
, $V \to \infty$, $N/V = n$.

A rigorous proof of the existence of the thermodynamic limit appeared to be a very difficult problem.^{9,15} To clarify the nature of the difficulties, it is worth noting that the distribution functions $F_{N,\Lambda}$ are equal to the ratio of the variables which diverge as N^N in the thermodynamic limit. Thus it was necessarily to prove that these divergences compensate each other and that the limiting distribution functions will be really well defined as a mathematical object. The main formulas obtained for equilibrium distribution functions correspond to Gibbs results, however the problem of justification of the thermodynamic limit procedure remained unsolved for about 50 years because of the difficulties described above. Only in 1949 did Bogoliubov propose the solution of this problem.¹⁷ He reduced it to the functional-analysis problem of proving the existence of solutions to certain operator equations and investigating their limiting properties. This program was realized on the basis of equations for distribution functions.^{18,19,20}

In the present topical review a brief survey of some important questions concerning the thermodynamic limit and related problems will be carried out. Our main intention is to sketch here the physical results rather than a mathematical formalism. Hence, we will stay away from technicalities and will concentrate on the essence of the problems from the physical viewpoint.

2 Interrelation of Statistical Mechanics and Thermodynamics

Before considering of special questions a very brief summary of the interrelation of statistical mechanics and thermodynamics will be instructive.

The aim of statistical mechanics is to give a consistent formalism for a microscopic description of macroscopic behavior of matter in bulk.^{1,21,22,23,24,25,26,27} The central problem in the statistical physics of matter is that of accounting for the observed equilibrium and nonequilibrium properties of fluids and solids from a specification of the component molecular species, knowledge of how the constituent molecules interact, and the nature of their surrounding. The methods of equilibrium and nonequilibrium statistical mechanics have been fruitfully applied to a large variety of phenomena and materials. From the other side, during the last decades there was a substantial progress in mathematical foundations of statistical mechanics^{8,9,28,29,30,31,32,33,34,35,36,37,38} and in studies of ergodic theory and theory of dynamical systems.^{37,38}

It is known that thermodynamic properties of many-particle systems are the physical characteristics that are selected for a description of systems on a macroscopic scale.^{4,24,21,22,39} Classical thermodynamics³⁹ considers the systems (i.e. a region of the space set apart from the remainder part for special study) which are in an equilibrium state. Thermodynamic equilibrium is a state of the system where, as a necessary condition, none of its properties changes measurably over a period of time exceedingly long compared to any possibly observations on the system. Classical equilibrium thermodynamics deals with thermal equilibrium states of a system, which are completely specified by the small set of variables, e.g., by the volume V, internal energy E and the mole numbers N_i of its chemical components.

In classical statistical mechanics one considers the number of particles N which is very large (typically of order 10^{23}), enclosed in a finite but macroscopically large volume V. A reduced description requires much smaller number of variable to operate with. Thus, construction of statistical ensembles^{1,4,21,22} in the case of statistical equilibrium is based on the appropriate choice of relevant integrals of motion on which the distribution function can depend.

The statistical ensemble is specified by the distribution function f(p, q, t), which has the meaning of the *probability density* of the distribution of systems in phase space (p, q). More precisely, the distribution function should be defined in such a way that a quantity

dw = f(p, q, t)dpdq

can be considered as the *probability* of finding the system at time t in the element of phase space dpdq close to the point (p,q).

The thermodynamic variables with a *mechanical* origin such as the internal energy E, the volume V, and the number of particles N, are given well-defined values or **averages** of the mechanical quantities over the ensemble under consideration.^{1,4,21,22} On the contrary, thermodynamic variables such as the entropy S, the temperature T, and the chemical potential μ do not have a mechanical nature. Those values are usually introduced by identifying terms in the fundamental differential relation^{4,24,21,22,39} for the energy E

$$dE = TdS - PdV + \mu dN. \tag{2}$$

Here P is the pressure, one of the thermodynamic intensive variables, T is the temperature and μ is the chemical potential. Intensive (extensive) variables are the variables whose value is independent of (depends on) the size and the quantity of matter within the region which is being studied.³⁹ Contrary to this, the subject of statistical mechanics aims to base the statistical approach on the microscopic models of matter; it deals with those properties of many-particle systems which are

describable in average.^{1,4,21,22} There are mainly three methods used in equilibrium statistical mechanics, namely, the Boltzmann method^{25,40,41} of identifying the equilibrium state with the most probable one; the Gibbs ensemble method^{1,4} of *postulating* a canonical distribution, and the Darwin-Fowler method⁴² of identifying the equilibrium state with the average state. Schrödinger²³ termed the last approach by the *method* of mean values. It should be noted that the Darwin-Fowler method in statistical mechanics is a powerful method which allows in a straightforward way the evaluation of statistical parameters and distributions in terms of relatively simple contour integrals of certain generating functions in the complex plane.

As a result of the Gibbs ensemble method, the entropy S can be expressed^{4, 21, 22, 23, 42, 43, 44} in the form of an average for all the ensembles, namely,

$$S(N, V, E) = -k_B \sum_{i} p_i \ln p_i = -k_B \Omega\left(\frac{1}{\Omega} \ln \frac{1}{\Omega}\right) = k_B \ln \Omega(N, V, E), \tag{3}$$

where the summation over i denotes a general summation over all states of the system and p_i is the probability of observing state i in the given ensemble and k_B is the Boltzmann constant. This relation links entropy S and probability p_i . For thorough mathematical discussion and precise definition of Gibbs entropy see Ref.⁴⁵

Boltzmann has $used^{21,22,23,24,25}$ a logarithmic relation in the following form

$$S = k_B \ln \Omega. \tag{4}$$

Here Ω is the probability of a macroscopic state E and $k_B = R/N_A = 1.3806 \cdot 10^{-23} J K^{-1}$ is the ratio of the molar gas constant R to the Avogadro constant N_A and has the dimension of entropy. It was termed the Boltzmann constant; in essence this constant relates macroscopic and microscopic physics. Indeed, the ideal gas equations are $PV = Nk_BT$ and $U = xNk_BT$, where x = 3/2 for a monoatomic gas, x = 5/2 for a diatomic gas, and x = 6/2 for a polyatomic gas. Here U is the internal energy of the gas.

Note that original Boltzmann expression $S = k \ln W$ defines the entropy S, a macroscopic quantity, in terms of the multiplicity W of the microscopic degrees of freedom of a system. Since entropy is an additive quantity and probability is a multiplicative one, this relationship looks very natural (see Refs.^{43,44,45,46,47,48,49,50,51,52,53,54} for detailed discussion). It is easy to see that any monotonic function of W will have a maximum where W has a maximum. In particular, states that maximize W also maximize the entropy, $S = k \ln W$.

The assumption of complete statistics⁴⁹ implies that all states regarding the system is countable and known completely by us so that we have full knowledge of the interactions taking place in the system of interest, thereby implying the ordinary normalization condition $\sum_i p_i = 1$. An alternative procedure for the development of the statistical mechanical ensemble theory is to introduce the Gibbs entropy postulate which states that for a general ensemble the entropy is given by Eq.(3). Thus the postulate of equal probabilities in the microcanonical ensemble and the Gibbs entropy postulate can be considered as a convenient starting point for the development of the statistical mechanical ensemble theory in a standard approach. It is should be said that this course of development is workable when the Boltzmann *H*-theorem was first established.^{25,40,41,55} After postulating the entropy by means of Eq.(3), the thermodynamic equilibrium ensembles are determined by the following criterion for equilibrium:

$$(\delta S)_{E,V,N} = 0. \tag{5}$$

This variational scheme is used for each ensemble (microcanonical, canonical and grand canonical) with different constraints for each ensemble.^{4,21,22,23,24} In addition, this procedure introduces Lagrange multipliers which, in turn, must be identified with thermodynamic intensive variables (T, P) using by Eq.(5). From the other hand, the procedure of introducing Lagrange multipliers and the task of identifying them with the thermodynamic intensive properties can be clarified by invoking a more general criterion for thermodynamic equilibrium.^{39,54}

It is worth noting that a close relationship exists between the concepts of entropy and probability, $^{43, 44, 46, 47, 48, 49, 50, 51, 52}$ the most famous of which is associated with the name of Boltzmann.^{25, 40, 41} Thus entropy and probability are intrinsically related.⁴⁹ It can showed that the concavity property of the entropy^{56, 57, 58, 59, 60} is directly related to a given probability distribution function for an ideal gas in which binary collisions dominate. Concavity is directly related to the logarithm of a probability distribution. It is interesting that by relating the entropy directly to a probability distribution function, one can show that a non-equilibrium version of the entropy function may be deduced.

The very important statement of the Gibbsian statistical mechanics is the so-called *Gibbs' theorem* on canonical distribution. The theorem states that a small part of a microcanonical ensemble of

systems with many degrees of freedom is distributed canonically, i.e. according to the law

$$f(p,q) = Q^{-1}(\theta, V, N) \exp\left(-\frac{H(p,q)}{\theta}\right).$$
(6)

Here $Q(\theta, V, N)$ is the partition function and θ is the modulus of the canonical distribution which corresponds to the temperature in the phenomenological thermodynamics.³⁹ Thus the partition function $Q(\theta, V, N)$ is an essential characteristic of the canonical Gibbs ensemble, which determines the thermodynamic properties of the system. The partition function satisfies to the normalization condition

$$Q(\theta, V, N) = \int \exp\left(-\frac{H(p, q)}{\theta}\right) d\Gamma; \ d\Gamma = \frac{dpdq}{N!\hbar^{3N}}.$$
(7)

As it was mentioned earlier, a statistical ensemble of systems with a specified number of degrees of freedom N and volume V in contact with a thermal bath (which is a non-trivial notion^{12,61}) is called a canonical Gibbs ensemble. Note, that the Gibbs' postulate^{1,4,24,21,9} states that the canonical equilibrium distribution, of all the normalized distributions having the same mean energy, is the one with maximum entropy.^{43,44,46,47,48,49,50,51,52,54} In addition, the Gibbs' postulate rests on two assumptions. First, the stationary equilibrium distribution, being canonical, is of exponential form. Second, Gibbs assumed that all the compared distributions have the same mean energy values. Thus the use of a more general condition Eq.(7) instead of Eq.(5) as a criterion for thermodynamic equilibrium permitted us treat the thermodynamic temperature T directly in the framework of the statistical mechanical formulation.

Before closing this section, it will be informative to remind the important remark by Hugenholtz⁶² that "in the many body problem and in statistical mechanics one studies systems with infinitely many degrees of freedom. Since actual systems are finite but large, it means that one studies a model which not only is mathematically simpler than the actual system, but also allows a more precise formulation of phenomena such as phase transitions, transport processes, which are typical for macroscopic systems. How does one deal with infinitely large systems. The traditional approach has been to consider large but finite systems and to take the thermodynamic limit at the end."

3 The Thermodynamic Limit in Statistical Thermodynamics

The macroscopic equilibrium thermodynamics³⁹ can be considered as a limiting case of statistical mechanics. This limit was termed by the *thermodynamic limit*. The thermodynamic limit^{6,7,8,9,26,27,63,64} or infinite-volume limit gives the results which are independent of which ensemble was employed and independent of size of the box and the boundary conditions at its edge. Hence the thermodynamic limit is a mathematical technique for modeling macroscopic systems by considering them as infinite composition of particles (molecules). The question of existence of these thermodynamical limits is rather complicated and poses lots of mathematical problems.^{8,29,30,35,65} The mathematical theory of thermodynamic limit is too involved to go into here, but it was discussed thoroughly in Refs.^{8,29,30,35,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79} To simplify the problem, sometimes it is convenient to replace the thermodynamic limit by working directly with systems defined on classical configuration spaces of infinite volume. In this case, one may expects that since these systems tend to show continuous spectra the relevant functions become relatively well behaved functions. In a certain case the thermodynamic limit is equivalent

The essence of the continuum limit is that all microscopic fluctuations are suppressed. The

to a properly defined continuum limit.⁶⁴

thermodynamic limit excludes the influence of surface effects. It is defined by⁶⁴

$$\lim_{V \to \infty} \begin{cases} V \to \infty, \\ V/N, E/N \text{ constant (microcanonical ensemble)}, \\ V/N, T \text{ constant (canonical ensemble)}, \\ \mu, T \text{ constant (grand canonical ensemble)}. \end{cases}$$
(8)

Thus, in the thermodynamic limit, surface (boundary) effects becomes negligibly small in comparison with the bulk properties.^{6,7,8,9,26,27,63,64}

It is of importance to recall that N and V are extensive parameters. They are proportional to V when V/N = const. Contrary to this, the parameter $\theta = k_B T$ is intensive. It has a finite value as $V \to \infty$ when V/N = const. In order to describe infinite systems one normalizes extensive variables, i.e. those that are homogeneous of degree one in the volume, by the volume, keeps fixed the density, i.e. the number of particles per volume, and takes the limit for N, V tending to infinity. It is at the thermodynamic limit that the additivity property of macroscopic extensive variables is obeyed.

The core of the problem lies in establishing the very existence of a thermodynamic limit^{13, 14, 18, 19, 20} (such as $N/V = \text{const}, V \to \infty$) and its evaluation for the quantities of interest. Of course, the problem of existence of these thermodynamical limits is extremely complicated mathematical problem^{8, 29, 30, 35, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79} (sometime it could be convenient to replace the thermodynamic limit by working directly with systems defined on classical configuration spaces of infinite volume, etc.).

It was established⁶⁶ that the free energy is the thermodynamic potential of a system subjected to the constraints constant T, V, N_i . To clarify the problem of the thermodynamic limit, let us consider the logarithm of the partition function $Q(\theta, V, N)$

$$F(\theta, V, N) = -\theta \ln Q(\theta, V, N).$$
(9)

This expression determines the free energy F of the system on the basis of canonical distribution. The standard way of reasoning in the equilibrium statistical mechanics do not requires the knowledge of the exact value of the function $F(\theta, V, N)$. For real system it is sufficient to know the thermodynamic (infinite volume) limit^{13, 14, 17, 18, 19, 21, 22, 30, 35, 66, 29}

$$\lim_{N \to \infty} \frac{F(\theta, V, N)}{N}|_{V/N = \text{const}} = f(\theta, V/N).$$
(10)

Here $f(\theta, V/N)$ is the free energy per particle. It is clear that this function determines all the thermodynamic properties of the system.^{9,26,27,29} Thus, the thermodynamic behavior of a system is asymptotically approximated by the results of statistical mechanics as N tends to infinity, and calculations using the various ensembles used in statistical mechanics converge.^{9,21,22,26,27,77,79} The importance of thermodynamic limit or infinite-volume limit was first mentioned by N.N. Bogoliubov in his seminal monograph.^{13,14} That monograph describes methods which gave a rigorous mathematical foundation for the limiting transition in statistical mechanics, using the formalism of the Gibbs' canonical ensemble. A general formalism was developed for establishing of the limiting distribution functions in the form of formal series in powers of the density.

Later on, in 1949, N.N. Bogoliubov published (with B. I. Khatset) a short article on this subject¹⁷ where they formulated briefly their results. Here the foundations were developed for a rigorous mathematical description of infinite systems in statistical mechanics. These works^{13,14,17,18,19} gave, in principle, a full solution to the mathematical problem arising during consideration of the limiting transition $N \to \infty$ in systems described by a canonical ensemble, for the case of positive

binary particle interaction potential and sufficiently small density. In this approach the system of equations for the distribution functions was treated in essence as an operator equation in Banach space. Unfortunately, the methods developed in these papers were not known at that time to other investigators in mathematical statistical mechanics.

Independently L. Van Hove^{80,81,82} studied the behaviour of the statistical system in the limit in which the volume of the system becomes infinitely large. He analyzed the problem and found that in the grand ensemble it is only in this limit that phase transitions, in the form of mathematically sharp discontinuities, can appear. Thus the thermodynamic limit has reformulated as a pure mathematical problem from which certain complications should be removed. The proof of Van Hove contained some mathematical shortcomings and was improved by Ruelle^{67,68,71,29} and Fisher.^{66,69,70}

In his paper⁶⁷ Ruelle suggested a similar to the Bogoliubov-Khatset approach¹⁷ to the study of the systems of equations for distribution functions. He used the formal method of a large canonical ensemble, which simplified his task in formulating a basis for the limit transition. At the same time Ruelle was able to consider a more wide class of potential functions by using the very ingenious idea of making the original equations for the distribution functions symmetrical. Ruelle has considered the well-known Kirkwood-Salsburg equations,^{9,83,84,85,86,87} i.e. the set of integral equations which form a linear inhomogeneous system for the (generic) distribution functions $f_A(x)$. In his paper, Ruelle has taken advantage of the linear structure of the Kirkwood-Salsburg equations and has shown how these equations may be transformed into a single equation for $f_A(x)$ in the Banach space. This work has stimulated a series of articles devoted to studies of the thermodynamic limit in various systems. For example, G. Gallavotti and S. Miracle-Sole⁷² studied the thermodynamic limit for a classical system of particles on a lattice and proved the existence of infinite volume correlation functions for a "large" set of potentials and temperatures.

The complete mathematical treatment of the thermodynamic limit problem was given by N.N. Bogoliubov and collaborators in 1969 in their fundamental paper.¹⁸ That paper formulated a rigorous mathematical description of the equilibrium state of the infinite system of particles on the basis of canonical ensemble theory. A proof is given of the existence and uniqueness of the limiting distribution functions and their analytical dependence on density. Results have been achieved by using the methods which were based on the application of the theory of Banach spaces to the study of the equation for the distribution functions.

Bogoliubov and co-authors showed that in order to obtain thermodynamic relations on the basis of statistical mechanics one requires to study systems with an infinite number of degrees of freedom. Such systems are derived from finite systems when there is an infinite increase in the number of particles N accompanied by a proportional increase in the volume V. Here difficult problems arose, associated with the rigorous mathematical basis for the limiting transition as $N \to \infty$. To solve these problems, as authors showed,¹⁸ the formalism of the canonical ensemble supplied with the mechanism of distribution functions is appropriate for the case.

They gave a rigorous mathematical description, based on the theory of the canonical ensemble, of the equilibrium state (at low density) of infinite systems of particles, whose interaction potential is free from the restriction of positiveness, and satisfies the Ruelle condition.⁶⁷ Both the methods, i.e., the method of Bogoliubov-Khatset, and the Ruelle method of symmetrization were used. For this aim the relations between the distribution functions in a finite volume, which for the limit transition become the Kirkwood-Salsburg equations were derived. In contrast with the case of a large canonical ensemble, for a Gibbsian ensemble in a finite volume there are generally no equations for the distribution functions: the appropriate equations appear only after the limit transition to infinite volume. This led to new problems, in comparison with the case of a large canonical ensemble. Then a theorem for the existence and uniqueness of a solution of the Kirkwood-Salsburg equations for the potentials satisfying the Ruelle condition was proved. In

addition, a clear estimate was given for the densities for which the solution is a series of interactions. As result of their analysis, a theorem was established concerning the analytical nature of the dependence of the limit distribution functions on the density. A proof of the existence of limit distribution functions when the number of particles in the system tends to infinity was given as well. The uniqueness of these limit functions was established and proved rigorously. Thus the paper by Bogoliubov, Petrina and Khatset¹⁸ and also the classical paper of Bogoliubov and Khatset¹⁷ have established the existence of limiting distribution functions for the microcanonical ensemble in the case of low densities.

In the paper by Simyatitskii,⁸⁸ some of the arguments and proofs in the paper by Bogoliubov. Petrina and Khatset¹⁸ were simplified. He obtained the same results using essentially the same methods but by a somewhat shorter path. The simplifications were achieved by the use of the apparatus of correlation functions rather than distribution functions. In addition, a more detailed investigation was made of the question of the equality of the limiting correlation functions of the microcanonical and grand canonical ensembles in the case of low densities. In addition, Simyatitskii⁸⁸ have been able to avoid many tedious estimates by referring simply to the results by Dobrushin and Minios,^{89,90} who proved an important theorem about the existence of a limit of the ratios of the microcanonical partition functions. On the basis of these results, Simvatitskii also investigated in detail the question of the equality of the limiting correlation functions of the grand canonical and microcanonical ensembles for the usual thermodynamic relationship between the density n and the activity z in agreement with the result by Bogoliubov, Petrina and Khatset.^{18,19} Kalmykov⁹¹ analyzed the problem further. The main aim of his paper was to derive an expression for the thermodynamic potential in terms of the limit correlation functions for classical systems of identical monatomic molecules. For single-component systems of hard spheres with binary interaction, the free energy was expressed in terms of the limit correlation functions of the canonical ensemble. Some properties of the configuration integral were investigated and estimates obtained for the correlation functions. His work was based also on the classical results by Bogoliubov, Petrina and Khatset^{18,19} and Dobrushin and Minlos.^{89,90}

It is known that in specific physical applications it is important to have approximate equations for some quantities from which correlation functions and the equation of state may easily be obtained. Gonchar and Rudyk⁹² used this idea to made a further progress. A new set of strict equations for correlation functions of equilibrium classical statistical mechanics was proposed. The solution was constructed for the pair repulsive interaction potential at arbitrary values of activity z and temperature with the help of some nonlinear monotonically increasing map L. In addition, Gonchar and Rudyk proved that the radial distribution function oscillates at low density in a system with a short-range nonnegative potential and investigated the branching of the solutions of an approximate equation of state.

The existence of thermodynamics for real matter with Coulomb forces was proved by Lieb and Lebowitz.^{93,94} They established the existence of the infinite volume (thermodynamic) limit for the free energy density of a system of charged particles, e.g., electrons and nuclei. These particles, which are the elementary constituents of macroscopic matter, interact via Coulomb forces. The long range nature of this interaction necessitates the use of specific methods for proving the existence of the limit. It was shown that the limit function has all the convexity (stability) properties required by macroscopic thermodynamics. They found that for electrically neutral systems, the limit functions was domain-shape independent, while for systems having a net charge the thermodynamic free energy density was shape dependent in conformity with the well-known formula of classical electrostatics. The analysis was based on the statistical mechanics ensemble formalism of Gibbs and may be either classical or quantum mechanical. The equivalence of the microcanonical, canonical and grand canonical ensembles was demonstrated also.

H. Moraal⁹⁵ shown, that the configurational partition function for a classical system of molecules

interacting with nonspherical pair potential is proportional to the configurational partition function for a system of particles interacting with temperature-dependent spherical k-body potentials. Therefore, the thermodynamic limit for nonspherical molecules exists if the effective k-body interaction is stable and tempered. A number of criteria for the nonspherical potential were developed which ensure these properties. In case the nonsphericity is small in a certain sense, stability and temperedness of the angle-averaged nonspherical potential are sufficient to ensure thermodynamic behaviour.

Heyes and Rickayzen⁹⁶ have investigated in detail a role of the interaction potential $\Phi(r)$ between molecules (where r is the pair separation). This quantity is the key input function of statistical mechanical theories of the liquid state. They applied the pair interaction stability criteria of Fisher and Ruelle⁷⁰ to establish the range of thermodynamic stability for a number of simple analytic potential forms used for condensed matter theory and modelling in the literature. In this way they identified the ranges of potential parameters where, for a given potential, the system is thermodynamically stable, unstable and of uncertain stability. This was further explored by carrying out molecular dynamics simulations on the double Gaussian potential in the stable and unstable regimes. It was shown that, for example, the widely used exponential-6 and Born-Mayer-Huggins alkali halide potentials produce many-particle systems that are thermodynamically unstable. Thus they have been able to decide the stability or instability of potentials which are the difference of two Gaussians or of two exponentials for all real positive values of their parameters. The parameter ranges of instability of the generalized separation-shifted Lennard-Jones and so-called *SHRAT* potential systems were established in this work.

Additional discussion of the applications of the thermodynamic limit in concrete situations were considered by Styer.^{97,98} In particular, it was demonstrated that the widely used microcanonical "thin phase space limit" must be taken *after* taking the thermodynamic limit.

Some important aspects of the nonequilibrium, thermostats, and thermodynamic limits were studied thoroughly by Gallavotti and Presutti.⁹⁹ They studied many important aspects of the problem, but left open the main problem, namely what can be said about the limit $t \to \infty$, i.e., the study of the stationary states reached at infinite time. Instead, a conjecture has been proposed: the limit will be an equilibrium Gibbs distribution at some intermediate temperature.

4 Equipartition of Energy

In spite of that the problem of equipartition of energy² in classical statistical mechanics is an old issue, it is still of interest because it can be used to understand better some of the background of statistical mechanics. The essential problem in statistical thermodynamics is to calculate the distribution of a given amount of energy E over N identical systems. The basic statement in statistical mechanics, which also known as the equal *a priori* probability conjecture, is the one of the main postulates of the equilibrium statistical mechanics.^{2,4,21,22} The equipartition conjecture rests essentially upon the hypothesis that for any given isolated system in equilibrium, it is valid that the system is found with equal probability in each of its accessible microstates. The equipartition hypothesis (or theorem) originated in the molecular theory of gases.² The equipartition theorem states that each degree of freedom contributes 1/2RT to the molar internal energy, E, of a gas. It will be of interest to give here the original Jeans² formulation:

The energy to be expected for any part of the total energy which can be expressed as a sum of squares is at the rate of 1/2RT for every squared term in this part of the energy.

A gas that consists of individual atoms (like He, Ne, Ar) has a low heat capacity because it has few degrees of freedom. The atoms can move freely in space in the x-, y-, or z-directions.

This translational motion corresponds to n = 3 degrees of freedom. However, atoms have no other types of internal motions such as vibrations or rotations, so the total number of degrees of freedom for a monatomic system is equal to 3. Once the degrees of freedom are determined, the internal energy is calculated from the equipartition theorem,

$$E = n(1/2RT). \tag{11}$$

For example, the monatomic gas exhibits only 3 degrees of freedom. Therefore, the prediction from the equipartition theorem for the molar internal energy is E = (3/2RT).

For diatomic molecules along with linear and nonlinear polyatomic molecules in the gas phase, the number of degrees of freedom can be determined and therefore the theoretical internal energy and heat capacity can be predicted. In addition to the 3 translational degrees of freedom, contributions from rotational and vibrational degrees of freedom must be considered.

For diatomic and linear polyatomic molecules, rotational motion contributes 2 degrees of freedom to the total, while for nonlinear polyatomic molecules, rotational motion contributes 3 degrees of freedom. For diatomic and linear polyatomic molecules, vibrational motion contributes 2(3N-5)degrees of freedom to the total, while for nonlinear polyatomic molecules, vibrational motion contributes 2(3N-6) degrees of freedom, where N is the number of atoms in the molecule. Using these rules, the total number of degrees of freedom can be determined and the equipartition theorem can then be used to determine a theoretical prediction for the molar internal energy and the heat capacities.

Thus the classical energy equipartition theorem constitutes an important point in equilibrium statistical physics, which has been widely discussed and used.

In its simplest version the equipartition principle deals with the contribution to the *average energy* of a system in thermal equilibrium at temperature T due to quadratic terms in the Hamiltonian. More precisely, it attests that any canonical variable x entering the Hamiltonian through an additive term proportional to x^2 has a thermal *mean energy* equal to $k_BT/2$, where k_B is the Boltzmann constant. The most familiar example is provided by a three dimensional classical ideal gas.

Thus, it should be emphasized that the equipartition principle is a consequence of the quadratic form of terms in the Hamiltonian, rather than a general consequence of classical statistical mechanics. Note, however, that the principle of equipartition is a strictly classical concept, that is, the degree of freedom contributed much should be such that $\Delta \varepsilon / k_B T$ is small in passing from one level to another.

The generalized equipartition principle^{4, 21, 22, 24} formulates its essence in the following form. Let us consider a classical many-particle system of N interacting particles with the Hamiltonian H(p,q). Let x_j be one of the 3N momentum components or one of the 3N spatial coordinates. Then the following equality will be hold

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T \delta_{ij}. \tag{12}$$

Here $\langle \ldots \rangle$ is the relevant ensemble average. It is clear that this equality can only hold asymptotically in the thermodynamic limit.

There are more general and advanced formulations^{100, 101, 102} of the generalized equipartition principle. Nevertheless, the equipartition, in principle, should be valid in the thermodynamic limit only. In addition, the equipartition principle yields a direct and intrinsic method for the definition of the absolute temperature,^{4, 21, 22, 24, 103} irrespective of the interaction or the phase state. The problem of the consistent definition of the temperature for small systems, such as clusters, etc., is under current intensive investigation.^{103, 104, 105, 106} There are many various applications of the generalized equipartition principle, for example, application to the phenomenon of laser cooling and the equipartition of energy in the case of radiation-atom interaction.¹⁰⁷ These are the conclusions arrived at from a study of the equipartition of energy in many-particle systems based on the classical dynamics of systems studied. Moreover, the presence of the quadratic form of terms in the Hamiltonian was established as decisive. Since the mid fifties the intensive studies of the equipartition of energy for nonlinear systems began.^{108, 109} Nonlinear effects are of the greatest importance in various fields of science. In the last decades a remarkable and fundamental development has occurred in the theory of nonlinear systems, leading to a deeper understanding of the interrelation of classical and quantum mechanics and statistical mechanics.^{110, 111, 112, 113}

The general importance of the nonlinearity for many-particle systems was demonstrated clearly by Ulam, Fermi and Pasta in their seminal study.^{108, 109} It was shown that the lack of equipartition of energy observed by Ulam, Fermi and Pasta for certain nonlinear systems has serious and deep reasons. Numerous authors have investigated and explored this fascinating field,^{110, 111, 112, 113, 114, 115, 116, 117, 118, 119} covering much the same ground of the interrelation of classical and quantum mechanics and statistical mechanics.

Galgani¹¹² has presented the point of view of L. Boltzmann on energy equipartition, which is not so well known. Boltzmann was confronted with the essential qualitative difficulties of classical statistical mechanics of his time.¹²⁰ The main message is that, according to Boltzmann, the two questions, equipartition and Poincare recurrence,^{121,122,123,124,125} "should be treated on the same foot". Roughly speaking, in connection with the problem of equipartition of energy, which seemed to demolish classical statistical mechanics, Boltzmann foresaw a solution of the same type he had afforded for the Poincare recurrence paradox,^{121,122,123,124,125} in the sense that the problem does not occur for finite, "enormously long", times.

An averaging theorem for Hamiltonian dynamical systems in the thermodynamic limit was derived by A. Carati¹²⁶ in connection with the the foundations of statistical mechanics. This theorem helps to understand better some essential feature of the Fermi-Pasta-Ulam phenomenon: the energy remains confined to the low frequency modes, while the energies (i.e., up to a factor, the actions) of the high frequency modes remain frozen up to very large times. It was shown how to perform some steps of perturbation theory if one assumes a measure-theoretic point of view, i.e. if one renounces to control the evolution of the single trajectories, and the attention is restricted to controlling the evolution of the measure of some meaningful subsets of phase space. For a system of coupled rotators, estimates uniform in N for finite specific energy were obtained in quite a direct way. This was achieved by making reference not to the *sup* norm, but rather, following Koopman and von Neumann, to the much weaker L^2 norm.

Hence, it was established that there are various reasons for lack of the equipartition of energy.^{11,12,127,128} In this context, it was said¹²⁸ that "one of the basic problem of statistical mechanics is to decide its range of applicability, in particular, the validity of the equipartition of energy. Deciding what are the boundaries of applicability of statistical mechanics has become one of the fundamental problems not only for the foundations but, indeed, for the applications".

5 Ensemble Equivalence and Nonequivalence

It is well known that the equilibrium thermodynamics^{21, 22, 27, 24} of any type of *normal* large system (e.g. a monoatomic gas) can be derived using any one of the statistical equilibrium Gibbs ensembles (microcanonical, canonical and grand canonical). However, there some subtleties, which should be taken into account properly. To see this point clearly, it will be useful to remind that, when considering a monoatomic ideal gas, each of the three ensembles will lead to the known equation of state $PV = Nk_BT$. From the other hand, it is also well known that in canonical ensemble the number of particles N is fixed, whereas in grand canonical ensemble N is not fixed and can fluctuate. All the standard considerations^{21, 22, 27, 24} of the ensemble equivalence in Gibbs'

statistical mechanics are based on the fact that the fractional fluctuations of N are very small, $\Delta N/N \sim 1/\sqrt{N}$.

The conceptual basis of statistical mechanics and thermodynamics is relatively well established^{129, 130} and it was shown in various ways^{131, 132, 133, 134, 135, 136} that *normal* systems with huge degrees of freedom satisfy the laws of statistical mechanics.

The question of the ensembles equivalence was considered by various authors. Considerable literature has developed on this subject.^{77,79,137,138,139,140,141,142,143,144,145,146} A. M. Khalfina¹⁴³ investigated the limiting equivalence of the canonical and grand canonical ensembles for the low density case. In that paper it was shown that the limiting Gibbs distribution, whose existence was established previously by starting from the grand canonical ensemble, can also be obtained by starting from the canonical ensemble, and both distributions coincide when a certain relation exists¹⁴⁴ between the parameters β and μ (for fixed β). The proof was based on the local limit theorem for the number of particles.

It was shown by Adler and Horwitz,¹⁴⁶ that complex quantum field theory can emerged as a statistical approximation to an underlying generalized quantum dynamics. Their approach was based on the already established formalism of application of statistical mechanical methods to determination of the canonical ensemble governing the equilibrium distribution of operator initial values. Their result was obtained by the arguments based on a Ward identity (analogous to the equipartition theorem of classical statistical mechanics). Adler and Horwitz¹⁴⁶ constructed in their work a microcanonical ensemble which forms the basis of this canonical ensemble. That construction enabled to them to define the microcanonical entropy and free energy of the field configuration of the equilibrium distribution and to study the stability of the canonical ensemble. They also studied the algebraic structure of the conserved generators from which the microcanonical and canonical ensembles were constructed, and the flows they induce on the phase space.

Although the ensemble equivalence holds for *normal* large system, we will mention, mainly by reference only, a few examples of systems where the nonequivalence of Gibbs ensembles occur^{147, 148, 149, 150} by various reasons.

Some objection to the standard arguments of the ensembles equivalence were put forward recently.^{147,148,149} According to this point of view some researchers have found examples of statistical mechanical models characterized at equilibrium by microcanonical properties which have no equivalent within the framework of the canonical ensemble. The nonequivalence of the two ensembles has been observed for these special models both at the thermodynamic and the macrostate levels of description of statistical mechanics of these systems. This is a contradiction with J. W. Gibbs,¹ who insisted that the canonical ensemble should be equivalent to the microcanonical ensemble in the thermodynamic limit. In this limit, *the thermodynamic limit*, the system **should** thus appear to observation as having a definite value of energy - the very *conjecture* which the microcanonical ensemble is based on. The conclusion then apparently follows, namely: both the microcanonical and the canonical ensembles should predict the same equilibrium properties of many-body systems in the thermodynamic limit of these systems independently of their nature. The fluctuations of the system's energy should become negligible in comparison with its total energy in the limit where the volume of the system tends to infinity.

H. Touchette and co-authors^{147, 148, 149} attempted to give relevant physical interpretation and an accessible explanation of the phenomenon of nonequivalent ensembles.

In particular, H. Touchette and co-authors^{147,148,149} investigated various aspects of generalized canonical ensembles and corresponding ensemble equivalence. They introduced a generalized canonical ensemble obtained by multiplying the usual Boltzmann weight factor $\exp(-\beta H)$ of the canonical ensemble with an exponential factor involving a continuous function g of the Hamiltonian H. They focused on a number of physical rather than mathematical aspects of the generalized canonical ensemble. The main result obtained is that, for suitable choices of g, the generalized canonical ensemble reproduces, in the thermodynamic limit, all the microcanonical equilibrium properties of the many-body system represented by H even if this system has a nonconcave microcanonical entropy function. This is something that in general the standard (g = 0) canonical ensemble cannot achieve. Thus a virtue of the generalized canonical ensemble is that it can often be made equivalent to the microcanonical ensemble in cases in which the canonical ensemble cannot. The case of quadratic g functions was discussed in detail; it leads to the so-called Gaussian ensemble.

Very recently it was pointed by G. De Ninno and D. Fanelli,¹⁵⁰ that classical statistical mechanics most commonly deals with large systems, in which the interaction range among components is much smaller than the system size. In such "short-range" systems, energy is normally additive and statistical ensembles are equivalent. The situation may be radically different when the interaction potential decays so slowly that the force experienced by any system element is dominated by the interaction with far-away components. In these "long-range" interacting systems energy is not additive. Well-known examples of non-additive "long-range" interacting systems are, for instance, found in cosmology (self-gravitating systems) and plasma physics applications, where Coulomb interactions are at play. The lack of additivity, together with a possible break of ergodicity, may be at the origin of a number of peculiar thermodynamic behaviours: the specific heat can be negative in the microcanonical ensemble, and temperature jumps may appear at microcanonical first-order phase transitions. When this occurs, experiments realized on isolated systems give a different result from similar experiments performed on systems in contact with a thermal bath. As a consequence, the canonical and microcanonical statistical ensembles of long-range interacting systems may be non-equivalent.

G. De Ninno and D. Fanelli,¹⁵⁰ discussed out-of-equilibrium statistical ensemble nonequivalence. They considered a paradigmatic model describing the one-dimensional motion of N rotators coupled through a mean-field interaction, and subject to the perturbation of an external magnetic field. The latter was shown to significantly alter the system behaviour, driving the emergence of ensemble nonequivalence in the *out-of-equilibrium phase*, as signalled by a negative (microcanonical) magnetic susceptibility. The thermodynamic of the system was analytically discussed, building on a maximum-entropy scheme justified from first principles. Simulations confirmed the adequacy of the theoretical picture. Ensemble nonequivalence was shown to rely on a peculiar phenomenon, different from the one observed in previous works. As a result, the existence of a convex intruder in the entropy was found to be a necessary but not sufficient condition for nonequivalence to be (macroscopically) observed. Negative-temperature states were also found to occur. These intriguing phenomena reflect the non-Boltzmanian nature of the scrutinized problem and, as such, bear traits of universality that embrace equilibrium as well as out-of-equilibrium regimes. However, it should be amphasized that this field of researches is still under debates and the

However, it should be emphasized that this field of researches is still under debates and the thorough additional investigations in this direction should be carried out.^{151,152,153,154}

6 Phase Transitions

The aim of statistical mechanics is to derive the properties of macroscopic systems from the properties of the individual particles and their interactions. In particular it is the task of statistical mechanics to give an explanation of phase transitions, transport phenomena and the approach to equilibrium in the course of time for a non-equilibrium system. Physicist have been trying to understand the occurrence of phase transitions by use of statistical mechanics since the famous dissertation of van der Waals in 1873.

The problem of phase transitions in the interacting many-particle systems has been studied intensively during the last decades from both the experimental and theoretical viewpoints.^{30, 32, 155, 156, 157, 158, 159, 160} Phase transitions occur in both, equilibrium and nonequilibrium systems. Typical examples of the equilibrium phase transitions are the transitions between different states of matter (solid, liquid, gaseous, etc.) or the transition from normal conductivity to superconductivity.

In the vicinity of a phase transition point,^{158,159} a small change in some external control parameter (like pressure or temperature) results in a dramatic change of certain physical properties (like specific heat or electric resistance) of the system under consideration. Many aspects of the theory of phase transitions are related in one way or another with the thermodynamic limit transition procedure.^{30,35} This is rather evident from the fact that an equilibrium phase transition is defined as a nonanalyticity of the free-energy density F/N.

Phase transitions have been an important part of statistical mechanics for many years. During the last decades the mathematical theory of the phase transitions^{30, 32, 33, 155, 156, 157} achieved a marked progress, in particular in a systematic study of the (quantum) mechanics of systems with infinitely many degrees of freedom. The theory of operator algebras, in particular C^* -algebras,^{62, 161} plays an important part in these developments.

Although, in certain models, one can prove the existence of a phase transition, for instance in the Ising model in two and more dimensions with zero external field,^{30,32,155,156,157,158,159,160} theoretically the situation with respect to phase transitions in general still is not fully understood. More recently phase transitions have become an object of intensive studies in computer science (study of 3-satisfiability), combinatorics (birth of the giant component for various random graph models) and probability theory (cutoff phenomena for Markov chains).

Here we touch briefly of some issues only from the physical viewpoint. Such a physical viewpoint on the essence of the phase transitions was formulated recently by M. E. Fisher and C. Radin.¹⁶² We shall follow to that work reasonably close because of its remarkable transparency and clarity. According to M. E. Fisher and C. Radin,¹⁶² there are various thermodynamic variables one can use to describe matter in thermal equilibrium, some of the common ones being: mass or number density N/V, energy density E/N, temperature T, pressure P, and chemical potential μ . By definition the states of a "simple" system can be parameterized by two such (independent) variables, in which case the others can be regarded as functions of these. We will assume we are modelling a simple material. Then a particularly good choice for independent variables is T and μ .

M. E. Fisher and C. Radin¹⁶² remarked that it is a fundamental fact of thermodynamics that the pressure P is a convex function of these variables, and, in particular, this convexity embodies certain mechanical and thermal stability properties of the system. Moreover, all thermodynamic properties of the material can be obtained from P as a function of T and μ by differentiation.

It is worth reminding that the question of a convexity of thermodynamic variables was investigated in detail by L. Galgani and A. Scotti.^{56,57,58} They considered the usual basic postulate of increase of entropy for an isolated system. In addition, it was pointed out that that postulate can be formalized mathematically as a superadditivity property of entropy. This fact has two kinds of implications. It allows one to deduce in a very direct and mathematically clear way stability properties such as $c_V \geq 0$ and $K_T \geq 0$. Here $c_V = (T\partial S/\partial T)_V$ is a specific heat and $K_T = -1/V (\partial P/\partial V)_T$; the entropy S was defined through the functional relation S = S(E, V, N). On this basis L. Galgani and A. Scotti^{56,57,58} were able to justify of the equivalence of various thermodynamic schemes as expressed for example by the fact that the *minimum* property of the free energy is a consequence of the *maximum* property of entropy.

The following definitions given below were straightforwardly adapted from Ref.¹⁶²

A thermodynamic phase of a simple material is an open, connected region in the space of thermodynamic states parametrized by the variables T and the pressure P being analytic in T and μ . Specifically, P is analytic in T and μ , at (T_0, μ_0) if it has a convergent power series expansion in a ball about (T_0, μ_0) that gives its values. Phase transitions occur on crossing a phase boundary. The graph of $P = P(T, \mu)$ is not only convex but (for all reasonable physical systems) also has no (flat) facets. M. E. Fisher and C. Radin¹⁶² used this fact in their definition of phase; without this property there would typically be open regions of states representing the coexistence of distinct phases. The essential point is the choice of independent variables, which can lead to the appearance of domains representing two or more coexisting phases. They noted also that in particular the isothermal (i.e., constant T) "tie lines" connecting the distinct phases that can coexist at the range of overall intermediate densities spanned at a fixed temperature.

On their phase diagram^{158,159,160,162} an intrinsic difference between vapor and liquid "phases", which can be analytically connected, and between these regions of the fluid phase and the solid phase, which cannot be so connected may be clearly seen.

M. E. Fisher and C. Radin¹⁶² mentioned that in the modern literature an important distinction is made between "field" variables and "density" variables, which helps to explain various consequences of the choice of independent and dependent variables. The foregoing constitutes a "thermodynamic" description of phases and phase transitions. There is a deeper description, that of statistical mechanics, deeper in that it allows natural ("molecular") models from which one can in principle compute the pressure as a function of T and μ .

In the statistical mechanical description the thermodynamic states are realized or represented as probability measures on a certain space and the measures still parameterized by thermodynamic variables, e.g. the two variables, specifically temperature T and chemical potential μ). M. E. Fisher and C. Radin¹⁶² considered first a finite system of N particles contained in a reasonably shaped domain, say Λ of volume V. In this case the probability densities in the phase space (\mathbf{x}, \mathbf{p}) for particles, will be proportional to the weights $f_N(T, \mu, \mathbf{x}, \mathbf{p})$.

The structure of the energy E_N is determined only when one settles on the type of "interactions" the constituent particles can undergo; that not only depends on the material being modelled but also on what environment. Then they considered the grand canonical pressure of the finite-volume system, which is given by $P_V(T,\mu)$. For reasonable interaction potentials Φ the pressure P_V as a function of T and μ will be everywhere analytic. In order to model a sharp phase transition they considered the thermodynamic limit

$$P(T,\mu) = \lim_{V \to \infty} P_V(T,\mu).$$
(13)

Then $P(T, \mu)$ may be identified as the thermodynamic pressure to which the above definitions of a phase and a phase transition applies. The proof of the existence of the thermodynamic limit requires certain conditions on the interaction potential.

In the present context, this very clear but terse formulation of the role of the thermodynamic limit requires an additional comment. First, a a few general remarks will be useful. It is known¹⁶³ that to discuss a certain phase transition of interest with the above definition, the free energy density has to be considered as a function of the relevant control parameters, i. e. those which, upon variation, give rise to the phase transition.

The number of independent intensive variables, r, which determine the state of a heterogeneous system is given by the Gibbs phase rule,³⁹

$$r = c - \phi + 2,$$

where c is the number of independent components and ϕ is the number of phases in the system. For the phase transitions between the aggregate states of, say, water, the (Gibbs) free-energy density as a function of temperature and pressure is a suitable choice. For spin systems there are at most two such relevant control parameters, the temperature T and an external magnetic field H_{ext} , and therefore the free-energy density $f(T, H_{\text{ext}})$ will be a function of the inverse temperature $\beta = 1/(k_B T)$ and the magnetic field H_{ext} . Quantities like the specific heat or caloric curves which are typically measured in an experiment are then given in terms of derivatives of the free-energy density. Nonanalyticities of derivatives may hence lead to discontinuities or divergences in these quantities, which are experimental hallmarks of phase transitions.

Our special interest will be in the emphasizing of the main difficulty in the theory of phase transition in the many-particle interacting systems. This is the task of the evaluation of partition functions associated with particular physical systems of interest. In this context it will be of instruction to discuss the concept of the isothermal-isobaric (or T - P) ensemble,^{21,22,164,165} which is used in the condensation theory.^{21,22,166}

A system (consisting of N molecules) in the isothermal-isobaric ensemble of temperature T and pressure P is described by means of partition function^{21,22,164,165}

$$R_N(P,T) = \int_0^\infty dV \sum_i \omega_i \exp\left(\frac{-PV - E_i}{k_B T}\right). \tag{14}$$

The equation of state for the imperfect gas was deduced^{164,165} in terms of the cluster concept. Then the properties of imperfect gases and the condensation phenomena were investigated and described in the limit $N \to \infty$, employing the concepts of "small", "large", and "huge" clusters. What is remarkable, when authors in their theory¹⁶⁴ have neglected the volume dependence of the cluster integral the obtained an unrealistic result: the lower limit of the range of fluctuation in v = V/N has become zero. When, however, they introduced¹⁶⁵ the volume dependence of the cluster integrals, this lower limit becomes a certain positive value, corresponding to the volume of the pure liquid. As vas stressed above, phase transitions of a physical systems stem from the singularities of a **limiting functions** related to the partition functions of the system. The limit $\langle v \rangle_{\infty}$ (for $N \to \infty$) of the ensemble average $\langle v \rangle$ of the specific volume v = V/N, which fluctuates in the (T - P) ensemble, was calculated in the form^{164,165}

$$\langle v \rangle_{\infty} = \lim_{N \to \infty} \langle v \rangle = -\lim_{N \to \infty} \frac{k_B T}{N} \left(\frac{\partial}{\partial P} \ln R_N(P, T) \right)_T = k_B T \left(\frac{\partial \ln z}{\partial P} \right)_T,\tag{15}$$

where z is the activity.

This example shows clearly that the procedure of taking the thermodynamic limit requires very careful performance.

7 Small and Non-Standard Systems

Statistical physics derives observable (or emergent) properties of macroscopic matter from the atomic structure and the microscopic dynamics. Those characteristics are temperature, pressure, mean flows, dielectric and magnetic constants, etc., which are essentially determined by the interaction of many particles (atoms or molecules). The central point of statistical physics is the introduction of probabilities into physics and connecting them with the fundamental physical quantity entropy. A special task of this theory was to connect microscopic behavior with thermodynamics.

From the brief sketch of the statistical thermodynamics, already given above, it should be clear that the "normal" thermodynamic systems must be large enough to avoid the influence of the boundary effects. In statistical mechanics¹⁶⁷ one studies large systems and the aim is to derive the macroscopic, or thermodynamical properties of such systems from the equation of motion of the individual particles. Due to their large size, such systems have features such as phase transitions, ^{30, 32, 155, 156, 157, 158, 159, 160, 168} transport phenomena, ^{27, 38} which are absent in small systems. To exhibit such features in full measure one has to consider the limiting case of infinitely large systems, i.e., systems with infinitely many degrees of freedom. This means that one has to consider large, but finite, systems and take the thermodynamic limit at the end.

However, small systems^{169,170,171,172,173,174,175,176} are becoming increasingly interesting from both

the scientific and applied viewpoints. Small systems are those in which the energy exchanged with the environment is a few times k_BT and energy fluctuations are observable. For example, nanoscience^{177,178,179} demands a progressive reduction in the size of the systems, and the fabrication of the new materials requires an accurate control over condensation and crystallization.¹⁷² Small systems found throughout physics, chemistry, and biology manifest striking properties as a result of their tiny dimensions.¹⁷³ Examples of such systems include magnetic domains in ferromagnets, which are typically smaller than 300 nm, quantum dots and biological molecular machines that range in size from 2 to 100 nm, and solid-like clusters that are important in the relaxation of glassy systems and whose dimensions are a few nanometers. There are a big interest in understanding the properties of such small systems.^{169,170,171,172,173,174,175,176}

There are a lot of specificities in describing such systems.^{104, 105, 106, 154, 174, 175, 176} For examples, J. Naudts¹⁷⁵ showed by slight modification of the Boltzmann's entropy that it is possible to make it suitable for discussing phase transitions in finite systems. As an example, it was shown that the pendulum undergoes a second-order phase transition when passing from a vibrational to a rotating state.

There is an interest in phase transitions in pores and in the so-called melting of small clusters.¹⁷² Although these clusters are equilibrated in a heat bath before being isolated, when they are isolated each cluster corresponds to a microcanonical ensemble in which a "microcanonical temperature" (c.f. Ref.¹⁷⁰) must be defined via reference to entropy.¹⁷² The act of "melting" then becomes a matter of definition, etc.

These topics form the new branch of thermodynamics,¹⁸⁰ the so-called nanothermodynamics and non-extensive thermodynamics. They are used to study of those physical systems that have not the property of extensivity and are characterized by a small size.

8 Concluding Remarks

This review was limited to selected topics of the statistical mechanics. The emphasis was on the thermodynamic limit, equipartition of energy and equivalence and nonequivalence of ensembles. The analysis carried out in the previous sections shows that from the statistical mechanics point of view, a thermodynamic system is one whose size is large enough so that fluctuations are negligible. This was shown very clearly by many authors, e. g., by T. L. Hill^{21, 22} and D. N. Zubarev²⁷ in their books on statistical mechanics and thermodynamics.^{21, 22} This is a conclusion arrived at from the present study of the problem of the thermodynamic limit.

To sum up, the statistical mechanics is best applied to large systems. Formally, its results are exact only for infinitely large systems in the thermodynamic limit. However, even at the thermodynamic limit, there are still small detectable fluctuations in physical quantities, but this has a negligible effect on most sensible properties of a system. The thermodynamic functions calculated in statistical mechanics should be independent of the ensemble used in the calculation. But as to the fluctuations, the situation is different. For each environment, i.e. for each ensemble the problem is different. Moreover, the variable which fluctuate are different.²⁷

It is the hope of the author that the present short review will serve, nevertheless, as a quick introduction to the subject and will help reader to appreciate vividly a beauty and elegance of statistical mechanics as an actual and developing branch of contemporary science.

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References

- [1] J. W. Gibbs, Elementary Principles in Statistical Mechanics Developed with Especial Reference to the Rational Foundations of Thermodynamics (Dover Publ., New York, 1960).
- [2] J. H. Jeans, The Dynamical Theory of Gases, (Cambridge University Press, Cambridge, 1925).
- [3] J. Rice, Introduction to Statistical Mechanics (Constable Publ. Co., London, 1930).
- [4] R. C. Tolman, The Principles in Statistical Mechanics (Dover Publ., New York, 1979).
- [5] P. M. Morse, *Thermal Physics*, 2nd ed. (W. A. Benjamin, Inc., New York, 1969).
- [6] D. Ya. Petrina, Mathematical Foundations of Quantum Statistical Mechanics (Kluwer Academic Publ., Dordrecht, 1995).
- [7] B. Widom, *Statistical Mechanics. A Concise Introduction for Chemists* (Cambridge University Press, Cambridge, 2002).
- [8] T. C. Dorlas, Statistical Mechanics. Fundamentals and Model Solutions (Taylor and Francis, London, 1999).
- [9] D. Ya. Petrina, V. I. Gerasimenko and P. V. Malyshev, *Mathematical Foundations of Classical Statistical Mechanics*, 3rd ed. (Taylor and Francis, London, 2002).
- [10] P. B. M. Vranas, Epsilon-ergodicity and the success of equilibrium statistical mechanics. *Philosophy of Science* 65, 688 (1998).
- [11] A. Carati, L. Galgani and A. Giorgilli, Dynamical systems and thermodynamics. in: Encyclopedia of Mathematical Physics (Elsevier, Oxford, 2006).
- [12] V. V. Kozlov, Gibbs ensembles, equidistribution of the energy of sympathetic oscillators and statistical models of thermostat. *Regular and Chaotic Dynamics* 13 (3), 141 (2008).
- [13] N. N. Bogoliubov, Problems of Dynamical Theory in Statistical Physics (Gostekhizdat, Moscow, 1946) [in Russian].
- [14] N. N. Bogoliubov, in *Studies in Statistical Mechanics*, J. de Boer and G. E. Uhlenbeck, eds., (North-Holland, Amsterdam, 1962), vol.1, p.1.
- [15] D. Ya. Petrina, Stochastic Dynamics and Boltzmann Hierarchy (Walter de Gruyter, Berlin, New York, 2009).
- [16] C. Cercignani, V. I. Gerasimenko and D. Ya. Petrina, Many-Particle Dynamics and Kinetic Equations (Springer, Berlin, 1997).
- [17] N. N. Bogoliubov and B. I. Khatset, On some mathematical problems in the theory of statistical equilibrium. Dokl. Akad. Nauk SSSR 66, 321 (1949).
- [18] N. N. Bogoliubov, D. Ya. Petrina, and B. I. Khatset, Mathematical description of equilibrium state of classical systems on the basis of canonical formalism. *Teor. Mat. Fiz.* 1, 251 (1969).

- [19] D. Ya. Petrina, The thermodynamic limit of solutions of the Bogoliubov equations. in: Statistical Mechanics and the Theory of Dynamical Systems. Collection of papers. Dedicated to Academician N. N. Bogolyubov on his 80th birthday. Trudy Mat. Inst. Steklov, (Nauka, Moscow, 1989) Vol. 191, p.192.
- [20] D. Ya. Petrina, Memories about the joint work with N. N. Bogoliubov. Ukr. J. Phys. 54, 919 (2009).
- [21] T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).
- [22] T. L. Hill, An Introduction to Statistical Thermodynamics (Addison-Wesley, New York, 1960).
- [23] E. Schrodinger, *Statistical Thermodynamics* (Dover Publ., New York, 1989).
- [24] D. A. McQuarrie, *Statistical Mechanics* (University Science Books, California, 2000).
- [25] G. Gallavotti, Statistical Mechanics. A Short Treatise (Springer, Berlin, 1999).
- [26] N. N. Bogoliubov and N. N. Bogoliubov, Jr., Introduction to Quantum Statistical Mechanics, 2nd ed. (World Scientific, Singapore, 2009).
- [27] D. N. Zubarev, Nonequilibrium Statistical Thermodynamics (Consultant Bureau, New York, 1974).
- [28] A. I. Khinchin, Mathematical Foundations of Statistical Mechanics (Dover Publ., New York, 1949).
- [29] J. L. Lebowitz, Statistical mechanics: a review of selected rigorous results Annu. Rev. Phys. Chem. 19, 389 (1968).
- [30] R. A. Minlos, *Introduction to Mathematical Statistical Physics* (University Lecture Series) (American Mathematical Society, 1999).
- [31] V. A. Malyshev and R. A. Minlos, Gibbs Random Fields. The Cluster Expansion Method (Kluwer Publ., Boston, London, 1991).
- [32] R. L. Dobrushin, A mathematical approach to foundations of statistical mechanics. Preprint ESI 179 (ESI Publ., Vienna, 1994).
- [33] On Dobrushin's Way: From Probability Theory to Statistical Physics (American Mathematical Society Translations, Series 2) eds. R. A. Minlos, S. Shlosman, and Yu. M. Suhov (American Mathematical Society, 2000).
- [34] O. Penrose, Foundations of Statistical Mechanics: A Deductive Treatment (Dover Publ., New York, 2005).
- [35] D. Ruelle, *Statistical Mechanics. Rigorous Results*, 2nd ed. (World Scientific, Singapore, 1999).
- [36] D. Ruelle, Thermodynamic Formalism: The Mathematical Structure of Equilibrium Statistical Mechanics, 2nd edn. (Cambridge University Press, Cambridge, 2004).
- [37] G. Gallavotti, F. Bonetto, and G. Gentile, Aspects of Ergodic, Qualitative and Statistical Theory of Motion (Springer, Berlin, New York, 2004).

- [38] A. L. Kuzemsky, Theory of transport processes and the method of the nonequilibrium statistical operator. Int. J. Mod. Phys. B 21, 2821 (2007).
- [39] J. M. Honig, *Thermodynamics*, 3rd ed. (Elsevier, Amsterdam, 1991).
- [40] L. Boltzmann, *Lectures on Gas Theory* (University of California Press, Berkeley, 1964).
- [41] The Kinetic Theory of Gases. (An Anthology of Classical Papers with Historical Commentary by S. G. Brush), N. S. Hall, ed., (Imperial College Press, London, 2003).
- [42] K. Huang, Statistical Mechanics, 2nd ed. (John Wiley and Sons, New York, 1987).
- [43] E. T. Jaynes, Gibbs vs. Boltzmann entropies. Am. J. Phys. 33, 391 (1965).
- [44] W. T. Grandy, Entropy and the Time Evolution of Macroscopic Systems (Oxford University Press, New York, 2008).
- [45] M. C. Mackey and M. Tyran-Kaminska, Temporal behavior of the conditional and Gibbs' entropies. J. Stat. Phys. 124, 1443 (2006).
- [46] E. T. Jaynes, Information theory and statistical mechanics. *Phys. Rev.* **106**, 620 (1957).
- [47] E. T. Jaynes, Information theory and statistical mechanics II. *Phys. Rev.* 108, 171 (1957).
- [48] E. T. Jaynes, E. T. Jaynes: Papers on Probability, Statistics and Statistical Physics, ed. R. D. Rosenkrantz (Reidel Publ., Dordrecht, Holland, 1989).
- [49] E. T. Jaynes, Probability Theory: The Logic of Science, ed. G. Larry Bretthorst (Cambridge University Press, Cambridge, 2003).
- [50] A. Katz, *Principles of Statistical Mechanics: The Information Theory Approach* (W. H. Freeman and Co., San Francisco, 1967).
- [51] W. T. Grandy, Foundations of Statistical Mechanics: Equilibrium Theory, vol.1, (Reidel Publ., Dordrecht, Holland, 1987).
- [52] W. T. Grandy, Foundations of Statistical Mechanics: Nonequilibrium Phenomena, vol.2, (Reidel Publ., Dordrecht, Holland, 1988).
- [53] N. G. van Kampen, Views of a Physicist. Selected Papers of N. G. van Kampen (World Scientific, Singapore, 2000).
- [54] A. Thess, *The Entropy Principle: Thermodynamics for the Unsatisfied* (Springer, Berlin, 2011).
- [55] H. R. Brown, W. Myrvold and J. Uffink, Boltzmann's *H*-theorem, its discontents, and the birth of statistical mechanics. *Studies in History and Philosophy of Modern Physics* 40, 174 (2009).
- [56] L. Galgani and A. Scotti, Remarks on convexity of thermodynamic functions. *Physica* 40, 150 (1968).
- [57] L. Galgani and A. Scotti, Further remarks on convexity of thermodynamic functions. *Physica* 42, 242 (1969).
- [58] L. Galgani and A. Scotti, On subadditivity and convexity properties of thermodynamic functions. Pure and Applied Chem. 22, 229 (1970).

- [59] P. T. Landsberg and D. Tranah, Entropies need not be concave. *Phys. Lett.* A 78, 219 (1980).
- [60] S. Prestipino and P. V. Giaquinta, The concavity of entropy and extremum principles in thermodynamics. J. Stat. Phys. 111, 479 (2003).
- [61] G. Gallavotti, Thermostats, chaos and Onsager reciprocity. J. Stat. Phys. 134, 1121 (2009).
- [62] N. M. Hugenholtz, Quantum mechanics of infinitely large systems. in: E. G. D. Cohen ed., Fundamental Problems in Statistical Mechanics II (North-Holland, Amsterdam, 1968).
- [63] A. Münster, Some aspects of the thermodynamic limit. Pure and Applied Chem. 22, 293 (1970).
- [64] A. Compagner, Thermodynamics as the continuum limit of statistical mechanics. Am. J. Phys. 57, 106 (1989).
- [65] N. M. Hugenholtz, C*-algebras and statistical mechanics, in: Operator Algebras and Applications, Part II, ed. R. V. Kadison, (AMS, Providence, 1982), p.407.
- [66] M. E. Fisher, The free energy of a macroscopic system. Arch. Rat. Mech. Anal. 17, 377 (1964).
- [67] D. Ruelle, Correlation functions of classical gases. Ann. Phys. (N. Y.) 25, 209 (1963).
- [68] D. Ruelle, Cluster property of the correlation functions of classical systems. Rev. Mod. Phys. 36, 580 (1964).
- [69] M. E. Fisher, Correlation functions and the coexistence of phases. J. Math. Phys. 6, 1643 (1965).
- [70] M. E. Fisher and D. Ruelle, The stability of many-particle systems. J. Math. Phys. 7, 260 (1966).
- [71] D. Ruelle, States of classical statistical mechanics. J. Math. Phys. 8, 1657 (1967).
- [72] G. Gallavotti and S. Miracle-Sole, Statistical mechanics of lattice systems. Commun. Math. Phys. 5, 317 (1967).
- [73] J. L. Lebowitz and O. Penrose, Analytic and clustering properties of thermodynamic functions for classical lattice and continuum systems. *Commun. Math. Phys.* 11, 99 (1968).
- [74] G. Gallavotti, O. E. Lanford and J. L. Lebowitz, Thermodynamic limit of time-dependent correlation functions for one-dimensional systems. J. Math. Phys. 11, 2898 (1970).
- [75] H. Araki and E. H.Lieb, Entropy Inequalities. Commun. Math. Phys. 18, 160 (1970).
- [76] A. Lenard, ed. Statistical Mechanics and Mathematical Problems, (Lecture Notes in Physics, vol. 20) (Springer, Berlin, New York, 1973).
- [77] R. Rechtman and O. Penrose, Continuity of the temperature and derivation of the Gibbs canonical distribution in classical statistical mechanics. J. Stat. Phys. 19, 359 (1978).
- [78] R. B. Griffiths and M. Kaufman, Spin systems on hierarchical lattices. Introduction and thermodynamic limit. *Phys. Rev. B* 26, 5022 (1982).
- [79] H.-O. Georgii, The equivalence of ensembles for classical systems of particles. J. Stat. Phys. 80, 1341 (1995).

- [80] L. Van Hove, Quelques proprietes generales de l'integrale de configuration d'un systeme de particules avec interaction. *Physica* 15, 951 (1949).
- [81] L. Van Hove, Sur l'integrale de configuration des systemes de particules a une dimension. *Physica* 16, 137 (1950).
- [82] A. Giovannini ed., The Legacy of Leon Van Hove (World Scientific Series in 20th Century Physics, vol. 28) (World Scientific, Singapore, 2000).
- [83] H.J. Brascamp, The Kirkwood-Salsburg equations: solutions and spectral properties. Commun.Math.Phys. 40, 235 (1975).
- [84] R. H. Swendsen and W. Klein, Solution of a truncated Kirkwood- Salsburg equation for the hard-sphere gas. *Phys. Rev.* A 13, 872 (1976).
- [85] H. Moraal, Derivation and spectrum of a generalized Kirkwood-Salsburg operator. *Physica* A 81, 469 (1975).
- [86] H. Moraal, Spectral properties of the Kirkwood-Salsburg operator. *Physica A* 87, 331 (1977).
- [87] H. Moraal, On the Kirkwood-Salsburg and Mayer-Montroll equations and their solutions for many-body interactions. *Physica A* 105, 286 (1981).
- [88] I. L. Simyatitskii, Comments on the paper "Mathematical description of the equilibrium state of classical systems on the basis of the canonical ensemble formalism" by N. N. Bogolyubov, D. Ya. Petrina, and B. I. Khatset. *Teor. Mat. Fiz.* 6, 230 (1971).
- [89] R. L. Dobrushin and R. A. Minlos, The existence and the continuity of the pressure in classical statistical physics. *Teoriya Veroyatnostei i ee Primeneniya* 12, 595 (1967).
- [90] R. A. Minlos, The lectures on statistical physics. Usp. Matem. Nauk 23, 153 (1968).
- [91] G. I. Kalmykov, Thermodynamic limit for a classical system of particles with hard cores. *Teor. Mat. Fiz.* 36, 89 (1978).
- [92] N. S. Gonchar and A. B. Rudyk, Oscillation of the radial distribution function. J.Stat.Phys. 68, 1065 (1992).
- [93] J. L. Lebowitz and E. H. Lieb, Existence of thermodynamics for real matter with Coulomb forces. *Phys. Rev. Lett.* 22, 631 (1969).
- [94] E. H. Lieb and J. L. Lebowitz, The constitution of matter, existence of thermodynamics for systems composed of electrons and nuclei. Adv. Math. 9, 316 (1972).
- [95] H. Moraal, On the existence of the thermodynamic limit for classical systems with nonspherical potentials. *Physica A* 79, 75 (1975).
- [96] D. M. Heyes and G. Rickayzen, The stability of many-body systems. J. Phys.: Condens. Matter 19, 416101 (2007).
- [97] D. F. Styer, What good is thermodynamic limit? Am. J. Phys. 72, 25 (2004).
- [98] D. F. Styer, Erratum: What good is thermodynamic limit? Am. J. Phys. 72, 1110 (2004).
- [99] G. Gallavotti and E. Presutti, Nonequilibrium, thermostats, and thermodynamic limit. J. Math. Phys. 51, 015202 (2010).

- [100] P. T. Landsberg, Generalized equipartition. Am. J. Phys. 46, 296 (1992).
- [101] G. D. J. Phillies, A second generalized equipartition theorem. J. Chem. Phys. 78, 1620 (1983).
- [102] J. A. S. Lima and A. R. Plastino, On the classical energy equipartition theorem. Braz. J. Phys. 30, 176 (2000).
- [103] M. Fannes, Ph. Martin and A. Verbeure, On the equipartition law in quantum statistical mechanics. J. Phys. A: Math. Gen. 16, 4293 (1983).
- [104] G. N. Makarov, Cluster temperature. Methods of its measurement and stabilization. Uspekhi Fiz. Nauk. 178, 337 (2008).
- [105] M. Falconi, D. Villamaina, A. Vulpiani, A. Puglisi and A. Sarracino, Estimate of temperature and its uncertainty in small systems. Am. J. Phys. 79, 777 (2011).
- [106] L. F. Cugliandolo, The effective temperature. J. Phys. A: Math. Theor. 44, 483001 (2011).
- [107] V. J. Menon and D. C. Agrawal, Crawford's technique applied to laser cooling and equipartition. Am. J. Phys. 57, 240 (1989).
- [108] J. Ford, Equipartition of energy for nonlinear systems. J. Math. Phys. 23, 387 (1961).
- [109] J. Ford, The Fermi-Pasta-Ulam problem: paradox turns discovery. Phys. Rep. 213, 271 (1992).
- [110] L. Galgani, Ordered and chaotic motions in Hamiltonian systems and the problem of energy partition. in: J. R. Buchler et al., eds., *Chaos in Asrophysics* (Reidel Publ. Co., Dordrecht, Holland, 1985), p.245.
- [111] L. Galgani, A. Giorgilli, A. Martinoli and S. Vanzini, On the problem of energy equipartition for large systems of the Fermi-Pasta-Ulam type: analytical and numerical estimates. *Physica* D 59, 334 (1992).
- [112] L. Galgani, Boltzmann and the problem of equipartition of energy. in: G. Batimelli et al., eds., Proc. of the Int. Symp. on Ludwig Boltzmann (Verlag der Oster. Acad. Wissensch., Wien, 1993), p.193.
- [113] A. Carati, P. Cioriani and L. Galgani, On the definition of temperature in FPU systems. J. Stat. Phys. 115, 1101 (2004).
- [114] J. De Luca, A. J. Lichtenberg and S. Ruffo, Energy transitions and time scales to equipartition in the Fermi-Pasta-Ulam oscillator chain. *Phys. Rev. E* 51, 2877 (1995).
- [115] J. De Luca, A. J. Lichtenberg and S. Ruffo, Universal evolution to equipartition in oscillator chains. *Phys. Rev. E* 54, 2329 (1996).
- [116] L. Casetti, M. Ceruti-Sola, M. Pettini and E. G. D. Cohen, The Fermi-Pasta-Ulam problem revisited: stochasticity thresholds in nonlinear Hamiltonian systems. *Phys. Rev.* E 55, 6566 (1997).
- [117] J. De Luca, A. J. Lichtenberg and S. Ruffo, Finite times to equipartition in the thermodynamic limit. *Phys. Rev. E* 60, 3781 (1999).

- [118] D. K. Campbell, P. Rosenau and G. M. Zaslavsky, The Fermi-Pasta-Ulam problem The first fifty years. *Chaos* 15, 015101 (2005).
- [119] A. Carati, L. Galgani and A. Giorgilli, The Fermi-Pasta-Ulam problem as a challenge for the foundations of physics. *Chaos* 15, 015105 (2005).
- [120] Ta-You Wu, Boltzmann's H theorem and the Loschmidt and the Zermelo paradoxes. Int. J. Theor. Phys. 14, 289 (1975).
- [121] H. L. Frisch, Poincare recurrence. *Phys. Rev.* **104**, 1 (1956).
- [122] P. C. Hemmer, L. C. Maximon and H. Wergeland, Recurrence time of a dynamical system. *Phys. Rev.* 111, 689 (1958).
- [123] C. Cercignani, Ludwig Boltzmann. The Man Who Trusted Atoms (Oxford University Press, Oxford, 1998).
- [124] D. A. Lavis, Boltzmann, Gibbs and the concept of equilibrium. Philosophy of Science 75, 682 (2008).
- [125] G. Gallavotti, W. L. Reiter and J. Yngvason (eds.), Boltzmann's Legacy (European Math. Soc. Vienna, 2008)
- [126] A. Carati, An averaging theorem for Hamiltonian dynamical systems in the thermodynamic limit. J. Stat. Phys. 128, 1057 (2007).
- [127] A. Carati and L. Galgani, Analog of Planck's formula and effective temperature in classical statistical mechanics far from equilibrium. *Phys. Rev. E* 61, 4791 (2000).
- [128] A. Haro and R. de la Llave, New mechanisms for lack of equipartition of energy. *Phys. Rev. Lett.* 85, 1859 (2000).
- [129] A. Isihara, Developments and outlook of statistical physics at the turn of the century. Prog. Theor. Phys. 97, 709 (1997).
- [130] A. Isihara and H. Hara, Fundamental aspects of statistical mechanics. Interdisciplinary Information Sciences 4, 65 (1998).
- [131] S. Albertoni, P. Bocchieri and A. Loinger, New theorem in the classical ensemble theory. J. Math. Phys. 1, 244 (1960).
- [132] P. Bocchieri and A. Loinger, Remarks on a theorem in classical ensemble theory. *Phys. Lett.* 4, 188 (1963).
- [133] R. Sorkin, On the meaning of the canonical ensemble. Int. J. Theor. Phys. 18, 309 (1979).
- [134] J. F. Fernandes and J. Rivero, Model for the derivation of the Gibbs distribution. Nuovo Cimento, B 109, 1135 (1994).
- [135] U. Balucani, M. H. Lee and V. Tognetti, Dynamical correlations. *Phys. Rep.* 373, 409 (2003).
- [136] G. E. Norman and V. V. Stegailov, Stochastic theory of the classical molecular dynamics method. Mathematical Models and Computer Simulations, 5, 305 (2013).
- [137] J. Van Der Linden, On the asymptotic problem of statistical thermodynamics for a real system. *Physica* **32**, 642 (1966).

- [138] J. Van der Linden and P. Mazur, On the asymptotic problem of statistical thermodynamics for a real system II. Equivalence of canonical and pressure ensemble. *Physica* 36, 491 (1967).
- [139] J. Van der Linden, On the asymptotic problem of statistical thermodynamics for a real system: III. Questions concerning chemical potential and pressure. *Physica* 38, 173 (1968).
- [140] L. Galgani, L. Manzoni and A. Scotti. Comment on Van der Linden's proof of the asymptotic equivalence of equilibrium ensembles. *Physica* 41, 622 (1969).
- [141] L. Galgani, A. Scotti and F. Valz Gris, Asymptotic equivalence of classical ensembles by the method of the maximum. *Physica* 47, 601 (1970).
- [142] L. Galgani, L. Manzoni and A. Scotti. Asymptotic equivalence of equilibrium ensembles of classical statistical mechanics. J. Math. Phys. 12, 933 (1971).
- [143] A. M. Khalfina, The limiting equivalence of the canonical and grand canonical ensembles (low density case). Mat. Sb. (N.S.) 80, 3 (1969).
- [144] R. A. Minlos and A. Khaitov, Equivalence in the limit of thermodynamic ensembles in the case of one-dimensional classical systems. *Functional Analysis and Its Applications* 6, 337 (1972).
- [145] V. Gurarie, The equivalence between the canonical and microcanonical ensembles when applied to large systems. Am. J. Phys. 75, 747 (2007).
- [146] S. L. Adler and L. P. Horwitz, Microcanonical ensemble and algebra of conserved generators for generalized quantum dynamics. J. Math. Phys. 37, 5429 (1996).
- [147] M. Costeniuc, R. S. Ellis, H. Touchette and B. Turkington, The generalized canonical ensemble and its universal equivalence with the microcanonical ensemble. J. Stat. Phys. 119, 1283 (2005).
- [148] M. Costeniuc, R. S. Ellis, H. Touchette and B. Turkington, Generalized canonical ensembles and ensemble equivalence. *Phys. Rev. E* 73, 026105 (2006).
- [149] H. Touchette, The large deviation approach to statistical mechanics. Phys. Rep. 478, 1 (2009).
- [150] G. De Ninno and D. Fanelli, Out-of-equilibrium statistical ensemble inequivalence. Europhysics Lett. 97, 20002 (2012).
- [151] E. Smith, Large-deviation principles, stochastic effective actions, path entropies, and the structure and meaning of thermodynamic descriptions. *Rep. Prog. Phys.* **74**, 046601 (2011).
- [152] C. Callender, Hot and heavy matters in the foundations of statistical mechanics. Found. Phys. 111, 960 (2011).
- [153] T. Petrosky and I. Prigogine, Thermodynamic limit, Hilbert space and breaking of time symmetry. *Chaos, Solitons and Fractals* 11, 373 (2000).
- [154] M. H. Lee, Nonextensivity in ordinary thermodynamics. Chaos, Solitons and Fractals 13, 545 (2002).
- [155] C. Domb, M. S. Green and J. Lebowitz, eds., Phase Transitions and Critical Phenomena, Vols. 1-20 (Academic Press, New York, 1972-2001).

- [156] Ya. G. Sinai, *Phase Transitions: Rigorous Results* (Pergamon Press, Oxford,, 1982).
- [157] H.-O. Georgii, *Gibbs Measures and Phase Transitions* (Springer, Berlin, New York, 1988).
- [158] C. Domb, *The Critical Point* (Taylor and Francis, London, 1996).
- [159] I. Herbut, A Modern Approach to Critical Phenomena (Cambridge University Press, Cambridge, 2007).
- [160] R. V. Sole, *Phase Transitions* (Princeton University Press, Princeton, 2011).
- [161] N. M. Hugenholtz, The how, why and wherefore of C*-algebras in statistical mechanics. Advances in Solid State Physics 12, 641 (1972).
- [162] M. E. Fisher and C. Radin, Definition of thermodynamic phases and phase transitions, in eds. P. Diaconis, D. Fisher, C. Moore and C. Radin, *American Institute of Mathematics Workshop on Phase Transitions*, (Palo Alto, California, 2006), p.1.
- [163] M. Kastner, On the origin of phase transitions in long- and short-range interacting systems, in *Long-Range Interacting Systems*. Lecture Notes of the Les Houches Summer School, Vol.90, eds. T. Dauxois, S. Ruffo, and L. F. Cugliandolo (Oxford University Press, Oxford, 2010), p. 329.
- [164] K. Ikeda, On the theory of isothermal-isobaric ensemble. I. Prog. Theor. Phys. 38, 584 (1967).
- [165] K. Ikeda and S. Kamakura, On the theory of isothermal-isobaric ensemble. II. Prog. Theor. Phys. 38, 611 (1967).
- [166] M. B. Lewis and A. J. Siegert, Extension of the condensation theory of Yang and Lee to the pressure ensemble. *Phys. Rev.* 101, 1227 (1956).
- [167] R. Haag, N. M. Hugenholtz and M. Winnik, On the equilibrium states in quantum statistical mechanics. Commun. Math. Phys. 5, 215 (1967).
- [168] L. Van Hove, Statistical mechanics: a survey of recent lines of investigation, *Rev. Mod. Phys.* 29, 200 (1957).
- [169] T. L. Hill, *Thermodynamics of Small Systems* (Dover Publ., New York, 2002).
- [170] H. Feshbach, Small systems: when does thermodynamics apply? *IEEE J. Quant. Electron.* 24, 1320 (1988).
- [171] D. H. E. Gross, Microcanonical Thermodynanics. Phase Transitions in Small Systems (World Scientific, Singapore, 2001).
- [172] D. Reguera, R. K. Bowles, Y. Djikaev and H. Reiss, Phase transitions in systems small enough to be clusters. J. Chem. Phys. 118, 340 (2003).
- [173] C. Bustamante, J. Liphardt and F. Ritort, The nonequilibrium thermodynamics of small systems. *Phys. Today* N 7, 43 (2005).
- [174] M. Pleimling and H. Behringer, Microcanonical analysis of small systems. *Phase Transitions* 78, 787 (2005).

- [175] J. Naudts, Boltzmann entropy and the microcanonical ensemble. Europhysics Lett. 69, 719 (2005).
- [176] D. P. Sheehan and D. H. E. Gross, Extensivity and the thermodynamic limit: Why size really does matter. *Physica* A **370**, 461 (2006).
- [177] E. Roduner, Size matters: why nanomaterials are different. Chem. Soc. Rev. 3, 583 (2006).
- [178] E. Roduner, *Nanoscopic Materials: Size-Dependent Phenomena* (Royal Society of Chemistry, Cambridge, 2006).
- [179] K. D. Sattler, (ed.), Handbook of Nanophysics: Functional Nanomaterials (CRC Press, 2010).
- [180] J. Naudts, Generalised Thermostatistics (Springer, Berlin, 2011).