

Temporal evolution, directionality of time and irreversibility

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Summary. — The aim of the present interdisciplinary review is to carry out a comparative analysis of the notions of thermodynamic entropy, information entropy and entropy of non-equilibrium states and flow of entropy from a critical perspective. The problems of temporal evolution and time directionality are discussed in this context as well. The interrelation of these notions is studied with focusing on the non-equilibrium entropy. The paper is aimed to clarify the notion of entropy, entropy production and its generalizations. The Boltzmann, Gibbs, von Neumann, Shannon, Renyi, Tsallis and others types of entropy are considered concisely. The notions of the steady state, local state and local equilibrium are analyzed thoroughly to expose similarities and dissimilarities of various approaches to the definition of the entropy of nonequilibrium states. The extremal principles for entropy and entropy production are analyzed and discussed in this connection. The purpose of the present study is to elucidate certain aspects of the non-equilibrium statistical mechanics, namely the principal role of the correct description of the temporal evolution of a system and the corresponding procedure of averaging. We also touch tersely the intriguing problems of directionality of time and causality as well as relevance of constructal law that accounts for the phenomenon of evolution.

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1. – Introduction

*For what is time? Who can readily and briefly explain this?
Who can even in thought comprehend it, so to utter a word about it?*

St. Augustine

The objective of this paper is to provide a thorough discussion on the time evolution and its implications with regard to approach to equilibrium of open systems in the context of non-equilibrium statistical thermodynamics. It is known that the irreversibility in time of all processes occurring in nature plays an important role from various points of view. The theory of non-equilibrium phenomena and irreversible processes is aimed to formulate an adequate formalism for their description. By definition evolution is the alteration of the state of the system with the passage of time. In general, this alteration is a random process. Thermodynamic properties of many-particle systems may be derived through appropriate thermodynamic functions and macroscopic (thermodynamic) entropy. Entropy is a non-conservative quantity and as such is a basic concept of thermodynamics and distinctive, marked characteristic of thermal phenomena in the real world. According to the laws of thermodynamics, reversible evolution is an evolution with constant entropy. In the thermodynamic approach entropy generation is a measure of the irreversibility. In other words, entropy changing characterizes the irreversible behavior in a system during the process. For quantum systems the entropy should include quantum-mechanical correlations arising from the off-diagonal elements of density matrix.

It is worth mentioning that a close relationship exists between the concepts of entropy and probability, the most famous of which is associated with the name of Boltzmann. Hence entropy and probability are intrinsically related. It can be showed that the concavity property of the entropy is related directly to a given probability distribution function for an ideal gas in which binary collisions dominate. Concavity is directly related also 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.

In the last decades essential progress has been made in our understanding of entropy and entropy generation in both the fundamental aspects and application to concrete problems. In order to understand how the complex concept of entropy emerged, we will discuss some of these results in terse form.

The concept of entropy was introduced by Clausius in 1876. Then Planck in four seminal papers entitled “On the principle of increasing of the entropy” (1887-1891) has analyzed the temporal behavior of the entropy. He concluded that “. . . for each process in nature there is corresponding increasing of the entropy” [1]. Nevertheless it has become clear that rather deep ideas will be required if one starts with the reversible equations of motion and then, after averaging, ends up with the irreversible ones.

Boltzmann conjectured [2] that the second law of thermodynamics is a consequence of the dynamical behavior (collisions) of the particles of a gas. Boltzmann proposed a statistical analogue of thermodynamic entropy linking the concept of entropy with molecular disorder or chaos [2]. In the Boltzmann approach [2] the irreversibility feature was connected with the assumption that *information about individual molecular dynamics is forgotten* after the collisions. In contrast, only the probability distribution of velocities among the particles was remembered. Hence, this lack of memory (or continual randomization) may be considered as the real source of irreversibility. As it was shown clearly

by Bogoliubov [3], the system should be large enough [4] in order for the randomization assumption to be reasonably applicable. The concept of Boltzmann entropy stimulated interest to the foundation of statistical mechanics [5].

P. Ehrenfest and T. Ehrenfest [6] raised the question whether a function exists which, like entropy in the equilibrium state of an isolated system, achieves its extreme value in a stationary non-equilibrium state. In their words [6]: “Consider an irreversible process which, with fixed outside constraints, is passing by itself from the non-stationary to the stationary state. Can we characterize in any sense the resulting distribution of state as the ‘relatively most probable distribution’, and can this be given in terms of the minimum of a function which can be regarded as the generalization of the H -function?” Unfortunately that paper [6] contained an essential disadvantage. It may lead to the conclusion that the Boltzmann expression only is directly related to the entropy, whereas the Gibbs entropy is unfounded. The problem of the proper description of irreversible processes is disputable up to now. Mehra and Sudarshan [7] noted that “. . . the current situation in statistical mechanics, especially in the treatment of irreversibility, is rather confused in its conceptual structure and mathematical formulation”.

In the thermodynamics of thermal processes it is convenient to consider two types of systems, namely *closed* and *open*. In classical mechanics the closed systems have quasi-periodic orbits, whereas the open systems have at least some aperiodic orbits which extend to infinity. It is worth mentioning that the classical statistical mechanics, which deals with many particles, incorporates an additional important notion, namely the concept of probability [8-13]. It turns out that it is possible to characterize a system by the Hamiltonian flow in $6N$ -dimensional phase space Γ .

The notion of entropy is tightly related with the concepts of the irreversibility and the open and closed systems. Indeed, the entropy of thermally isolated systems does not increase. The idea of entropy provided a new look on the treatment of the irreversible behavior in macroscopic thermodynamics [14-16]. In statistical mechanics the concept of entropy is closely related to information theory and information entropy [5, 8-13, 17-20].

Energy, entropy, and information are all around us [12, 21-36]. Entropy and entropy generation [37-41] are the basic notions when we describe diverse phenomena ranging from physics and chemistry to cosmology and biology [42-44]. Their importance is clearly visible in many areas of practical interest [45-54], such as kinetic of chemical reactions, thermal conductivity and gas flow, transport and dissipative phenomena, theory of turbulence, simulated annealing, information and biological aspects, global energy, etc.

Entropy and entropy production (generation) also form the basis of various advanced formulations of both equilibrium and non-equilibrium statistical mechanics and thermodynamics of irreversible processes [54-61]. It is well known also that the principles of extremum of the entropy and entropy production play a fundamental role in equilibrium and non-equilibrium statistical physics [8-13, 17, 18, 51, 60, 62-72].

As was mentioned above, the notion of entropy was introduced by Clausius in the context of the interpretation of the second law of thermodynamics [34-36] and was analyzed further by Boltzmann, Gibbs and Planck. Nowadays, the problem of the notion of entropy is still under meticulous attention of many researchers. The subject is well explored and the literature is vast [37-41]. In spite of this, the last decades showed that there is scope for further extension of the existing methods and principles [5, 8-13, 17, 18].

For example, Thurner, Corominas-Murtra and Hanel [60] noticed the fact that there are at least three distinct ways to conceptualize entropy: entropy as an extensive thermodynamic quantity of physical systems (Clausius, Boltzmann, Gibbs), entropy as a mea-

sure for information production of ergodic sources (Shannon), and entropy as a means for statistical inference on multinomial processes (Jaynes maximum entropy principle). Even though these notions represent substantially different concepts, the functional form of the entropy for thermodynamic systems in equilibrium, for ergodic sources in information theory, and for independent sampling processes in statistical systems, is degenerate, $H(p) = -\sum_k p_k \log p_k$. They emphasized that for many complex systems, which are typically history-dependent, non-ergodic, and non-multinomial, this is no longer the case. Authors attempted to show that for such processes, the three entropy concepts lead to different functional forms of entropy, which they proposed refer to as *SEXT* for extensive entropy, *SIT* for the source information rate in information theory, and *SMEP* for the entropy functional that appears in the *maximum entropy principle*, which characterizes the most likely observable distribution functions of a system. Authors explicitly computed these three entropy functionals for three concrete examples: for *Polya urn processes*, which are simple self-reinforcing processes, for *sample-space-reducing processes*, which are simple history-dependent processes that are associated with power-law statistics, and finally for multinomial mixture processes.

Lieb and Yngvason [73] presented a foundation for the second law of classical thermodynamics in terms of the entropy principle. Their starting point was the basic empirical fact that under “*adiabatic conditions*” certain changes of the equilibrium states of thermodynamical systems are possible and some are not. The second law of thermodynamics in their opinion is the assertion that the possible state changes are characterized by the increase (non-decrease) of an (essentially) unique state function, called *entropy*, which is extensive and additive on subsystems. More precisely, they provided an empirically accessible *axiomatic derivation* of an entropy function defined on all equilibrium states of all systems that has the appropriate additivity and scaling properties, and whose increase is a necessary and sufficient condition for an adiabatic process between two states to be possible. In a subsequent paper [58] they discussed the question of defining entropy for non-equilibrium states. Lieb and Yngvason [58] carried out a careful analysis of the problem and pointed out some of the problems connected with defining entropy in non-equilibrium situations. Their conclusion was that it is generally not possible to find a *unique entropy* that has all relevant physical properties. They did show, however, that one can define two entropy functions, called S_- and S_+ , which, taken together, delimit the range of adiabatic processes that can occur between non-equilibrium states. The concept of *comparability* of states with respect to adiabatic changes plays an important role in that line of reasoning.

In a complementary study Marsland, Brown and Valente [74] analyzed thoroughly the problem of time and irreversibility in thermodynamics which is the paradigm example in physics of a time-asymmetric theory. They concluded that the origin of the asymmetry lies deeper than the second law. In their opinion a primordial arrow can be defined by the way of the equilibration principle. By appealing to this arrow, the nature of the known ambiguity in the Caratheodory version of the second law becomes somewhat clearer. It is worth mentioning that Caratheodory [75] offered the first systematic and contradiction-free formulation of thermodynamics on the basis of his mathematical work on Pfaff forms. Moreover, his work on measure theory provided the basis for later improved formulations of thermodynamics and physics of continua where extensive variables are measures and intensive variables are densities. Caratheodory was the first to see that measure theory and not topology is the natural tool to understand the difficulties (ergodicity, approach to equilibrium, irreversibility) in the problem of foundations of statistical physics. He gave a measure-theoretic proof of Poincaré recurrence theorem in 1919. This work provided the

way for Birkhoff to identify later ergodicity as *metric transitivity* and for Koopman and von Neumann to introduce the spectral analysis of dynamical systems in Hilbert spaces. Mixing provided an explanation of the approach to equilibrium but not of irreversibility. The subsequent extension of spectral theory of dynamical systems to locally convex spaces provided the non-trivial time-asymmetric spectral decompositions for unstable and non-integrable systems. In this way irreversibility may be interpreted in a natural way. Following Caratheodory seminal work [76-78], formulations of thermodynamics have gained ground that highlight the role of the binary relation of adiabatic accessibility between equilibrium states.

Maes [79] has analyzed various forms of non-equilibrium entropies from the unified standpoint to contrast the notion of entropy in equilibrium theory and its extension in the light of non-equilibrium thermodynamics. He pointed out that in contrast to the established entropy concept which is used for systems in thermodynamic equilibrium, there is a variety of distinct entropies, suitable for non-equilibrium systems, which represent different physical models. Maes characterized systematically these entropies as they related to heat, fluctuations, response, time asymmetry, variational principles, monotonicity, volume contraction or statistical forces. What is remarkable, he found that not all of those extensions yield state quantities as understood thermodynamically. He also showed that these entropies do not fit well to a construction of non-equilibrium statistical thermodynamics. Maes discussed also how aspects of dynamical activity can take over for obtaining an extended Clausius relation [34-36].

In view of the above-mentioned problems connected with defining entropy in non-equilibrium situations it will be of use to discuss and compare some selected aspects of temporal evolution and entropy production principle in the context of Zubarev method of the non-equilibrium statistical operator [8]. This method related deeply with the extremum of information entropy [8-12] and, as such, may provide a background for non-equilibrium statistical thermodynamics and also elucidate the wide scope of the whole problem of irreversibility. A comparative study of various approaches is the main point of our survey. The present review is the direct continuation of our previous paper [12].

2. – Temporal evolution and arrow of time

In this review, we draw attention to the connection of temporal evolution and directionality of time which is one of the big open questions in physics. In the context of temporal evolution [39], it is of importance to emphasize that in the structure of thermodynamics one of its basic laws, namely the second law [7], differs very much from other general laws of physics. It is not an equation, but instead states an inequality, which becomes an equality only in the limiting case of a reversible process. There are difficulties with the realization of this limit, because a reversible process is one in which the thermodynamic system never deviates appreciable from equilibrium. However, a finite time process involves a disturbance of equilibrium. As a result, it is difficult (if not impossible) to derive the fully correct equations concerning temporal evolution. It was even said sometimes that time appears in thermodynamics not as a quantity but only as the indicator of the sense of a quantity, the change of entropy. The second law of thermodynamics states that for a closed system the entropy does not change. In general, the total entropy of a system can not decrease without increasing the entropy of some other systems. From the other side, *time* is not the usual physical time variable, but it is a special *device* used for the temporal ordering of states. However, the entropy increase is not the unique source of temporality. Many questions concerning the nature of time and

its directionality are still under intensive debates [80-97] and require separate thorough consideration.

As it was shown above, the time directionality of physical processes is related deeply with the second law of thermodynamics. From the mechanical point of view taking into consideration the dissipative forces, *e.g.* such as those which depend on velocity, may lead to explicit time direction on the Hamiltonian. To resolve the problem of entropy increase and the approach to equilibrium, a few different schemes were used [8, 98, 99]. One of the possible treatments employed a coarse-graining method. The other methods were based on the derivation of generalized master equations.

There are hot discussions in the literature [80-97] relating to the intrinsic sources of the arrow of time in thermodynamics and the temporal ordering and temporal direction of thermodynamic and quantum processes. The common wisdom is that the thermodynamic arrow of time is directed by the second law of thermodynamics [97, 100]. Or, in other words, this arrow expresses itself via the second law, which states that entropy tends to increase toward the future. This statement has been criticized by various authors, *e.g.* by Hawking [101] and others, who pointed out that we attribute to time that direction in which entropy increases.

In addition, as was demonstrated in refs. [89, 90], there are over two dozen theoretical challenges to the second law, many of them laboratory testable. These facts may have cast serious doubt on the continued universality of that law. Sheehan [90] reviewed some representative challenges and considered the possibility that the thermodynamic arrow of time might be reversed on local or global scales. Experiments were proposed to test the connections between retrocausation and a reversed thermodynamic arrow. Hence the problem of directionality still is in a fog.

The most debatable question remains, what is the reason or origin of the arrow of time [80-82, 84-88, 90-95, 100, 102, 103]. Many hypotheses were proposed to fix a proper origin. Zeh [91] investigated irreversible phenomena and their foundation in classical, quantum and cosmological perspective. Conceptual problems regarding the arrow of time in classical physics, quantum physics, cosmology, and quantum gravity were discussed. Particular attention was paid to the dynamical role of the quantum indeterminism, and to various concepts of timelessness. Zeh book contains an analysis of the physical concept of time, a detailed treatment of radiation damping as well as discussion on quantum entanglement and decoherence, arrows of time hidden in various interpretations of quantum theory, and the emergence of time in quantum gravity. The author addressed these and similar problems expressing the asymmetric evolution of time.

It should be stressed that entropy is a concept equally applicable to deterministic as well as stochastic processes [12]. A specific approach to the arrow of time problem was formulated in refs. [102, 103]. It was shown that the entropy S , defined as

$$(1) \quad S = \langle \chi \ln \chi \rangle - \langle \chi \rangle \ln \langle \chi \rangle,$$

where χ stands for the natural time, may be of use for the study of the dynamical evolution of a complex system. The notion of *natural time* was introduced by ascribing to the k -th pulse of an electric signal consisting of N pulses the value $\chi_k = k/N$. This entropy exhibits positivity and concavity as well as stability or experimental robustness. Authors claimed that certain experimental results reveal the reasonable workability of considering the true time arrow in natural processes on the basis of their “entropic” approach.

Tuisku, Pernu and Annala [94] examined the concept of time by using the second law of thermodynamics that was reformulated as an equation of motion. They speculated that, according to the statistical notion of increasing entropy, flows of energy diminish the differences between energy densities that form space. They identified the flow of energy with the *flow of time*. The *non-Euclidean energy landscape*, *i.e.* the curved space-time, is in evolution when energy is flowing down along gradients and equalizing the density differences. The flows along the steepest descents, *i.e.* geodesics, were derived from the *principle of least action* for mechanics, electrodynamics and quantum mechanics. The *arrow of time*, associated with the expansion of the Universe, was identified with dissipation of energy when high-energy densities transform by various mechanisms to lower densities in energy and eventually to ever-diluting electromagnetic radiation. Moreover, according to this approach, time in a quantum system takes an increment forward in the detection-associated dissipative transformation when the stationary-state system begins to evolve pictured as the wave function collapse. The energy dissipation is understood to underlie causality so that an energy gradient is a cause and the resulting energy flow is an effect. The account of causality by the concepts of physics does not imply determinism; on the contrary, evolution of space-time as a causal chain of events is non-deterministic. In summary, based on the above-mentioned common characteristics of evolutionary processes, Tuisku, Pernu and Annala [94] proposed that the *flow of time* is the flow of energy. The net energy flow is the basis of irreversibility.

Haddad [95] attempted to combine the two universalisms of thermodynamics and dynamical systems theory to develop a kind of dynamical system formalism for classical thermodynamics. Specifically, using a compartmental dynamical system energy flow model, Haddad developed a state-space dynamical system model that captures the key aspects of thermodynamics, including its fundamental laws. In addition, he established the existence of a unique, continuously differentiable *global entropy function* for his dynamical system model, and using Lyapunov stability theory, Haddad concluded that the proposed thermodynamic (dynamic) model has finite-time convergent trajectories to Lyapunov stable equilibria determined by the system initial energies. Finally, using the system entropy, Haddad claimed the absence of Poincaré recurrence for his thermodynamic model and formulated certain criteria of the connections between irreversibility, the second law of thermodynamics, and the entropic arrow of time. Moreover, Haddad [95] claimed that perhaps a better expression for the evolution of time in this context is the *geodesic arrow of time*, since, as Einstein theory of relativity shows, *time and space are intricately coupled*, and hence one cannot curve space without involving time as well. Thus, time has a shape that goes along with its directionality.

From the other side, Ford [96] considered related complementary problems, namely he pointed out that if a dynamical system is sufficiently complex, then as time progresses it will share out energy and other properties amongst its component parts to eliminate any initial imbalances, retaining only fluctuations. This is known as energy dissipation and it is closely associated with the concept of *thermodynamic irreversibility*, measured by the increase in entropy according to the second law [97]. Ford argued that it is of interest to quantify such behavior from a *dynamical* rather than a thermodynamic perspective and to this end stochastic entropy production and the time-integrated dissipation function have been introduced as analogous measures of irreversibility, principally for stochastic and deterministic dynamics, respectively. He attempted to compare these measures. First he modified the dissipation function to allow it to measure irreversibility in situations where the initial probability density function of the system is asymmetric as well as symmetric

in velocity. Ford proposed that it will test for failure of what is possible to call the *obversibility* of the system, to be contrasted with *reversibility*, the failure of which was assessed by stochastic entropy production. He noted that the essential difference between stochastic entropy production and the time-integrated modified dissipation function lies in the sequence of procedures undertaken in the associated tests of irreversibility. Ford argued that an assumed symmetry of the initial probability density function with respect to velocity inversion (within a framework of deterministic dynamics) can be incompatible with the *past hypothesis*, according to which there should be a statistical distinction between the behavior of certain properties of an isolated system as it evolves into the far future and the remote past. Imposing symmetry on a velocity distribution is acceptable for many applications of statistical physics, but may introduce difficulties when discussing irreversible behavior.

Roduner and Radhakrishnan [104] discussed an interesting aspect of the problem of directionality and arrow of time. Their starting point is the second law of thermodynamics which determines the direction of spontaneous processes in the laboratory, life and the universe. They attracted attention to an important effect of kinetic barriers which intercept equilibration and may preserve highly ordered, high energy non-equilibrium states. Examples of such states are many modern materials produced intentionally for technological applications. Furthermore, all living organisms fuelled directly by photosynthesis and those fuelled indirectly by living on high energy nutrition represent preserved non-equilibrium states. The formation of these states represents the local reversal of the arrow of time which only seemingly violates the second law. Since the works of Prigogine, it is known that the stabilization of these states requires the dissipation of energy in the form of dispersal heat. It is this feature of heat dissipation following the input of energy that drives all processes occurring at a finite (non-zero) rate. Photosynthesis, replication of living organisms, self-assembly, crystal shape engineering and distillation have this principle in common with the well-known Carnot cycle in the heat engine. On the basis of this analogy, authors proposed to call these essential and often sophisticated driven processes by the term *machinery of life*.

Lucia [105] re-considered the relation between macroscopic irreversibility and microscopic reversibility by considering atoms as open systems. The notion of *constructal law* was used to formulate analytically Einstein's, Schrodinger's, and Gibbs' considerations on the interaction between particles and thermal radiation (photons). The result leads to consider the atoms and molecules as open systems in continuous interaction with flows of photons from their surroundings. The conjecture was that, in any atomic transition, the energy related to the microscopic irreversibility may be considered as negligible. From the other hand, when a big number of atoms (of the order of Avogadro's number) is considered, this energy related to irreversibility becomes so large that its order of magnitude must be taken into account. It was concluded [105] that macroscopic irreversibility results related to microscopic irreversibility by flows of photons and amount of atoms involved in the processes.

It is worth mentioning that the concept of *constructal law* was invented by Bejan [106-110] in 1995 while reviewing entropy generation minimization for a symposium paper. Bejan stated it as: "The constructal law is the law of physics that accounts for the phenomenon of evolution (configuration, form, design) throughout nature, inanimate flow systems and animate systems together". Or, in another form, "For a finite-size system to persist in time (to live), it must evolve in such a way that it provides easier access to the imposed currents that flow through it."

Hence the constructal law may be considered as a principle of physics of life and

evolution [106-110]. Moreover, the constructal law accounts for the arrow of time [109], which is, in Bejan's opinion, the direction of the evolution of flow organization over time. Bejan conjectured [109] that the arrow of time is painted much more visibly on another self-standing phenomenon, namely the occurrence and change of flow organization throughout nature, which he called the "other time arrow".

The approach of Bejan to evolution processes accumulated many notions and concepts of physics, biology, technology, and social sciences. It is complementary, in certain sense, to the concept of complexity [111,112]. The *constructal law* is a stimulating concept, but includes many delicate aspects. It raised hot discussions in the literature [113-117], which shows that there exist essential differences in understanding of macroscopic irreversibility and underlying microscopic dynamical behavior and the nature of irreversibility in complex systems.

To summarize, the nature of irreversibility in complex systems is not yet fully clear and its description depends strongly on the particular model selected to it. To clarify partially these complicated issues, we will discuss below some topics of non-equilibrium statistical thermodynamics relevant for our purposes in terse form.

3. – Entropy and statistical thermodynamics

The second law of thermodynamics and the concept of entropy arose mainly from practical studies of thermal engines and other devices [34,35]. What will be provided here is a sketchy reminder.

The general expression for entropy difference between the two states is

$$(2) \quad \Delta S = \int_A^B \frac{dQ}{T}.$$

This expression says that the difference in entropy between the equilibrium states A and B of a physical system may be determined by measuring the heat flow ΔQ over an arbitrary reversible path connecting the states. Thermodynamic entropy is dimensionless: $[S] = L^2 T^{-2} M \Theta^{-1}$, where Θ is the temperature.

The condition of thermodynamic reversibility in terms of the free energy G or the entropy S is expressed as $\Delta G = 0$ or $\Delta S = 0$. For an isothermal reversible process (temperature T is a constant) one can write down the equality $T\Delta S = \Delta Q = 0 = \Delta W$. Here W is the work done by the system and Q is the heat that the system exchanges with a thermal reservoir. Note that the term *reversible process* means here the quasi-static process. Hence, to find the entropy of a system, the thermodynamic definition of temperature, $T^{-1} = dS/dE$ should be used, where E is the energy.

In this connection it is of use to remember that in order to realize the entropy increase in a system, heat (or a flux of heat) should be provided in some way for the system itself. As a result, the temperature T will decrease: $(\partial T/\partial z) < 0$, where z is some relevant variable of a process.

It is worth mentioning that there is a conceptual distinction [118,119] between thermodynamic (empirical) entropy S and statistical entropy \mathcal{S} . The statistical entropy is by definition

$$(3) \quad \mathcal{S} = - \sum_k p_k \ln p_k.$$

Here p_k is the probability that the system under study is in the k -th state. In other words, in terms of statistical physics, entropy is related to the number of microstates that many-particle system can have for a given state which some selected set of macroscopic variables are characterized (volume, temperature, pressure, etc.).

For establishing a connection between empirical (macroscopic) and statistical (microscopic) description of complex many-particle systems it was necessary to make an important step and write down that

$$(4) \quad S = k_B \mathcal{S},$$

where k_B is Boltzmann constant. The Boltzmann constant is equal to the ratio of the gas constant R to Avogadro number N_A

$$(5) \quad k_B = \frac{R}{N_A} = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}} = 86.3 \text{ meV}.$$

This formula permits one to compute the thermodynamic entropy of isolated systems. Entropy is a function of state; it is also, as a rule [119], an extensive variable. There is a line of reasoning, proposed by Callen [120] which stresses that one of the most important aspects of entropy is to see it as a thermodynamic potential like the others.

The notion of statistical entropy suggests, in particular, that the statistical mechanics of a system in thermal equilibrium should be based on dynamics of particles and the concept of phase space [8, 121-124]. Statistical entropy is the quantity of fundamental importance. Let us consider the logarithm of the distribution function $f(p, q, t)$ with a minus sign

$$(6) \quad \eta = -\ln f(p, q, t).$$

This quantity is additive for multiplicative distribution functions and is related to the entropy of the system. Indeed, η , like f , satisfies the Liouville equation

$$(7) \quad \frac{\partial}{\partial t} f(p, q, t) = iL f(p, q, t); \quad \frac{\partial}{\partial t} \eta = \{H, \eta\}.$$

Here L is a linear operator $iL f = \{H, f\}$ and H is the total Hamiltonian. The average value of η

$$(8) \quad S = \langle \eta \rangle = - \int f(p, q, t) \ln f(p, q, t) d\Gamma$$

plays a special role in statistical mechanics. It is called Gibbs entropy [8].

Let us consider now a rarefied gas, in which the states of the different particles are nearly statistically independent. Hence the total distribution function can be represented as a product of the distribution functions for the single particles

$$(9) \quad f(p, q, t) \propto \prod_{i=1}^N f_1(p_i, q_i, t); \quad \int f_1(p_1, q_1, t) d\Gamma_1 = N.$$

The Boltzmann entropy is defined as

$$(10) \quad S_B = - \int f_1(p_1, q_1, t) \ln \frac{f_1(p_1, q_1, t)}{e} d\Gamma_1.$$

It is worth noting that in the general case, when the multiplicative property (9) does not hold, the Boltzmann entropy may also be formally defined by formula (4). It can be shown that if the function $f_1(p_1, q_1, t)$ satisfies Boltzmann kinetic equation [2], then the Boltzmann entropy increases. In the case of statistical equilibrium it is constant. What is the most important in this context is the fact that the Boltzmann definition of the entropy is adequate for the strongly rarefied gas only. It is less adequate in general case. Contrary to this, the Gibbs definition of the entropy is more suitable, since in the equilibrium case it gives the correct expression for the entropy as a thermodynamic function [8]. It is well known that the entropy can be obtained by a suitable phase-space averaging in different ensembles [8, 13]. According to Gibbs, the entropy is defined as the Boltzmann constant times the logarithm of the total phase space volume less than a given energy. Indeed, the Gibbs entropy is defined (for a microcanonical ensemble) as

$$(11) \quad S(E, N, V) = \ln \Omega(E, N, V).$$

Here Ω is the statistical weight. Thus, for a microcanonical ensemble, when energy is considered as a single integral of motion, the entropy is equal to the logarithm of the statistical weight [8]. In general case when, in addition to the energy, there exist a few additive integrals of motion P_s , the Gibbsian distribution takes the form

$$(12) \quad f(p, q) = Q^{-1}(\theta, F_1, \dots, F_s) \exp \left\{ -\frac{H(p, q)}{\theta} - \sum_{1 \leq n \leq s} F_n P_n(p, q) \right\}.$$

Here Q is the partition function (or statistical integral) which is determined from the normalization condition of the canonical distribution [8]. It is convenient to rewrite this expression in the form

$$(13) \quad f(p, q) = \exp \left\{ -\Phi(F_0, \dots, F_s) - \sum_{0 \leq n \leq s} F_n P_n(p, q) \right\}.$$

Here we denote that

$$(14) \quad P_0(p, q) = H(p, q), \quad F_0 = \frac{1}{\theta}, \quad \Phi(F_0, \dots, F_s) = \ln Q.$$

The thermodynamic potential $\Phi(F_0, \dots, F_s)$ is called the Massieu-Planck thermodynamic function [8]. Then we obtain the thermodynamic equalities and the most general expression for the entropy S in the form

$$(15) \quad \langle P_n \rangle = -\frac{\partial \Phi}{\partial F_n}, \quad F_n = \frac{\partial S}{\partial \langle P_n \rangle},$$

$$(16) \quad S = \Phi + \sum_n F_n \langle P_n \rangle = \Phi - \sum_n F_n \frac{\partial \Phi}{\partial F_n}.$$

It is known that the Boltzmann original definition of the entropy

$$(17) \quad S = k_B \ln W$$

was written in terms of the probabilities of available microscopic states of composite systems. Here W is the number of microstates which correspond to a macrostate of the system (*the thermodynamical probability of the macrostate*). In spite of its popularity, the Boltzmann approach led to hot discussions [5, 105].

The Boltzmann formula was analyzed from various sides in general form [5, 8, 60, 121, 122, 124, 125] to characterize it uniquely by physically plausible properties. In spite of this, it should be considered as a kind of postulate [126]. In particular, the Boltzmann formula was criticized in the literature on the ground that it gives a non-sufficient dynamical foundation in view of the thermal motion of the particles, out of which a physical system consists. There is numerous literature on Boltzmann entropy and its comparison with Gibbs entropy [5, 60, 127-134], where there are various and controversial statements on the interrelation of both the entropies (Boltzmann and Gibbs).

Vilar and Rubio [131] analyzed this interrelation critically. They compared the Boltzmann definition of entropy $S(E) = k_B \ln \Omega(E)$ in terms of the number of microstates $\Omega(E)$ with energy E with the expression $S_G(E) = k_B \ln \sum_{E' < E} \Omega(E')$ examined by Gibbs. They shown that $S_G(E)$ is either equivalent to S in the macroscopic limit or becomes independent of the energy exponentially fast as the system size increases. The resulting exponential scaling makes the realistic use of $S_G(E)$ unfeasible and leads in general to temperatures that are inconsistent with the notions of hot and cold. In other words, Vilar and Rubio showed that $S_G(E)$, in contrast to S , ceases to be a function of the energy for decreasing $\Omega(E)$ in the macroscopic limit and that it does so exponentially fast. Such exponential dependence makes a meaningful use of $S_G(E)$ unfeasible not only for macroscopic systems but also for small systems with over tens of elements and leads to temperatures that are inconsistent with the notions of hot and cold.

Another delicate problem is the extensivity of entropy. Dunning-Davies [127] have shown that the traditional approach using Carnot cycles to the problem of establishing the existence of absolute temperature and entropy and to deriving the relation $d'Q = TdS$ remains valid for systems whose entropy is *non-extensive* as well as for systems whose entropy is *extensive*. However, it is seen that the analytical approach to this problem is valid only for systems whose entropy is extensive. Dunning-Davies presented two methods for resolving this difficulty.

Addison and Gray [128] have examined the role of linearity in the definition of entropy. They noted that, while discussions of entropy often treat extensivity as one of its fundamental properties, the extensivity of entropy is not axiomatic in thermodynamics. It was shown that systems in which entropy is an extensive quantity are systems in which entropy obeys the generalized principle of linear superposition.

Mannaerts [129] reconsidered the notion of *extensive quantity* (or extensive property) and claimed that a literature survey shows little consistency in the definitions of this term as used in thermodynamics. The majority assumes that extensive quantities are those that are proportional to mass. Taking the mathematical meaning of proportional and taking the “*mass*” to be that of the system or subsystem, it was shown that the proportionality assumption is only correct for a few extensive quantities under the condition of constant composition. A large subset of extensive quantities are completely independent of mass; for most systems extensive quantities are not proportional to mass,

but mass is the (extensive) constant of proportionality. The common wisdom, based on the *additivity of extensive quantities*, is the main leading principle for discussing this subject. It was noted however, that two types of additivity need to be distinguished and that a few intensive quantities are also additive.

Diebner and Rossler [130] have analyzed in detail a deterministic entropy to examine the evolution of microscopically simulated out-of-equilibrium structures. They considered the H -function introduced by Boltzmann, who conjectured a way to define a *deterministic microscopic entropy* valid close to equilibrium. According to authors [130], his original idea was the following: Replace the N -particle system by N overlaid one-particle systems —as if each particle were alone. Then look only at the differences between the state points of neighbouring particles. Boltzmann himself only looked at the momentum subspace. As the system of particles approaches equilibrium, the mean value, taken over all the individual differences, becomes a maximum. The same fact still holds true for the logarithm of the same sequence of mean values obtained on the way towards equilibrium. The absolute value of the resulting function, which becomes maximal at equilibrium, is reduced to the H -function with minus sign; its positive obviously qualifies as a *deterministic entropy*, valid close to equilibrium. It is known that the H -function formalism can be well applied only close to equilibrium. Diebner and Rossler [130] concluded that “The cosmos seems live on entropy according to Boltzmann.”

Byung Chan Eu [132] carried out a deep analysis of these problems and concluded that generalized thermodynamics or *extended irreversible thermodynamics* assumes the existence of thermodynamic intensive variables (*e.g.*, temperature, pressure, chemical potentials, generalized potentials) even if the system is removed from equilibrium. He emphasized the necessity to properly understand the nature of such intensive variables and, in particular, of their fluctuations, that is, their deviations from those defined in the extended irreversible thermodynamic sense. The meaning of temperature was examined by means of a kinetic theory of macroscopic irreversible processes to assess the validity of the generalized (or extended) thermodynamic method applied to non-equilibrium phenomena. The Boltzmann equation was used to that aim. Since the relative Boltzmann entropy has been known to be intimately related to the evolution of the fluctuations in the intensive thermodynamic variables, Eu derived the evolution equations for such fluctuations of intensive variables to lay the foundation for investigating the physical implications and evolution of the *relative Boltzmann entropy*. In this way the range of validity of the thermodynamic theory of irreversible processes may be clarified. In addition, Eu examined also a special case of the evolution equations for the fluctuations of intensive variables, which also facilitate the investigation of the molecular theory meaning of the zeroth law of thermodynamics. On this basis Eu derived an evolution equation describing the relaxation of temperature fluctuations from its local value and presented a formula for the temperature relaxation time.

By adopting the Boltzmann definition of the entropy, Sinha [133] gave a formulation of entropy as a difference between the changes in Hamiltonian and potential energy. He presented a derivation of a new formula of entropy from Boltzmann formula while incorporating potential energy changes. Thermal energy applied to particles in conservative vector fields resulted in an increase in the potential and kinetic energy causing an increase in entropy. However, in his approach, conservative fields associated with potential energy gradients of the system act in opposition to the kinetic energy gradients reducing the overall accessible states of the system and its entropy. Hence, entropy can be expressed

as the ratio of difference between the input energy and potential energy of the system to its temperature. As the input energy represents the changes in Hamiltonian of the system, entropy can also be expressed as the difference in changes of its Hamiltonian and potential energy. Hence, the formulation of entropy in terms of the changes in system Hamiltonian and potential energy changes may provide some additional understanding about the role of potential fields in determining entropy rate and its impact on order and equilibrium.

4. – Variety of entropies

Grad [16] long ago pointed out that there are *many faces of entropy*. Since that time the concept of entropy [37-41] was deepened and generalized greatly [50, 123, 135-140], especially in the context of complex systems [141]. However, it was widely recognized that there is no systematic single valued way of deriving the *right entropy* for a given dynamical (statistical) system.

Thurner and Hanel [55, 56] re-analyzed the definition of entropy for complex statistical systems. Many complex systems are characterized by non-Boltzmann distribution functions of their statistical variables. In case if one wants to —justified or not— hold on to the maximum entropy principle for complex statistical systems (non-Boltzmann), Thurner and Hanel demonstrated how the corresponding entropy has to look like, given the form of the corresponding distribution functions. By two natural assumptions that i) the maximum entropy principle should hold and that ii) entropy should describe the correct thermodynamics of a system (which produces non-Boltzmann distributions). As a result the existence of a class of fully consistent entropies was deduced. Classical Boltzmann-Gibbs entropy was recovered as a special case for the observed distribution being the exponential, Tsallis entropy [123] the special case for q -exponential observations.

Entropy in a broad sense is a *measure of uncertainty*. Hence, the entropy of a random variable can be treated as a measure of uncertainty associated with that random variable [12, 142, 143]. Indeed, when the uncertainty of the value of that random variable is large the corresponding entropy will be large. When the state of a physical system is not fully determined by available data, it may be possible to some extent to make a reasonable guess concerning the unknown state by applying the formalism of information theory [12, 21-33]. The general theory of information [28-33] provides a unified context for various directions in information studies, making it possible to elaborate on a comprehensive definition of information [12]. Moreover it is of use in establishing relations between information, data, and knowledge to establish how different mathematical models of information and information processes are related. The information-theoretic entropy concept was formulated as the fundamental notion of this formalism [12]. This line of reasoning was developed by numerous researchers [5, 9-11, 17-20] and was applied successfully to statistical physics [8, 12, 13, 52, 144-147].

Information theory was developed by Shannon [12, 19, 21, 22, 27-33, 145-147], who introduced the quantitative measure for the *missing information* (or an uncertainty measure) in the discrete probability distribution $\{p_{s_i}\}$

$$(18) \quad H(S) = - \sum_{i=1}^n p_{s_i} \log p_{s_i}.$$

Here $H(s)$ means the entropy of the source and $\{p_{s_i}\}$ is the set of probabilities p_{s_i} of the

occurrence of state s_i ; the amount of information is $I(s_i) = -\log p_{s_i}$. This expression can be rewritten also in the form

$$(19) \quad H = -k \sum_i p_i \ln p_i.$$

Here k is a positive constant. For a continuous case $H(X)$ may be defined as

$$(20) \quad H(X) = - \int_{-\infty}^{\infty} p(x_i) \log(p(x_i)).$$

However, Hobson [148] argued that the generalization Shannon definition to continuous probability distributions $f(x)$ has certain caveats. In order to escape the difficulties associated with Shannon definition, Hobson [148] has proposed a generalized expression for the basic information measure

$$(21) \quad H(p_1, \dots, p_n; p_1^0, \dots, p_n^0) = k \sum_i p_i (\ln p_i / p_i^0).$$

Here k is a positive constant. Hobson [148] considered a random experiment whose possible outcomes were z_1, z_2, \dots, z_n . The prior probabilities were denoted as p_1^0, \dots, p_n^0 , and the posterior probabilities as p_1, \dots, p_n . This expression seems to have all the properties desired in an information measure [148, 149]. It was shown also that, subject to certain prescribed and intuitively reasonable conditions, this formula is the unique expression for the information contained in a message which alters the probabilities from the p_i^0 to the p_i .

It is of importance to mention in this context the notion of the entropy in quantum physics. Quantum physics uses two basic ideas, namely, the “state” and the “observable”. After measuring an observable and getting a particular outcome, which is called by an eigenvalue, the state of the system is the corresponding eigenvector. The state of a system (consisting of one particle or many particles) in quantum mechanics is fully described by a function $\psi(\mathbf{r}, t)$ (or $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, t)$). The function $\psi(\mathbf{r}, t)$ is a basic notion of quantum physics. It is termed the wave function of the system. The wave function is defined so that the probability of finding the particle in the interval x to $x + dx$ is $P(x)dx = |\psi|^2 dx = \psi^* \psi dx$. In quantum mechanics two kinds of states occur: the pure state, represented for instance by a wave function $\psi(\mathbf{r}, t)$, and the mixed state, represented by a density matrix ρ_{nm} . A mixed state may be regarded as a probability distribution over a set of pure states. Similarly, in classical mechanics a pure state is represented by a point in phase space and a mixed state by a probability distribution over phase space.

Let us consider a quantum system which is characterized by some unknown pure state $|\Psi\rangle$. It belongs to the set of orthonormal functions $\{|\psi_n\rangle\}$. Hence the quantal state proposition is that the system under consideration is in state $|\psi_n\rangle$. In terms of information theory a subjective probability distribution $\{P_n\}$ may be defined over the proposition, which satisfies the constraint $\sum_i P_i = 1$. The information-theoretic entropy, or missing information function, may then be defined as

$$(22) \quad H = -k \sum_i P_i \ln P_i.$$

From the point of view of the quantum mechanical density operator formalism, it was said that it may be interpreted as a compact invention for describing the informational situation wherein each subjective probability in $\{P_n\}$ represents the likelihood that its associated state vector in $\{|\psi_n\rangle\}$ is the correct one to be characterized by the density operator

$$(23) \quad \rho = \sum_n P_n |\psi_n\rangle \langle \psi_n|.$$

It was von Neumann [150] who connected an entropy quantity to a statistical operator ρ . In other words, to calculate the statistical entropy one must find the volume of phase space occupied by the system; the statistical entropy in this case will be written as

$$(24) \quad \mathcal{S} = -\text{Tr } \rho \ln \rho,$$

where ρ is the density matrix. The introduction of entropy in quantum mechanics gives in a compact form all the classical definitions of entropy. The temporal evolution of the von Neumann entropy is governed by the Liouville-von Neumann equation [8, 13] for isolated quantum systems.

In the von Neumann approach, the process of measurement can be described as the determination of statistical correlations between the state of the object and that of the measuring apparatus. The measurement process [151, 152] in quantum mechanics involves a system and an apparatus which interact between themselves at some time and then should be separated. Hence, the system under consideration is not isolated, *i.e.* is open. However, the von Neumann approach describes the measuring process and irreversibility in a somewhat idealized manner. The von Neumann entropy is invariant under the unitary dynamics. In other words, the changes in the entropy of the system during the measurement process should be estimated very carefully [151, 152], since even if the quantum measurement process is irreversible, such irreversibility may be not quantified by an increase of the von Neumann entropy. The property of concavity (see ref. [153]) in combination with comparison of the initial von Neumann entropy with the weighted final entropy showed that the final entropy may be lower than the initial one. Klein's inequality [153] and related inequalities permitted one to establish that the Shannon entropy corresponding to the probabilities pertaining the measurement outcomes of a non-degenerate observable is always larger than or equal to the von Neumann entropy. However, the detailed consideration of the quantum measurement processes [151, 152] is beyond the scope of the present review.

Stotland *et al.* [20] pointed out that a Shannon-based definition of information entropy leads in the classical case to the Boltzmann entropy. Hence, it is tempting to regard the von Neumann entropy as the corresponding quantum mechanical definition. But the latter is problematic from quantum information point of view. Indeed, the information entropy $S[\rho]$ is a measure for the amount of extra information which is required in order to predict the outcome of a measurement. If no extra information is needed one can say that the system is in a definite statistical state with $S = 0$. A classical system can be in principle prepared in a definite state. But this is not true for a quantum mechanical system. Consequently Stotland *et al.* [20] introduced a new definition of entropy that reflects the *inherent uncertainty* of quantum mechanical states. They derived for it an explicit expression, and discussed some of its general properties. Authors pointed out

TABLE I. – *Variety of entropies.*

Entropy	Formula	Reference
Boltzmann entropy	$S_B = - \int f_1(p_1, q_1, t) \ln \frac{f_1(p_1, q_1, t)}{e} d\Gamma_1$	Zubarev [8]
Gibbs entropy	$S = k_B \ln \Omega(E, V, N)$	Zubarev [8]
von Neumann entropy	$S = - \text{Tr } \rho \ln \rho$	Zubarev [8]
Shannon entropy	$H = -k \sum_i p_i \ln p_i$	Shannon [21, 22], Lesne [147]
Fisher information	$I = \int d\mathbf{r} \nabla p \nabla p / p$	Frieden [154]
Kullback measure	$I_k[P : P^0] := \sum_i p_i \ln(p_i/p_i^0)$	Kullback [155], Hobson [156]
Kolmogorov entropy	$H(P) = - \sum_i f(P_i) \log f(P_i)$	Kolmogorov [157, 158]
Jauch-Baron entropy	$H(\mu, \nu) = \int_X f \ln(f) d\nu$	Jauch and Baron [149, 159]
Sharma-Mittal entropy	$H_{SM}(P; \alpha, \beta) = \frac{1}{2^{1-\beta}-1} \left[\left(\sum_{k=1}^n p_k^\alpha \right)^{\frac{\beta-1}{\alpha-1}} - 1 \right]$	Sharma and Mittal [160]
Renyi entropy	$H_q(p) = \frac{1}{1-q} \log \left(\int p(x)^q dx \right)$	Renyi [161]
Tsallis entropy	$S_T(P, q) = \frac{1}{1-q} \sum_i p_i (1 - p_i^{q-1})$	Tsallis [123]
Abe entropy	$S_q^S = \frac{(q-1)S_q^T - (q^{-1}-1)S_q^T}{q - q^{-1}}$	Abe [162-164]
Kaniadakis entropy	$S_\kappa(p_i) = \sum_i p_i \ln_\kappa(1/p_i)$	Kaniadakis [165-168]
Edwards granular entropy	$S_{Ed} \propto - \int P \log P \prod_\omega dA(\omega)$	Edwards [169, 170]

distinctions between the minimum uncertainty entropy of pure states, and the excess statistical entropy of mixtures.

Beck [135] showed that the formalism of statistical mechanics can be generalized by starting from more general measures of information than the Shannon entropy and maximizing those subject to suitable constraints. He discussed some of the most important examples of information measures that are useful for the description of complex systems [154-156, 159, 161-164, 171-174]. Examples treated are the Renyi entropy [161], Tsallis entropy [123, 174], Abe entropy [162-164], Kaniadakis entropy [165-168], Sharma-Mittal entropies [135], and a few more. Important concepts such as the axiomatic foundations, composability and Lesche stability of information measures were discussed as well. Potential applications in physics include complex systems with long-range interactions and metastable states, scattering processes in particle physics, hydrodynamic turbulence, defect turbulence, optical lattices, and quite generally driven non-equilibrium systems with fluctuations of temperature.

It will be of use to summarize the various entropies (incomplete list) in the form of table I. A few remarks will not be out of place here. The trace of the Fisher informa-

tion [143, 154, 171, 172] matrix

$$(25) \quad I = \int \mathrm{d}\mathbf{r} \nabla p \nabla p / p$$

is a scalar *information quantity* that has been shown [143, 154, 171, 172] to be a workable tool for the description of various physical phenomena. This includes such diverse phenomena as the complex Schrödinger wave equation, the Maxwell-Boltzmann distribution law, and Maxwell's equations. In eq. (25), p is a probability density function $p(x)$ for a coordinate x whose unit specifies the physical situation, *e.g.*, a length in quantum mechanics, or a velocity in classical particle statistics.

Fisher information is related to the asymptotic variability of a maximum likelihood estimator [173]. The idea being that higher Fisher information is associated with lower estimation error. Shannon information [21, 22] is totally different, and refers to the content of the message or distribution, not its variability. It was assumed sometimes that the higher entropy distributions convey less information because they can be transmitted with fewer bits. In fact, in the realm of communication theory, Shannon entropy effectively bounds the performance of the strongest lossless compression possible. Hence, according to noiseless coding theorem [28, 31-33, 154], a data source with higher entropy requires a communication channel with higher capacity for reliable error-free communication.

There is a relationship between Fisher information and relative entropy. The book by Frieden [154] defines and develops a unifying principle of physics, that of “*extreme physical information*”. The information in question is not Shannon or Boltzmann entropy but, namely, Fisher information. Both statistical and physical properties of Fisher information have been considered. Fisher information was shown to be a physical *measure of disorder*, sharing with entropy the property of monotonic change with time. The information concept was applied “phenomenally” to derive most known physics, from statistical mechanics and thermodynamics to quantum mechanics, the Einstein field equations, and quantum gravity. Many new physical relations and concepts were reconsidered, including new definitions of disorder, time and temperature. The information principle was based upon a new theory of measurement, one which incorporates the observer into the phenomenon that he observes. The “*request*” for data creates the law that, ultimately, gives rise to the data. In that sense the observer creates his local reality.

As regards Kullback measure [155], Hobson and Bin-Kang Cheng [156] have analyzed and compared two widely used information measures. It was shown that the Kullback measure, unlike the Shannon measure [21], provides the basis for a consistent theory of information which extends to continuous sample spaces and to non-constant prior distributions. It was shown also that the Kullback measure is a generalization of the Shannon measure, and that the Kullback measure has more reasonable additivity properties than does the Shannon measure. The results lend support to Jaynes's entropy maximization procedure [11].

Kolmogorov in 1958 proposed the use of information characteristics (namely entropy characteristics) in the study of both metric spaces and of dynamical systems. He introduced an entirely new metric invariant, coming from information theory, the entropy of the dynamical system [175]. Kolmogorov showed in the context of ergodic theory how Shannon concept of entropy could be extended to obtain an invariant for measure-preserving transformations. He proposed that the entropy of a finite partition P can be

written in the form

$$(26) \quad H(P) = - \sum_i f(P_i) \log f(P_i).$$

Kolmogorov entropy approach stimulated activity in that direction. Entropies of many transformations of interest were calculated and a wide class of transformations were shown to have completely positive entropy. In this line of reasoning the notion of *topological entropy* has been formulated as an analog to measure-theoretic entropy. Topological entropy was defined by various authors to characterize dynamical systems resulting from continuous mappings. However, this notion is out of the scope of the present study.

In his papers of 1955-1956 Kolmogorov introduced the notion of ϵ -entropy of sets in a metric space and thus obtained a means to estimate the *metric mass* of functional classes and spaces. Using this notion, Kolmogorov gave an entropy interpretation of the former results on the non-representability of functions in n variables of smoothness r as the superposition of function of m variables of smoothness l if $n/r > m/r$. The thing is, the ϵ -entropy of any class of functions is, roughly speaking, the amount of information which allows to indicate a function of this class with precision ϵ .

Kolmogorov formulated also a reconstruction of information theory itself [176], a reconstruction based on the algorithmic approach. In the fundamental papers [157, 158] Kolmogorov invented *the algorithmic theory of information*. The central position in this theory was the notion of complexity of a finite object for a fixed (algorithmic) method of its description [177, 178]. This complexity was defined in a very natural way, as the minimal volume of description. Kolmogorov theorem established that among all possible algorithmic methods of description there exist optimal ones, those for which the complexity of the objects described turns out to be relatively small. Although the optimal method is not unique, for two given optimal methods, the corresponding complexities differ no more than an additive constant. The new notions turn out to be at the same time quite natural, unexpected and simple. In the framework of these ideas it turned out to be possible, in particular, to define the notion of individual random sequence (which is impossible in terms of classical probability theory). One must call random any sequence whose complexity (under any optimal method of description of its initial segment) grows sufficiently fast as the length of the segment increases. It should be noted that Kolmogorov complexity and Shannon entropy of an information source have different definitions.

Skagerstam [149] analyzed some of the historical reasons for the "identification" of the information-theoretical and thermodynamic entropy concepts. He considered the question what is the connection between the entropy concept used in information theory and that used, *e.g.*, in statistical mechanics and other disciplines. His conclusion was that in general they are different both as fundamental concepts and quantitative instruments for analyzing the properties of physical systems.

Jauch and Baron [159] discussed similar questions and they also constructed an entropy function that gives the standard formulas for entropy as defined by Boltzmann in statistical mechanics or by Shannon in information theory. Skagerstam also discussed the Jauch-Baron entropy concept [159] and explicitly showed that, for classical systems in thermodynamic equilibrium, there exists a very simple connection between this general definition and the ordinary experimental entropy. He also noticed that the problem of giving a precise meaning for entropy so that it can be applied to the description of irreversible processes in physics is perhaps, at present, not a well-defined question. This is so because we do not have any general universal method for treating such processes.

Various specific definitions of the entropy concept were studied in the last decades. Consider the Shannon entropy of a n -dimensional random vector with density p , defined as

$$(27) \quad H(p) = - \int p(x) \log p(x) dx.$$

The Shannon measure has been generalized by various authors and has found numerous applications in various disciplines ranging from physics to economics. Sharma and Mittal [160] generalized the Shannon entropy in the following form:

$$(28) \quad H_{SM}(P; \alpha, \beta) = \frac{1}{2^{1-\beta} - 1} \left[\left(\sum_{k=1}^n p_k^\alpha \right)^{\frac{\beta-1}{\alpha-1}} - 1 \right].$$

The Renyi entropies also generalize the Shannon entropy. Renyi [161] found that the Shannon expression does not represent the only possible measure of uncertainty. He formulated certain axioms and showed that these axioms are satisfied by a more general definition, namely

$$(29) \quad S_R(P, q) = \frac{1}{1-q} \log \left(\sum_i p(x)^q \right),$$

for discrete case and for continuous case as

$$(30) \quad S_R(P, q) = \frac{1}{1-q} \log \left(\int p(x)^q dx \right).$$

Here S_R is the q -Renyi entropy (or Renyi entropy of order q , where $q \neq 1$). The limit of Renyi entropy for $q \rightarrow 1$ gives the Shannon entropy, namely

$$(31) \quad \lim_{q \rightarrow 1} S_R(P, q) \longrightarrow - \int p(x) \log p(x) dx.$$

Tsallis [123] proposed a generalization of Shannon entropy to non-extensive systems, *e.g.* self-organized critical systems, etc., as

$$(32) \quad S_T(P, q) = \frac{1}{1-q} \sum_i p_i \left(1 - p_i^{q-1} \right).$$

Note that the Shannon measure is additive, whereas the Tsallis one is pseudo-additive. Tsallis entropy leads to Shannon entropy as well. The limit for $q \rightarrow 1$ gives the Shannon entropy. The relationship between Renyi entropy and Tsallis entropy is

$$(33) \quad S_R(P, q) = \frac{1}{1-q} \log(1 + (1-q)S_T(P, q)).$$

Hence, the parameter q describes the deviations of Renyi and Tsallis entropies from the standard Shannon entropy.

Abe [162-164] showed that a connection between the generalized entropy and theory of quantum groups, pointed out by Tsallis, can naturally be understood in the framework of q -calculus. Abe presented a new entropy which has $q \leftrightarrow q^{-1}$ invariance and discussed its basic properties. In his work [162], Abe showed, using q -calculus, that Tsallis postulate for the entropy, in fact, contains the q -deformation structure in itself. In a sense, this observation turns out to be more fundamental than the above-mentioned similarity. Based on this idea, Abe then presented a new generalized entropy of the form

$$(34) \quad S_q^S = \frac{(q-1)S_q^T - (q^{-1}-1)S_{-q}^T}{q - q^{-1}}.$$

This expression can be interpreted as the $q \leftrightarrow q^{-1}$ symmetric modification of Tsallis entropy S_T . Hence Abe showed the possibility of a consistent q -deformation-theoretic approach to constructing a class of extended thermodynamics.

Kaniadakis [165-168] proposed “a consistent framework for generalized statistical mechanics” by considering two-parameter deformations of logarithm, exponential, and entropy of the form

$$(35) \quad S_\kappa(p_i) = \sum_i p_i \ln_\kappa(1/p_i).$$

A consistent generalization of statistical mechanics was obtained [165-168] by applying the maximum entropy principle to a trace-form entropy and by requiring that physically motivated mathematical properties were preserved. The emerging differential-functional equation yielded a two-parameter class of *generalized logarithms*, from which entropies and power-law distributions follow. These distributions potentially could be relevant in many anomalous systems. Within the specified range of parameters, these entropies possess positivity, continuity, symmetry, expansibility, decisivity, maximality, concavity, and are Lesche stable. The Boltzmann-Shannon entropy and some one-parameter generalized entropies already known belong to this class. The two-parameter class of deformed logarithms includes an infinity of one-parameter deformed logarithms that can be specified by selecting a relation between specific parameters. These entropies and their distribution functions were compared, and the corresponding deformed algebras were discussed.

It is worth noting that Lesche stability criterion [102, 103], which states that an entropic measure is stable if its change upon an arbitrarily small deformation of the distribution representing fluctuations of experimental data remains small. By means of this stability criterion, Lesche showed that the Boltzmann-Gibbs-Shannon entropy is stable, while the Renyi entropy is unstable. Abe later proved that the Tsallis entropy is also stable, while the escort entropy [123, 164] is not. Finally, the stability was also shown for the Kaniadakis entropy.

Recently Deng [179] reconsidered Dempster-Shafer evidence theory which has been widely used in many applications due to its advantages to handle uncertainty. However, how to measure uncertainty in evidence theory has been until recently an open issue. The main contribution of Deng paper [179] was that a new entropy, named as *Deng entropy*, was presented to measure the uncertainty of a basic probability assignment (BPA). Deng entropy is the generalization of Shannon entropy since the value of Deng entropy is identical to that of Shannon entropy when the BPA defines a probability measure. Numerical examples were considered to illustrate the efficiency of Deng entropy.

Abellan [180] continued this line of reasoning by considering the theory of evidence (or Shafer-Dempster theory) which has been widely used in applications. The Shafer-Dempster theory was based on the concept of a basic probability assignment. An important part of this theory was the quantification of the information-based uncertainty that this function represents. Abellan [180] discussed the measure of uncertainty (or *information*) in this theory, called the Deng entropy, which has appeared as a useful alternative to the measures presented so far. This measure quantifies both types of uncertainty found in Shafer-Dempster theory, then it was considered as a total uncertainty measure. It was shown that this measure does not verify some of the essential properties for a total uncertainty measure in Shafer-Dempster theory such as monotonicity, additivity and subadditivity. Also, the definition of this new measure produces other debatable situations. These shortcomings call in question the utility of this measure in applications. For details on the Deng entropy we refer to papers [179,180].

An especial and tricky example of the generalized “entropy” was proposed by Edwards in the context of theory of granular or glassy systems. He called it “new kinds of entropy” [169,170,181-183]. It should be noted that statistical mechanics of jammed granular states is rather non-trivial. In granular materials particles only interact when they touch. There are particles with hard cores and particles with soft cores. The last are deformable particles which repel with a finite force when they overlap. Inter-particle scattering processes are inelastic and do not conserve energy.

To deal with such complicated systems Edwards proposed two new entropies in his papers [169,170]. Both of them do not belong to the “traditional conservative statistical mechanics”. The first deals with the states of granular or glassy systems which may be, in principle, confined by a suitable experimental pathway. This assumption implies that an entropy may be defined [169,170] for them by deriving an appropriate analog of Boltzmann equation in which the pathway to the steady state has an increasing entropy until the state characterized by a compactivity (or compactness) $X = (\partial V)/(\partial S)$ is reached. Here V is the volume and S is the “entropy”.

The second problem in Edwards’ opinion [169] was to consider a state where energy *flows in* and *flows out*, leaving a steady state, *e.g.*, a steady turbulent flow. Time-dependent correlation functions may be reasonably well defined and hence a probability of the history of the system may be defined. Author investigated whether such systems will possess *an entropy* defined by the usual $\int P \log P$, but now P is the probability of the entire history of the system and the integral is over all histories. In other words, it was conjectured [169,170] that all jammed states of equal volume have equal probabilities so that the probability of finding a given configuration i may be written as $P_i \propto \exp(S/\lambda)$, where λ is the analog of the Boltzmann constant. Authors claimed that their entropy S is extensive and the compactivity X is equivalent to the temperature in a thermal system. This direction of researches is developed very rapidly [169,170,181-183] and many complicated questions should be still answered. Among them one may select especially the problem of temporal evolution of a system, which require a corresponding dynamics that allowed the system to move directly between jammed states at fixed volume and, as a result, an appropriate change of the generalized entropy.

5. – Irreversible processes and thermodynamic fluxes

One of the purposes of this paper is to analyze the relationship between the concepts of entropy and entropy generation in the standard sense of statistical thermodynamics and the entropy production in the approach of the method of the non-equilibrium statistical

operator [8]. Entropy production of steady-state irreversible processes can be expressed as the product of thermodynamic fluxes and thermodynamic forces. Here we remind very briefly the underlying macroscopic basis of the theory of irreversible processes [8, 13, 52, 53, 184-186] to introduce the necessary macroscopic notions.

The irreversible process in thermodynamics is described by the Clausius inequality [184-186]

$$(36) \quad \oint \frac{dQ}{T} \leq 0.$$

Hence it is possible to say that entropy characterizes the *degradation* of energy as a result of the *dissipation* [187, 188] of mechanical energy to thermal energy due to friction or the degradation of thermal energy due to temperature homogenizing in a system. In an irreversible transition change of entropy, dS of a closed system during the process is

$$dS \geq \frac{dQ}{T}.$$

The entropy generation S_g is defined as the entropy which appears during a process (transition from A to B)

$$(37) \quad \Delta S = \int_A^B \frac{\delta Q}{T} + S_g.$$

Thus the entropy production has the property

$$(38) \quad S_g = \begin{cases} > 0, & \text{irreversible,} \\ = 0, & \text{reversible,} \\ < 0, & \text{impossible.} \end{cases}$$

In other words, for the system in equilibrium only a small number of variables such as temperature, volume, pressure, composition, etc., are required to determine the properties of the thermodynamic system [8, 13, 52]. The adequate description of the non-equilibrium system and irreversible processes is a complicated task [189]. The important advance was given by Onsager [190-193]. He elaborated a macroscopic approach to irreversible thermodynamics, based on achievements of fluctuation theory and statistical mechanics [194]. The theory of irreversible processes after the works of Onsager was developed substantially in more general fashion and more firmly based on experiment. The main ideas of these advances were related to the formulation of the theory of the *production of entropy* in irreversible processes and its relation to known linear laws such as Fick law and Ohm law and their generalizations [8, 13, 52, 195].

For describing the change of a system it is necessary to compute the rate at which entropy is produced during an irreversible process [189]. The entropy production is defined as the rate at which entropy is produced inside the system (it is important not to mix the entropy produced inside the system with the entropy change of the system). According to the second law of thermodynamics eq. (37) hold valid in any irreversible process. The quantity $\delta Q/T$ is the entropy added to the system by heat transport across its boundaries. Since ΔS is the total entropy change of the system, the quantity

$\Delta S - \int \delta Q/T = \Delta S_i$ must represent the entropy produced *inside* the system. Thus we have

$$(39) \quad \Delta S = \int \frac{\delta Q}{T} + \Delta S_i; \quad \Delta S_i = \int \frac{\delta Q_i}{T},$$

where Q_i is the Clausius uncompensated heat [15, 35, 36, 185, 186]. It is obvious that ΔS_i and Q_i must always be positive in an irreversible process. Equation (39) is the entropy balance equation. The entropy production for the electrical conduction and heat conduction were analyzed in details in refs. [13, 42, 44, 52, 195-197].

Let us consider in the present context a typical pedagogical example [198] of heat conduction. For simplicity it is of convenience to consider a sample (a bar) of uniform cross section whose ends are at different temperatures, $T_L \neq T_R$. The temperatures may not be fixed; the sample is in a steady state. It may be assumed that the heat was transmitted through the sample if the surface of the sample is well insulated. It was supposed also that the system is in the *local equilibrium* state. Then, dS is given by

$$(40) \quad dS = \frac{d(\Delta Q)}{T}.$$

Here ΔQ is the quantity of heat which leaves the section of a sample at point x (which is at a temperature T) during the time dt . At $x + dx$ an amount of entropy $[\Delta Q + d(\Delta Q)]/(T + dT)$ enters, and at x an amount $\Delta Q/T$ leaves. Then dS_i is found to be

$$(41) \quad dS_i = \frac{d(\Delta Q)}{T} - d\left(\frac{\Delta Q}{T}\right) = \frac{(\Delta Q)dT}{T^2} > 0.$$

Hence the entropy production dS/dt will take the form

$$(42) \quad T\dot{S} = \frac{T}{V} \frac{dS_i}{dt} = \frac{1}{C} \frac{\Delta Q}{dt} \left(\frac{1}{T} \frac{dT}{dx} \right) = \mathbf{J}_q \mathbf{X}_q.$$

Here the heat flux \mathbf{J}_q and force \mathbf{X}_q may be written as follows:

$$(43) \quad \mathbf{J}_q = - \left(\frac{1}{C} \right) \frac{\Delta Q}{dT}; \quad \mathbf{X}_q = - \left(\frac{1}{T} \right) \frac{dT}{dx}.$$

In three dimensions the entropy production would be written as

$$(44) \quad T\dot{S} = -\mathbf{Q} \frac{\text{grad } T}{T}.$$

It is known that there exists a linear dependence of the flux of heat with the temperature gradient. It is the Fourier law of heat conduction (see discussion in refs. [13, 42, 44, 195-197])

$$(45) \quad \left(\frac{1}{C} \right) \frac{\Delta Q}{dT} = -\kappa \frac{dT}{dx},$$

where κ is the conductivity coefficient. With the aid of introducing the quantities \mathbf{J}_q and \mathbf{X}_q , this equation can be rewritten as follows:

$$(46) \quad \mathbf{J}_q = \hat{L}_q \mathbf{X}_q; \quad L_q = -\kappa T.$$

Transport of mass, energy, momentum, volume and electric charges happens when driven forces of various nature are applied [13, 42, 44, 52, 195, 196]. These forces are the concentration, temperature, velocity, pressure and voltage gradients. Thermodynamic systems may be prevented from relaxing to equilibrium because of the application of a mechanical field (*e.g.*, electric or magnetic field), or because the boundaries of the system are in relative motion (shear) or maintained at different temperatures, and so on. Hence it may be reasonable to consider (at least in the first approximation) two types of non-equilibrium systems, namely, mechanical non-equilibrium systems and thermal non-equilibrium systems [8, 13, 52, 199].

The well-known example of a mechanical transport process is the electrical conduction which is described by the Ohm law [13, 52, 195], which states that at least for sufficiently small applied voltages, the current I is linearly proportional to the applied voltage V , $I = \sigma V$. The coefficient of proportionality is the electrical conductivity which is the reciprocal of the electrical resistance. As the applied voltage increases one may expect to see deviations from linear behavior.

The known example of a thermal transport process is the Newton law of viscosity [200] which states that the shear stress P_{xy} is linearly proportional to the strain rate. The strain rate Γ is the rate of change streaming velocity in the x -direction, with respect to the y -coordinate, $\Gamma = \partial u_x / \partial y$. The law of viscosity states

$$(47) \quad P_{xy} = \eta \Gamma.$$

As the strain rate increases, one may expect to see deviations from linear behavior

$$P_{xy} = \eta(\Gamma)\Gamma.$$

Another well-known thermal transport process is the Fourier law of heat conduction [196], which states that the heat flux between two bodies maintained at different temperatures is proportional to the temperature gradient (the temperature difference divided by the spatial separation). Thus, regardless of whether transport processes are caused thermally or mechanically, in the small field limit it is expected that a flux will be linearly proportional to an applied field. In such a case the flux and the force are said to be conjugate to each other. The relation between a thermodynamic force and its conjugate thermodynamic flux is called a linear constitutive relation,

$$(48) \quad \mathbf{J} = \hat{L}(\mathbf{X}_{\text{ext}} = 0) \mathbf{X}_{\text{ext}},$$

where $\hat{L}(0)$ is called a linear transport coefficient.

Transport equations express the *generalized forces* required to maintain a small steady flux of particles, charge, and heat, respectively. They may also be used to describe the approach to equilibrium of a system initially in non-equilibrium due to the presence of gradients in concentration n , electrostatic potential ϕ , or temperature T . The constants of proportionality are termed linear transport coefficients: diffusion D , electrical conductivity σ , thermal conductivity κ .

It was mentioned above that a typical example [198] of heat current may be described as follows. Let us consider a solid cylinder through which a stationary heat current \mathbf{J}_Q flows. The current may be produced by coupling the cylinder at its right and left ends to thermal reservoirs at temperatures T_R and T_L , respectively. It is known that the linear relation between the quantity $\text{grad}(1/T)$ and the current \mathbf{J}_Q and the linear response coefficient $\mathbf{L}_Q = \mathbf{L}_Q(T)$ may be used. Then heat current may be written as

$$(49) \quad \mathbf{J}_Q = \mathbf{L}_Q \text{grad} \frac{1}{T} = \kappa \text{grad} T.$$

The mean entropy production \tilde{S} in the material will take the form

$$(50) \quad \tilde{S} = \mathbf{J}_Q \text{grad} \frac{1}{T} = \kappa T^2 \left[\text{grad} \frac{1}{T} \right]^2.$$

In the case of weak deviation from equilibrium we can suppose that the entropy of the material remains nearly constant (its macrostate is unchanged). Hence all the produced entropy will be carried away by means of the *entropy current* \mathbf{J}_S and transmitted into the reservoirs. The relation between entropy current and entropy production was formulated in the thermodynamics of irreversible processes with the aid of the entropy balance equations [50, 201, 202]. Indeed, after integration of the entropy production over the material volume, it may be shown [198] that the entropy of the reservoirs is changed by

$$(51) \quad \frac{dS}{dt} = \mathbf{J}_S \left(\frac{1}{T_R} - \frac{1}{T_L} \right) a.$$

Here a is the cross-sectional area of the cylinder.

In this context it is worth mentioning that the second law of thermodynamics governs the direction of heat transport, which provides the foundational definition of thermodynamic Clausius entropy [203]. Shu-Nan Li and Bing-Yang Cao showed [203] that the definitions of entropy can be further generalized for the phenomenological heat transport models in the frameworks of classical irreversible thermodynamics and extended irreversible thermodynamics. In their work [203], entropic functions from mathematics were combined with phenomenological heat conduction models and connected to several information-geometrical conceptions. It was shown that the long-time behaviors of these mathematical entropies exhibit a wide diversity and physical pictures in the phenomenological approach to heat conduction, including the tendency to thermal equilibrium, and exponential decay of non-equilibrium and asymptotics, which may provide a bridge between the macroscopic and microscopic modelings. In contrast with the extended irreversible thermodynamics entropies, the mathematical entropies expressed in terms of the internal energy function can avoid singularity paired with non-positive local absolute temperature caused by non-Fourier heat conduction models.

Now let us consider briefly the notion of entropy current [189, 201, 202]. In thermodynamics derivation of the linear and quasi-linear transport equations is based on the entropy production, *i.e.* on the control of entropy balance in terms of classical continuum physics

$$S_{\text{tot}} \sim S_{\text{in}} - S_{\text{out}} + S_{\text{prod}}.$$

The first two terms in this equation on the right-hand side represent the entropy transfer between the system and its surroundings. The third term represents the entropy production in the system. Entropy can be transferred to or from a system in various ways but mainly by two mechanisms, namely the heat transfer and mass flow. It must be emphasized that no entropy may be transferred by work. Heat transfer to a system *increases* the entropy of the system, and heat transfer out of a system *decreases* the entropy of the system. Hence for establishing the entropy balance the knowledge both the entropy density (s) and entropy current density (\mathbf{J}_s) is necessary.

An important question in non-equilibrium thermodynamics is the appropriate definition of entropy current and what the entropy current density is related to. In general case this is a rather non-trivial task [189, 201, 202, 204-206] as well as the definition of entropy production for non-equilibrium steady states [50, 58]. The simplest way is to consider first the local-equilibrium (quasi-equilibrium) state. In this case the entropy current density is equal to the heat current density divided by the temperature

$$(52) \quad \mathbf{J}_s = \frac{1}{T} \mathbf{J}_q.$$

However, when diffusion is involved this definition should be modified as

$$(53) \quad \mathbf{J}_s = \frac{1}{T} \mathbf{J}_q - \sum_i \frac{\mu_i}{T} \mathbf{J}_i.$$

Here the summation is extended over all chemical components. This expression can be reformulated in a general form [201]. To this aim the specific entropy (entropy per unit mass) should be considered as a function, which depends on the specific values of the independent extensive quantities only.

Nyiri [202] showed that if the entropy current may depend only on the currents and the equilibrium state variables, then only the formula corresponding to Gibbs relation is acceptable. All other formulae of this type may lead to (physical) contradiction. If, however, nothing is assumed about the coefficients of the extensive quantity currents in the formula of the entropy current, then it is possible to get an extra set of constitutive equations for these coefficient tensors. These second-order tensors play the role of intensive quantities: their divergences are the *thermodynamical forces* conjugated to the *currents*, while their deviation from the equilibrium intensive quantities is induced by the current gradients. Thus, a *non-equilibrium entropy current*, converging to the classical equilibrium one as approaching equilibrium, was obtained. The Nyiri theory [202] applied to conductive energy transport contains a second-order tensor playing a role similar to reciprocal temperature. The heat transport equation obtained after eliminating this tensor from the equations contains an extra term. This modified “*heat conduction*” equation is identical to the classical one in stationary state, while its dynamic behavior predicts a characteristic length and time, both vanishing with the coefficient of the extra term. The theory permits coupling between viscous flow and conductive energy transport even in linear order. Hence the notion of the entropy current is rather a non-trivial concept [189, 201, 202, 204-206].

In hydrodynamics the existence of an entropy current with non-negative divergence is related to the existence of a time-independent solution in a static background. Recently there has been a proposal for how to construct an entropy current from the equilibrium partition function of the fluid system [207]. Bhattacharyya has applied that algorithm

for the charged fluid at second order in derivative expansion. From the partition function he first constructed one example of entropy current with non-negative divergence up to the required order. Finally he extended it to its most general form, consistent with the principle of *local entropy production*. In addition, author obtained the constraints on the second-order transport coefficients for a parity even charged fluid, but in some non-standard fluid frame.

6. – Temporal ordering and Clausius-Duhem inequality

Usually a foundation for the second law of thermodynamics is formulated in terms of the entropy principle. According to Gibbs, entropy characterizes the concept of equilibrium and its stability by means of variational principles. It is known that the notion of the entropy for non-equilibrium states and its evolution for macroscopic systems may lead to controversial conclusions. The reason for it is the fact that the notions of non-equilibrium state, non-equilibrium entropy and relevant observables cannot be defined in complete generality [8, 14, 15, 37, 42, 44-47, 54, 55, 58]. This circumstance does not allow us to develop a fully consistent formalism. As was discussed above, the laws of thermodynamics distinguish between the past and the future, *i.e.*, include an *arrow of time* [73, 74, 80, 83, 84, 87, 93, 97]. This directionality of time expresses itself primarily in the second law, which states that, roughly speaking, entropy tends to increase toward the future. Till now we do not know precisely what is the reason of this time-asymmetric law and what is the most adequate form for its expression. Some aspects of these questions were clarified within the axiomatic approach started by Caratheodory [75-78, 118, 119]. This approach was pursued further by Yngvason and Lieb [73] and others, but the rigorous foundations of the thermodynamic directionality of time still are under debates [73, 74, 80, 83, 84, 87, 93, 97].

It is worth mentioning that in the Caratheodory axiomatic approach to the foundation of thermodynamics [73, 75-78, 118, 119], the notion of the binary relation (*preorder*) between states associated with adiabatic accessibility has been used. Hence Caratheodory axioms included a possibility to take into account *irreversible processes* in which entropy may decrease or increase. From the other side there is the unresolved problem of incompatibility between thermodynamic irreversibility and time-reversal invariant dynamics. It is known that for Hamiltonian systems the dynamics is time-reversal invariant. The Liouville theorem states the conservation of probability under the Hamiltonian flow. Conservative forces assumed usually are non-dissipative.

On the other hand, dissipative forces, such as those which are velocity dependent, put an explicit time direction on the Hamiltonian. The important notion of *time arrow* is connected intimately with the general principles of thermodynamics and especially with the second law. In last decades the problem of an arrow of time has been placed in a new context [80-82, 87]. Entropy increasing dictated by the Clausius theorem and more generally by the Clausius-Duhem inequality [35, 36, 208-214] and requirement causality were interrelated by the prescription of thermodynamically admissible constitutive equations.

To simplify the problem, sometimes it is convenient to replace the thermodynamic limit of statistical mechanics [4] by working directly with systems defined on classical configuration spaces of infinite volume. In this case, one may expect that, since these systems tend to show continuous spectra, the relevant functions become relatively well-behaved functions. In a certain sense the thermodynamic limit is equivalent to a properly defined continuum limit [215]. The essence of the continuum limit is that all microscopic fluctuations are suppressed.

In this context it is of importance to consider briefly the Clausius-Duhem inequality [210,212-214], which appears in continuum mechanics when combining the momentum balance law and the two laws of thermodynamics. The thermodynamics of irreversible processes as a phenomenological theory describing processes in continua was initiated by Eckart [209] in 1940. His seminal works were reviewed thoroughly by Müller [210].

The Clausius-Duhem inequality [208-214] gathers quantities which should be chosen to build a predictive theory of some thermo-mechanical phenomena. It gives the quantities which are of significance. Moreover it points out the ones which are to be related: *e.g.*, the dissipative stress and the strain rate, or the heat flux and the gradient of temperature. All the classical dissipative constitutive laws and the classical thermal Fourier law may be formulated in this framework [216]. In terms of mathematics the various products are duality products between linear spaces, namely products between quantities describing the evolution, the thermal heterogeneity and quantities describing the interior forces and the heat flux. Hence the Clausius-Duhem inequality is essentially a global statement of the second law of *continuum thermodynamics* in the form

$$(54) \quad \dot{S}(\bar{V}_t) \geq \int_{\delta V_t} \theta^{-1} q \, da + \int_{V_t} \theta^{-1} h \, dm.$$

Here S is the total entropy pertaining to the actual volume V_t occupied by a material body at time t in physical Euclidean space \mathbf{R}^3 , δV_t being its boundary and \bar{V}_t its closure. The scalar $\theta > 0$ is the thermodynamic temperature, q is the heat flux per unit area, h is the mass density, dm is the mass element. Note that Clausius original form of inequality had zero for the right-hand side. The surface contribution was added by Duhem [208]. Later it was generalized by Truesdell [211] and others. The local form of the Clausius-Duhem inequality has the form [208-214]

$$(55) \quad \rho \dot{\eta} + \nabla \mathbf{S} - \theta^{-1} \rho h \geq 0.$$

Here $\eta(x, t)$ is the specific entropy such that $S(V_t) = \int_{V_t} \eta \, dm$, $dm = \rho(x, t) d\nu$ and ρ is the matter density of the actual placement x at absolute time t .

Various authors showed [34-36] that calculations and bounds on work production, Carnot efficiency, heat exchange, and the Clausius inequality are at the core of thermodynamics. Gaveau *et al.* [187] studied generalized Clausius relation and power dissipation in non-equilibrium stochastic systems. They extended the Clausius inequality to non-isothermal systems in the transient regime. In addition, they considered power production necessarily in a context involving time dependence and observed that maximal efficiency and optimal power production are in conflict, since to achieve the best Carnot efficiency the system must move infinitely slowly. Authors calculated spontaneous power production in a stationary non-equilibrium state and provided an upper bound for it. The time-dependent context necessarily goes beyond traditional thermodynamics. In the framework of the stochastic dynamics of open Markov systems, they derived an extension of the *Clausius inequality* for transitions between states of the system. The relation obtained [187] was an extension of the classical Clausius inequality, valid in the transient situation, which was thus derived in the framework of stochastic dynamics. Authors derived a formula for the power produced when the system is in its stationary state and related it to the dissipation of energy needed to maintain the system out of equilibrium. They deduced also that, near equilibrium, maximal power production requires an energy dissipation of the same order of magnitude as the power production.

Bertini *et al.* [217] carried out a quantitative analysis of the Clausius inequality. They derived an expansion of the energy balance in the context of driven diffusive systems, for thermodynamic transformations over a large but finite time window. In particular, authors characterized the transformations which minimize the energy dissipation and described the optimal correction to the quasi-static limit. In the case of transformations between homogeneous equilibrium states of an ideal gas, the optimal transformation is a sequence of inhomogeneous equilibrium states.

In regard to the temporal evolution, according to Maugin [212], “The *arrow of time* dictated by the Clausius-Duhem inequality and causality, represented mathematically by the hyperbolicity of the studied system of field equations, once closed by the prescription of thermodynamically admissible constitutive equations, are thus interrelated”.

7. – Steady state, local state and local equilibrium

In giving the physical specification of a system at any instant the concept of *local state* [218-220] has been used. The postulate that a local state exists is often taken as being equivalent to assuming some form of *local equilibrium*. For a justification of this postulate the notion of the relaxation time for fluctuations was used. The statement is that at the atomic scale the relaxation time is shorter compared with the timescale of the macroscopic processes under consideration. It is not a simple task to specify fully the local state in terms of measurable macroscopic variables. It was often assumed that there exist additional internal or *relevant* variables which complete the description of the local state. Assumption of a local state permits one to use safely the notions of equilibrium thermodynamics, such as the concepts of entropy and energy as scalar potentials as well as the Gibbs-Duhem and the Gibbs relations [184-186, 218-220]. Since the second law supposes the production of entropy for irreversible processes, it can be formulated by using appropriate constraints on the laws governing these processes, especially in relation to their stability. It should be stressed that the applications have been confined usually to processes in systems not very far from equilibrium, *i.e.* in terms of the linear thermodynamics of irreversible processes [37-39, 42, 53, 184-186, 218-220].

To clarify these statements we recall very tersely the description of continuous systems [218-220]. When a continuous system undergoes a process, the process is described as a reversible one if the process undergone by every subsystem, however small, is reversible, otherwise it is irreversible. The state of continuous system is described by a number of continuous functions of position (x, y, z) (at any given instant) or by a number of fields [184-186, 218-220], for example $\theta = \theta(x, y, z)$ and $P = P(x, y, z)$ and so on, at instant t . When time is in the fields as a variable $\theta = \theta(x, y, z, t)$ and $P = P(x, y, z, t)$, a process undergone by the continuous system is described. It is worth noting that the expressions *spontaneous change* and *spontaneous process* should not be used interchangeably. *Process* means the method of carrying out a given *change*. Hence a given spontaneous change, in principle, can be carried out by a reversible process or by an irreversible process.

When a system is in equilibrium at every step during the process, the rate of change of energy, $\dot{\epsilon}$, is a constant of the system and the same applies to the density ρ . Hence

$$(56) \quad \int_V \rho \dot{\epsilon} dV = \rho \dot{\epsilon} V = m \dot{\epsilon},$$

since $\rho V = m$. Thus we have

$$(57) \quad \dot{Q} - \dot{W} = m \frac{d}{dt} \epsilon; \quad dE = \left\{ \frac{d}{dt} \int_V \rho \epsilon dV \right\} dt,$$

which is identical with

$$(58) \quad dQ - dW = dE$$

for every homogeneous part. Here W is the work and Q is the heat; dW may be replaced by the appropriate expression for reversible work in terms of the properties of the system.

Steady state is an extension of the concept of equilibrium [184-186, 218]. Denbigh noted in his book [184] that "... there has been an important development, which has become known as the 'thermodynamics of irreversible processes'. A more appropriate name would be the 'thermodynamics of the steady state'!"

Eckmann, Pillet and Rey-Bellet analyzed the entropy production in nonlinear, thermally driven Hamiltonian systems [221]. They considered a finite chain of nonlinear oscillators coupled at its ends to two infinite heat baths which are at different temperatures. Using their earlier results about the existence of a stationary state, authors showed rigorously that for arbitrary temperature differences and arbitrary couplings, such a system has a *unique stationary state*. In all these cases, any initial state will converge (at an unknown rate) to the stationary state. It was shown that this stationary state *continually* produces entropy. The rate of entropy production is strictly negative when the temperatures are unequal and is proportional to the mean energy flux through the system.

The processes that are studied in continuous systems usually are such processes during which the local state at every point throughout the system is independent of time. A system of this kind, regardless of whether it is open or closed, is said to be in *steady state*. In steady-state systems, the local rate of change of specific energy is zero, so that

$$(59) \quad \frac{d}{dt} \int_V \rho \epsilon dV = \int_V \rho \dot{\epsilon} dV = 0.$$

Hence, in steady state $\dot{Q} - \dot{W} = 0$. In order to maintain a steady state it is, therefore, necessary to balance the rate of heat flow with the aid of the performance of work. More specifically, if work is done on the system ($\dot{W} < 0$), its equivalent must be extracted in the form of heat by cooling ($\dot{Q} < 0$). Hence, a system in steady state transforms heat into work or vice versa in the same way as a cycle. Note that in steady state the volume of a closed system should be constant. Thus, a closed system in steady state cannot perform work by deforming its boundary. Then a question arises how to describe system as being in a steady state when all its properties are invariant with respect to time. In such cases, a system will be classified as being in steady state when all local properties are time independent, that is, when all the fields depend on the coordinates (x, y, z) only *but not on time*, in complete analogy with a closed continual system.

There are numerous works on the thermodynamics of the steady state. A kinetic-molecular theory which connects dissipation and fluctuations was used to examine the second law of thermodynamics by Keizer [222]. Considerations were restricted to systems with stable equilibrium states and were based on a conservation condition satisfied by transport processes which obey microscopic reversibility. The conservation condition

leads to a statement about the accessibility of equilibrium states which is comparable to the Caratheodory statement of the second law. Insofar as the transport of heat into a system is the only process which violates microscopic reversibility, this statement is equivalent to the second law. The treatment also gives a simple kinetic proof of the Clausius inequalities $T_R dS/dt > dQ/dt$ and $dS/dt > 0$ for the entropy. Using the statistical aspects of the fluctuation-dissipation postulates, a class of state functions related to the equilibrium statistical distribution was defined, and it was verified that the entropy is one of these functions. A discussion was given of how to extend these results to systems with multiple phases or at non-equilibrium steady states.

In ref. [223] Keizer considered the fluctuation-dissipation postulates, which describe the kinetic effects of molecular processes, and used to characterize non-equilibrium steady states. Attention was restricted to stable, non-critical states which developed in systems with inputs that are time independent. For these systems it was shown that the steady-state distribution is Gaussian, which provides a generalization of the well-known Einstein formula for equilibrium states. For certain systems it was shown that the time dependence of the covariance matrix of the extensive variables gives a necessary and sufficient condition for the stability of a non-critical state. These considerations were illustrated for the steady states accompanying diffusion, heat transport, chemical reactions with linear coupling, and certain nonlinear chemical reactions. These examples showed that the covariance matrix is not necessarily related to the *local-equilibrium entropy*. When the covariance matrix is invertible, it can be used to construct generalized state functions which reduce to familiar thermodynamic functions at equilibrium. The generalization of the entropy, called the σ function, was related to stability, the probability density, and generalized “thermodynamic forces” in precisely the same way as the entropy is at equilibrium.

In a following paper [224], a discussion of how to extend equilibrium thermodynamics to non-equilibrium steady states was continued. The extension was based on molecular fluctuations of the extensive variables and gives rise to a state function, called the σ function. The σ function reduces to the entropy at equilibrium and can be constructed from a knowledge of the local-equilibrium entropy and the molecular fluctuations. The σ function depends on all the variables characterizing a steady state, including fluxes of the extensive variables and reservoir parameters. The theoretical analysis of non-equilibrium fluctuations predicts that the σ function is related to stability and the kinetics around a steady state just like the entropy is at equilibrium. Calculations of the σ function were outlined for several multicomponent systems of experimental interest. Using the fluctuation-dissipation theory, a *generalization of the Clausius inequality* was obtained. This leads to a class of extremum principles at steady state for Legendre transformations of the σ function.

Benofy and Quay [225] have developed a rigorous thermodynamic theory of steady-state systems by generalizing the methods which were used by Clausius and Kelvin in the development of classical thermodynamics (thermostatistics) [35, 36]. The zeroth law was extended to non-equilibrium situations and the concept of temperature generalized accordingly. The law of homogeneous circuits, shown to be complementary to *Kelvin’s principle*, can be combined with it to give a generalized second principle. The thermodynamic principles were applied to those conversions of heat to work that result from transitions between two or more steady states or from the activity of systems that remain in a single steady state. It was proved that these latter systems must be multiply connected if conversion is to be continuous. Authors proved the existence of both scalar and vector functions of state for all steady-state systems. Steady-state conversion coefficients

can be defined as derivatives of the vector functions of state, and useful relations among these coefficients were derived. These include not only generalized forms of Kelvin's relations for the thermocouple [35, 36] but similar relations for an analogous fluid system and, indeed, for any system in which potentials can be defined governing the flow of conserved quantities.

In ref. [226] Keizer investigated the properties of matter at non-equilibrium steady states using a thermodynamic formalism derived from molecular fluctuations. Based on the generalized Clausius inequality, Keizer extended the definition of "reversible" process to include transformations between steady states and related reversible work and heat to changes in state functions. The variable which is thermodynamically conjugate to the internal energy, that is, the inverse of the generalized thermodynamic temperature, is an integrating factor for the reversible heat. Keizer discussed the relationship of the generalized temperature to the Kelvin temperature, how the generalized intensive variables can be measured, defined generalized heat capacities, and obtained the *Gibbs-Duhem relationship* satisfied by the intensive variables. These ideas were illustrated for two simple steady-state systems, a fluid under homogeneous shear and a two-level gas which is pumped by radiation. Finally the author analyzed under appropriate conditions the electromotive force of a chemical reaction system held at a non-equilibrium state. Corrections were predicted to the Nernst equation which depend on how far the chemical reactions were removed from equilibrium.

Oono and Paniconi [227] constructed a phenomenological framework corresponding to equilibrium thermodynamics for steady states. All the key concepts, including entropy, were operationally defined. They showed that if a system is strictly linear, the resultant Gibbs relation justifies the postulated form in the extended irreversible thermodynamics. The resultant Maxwell's relations and stability criteria gave various *le-Chatelier-Braun*-type qualitative predictions. A phenomenological fluctuation theory around steady states was also formulated.

Let us consider briefly the complementary concept of local (or *quasi-equilibrium*) state [8, 13, 52]. A physical system is in an equilibrium state if all currents, of heat, momentum, etc., vanish, and the system is uniquely described by a set of state variables, which do not change with time. From the other side, it is possible to speak about irreversible processes by considering the energy increase ΔE and the entropy increase ΔS ; a process will be irreversible if

$$(60) \quad \Delta S > \int \frac{\delta Q}{T},$$

where Q is the heat absorbed by the system during the particular process of interest and T is the temperature at which the heat crosses the boundary of the system. The workable method for systems which are in steady states is the division of the system into small regions [219, 220, 228, 229]. In this approach the value of an intensive variable changes in total sample but the value remains constant in time in each small region. Then extensive quantities are found for the whole system by summing over all regions. For the treatment of non-steady states in systems with gradients, the system is divided up into small (infinitesimal) regions each of which can be described by a small number of variables. In addition, as the local values of the variables change in the region during the course of the process, it is assumed that they define at each moment a local quasi-equilibrium state. A combined approach which has been most used to treat steady states can be formulated in the following way [184-186]. Consider a system in a steady state,

i.e., the variables of state have time-independent values at every point. It is reasonable to expect that if at the steady state one or more of the total number of processes have come to an end, virtual displacements in these processes cause no change in entropy of the system and its environment. This statement is a workable conjecture which deserved, in principle, an additional firm theoretical and experimental basis [8, 13, 52].

Hence, in equilibrium the temperature T and chemical potential μ must be uniform throughout the system. If the variation of the driving forces is slow in space and time, then one may imagine that the system acquires a *local equilibrium* [8, 13, 52], which may be characterized by a *local* T and μ which are slowly varying functions of space and time

$$T = T(\mathbf{r}, t), \quad \mu = \mu(\mathbf{r}, t).$$

In contrast to a closed system, an open system exists in a state away from equilibrium even when it reaches its steady state. Zhang *et al.* [230] re-considered the concepts of equilibrium and non-equilibrium steady states as mathematical concepts associated with stationary Markov processes. For both discrete stochastic systems with master equations and continuous diffusion processes with Fokker-Planck equations, the non-equilibrium steady states were characterized in terms of several key notions which are originated from non-equilibrium physics: *time irreversibility, breakdown of detailed balance, free energy dissipation, and positive entropy production rate*. After presenting this non-equilibrium steady-state theory in suitable mathematical terms, the latter was applied to two widely studied problems: the stochastic resonance (also known as coherent resonance) and molecular motors (also known as Brownian ratchet). Although both areas have advanced rapidly on their own with a vast amount of literature, the theory of non-equilibrium steady states provides them with a unifying mathematical foundation.

To summarize, in the classical case a distribution function can be obtained which reflects knowledge of the initial spatial dependence of temperature, local velocity, and chemical potential. In all other respects it reflects local equilibrium or *quasi-equilibrium*. This distribution cannot be justified in the full measure for most non-equilibrium situations. Its use is only partial when the system is not in equilibrium, locally or otherwise [8, 13, 52, 218-220]. Characterization of close-to-equilibrium stationary states, both for macroscopic systems and for stochastic models may be provided by the minimum entropy production principle, which is a kind of an approximative variational method useful for the case.

8. – Extremal principles and entropy production

In the present section we will discuss very tersely some foundational statements concerning the entropy production concept and about its relevance for non-equilibrium statistical thermodynamics.

The principles of extremum of the entropy and entropy production (including information entropy) play a fundamental role in equilibrium and non-equilibrium statistical physics [8, 13, 231]. The information theoretic entropy is a probabilistic concept [12], contrary to the thermodynamic entropy [13, 52, 232]. Information entropy in problems of classical and quantum statistical mechanics was considered and analyzed in numerous articles and books [5, 9-13, 17, 18, 52, 144-147].

The maximum entropy approach to statistical thermodynamics was initiated by Jaynes [5, 9-11, 17, 18]. In this approach statistical mechanics [8, 13] was considered as general problem requiring prediction from incomplete or insufficient data. In this sense

equilibrium thermodynamics is a specific application of *inference* techniques rooted in information theory [12, 13, 21-23]. Such an approach is general to all problems requiring prediction from incomplete or insufficient data. According to Jaynes, statistical mechanics can be interpreted as a special type of statistical inference based on the principle of maximum entropy. The result of such an inference depends on the available information about a given physical system, but the principle itself does not decide what kind of information is essential and what is not. The Gibbs canonical state results from the principle when the statistical mean value of energy was supposed to be known [8, 13]. For other distributions an entropic measure, which was optimized by a given arbitrary distribution with the finite linear expectation value of a physical random quantity of interest, should be constructed. This offers a unified basis for a great variety of distributions observed in nature. The maximum entropy formalism has been applied to numerous practical problems and its operation ability was demonstrated. Hence the maximum entropy principle is a technique for evaluating probability distributions consistent with constraints. Or, in other words, the principle of maximum entropy is a method for analyzing the available information in order to determine a unique epistemic probability distribution. All these results lends support to Jaynes formalism as a common predictive framework for equilibrium and non-equilibrium statistical mechanics [5, 9-11, 17, 18, 39].

Information theory [12, 13], in conjunction with the techniques developed by Jaynes was used in various problems of statistical mechanics. The Gibbs distributions have a non-trivial common property: subject to certain constraints they maximize a functional known in statistical mechanics as entropy, and in information theory, probability theory and mathematical statistics as information. The approach based on the information theory in the spirit of the principle of maximum entropy has been used in numerous works on statistical mechanics [8, 12, 13, 33, 39] to derive the fundamental statistical mechanical distributions.

Maximum entropy formalism [5, 9-13, 17, 18, 146, 147] is a specific method which provides a way of finding probability distributions with the largest uncertainty on the basis of the available information. An inference from this way of reasoning is founded on our state of knowledge about the system only. The extremum entropy production principle has been stated in various ways and was confirmed as a workable tool. A common wisdom states that a system tends to be in an extremum entropy generation state allowed by corresponding constraints (steady-state or approaching one). In refs. [12, 13, 52, 233] the basic issues of maximum entropy formalism along with their consequences and various applications were considered in detail.

Entropy production and its role in thermodynamics of non-equilibrium processes in the physical, chemical and biological sciences was studied intensely during last decades [50, 64-67, 79, 124, 221, 234, 235], because of its crucial role for the second law of thermodynamics. However, there are some points at issue and also other features of the entropy production concept which are not fully clear [235].

Extremal principles [62, 70, 236] for entropy production, namely *maximum entropy production principle* due to Ziegler [64, 216] and *minimum entropy production principle* due to Prigogine [237], deserve a careful consideration. Ziegler principle [64, 216] states that the rate of entropy production under the influence of given forces should be maximum.

The minimum entropy production principle is an approximate variational characterization of steady states for thermodynamically open systems which are in an out-of-equilibrium state. Initially this statement was formulated by Prigogine [237] within the framework of linear irreversible thermodynamics [185, 186]. Later it was extended

to stochastic kinetics, *e.g.*, for systems not too far from equilibrium [238] described by a *master equation*. Usually the temporal evolution of non-equilibrium open quantum systems was investigated within the density-matrix techniques. The corresponding equations of evolution for density matrix lead to various forms of generalized master equations [13, 52, 239-249]. These master equations show that for weak coupling and in the thermodynamic limit [4] a perturbed system will approach equilibrium.

Klein and Meijer [238] used the principle of minimum entropy production which says that the steady state of an irreversible process, *i.e.*, the state in which the thermodynamic variables are independent of the time, is characterized by a minimum value of the rate of entropy production. This theorem, due to Prigogine [237], was proved by the methods of statistical mechanics for a particular process — the flow of matter and energy through a narrow tube connecting two containers of an ideal gas. The two containers were maintained at slightly different temperatures. Authors concluded that the resultant form for the entropy production in the steady state, and the method used in the proof, gave additional insight into the significance of the principle of minimum entropy production.

However, Callen [250] found that the calculations on particular models by Klein and Meijer have weak points. An analysis of magnetic resonance by Wangsness suggested certain modifications necessary in the case of a non-zero, non-stationary, magnetic field. In fact, Prigogine showed that in the steady state in which certain macroscopic affinities F_1, F_2, \dots, F_k were fixed and other macroscopic affinities $F_{k+1}, F_{k+2}, \dots, F_r$ were unconstrained, the values assumed by the unconstrained affinities were such as to minimize the rate of production of entropy. Callen [250] has shown that the complete microscopic density matrix of the system is that which minimizes the rate of entropy production subject to the imposed constraints. All magnetic fields were assumed to be zero. It was shown that the kinetic coefficients connecting Casimir's α -type and β -type variables always vanish. The validity of the minimum entropy production theorem in the absence of a magnetic field depends on this fact. The limitations on the validity of the minimum entropy production theorem in the presence of a magnetic field were established.

In other words, Prigogine showed that a system close to equilibrium and in a sufficiently stable environment evolves toward a steady state that minimizes the dissipation of energy. For open systems close to equilibrium the Prigogine principle permits a broader treatment of the law of irreversible increase of entropy in isolated systems. Roughly speaking, open systems should uphold their stationary (or quasi-equilibrium) state permanently. Minimum entropy production promotes the minimum dissipation of energy. Later on Glansdorff and Prigogine [251] formulated the stability criterion for the case of dynamical systems which may be, in principle, far from equilibrium, *e.g.*, the self-organization processes in a low-temperature, non-isotherm plasma, etc. Hence, an initial steady state may be triggered suddenly to other states through bifurcations. In this case, the thermodynamic behavior could be *quite different, in fact, even opposite* to that indicated by the theorem of minimum entropy production [251].

Glansdorff-Prigogine stability criterion raised controversial discussions in the literature [252-257]. In particular, the problem of applicable range and practical value of the Glansdorff-Prigogine criterion and of the theorem of minimum entropy production was discussed critically. It was pointed out that the Glansdorff-Prigogine criterion as a thermodynamic theory is consistent, but in the practical problem of many variables, it has applicable value to a less degree. Moreover, it was claimed that the applicable range of the theorem of minimum entropy production is smaller than that of other theorems in the linear non-equilibrium thermodynamics, therefore, to use it as a principle is less reliable.

Keizer and Fox [252] raised doubts concerning the range of validity of a stability criterion for non-equilibrium states which has been proposed by Glansdorff and Prigogine. They claimed that in the case of a particular autocatalytic reaction, the stability analysis presented by Glansdorff and Prigogine, and by Eigen and by Katchalsky in their reviews of this problem, does not agree with their analysis, which was based upon exact solution of the relevant rate equations. Keizer and Fox [252] also found disagreement between the analysis based upon the Glansdorff-Prigogine criterion and their analysis of a second example which involves non-equilibrium steady states. In their opinion, the situation is quite delicate because seemingly innocent approximations may lead to the impression that the scope of validity of the criterion is wider than it actually is. By considering the stability of the equilibrium state, Keizer and Fox concluded that the second differential of the entropy, which is at the heart of the Glansdorff-Prigogine criterion, is likely to be relevant for stability questions close to equilibrium only.

Prigogine and co-authors [253] in their reply have shown that the objections of Keizer and Fox [252] were based on a misunderstanding of the work of the Brussels group [258]. They summarized the formulation of the stability criterion in accordance with their published works. The differences with the presentation by Keizer and Fox were pointed out and it was shown that, when correctly applied, their approach does not lead to any contradiction with other methods available for studying stability.

The starting point of Keizer and Fox seems to be the belief that Glansdorff and Prigogine have claimed or implied that the threshold for instability coincides with the manifold of the parameter space where a certain quadratic form, namely the excess entropy production, ceases to be positive definite. In order to support their point Keizer and Fox analyzed two specific examples. They found contradictions between the exact treatment based on the solution of the rate equations, and the predictions they believe that the Glansdorff-Prigogine criterion would provide. In fact, the presentation of the stability criterion and its applications attributed to Glansdorff-Prigogine by Keizer and Fox arises from a misunderstanding of the whole subject. It was concluded [253] that, being a Lyapounov-type theory, the thermodynamic stability criterion provides sufficient stability conditions, along the appropriate manifold of solutions of the kinetic equations.

Nicolis and co-authors [254] made the next step. They developed a stochastic formulation of the stability of non-equilibrium states. Entropy balance equations, including the effect of both the macroscopic evolution and of the fluctuations, were discussed. In the linear region of thermodynamics Prigogine minimum entropy production theorem was extended to include the effect of fluctuations. The latter were shown to reinforce the return of the system to its steady-state distribution.

Di Vita [255] derived ten necessary criteria for stability of various dissipative fluids and plasmas from the first and the second principle of thermodynamics applied to a generic small mass element of the system, under the assumption that *local thermodynamic equilibrium* holds everywhere at all times. He investigated the stability of steady states of a mixture of different chemical species at the same temperature against volume-preserving perturbations. The author neglected both electric and magnetic polarization, and assumed negligible net mass sources and particle diffusion. He assumed also that both conduction- and radiation-induced heat losses increase with increasing temperature. Di Vita invoked no Onsager symmetry, no detailed model of heat transport and production, no "Extended Thermodynamics," no "Maxent" method, and no "new" universal criterion of stability for steady states of systems with dissipation. Each criterion takes the form *of —or is a consequence of a variational principle*. He retrieved maximization of entropy for isolated systems at thermodynamic equilibrium, as expected. If the boundary conditions keep

the relaxed state far from thermodynamic equilibrium, the stability criterion retrieved depends also on the detailed balance of momentum of a small-mass element. This balance may include the ∇_p -related force, the Lorenz force of electromagnetism and the forces which are gradients of potentials. In order to be stable, the solution of the steady-state equations of motion for a given problem should satisfy the relevant stability criterion. Retrieved criteria included (among others) Taylor's minimization of magnetic energy with the constraint of given magnetic helicity in relaxed, turbulent plasmas, Rayleigh's criterion of stability in thermoacoustics, Paltridge's maximum entropy production principle for Earth's atmosphere, Chandrasekhar's minimization of the adverse temperature gradient in Benard's convective cells, and Malkus' maximization of viscous power with the constraint of given mean velocity for turbulent shear flow in channels. It turns out that characterization of systems far from equilibrium, *e.g.*, by maximum entropy production, is not a general property but, just like minimum entropy production, is reserved to special systems. A *taxonomy* of stability criteria was derived, which clarifies what is to be minimized, what is to be maximized and with which constraint for each problem.

The paper of Di Vita [255] was commented by Sonnino, Tlidi and Evslin [256]. In their opinion, the author [255] attempted to derive ten necessary conditions for the stability of dissipative fluids and plasmas. Assuming the validity of the local-equilibrium principle, these criteria have been obtained solely from the first and second laws of thermodynamics. The Onsager reciprocity relations have not been invoked, and the author's results were supposed to be valid independent of the choice of the boundary conditions. In their comment Sonnino *et al.* [256] expressed agreement with the general theory established by Glansdorff and Prigogine in 1954 and 1970. They also showed that there is no variational principle expressing the necessary conditions for the stability of dissipative systems involving convective effects when the system is out of the Onsager region. In particular, Sonnino *et al.* [256] proved that the basic equations constituting the starting point of the analysis of Di Vita [255], attempting to derive ten necessary conditions for the stability involving magnetohydrodynamical effects, were incorrect and in contradiction with the laws of the thermodynamics of irreversible processes.

Maes and Netocny [257] re-considered the Glansdorff-Prigogine criterion for stability within irreversible thermodynamics on a new ground. Glansdorff and Prigogine proposed a decomposition of the entropy production rate, which now is known for Markov processes as the Hatano-Sasa approach. Their context was irreversible thermodynamics which, while ignoring fluctuations, still allows a somewhat broader treatment than the one based on the master or Fokker-Planck equation. Glansdorff and Prigogine were the first to introduce a notion of excess entropy production rate δ^2EP and they suggested as sufficient stability criterion for a non-equilibrium macroscopic condition that δ^2EP be positive. Authors found for nonlinear diffusions that their excess entropy production rate is itself the time-derivative of a local free energy which is the close-to-equilibrium functional governing macroscopic fluctuations. The positivity of the excess δ^2EP , for which a simple sufficient condition was proposed, is therefore equivalent with the monotonicity in time of that functional in the relaxation to steady non-equilibrium. There also appears a relation with recent extensions of the Clausius heat theorem close to equilibrium. The positivity of δ^2EP immediately implies a Clausius (in)equality for the excess heat. A final and related question concerns the operational meaning of fluctuation functionals, non-equilibrium free energies, and how they make their access in irreversible thermodynamics.

The inter-relation of Ziegler maximum entropy production principle and Prigogine minimum entropy production principle was analyzed by various authors [39, 42-44, 48, 50, 51, 54, 57, 59, 69, 71]. The consistency of both the principles is not evident. However,

it was clarified that both linear and nonlinear thermodynamics may be deduced using Ziegler principle. Moreover, this principle yields, as a particular case, Onsager variational principle [42, 64, 216], which is valid for linear non-equilibrium thermodynamics only. Whereas the Prigogine minimum entropy production principle follows in fact from the Onsager-Gyarmati principle [42, 185, 186, 237] as a special case. That principle is valid for stationary processes in the presence of free forces. Hence, Prigogine principle is less general and has a more restricted domain of applicability than Ziegler principle.

Gyarmati carried out a careful analysis of the theory of linear and nonlinear irreversible processes [259]. As a result he clarified and extended Onsager principle of least dissipation of energy, by formulating a more symmetric form known as *Gyarmati principle*.

Detail considerations showed that the minimum entropy production principle is consistent with but different from other non-equilibrium variational principles like the maximum entropy production principle [260-262] or the *least dissipation principle* due to Onsager and Machlup [192-194].

It was claimed by some authors [263] that Onsager principle of the least dissipation of energy may be considered as an equivalent to the maximum entropy production principle. For example, solutions of the linearized Boltzmann equation make an extremum of entropy production. Authors [263] argued that, in the case of stationary processes, this extremum is a *maximum* rather than a *minimum*. Paltridge [260-262] has formulated his maximum entropy production principle (which may be applied to nonlinear process) in the context of geophysical studies of the Earth climate. Paltridge has supposed that the steady state of the atmosphere is the state of maximum entropy production due to the specificity of heat transport.

In short, the principle of minimum entropy production is a workable scheme for linear non-equilibrium thermodynamics. It states that the steady state of an irreversible process, *i.e.*, the state in which the thermodynamic variables are independent of the time, is characterized by a minimum value of the rate of entropy production. A typical example of its effective applicability was considered by Zivi [264], who performed estimation of steady-state steam-void fraction by means of the principle of minimum entropy production. Zivi [264] carried out an analysis of steam-void fraction in a two-phase flow, utilizing the principle that in a steady-state thermodynamic process the rate of entropy production is minimum. The two-phase flow was idealized in the analysis to be a truly steady-state process. The effects of liquid entrainment and wall friction on the void fraction and slip ratio were evaluated. It was found that the slip ratio in an idealized two-phase flow with zero wall friction and zero entrainment equals $(\rho_f/\rho_g)^{1/3}$. Data from a number of experiments were found to be bracketed between this result and the result obtained by assuming complete entrainment (slip ratio = 1). It should be noted, however, that the Prigogine principle has some limitations. It can be applied to systems so close to equilibrium that there is only one steady state accessible.

Ziman formulated the variational principle of transport theory [265] as a general principle of the thermodynamics of irreversible processes. He proposed to consider all distributions of currents such that the intrinsic entropy production equals the extrinsic entropy production for the given set of forces. Then, of all current distributions satisfying this condition, the *steady-state distribution* makes the entropy production a maximum. He noted the difference between this principle and Prigogine minimum entropy production principle, which states that, if not all the forces acting on a system were fixed the free forces will take such values as to make the entropy production a minimum.

Jones [266] discussed the principle of minimum entropy production in microscopic

terms in the context of transport theory and showed that it may be considered as a full generalization of Kohler's principle for the solution of the semiclassical Boltzmann equation. The principle is thus in fact a general variational principle for the expressions of Kubo type [8] for the transport coefficients of a linear system. It was also shown that the usual principle of minimum entropy production in macroscopic terms due to Prigogine [237] follows from the general principle. When a magnetic field is present there is a sense in which the principle is still valid, but one must discuss together the original system and one identical to it except that the magnetic field is reversed.

From the other side, Niven [267] formulated a theory to predict the steady-state position of a dissipative flow-controlled system, as defined by a control volume. His approach was developed on the basis of the maximum entropy principle of Jaynes [5,9-11], involving minimization of a generalized free-energy-like potential. The analysis provided a theoretical justification of a local, conditional form of the maximum entropy production principle, which successfully predicts the observable properties of many such systems. The analysis revealed a very different manifestation of the second law of thermodynamics in steady-state flow systems, which provided a driving force for the formation of complex systems, including life.

There has been permanent interest in finding a general (universal) variational principle of statistical mechanics [233,267-273]. The development of the dynamical fluctuation theories provided a framework for formulation, unification and systematic improvement of various variational principles, namely energy dissipation and entropy production extremal principles (see table II).

Jaynes proposed [268,269] the so-called the *maximum caliber principle*. Maximum caliber is a general variational principle for non-equilibrium statistical mechanics [270,271]. Jaynes [268,269] gave evidence that the maximum caliber principle is indeed such a principle. His aim was to formulate the principles for prediction of macroscopic phenomena *in general*, and establish its relation to microscopic phenomena. In spite of the common wisdom that we have understood the laws of microphysics quite well, macroscopic phenomena were observed to have a rich variety that is difficult to understand. In Jaynes' words [269]: "We see not only lifeless thermal equilibrium and irreversible approaches to it, but lively behavior such as that of cyclic chemical reactions, lasers, self-organizing systems, biological systems."

In refs. [270,271] it was argued additionally that the maximum caliber principle may be considered as a such a principle. The maximum caliber principle, a variant of maximum entropy principle, predicts dynamical distribution functions by maximizing a path entropy subject to dynamical constraints, such as average fluxes. It was shown [270,271] that the maximum caliber principle leads to standard results for systems close to equilibrium, including the Green-Kubo relations, Onsager reciprocal relations of coupled flows, and Prigogine principle of minimum entropy production as particular cases. It was emphasized that the maximum caliber principle does not require any notion of "*local equilibrium*", or any notion of entropy dissipation, or even any restriction to material physics. In this sense, it is more general than many traditional approaches. Authors developed some generalizations of the Onsager and Prigogine results that can be applicable arbitrarily far from equilibrium.

Maes [273] carried out a systematic derivation of positive lower bounds for the expected entropy production rate in classical statistical mechanical systems obeying a dynamical large deviation principle. The logic was the same for the return to thermodynamic equilibrium as it was for steady non-equilibria working under the condition of *local detailed balance*. This approach permits to recover the recently studied "*uncer-*

TABLE II. – *Variational principles.*

Principle	Author(s)	Year	Refs.
Variational principle	Onsager	1931	[190, 191]
Minimum entropy production principle	Prigogine	1947	[237]
Principle of the least dissipation of energy	Onsager, Machlup	1953	[192, 193]
Variational principle of transport theory	Ziman	1956	[265]
Maximum entropy principle	Jaynes	1957	[9, 11]
Onsager-Gyarmati principle	Gyarmati	1967/70	[259]
Glansdorff-Prigogine stability criterion	Glansdorff-Prigogine	1970	[251]
Maximum entropy production principle	Paltridge	1979	[260, 261]
Maximum rate of entropy production principle	Ziegler	1987	[64, 216]
Maximum caliber principle	Jaynes	1980	[268, 269]
Principle of minimum “integrated” entropy production	Suzuki	2013	[274]

tainty” relations for the entropy production, appearing in studies about the effectiveness of mesoscopic machines. In general, Maes refinement of the positivity of the expected entropy production rate was obtained in terms of a positive and even function of the expected current(s) which measures the dynamical activity in the system, a time-symmetric estimate of the changes in the system’s configuration. Also underdamped diffusions may be included in the analysis. Many additional complementary studies of the entropy production of the steady non-equilibrium states were carried out in refs. [275-282]

9. – Linear response formalism and entropy production

Under the influence of the external driving forces $F_1(t), \dots, F_n(t)$, the energy and entropy of a system can increase. It is of importance to consider first [8] the change of the energy of a system with Hamiltonian H under the influence of the external perturbation $H_{\text{ext}}(t) = -\sum_i F_i(t)a_i$. Here $F_i(t) \sim \exp(\varepsilon t)$; $t \rightarrow -\infty$. The quantities a_i are dynamical variables, and $F_i(t)$ is a kind of force with which the external field acts on the variable a_i . Then the perturbation can be represented as $H_{\text{ext}}(t) = -(\mathbf{F}(t)\mathbf{a})$. It should be stressed that taking the perturbation in the above form, we assume that $F_i(t=0) = 0$ (or $\langle a_i \rangle_0 = 0$) for a state of statistical equilibrium [8].

The Hamiltonian of the total system is of the form

$$(61) \quad \mathcal{H} = H + H_{\text{ext}}.$$

The statistical operator ρ satisfies the quantum Liouville equation [8, 13]

$$(62) \quad i\hbar \frac{\partial}{\partial t} \rho = [H + H_{\text{ext}}(t), \rho].$$

The change of energy of the system under the influence of the perturbation $H_{\text{ext}}(t)$ is described by the *dynamical* variable

$$(63) \quad \frac{dH}{dt} = \frac{1}{i\hbar} [H, H + H_{\text{ext}}(t)] = \frac{1}{i\hbar} [H, H_{\text{ext}}(t)],$$

since H does not depend explicitly on time. Then we can write the average change of energy in the form

$$(64) \quad \left\langle \frac{dH}{dt} \right\rangle = \text{Tr} \left(\rho \frac{dH}{dt} \right) = \frac{d}{dt} \langle H \rangle = \frac{1}{i\hbar} \langle [H, H_{\text{ext}}(t)] \rangle = -\langle \dot{H}_{\text{ext}} \rangle.$$

The operator $\dot{H}_{\text{ext}}(t)$ has the meaning of the derivative of the operator with respect only to the time variable appearing in the Heisenberg picture. It is possible to rewrite the average change of energy in the form [8]

$$(65) \quad \frac{d}{dt} \langle H \rangle = \int_0^\beta \int_{-\infty}^t \langle \dot{H}_{\text{ext}}(t' - i\hbar\lambda) \dot{H}_{\text{ext}}(t) \rangle d\lambda dt' = \beta \int_{-\infty}^t \left(\dot{H}_{\text{ext}}(t') \dot{H}_{\text{ext}}(t) \right) dt'.$$

Thus, the rate of change of the energy of the system is determined by quantum time correlation function coupling the operators $H_{\text{ext}}(t)$ at different time.

The starting point for the linear thermodynamics of irreversible processes is the second law and the concept of entropy production in an irreversible process. In any irreversible change in a system, the rate of change in entropy consists of a part due to *entropy flow* from the surroundings and a part due to *changes within the system*. This second part is called the *rate of entropy production*, or simply the entropy production \dot{S} , and is denoted by s per unit volume. It was shown above that, according to the second law, s must be positive. In the energy representation of the evolution of the system, the corresponding quantity is called a *dissipation function* or potential, since it represents the rate at which irrecoverable energy or work must be supplied or done to maintain the process [37-39, 42, 53, 184-186, 218-220].

The entropy production $\dot{S}(t)$ factor appears in various problems of non-equilibrium statistical physics. It can be calculated approximately in a semi-phenomenological approach or with the help of various advanced methods of statistical mechanics. For example, as it was shown in paper [283], when we consider the scattering of neutrons on the non-equilibrium statistical medium, the generalized Van Hove scattering function $\mathcal{S}(\vec{k}, \omega, t)$ will contain an essential additional factor, connected with the entropy production $\dot{S}(t)$.

There were numerous attempts to resolve the problem of entropy production within the Kubo linear response theory [195, 199]. However, until recently, the consistent consideration and derivation of entropy production within the linear response formalism was not fully clear. We have considered above the effect of mechanical perturbation on the

change of energy of a system. Let us summarize the influence of mechanical perturbations on the change of entropy. To proceed, it is necessary to define entropy for a non-equilibrium state [8]. In the equilibrium case it has the form

$$(66) \quad \langle \eta \rangle = -\langle \ln \rho \rangle = -\text{Tr}(\rho \ln \rho),$$

where ρ is the statistical operator. However, $\langle \eta \rangle$ cannot describe the entropy of a non-equilibrium state. Indeed, $\eta = -\ln \rho$, as ρ satisfies the Liouville equation [8]

$$(67) \quad i\hbar \frac{\partial \eta}{\partial t} = [H + H_{\text{ext}}(t), \eta].$$

Consequently η is an integral of motion, *i.e.* $d/dt \langle \eta \rangle = 0$, and cannot possess the properties of the entropy of a non-equilibrium state. To proceed in the framework of linear response formalism [8] it should be assumed that the state of the system remains spatially uniform and stationary in time, *i.e.*, the energy evolved is drawn off. Then it is natural to define the entropy by *analogy with the equilibrium state* by the thermodynamic relation [8, 13]

$$(68) \quad S = \frac{\langle H \rangle - \mu \langle N \rangle - \Omega}{\theta},$$

but assuming that the averaging is performed *over the non-equilibrium state*. Then the entropy will be equal to minus the average of the logarithm of the equilibrium distribution

$$(69) \quad S = -\langle \ln \rho_0 \rangle = -\text{Tr}(\rho \ln \rho_0),$$

where $\rho_0 = \exp((\Omega - H + \mu N)\theta^{-1})$. The rate of change of the entropy with time is equal to

$$(70) \quad \frac{\partial S}{\partial t} = \frac{1}{\theta} \frac{d\langle H \rangle}{dt}.$$

The effect of mechanical perturbation on the change of entropy of a system takes the form [8]

$$(71) \quad \frac{\partial S}{\partial t} = \frac{1}{\theta} \sum_{i,k} \int_{-\infty}^t F_i(t) L_{ik}(t-t') F_k(t') dt'.$$

Here $L_{ik} = \beta(\dot{\alpha}_k(t'), \dot{\alpha}_i(t))$ are the kinetic coefficients and $\langle \dot{\alpha}_i \rangle = \sum_k L_{ik} F_k$ are the linear relations between the fluxes and the forces [8]. For a special form of external forces (*e.g.*, periodically varying with time) the average rate of change of entropy may lead to the generation of the entropy (or entropy production) in the system.

Suzuki [274, 284-288] re-analyzed the problem of irreversibility and entropy production in transport phenomena in details. He proposed a consistent derivation [284, 285] of entropy production which is directly based on the first principles by using the projected density matrix approach. His derivation clarified conceptually the physics of irreversibility in transport phenomena, using the symmetry of non-equilibrium states. This showed

also the duality of current and entropy production. Suzuki showed also that the linear response scheme *is not closed* within the first order of an external force, in order to manifest the irreversibility of transport phenomena. New schemes of *steady states* were presented by introducing relaxation-type (symmetry-separated) von Neumann equations. The concept of stationary temperature T_{st} was introduced, which is a function of the relaxation time τ_r characterizing the rate of extracting heat outside the system. The entropy production in this steady state depends on the relaxation time. A dynamical-derivative representation method to reveal the irreversibility of steady states was also proposed. This derivation of entropy production was directly based on the first principles of using the projected density matrix $\rho_2(t)$ or more generally the symmetric density matrix $\rho_{\text{sym}}(t)$, while the previous standard argument was due to the thermodynamic energy balance. The derivation proposed by Suzuki clarified conceptually the physics of irreversibility in transport phenomena, using the symmetry of non-equilibrium states, and this showed clearly the duality of current and entropy production.

In the next paper [286] Suzuki formulated a statistical-mechanical theory on steady states including thermal disturbance and energy supply. Some general aspects of nonlinear transport phenomena were discussed on the basis of two kinds of formulations obtained by extending Kubo perturbational scheme of the density matrix and Zubarev non-equilibrium statistical operator formulation [8]. Both formulations were extended up to infinite order of an external force in compact forms and their relationship was clarified through a direct transformation.

In order to make it possible to apply these formulations straightforwardly to thermal disturbance, its mechanical formulation was given by introducing the concept of a thermal field E_T which corresponds to the temperature gradient and by defining its conjugate heat operator A_H for a local internal energy h_j of the thermal particle j . This yields a transparent derivation of the thermal conductivity κ of the Kubo form and the entropy production $(dS/dt)_{\text{irr}}$. To describe the steady state of the system, a statistical-mechanical formulation was proposed with a special approach which includes energy supply to the system from outside by extending the symmetry-separated von Neumann equation given in the previous paper [284]. This yields a general theory based on the density-matrix formulation on a steady state with energy supply inside and heat extraction outside. Furthermore, this steady state gives a positive entropy production. The general formulation of the current yields a compact expression of the time derivative of entropy production, which yields the plausible justification of the principle of minimum entropy production in the steady state even for nonlinear responses.

A new variational principle of steady states was formulated by Suzuki [274] with the help of introducing an integrated type of energy dissipation (or entropy production) instead of instantaneous energy dissipation. This new principle is valid both in linear and nonlinear transport phenomena. Suzuki [274] called this new general principle of minimum “integrated” entropy production (or energy dissipation) by realization of the “Prigogine dream”. He claimed also that the new principle does not contradict the Onsager-Prigogine principle of minimum instantaneous entropy production in the linear regime, but it is conceptually different from the latter which does not hold in the nonlinear regime. Applications of this theory to electric conduction, heat conduction, particle diffusion and chemical reactions were considered. The irreversibility (or positive entropy production) and long time tail problem in Kubo formula were also discussed in this context. This constitutes the complementary explanation of the theory of entropy production given in the previous papers [284-286].

The mechanism of entropy production in transport phenomena was discussed by

Suzuki [288] again by emphasizing the role of symmetry of non-equilibrium states and also by reformulating Einstein theory of Brownian motion to derive entropy production from it. Separated variational principles of steady states for multi external fields $\{X_i\}$ and induced currents $\{J_i\}$ were proposed by extending the principle of minimum integrated entropy production found earlier for a single external field. The basic strategy of this theory on steady states was to take in all the intermediate processes from the equilibrium state to the final possible steady states in order to study the irreversible physics even in the steady states. As an application of this principle, Glansdorff-Prigogine evolution criterion inequality (or stability condition) was derived in the stronger form for individual force $\{X_i\}$ and current $\{J_i\}$ even in nonlinear responses which depend on all the external forces $\{X_k\}$ nonlinearly. This was called “*separated evolution criterion*”. Some explicit demonstrations of the general theory to simple electric circuits with multi external fields were given in order to clarify the physical essence of the theory and to realize the condition of its validity concerning the existence of the solutions of the simultaneous equations obtained by the separated variational principles.

To summarize, in the approach of Suzuki [274, 284-288], a workable invention has been used, namely the steady state of the system within the formalism of linear response theory. To describe the steady state of the system, a statistical-mechanical formulation was proposed with a special approach which includes energy supply to the system from outside.

It is worth noting that there exists a substantial distinction of the standard linear response theory and of the Zubarev’s method of the non-equilibrium statistical operator [8, 13, 52]. In essence, the linear response theory is an expansion from the *global* equilibrium state whereas the non-equilibrium statistical operator approach uses the expansion from the *local* (quasi-equilibrium) state. Hence it may provide a more consistent description of various non-equilibrium nonlinear processes.

10. – NSO method, extremal principles and entropy production

In the present section we discuss tersely the Zubarev method [8] of non-equilibrium statistical operator (NSO) viewed in the context of entropy production.

In equilibrium statistical mechanics the distribution function is chosen so that averages over the ensemble are in exact agreement with the incomplete (macroscopic) knowledge of the state of the system at some specified time. Then the expected development of the system at subsequent times is modelled via the average behavior of members of the representative ensemble.

In the NSO approach [8], the non-equilibrium statistical operator may be deduced from the extremum condition on the information entropy for fixed values of the thermodynamic coordinates at any past time. Note that it can be obtained also on the basis of other considerations. It was discussed above that the theorem of Prigogine on the minimum entropy production [237] and its generalization, namely the Glansdorff-Prigogine theorem [251], can be related to the condition of maximum entropy for a local-equilibrium (or quasi-equilibrium) distribution. For a precise definition of a local-equilibrium ensemble, it is necessary to define the distribution function for the statistical operator corresponding to it. We gave already convincing arguments that in a system situated in stationary external conditions, a certain stationary distribution is established, which we called a stationary local-equilibrium distribution. If the external conditions depend on time, the local-equilibrium distribution will be *non-stationary*. The assumption of *local equilibrium* is a basic and necessary assumption in linear irreversible thermody-

namics [8, 13]. It enables us to apply the equations of equilibrium thermodynamics, such as the Gibbs equation, to local volume elements in a system. The entropy and other thermodynamic properties of the system can then be defined in terms of local, intensive state variables. The assumption leads to the concept of an *entropy production* in a system subject to irreversible processes [57, 284-286].

The simplest method of constructing the local-equilibrium statistical operator (or distribution function) is based on information theory as was discussed in detail in refs. [8, 13]. The statistical operator is determined from the maximum of the information entropy, which is equal to [8]

$$(72) \quad S_{\text{inf}} = -\langle \ln \rho \rangle = -\text{Tr}(\rho \ln \rho), \quad (\text{Tr} \rho = 1).$$

For the construction of a non-equilibrium statistical operator [8, 13] the basic hypothesis is that after a small time interval τ the non-equilibrium distribution is established. Moreover, it is supposed that it is weakly time dependent by means of its parameters only. Then the statistical operator ρ for $t \geq \tau$ can be considered as an *integral of motion* of the quantum Liouville equation

$$(73) \quad \frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] = 0.$$

Here $\partial\rho/\partial t$ denotes time differentiation with respect to the time variable on which the relevant parameters F_m depend. It is important to note once again that ρ depends on t by means of $F_m(t)$ only. These parameters are given through the external conditions for our system and, therefore, the term $\partial\rho/\partial t$ is the result of the external influence upon the system; this influence causes the system to be non-stationary. In other words we may consider that the system is in thermal, material, and mechanical contact with a combination of thermal baths and reservoirs maintaining the given distribution of the parameters F_m . For example, it can be the densities of energy, momentum, and particle number for the system which is macroscopically defined by given fields of temperature, chemical potential and velocity. It is assumed that the chosen set of parameters is sufficient to characterize macroscopically the state of the system. Thus the choice of the set of the relevant parameters is dictated by the external conditions for the system under consideration.

Hence, it was assumed that a non-equilibrium statistical ensemble can be characterized by a small set of relevant operators $P_m(t)$ (quasi-integrals of motion) and that the NSO is a functional of these operators,

$$(74) \quad \rho(t) = \rho\{\dots P_m(t) \dots\}.$$

For the description of the hydrodynamic stage of the irreversible process the energy, momentum and number of particles densities, $H(x)$, $\mathbf{p}(x)$, $n_i(x)$ should be chosen as the operators $P_m(t)$. For the description of the kinetic stage the occupation numbers of one-particle states can be chosen [52, 289]. It is necessary to take into account that $\rho(t)$ satisfies the Liouville equation.

Hence the quasi-equilibrium (local-equilibrium) Gibbs-type distribution will have the form

$$(75) \quad \rho_q = Q_q^{-1} \exp\left(-\sum_m F_m(t) P_m\right),$$

where the parameters $F_m(t)$ have the meaning of time-dependent thermodynamic parameters, *e.g.*, of temperature, chemical potential, and velocity (for the hydrodynamic stage), or the occupation numbers of one-particle states (for the kinetic stage). The statistical functional Q_q is defined by demanding that the operator ρ_q be normalized and equal to

$$(76) \quad Q_q = \text{Tr} \exp \left(- \sum_m F_m(t) P_m \right).$$

In addition, it was shown that there exists a general method for choosing a suitable quasi-equilibrium distribution [8]. For the state with the extremal value of the *informational entropy* [8, 13]

$$(77) \quad S = - \text{Tr}(\rho \ln \rho),$$

provided that

$$(78) \quad \text{Tr}(\rho P_m) = \langle P_m \rangle_q; \quad \text{Tr} \rho = 1,$$

it is possible to construct a suitable quasi-equilibrium ensemble [8]. Here the notation used is $\langle \dots \rangle_q = \text{Tr}(\rho_q \dots)$. Then the corresponding quasi-equilibrium (or local equilibrium) distribution has the form [8]

$$(79) \quad \rho_q = \exp \left(\Omega - \sum_m F_m(t) P_m \right) \equiv \exp(-S(t, 0)),$$

$$\Omega = \ln \text{Tr} \exp \left(- \sum_m F_m(t) P_m \right),$$

where $S(t, 0)$ can be called the entropy operator. Indeed, the conditional extremum [8] of the functional (77) corresponds to the extremum of

$$(80) \quad \Phi(\rho) = - \text{Tr}(\rho \ln \rho) - \sum_m F_m \text{Tr}(\rho P_m) + \lambda \text{Tr} \rho,$$

where $F_m(t)$ and λ denote Lagrange multipliers. From the condition

$$(81) \quad \delta \Phi(\rho) = 0,$$

we find the expression for ρ_q .

The quasi-equilibrium statistical operator preserves the thermodynamic formulae for the parameters $F_m(t)$

$$(82) \quad \frac{\delta \Phi}{\delta F_m} = - \langle P_m \rangle_q,$$

but the Liouville equation is not satisfied.

In other words, the form of the quasi-equilibrium statistical operator was constructed in such a way that to ensure that the thermodynamic equalities for the relevant parameters $F_m(t)$

$$(83) \quad \frac{\delta \ln Q_q}{\delta F_m(t)} = \frac{\delta \Omega}{\delta F_m(t)} = -\langle P_m \rangle_q; \quad \frac{\delta S}{\delta \langle P_m \rangle_q} = F_m(t)$$

are satisfied. It is clear that the variables $F_m(t)$ and $\langle P_m \rangle_q$ are thermodynamically conjugate. Since the operator ρ_q itself does not satisfy the Liouville equation, it should be modified [8] in such a way that the resulting statistical operator satisfies the Liouville equation. This is the most delicate and subtle point of the whole method [8, 13, 289]. In the standard procedure [8] the suitable variables (*relevant operators*), which are time dependent by means of $F_m(t)$, should be constructed by means of taking the *invariant part* of the operators incoming into the logarithm of the statistical operator with respect to the motion with Hamiltonian H . Thus, by definition, a special set of operators should be constructed which depends on the time through the parameters $F_m(t)$ by taking the *invariant part* of the operators $F_m(t)P_m$ occurring in the logarithm of the quasi-equilibrium distribution, *i.e.*,

$$(84) \quad B_m(t) = \overline{F_m(t)P_m} = \varepsilon \int_{-\infty}^0 e^{\varepsilon t_1} F_m(t+t_1) P_m(t_1) dt_1 \\ = F_m(t)P_m - \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \left(F_m(t+t_1) \dot{P}_m(t_1) + \dot{F}_m(t+t_1) P_m(t_1) \right),$$

where ($\varepsilon \rightarrow 0$) and

$$\dot{P}_m = \frac{1}{i\hbar} [P_m, H]; \quad \dot{F}_m(t) = \frac{dF_m(t)}{dt}.$$

The parameter $\varepsilon > 0$ will be set equal to zero, but only *after the thermodynamic limit* [4] has been taken. Thus, the invariant part is taken with respect to the motion with Hamiltonian H . The operators $B_m(t)$ satisfy the Liouville equation in the limit ($\varepsilon \rightarrow 0$)

$$(85) \quad \frac{\partial B_m}{\partial t} - \frac{1}{i\hbar} [B_m, H] = \varepsilon \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \left(F_m(t+t_1) \dot{P}_m(t_1) + \dot{F}_m(t+t_1) P_m(t_1) \right).$$

The operation of taking the invariant part, or *smoothing* the oscillating terms, is used in the formal theory of scattering to set the boundary conditions which exclude the advanced solutions of the Schrödinger equation [8, 13]. It is most clearly seen when the parameters $F_m(t)$ are independent of time. Differentiating $\overline{P_m}$ with respect to time gives

$$(86) \quad \frac{\partial \overline{P_m(t)}}{\partial t} = \varepsilon \int_{-\infty}^0 e^{\varepsilon t_1} \dot{P}_m(t+t_1) dt_1.$$

$\overline{P_m(t)}$ can be called the integrals (or *quasi-integrals*) of motion, although they are conserved only in the limit ($\varepsilon \rightarrow 0$). It is clear that for the Schrödinger equation such a procedure excludes the advanced solutions by choosing the initial conditions. In the

present context this procedure leads to a selection of the retarded solutions of the Liouville equation.

Then the non-equilibrium statistical operator ρ can be written as

$$\begin{aligned}
 (87) \quad \rho &= \exp(\overline{\ln \rho_q}) = \exp\left(\varepsilon \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \exp\left(\frac{iHt_1}{\hbar}\right) \ln \rho_q(t+t_1) \exp\left(\frac{-iHt_1}{\hbar}\right)\right) \\
 &= \exp\left(-\overline{S(t,0)}\right) = \exp\left(-\varepsilon \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} S(t+t_1, t_1)\right) \\
 &= \exp\left(-S(t,0) + \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \dot{S}(t+t_1, t_1)\right).
 \end{aligned}$$

Here

$$\begin{aligned}
 (88) \quad \dot{S}(t,0) &= \frac{\partial S(t,0)}{\partial t} + \frac{1}{i\hbar}[S(t,0), H]; \\
 \dot{S}(t, t_1) &= \exp\left(\frac{iHt_1}{\hbar}\right) \dot{S}(t,0) \exp\left(\frac{-iHt_1}{\hbar}\right).
 \end{aligned}$$

It is required [8] that the normalization of the statistical operator ρ_q is preserved as well as the statistical operator ρ , and the constraint $\langle P_m \rangle^t = \langle P_m \rangle_q^t$ is fulfilled. For the particular choice of F_m which corresponds to the statistical equilibrium we obtain $\rho = \rho_q = \rho_0$. It determines the parameters $F_m(t)$ such that P_m and $F_m(t)$ are thermodynamically conjugate, *i.e.*

$$(89) \quad \frac{\delta \lambda}{\delta F_m} = -\langle P_m \rangle_q = -\langle P_m \rangle.$$

The method of the non-equilibrium statistical operator is a very useful tool to analyze and derive generalized transport and kinetic equations [8, 13, 52, 195, 239, 289]. In refs. [13, 52, 239, 289] the generalized kinetic equations for the system weakly coupled to a thermal bath have been derived. The aim was to describe the relaxation processes in two weakly interacting subsystems, one of which is in non-equilibrium state and the other is considered as a thermal bath. We took the quasi-equilibrium statistical operator ρ_q in the form

$$(90) \quad \rho_q(t) = \exp(-S(t,0)), \quad S(t,0) = \Omega(t) + \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta H_2.$$

Here $F_{\alpha\beta}(t)$ are the thermodynamic parameters conjugated with $P_{\alpha\beta}$, and β is the reciprocal temperature of the thermal bath; $\Omega = \ln \text{Tr} \exp(-\sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) - \beta H_2)$. The non-equilibrium statistical operator in this case has the form

$$\begin{aligned}
 (91) \quad \rho(t) &= \exp(-\overline{S(t,0)}); \\
 \overline{S(t,0)} &= \varepsilon \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \left(\Omega(t+t_1) + \sum_{\alpha\beta} P_{\alpha\beta} F_{\alpha\beta}(t) + \beta H_2 \right).
 \end{aligned}$$

The parameters $F_{\alpha\beta}(t)$ are determined from the condition $\langle P_{\alpha\beta} \rangle = \langle P_{\alpha\beta} \rangle_q$.

In the derivation of the kinetic equations we used the perturbation theory in a *weakness of interaction*. The kinetic equations for $\langle P_{\alpha\beta} \rangle$ were derived in the form [13, 52, 239, 289]

$$(92) \quad \frac{d\langle P_{\alpha\beta} \rangle}{dt} = \frac{1}{i\hbar}(E_\beta - E_\alpha)\langle P_{\alpha\beta} \rangle - \frac{1}{\hbar^2} \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \langle [[P_{\alpha\beta}, V], V(t_1)] \rangle_q.$$

The last term on the right-hand side of eq. (92) can be called the generalized *collision integral*. Thus, we can see that the collision term for the system weakly coupled to the thermal bath has the convenient form of a double commutator. It should be emphasized that the assumption about the model form of the Hamiltonian of a system (H_1) interacting with thermal bath (H_2) $H = H_1 + H_2 + V$ is non-essential for the derivation [13, 52, 239, 289]. Equation (92) will be fulfilled for the general form of the Hamiltonian of a small system weakly coupled to a thermal bath.

The change of the entropy during the evolution of the small subsystem to equilibrium has the form

$$(93) \quad S = -\langle \ln \rho_q \rangle = \beta \langle H_2 - \mu_2 N_2 \rangle + \sum_{\alpha\beta} F_{\alpha\beta}(t) \langle P_{\alpha\beta} \rangle - \ln Q_q.$$

After differentiation on time t we obtain

$$(94) \quad \frac{dS}{dt} = \beta \langle J_2 \rangle + \sum_{\alpha\beta} F_{\alpha\beta}(t) \frac{d\langle P_{\alpha\beta} \rangle}{dt}.$$

Now we substitute in this equation the expression

$$(95) \quad J_2 = \frac{1}{i\hbar} [(H_2 + V), H].$$

Then we obtain

$$(96) \quad \frac{dS}{dt} = \sum_{\alpha\beta} X_{\alpha\beta}(t) \frac{d\langle P_{\alpha\beta} \rangle}{dt},$$

which is the standard expression for the entropy production of the thermodynamics of irreversible processes [8, 185, 186]. Here the $X_{\alpha\beta}$ is the generalized “*thermodynamic force*”.

11. – Conclusions

We carried out in the present review a *comparative study* of the various approaches to the concepts of entropy and entropy production and analyzed tersely the extremal principles of statistical thermodynamics. The paper aims to clarify the notion of entropy, entropy production and its generalizations. We also touched briefly the intriguing problem of the directionality of time and causality. A discussion of those features was concentrated on the foundational issues of non-equilibrium statistical thermodynamics and the related conceptual problems of irreversibility.

We show that there exists a substantial distinction of the standard linear response theory and of Zubarev's method of non-equilibrium statistical operator [8, 13, 52]. This distinction is connected with the procedure of averaging in both methods. The linear response theory is an expansion from the *global* equilibrium state whereas the non-equilibrium statistical operator approach uses the expansion from the *local* (quasi-equilibrium) state. Hence it may provide a more consistent description of various non-equilibrium nonlinear processes.

We analyzed and compared the extremal principles of thermodynamics and demonstrated their interrelation and use. We concluded that information theory [12, 13], in conjunction with the techniques developed by Jaynes [11, 17, 18] is a useful tool in various problems of statistical thermodynamics. The Gibbs distributions have a non-trivial common property: subject to certain constraints they maximize a functional known in statistical mechanics as entropy, and in information theory, probability theory and mathematical statistics as information [146]. The approach based on the information theory in the spirit of the principle of maximum entropy has been used in numerous works on statistical mechanics [8, 12, 13, 33, 39] to derive the fundamental statistical mechanical distributions.

We show also that the effective approach to the construction of Gibbs-type ensembles for non-equilibrium systems is the method of non-equilibrium statistical operator developed by Zubarev [8]. In that method it was assumed that the chosen set of parameters $\{P_m\}$ is sufficient to characterize macroscopically the state of the system. The choice of the set of the relevant parameters is dictated by the external conditions for the system under consideration. It was argued that there exists a general method for choosing a suitable *quasi-equilibrium distribution* [8, 13] by considering the state with the extremal value of the informational entropy. The quasi-equilibrium distribution is not necessarily close to the stationary stable state. The form of the quasi-equilibrium statistical operator was constructed so to ensure that the thermodynamic equalities for the relevant parameters $F_m(t)$ are satisfied. Then it is possible to obtain the statistical operator in the form which corresponds to the extremum of the information entropy for given averages $\langle P_m \rangle^t$ in an arbitrary moment of the past.

Our comparative study shows that the non-equilibrium statistical operator method may offers several advantages over the standard technique for the description of non-equilibrium phenomena and for the description of time evolution.

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