Maximum entropy production principle in physics, chemistry and biology

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Abstract

The tendency of the entropy to a maximum as an isolated system is relaxed to the equilibrium (the second law of thermodynamics) has been known since the mid-19th century. However, independent theoretical and applied studies, which suggested the maximization of the entropy production during nonequilibrium processes (the so-called maximum entropy production principle, MEPP), appeared in the 20th century. Publications on this topic were fragmented and different research teams, which were concerned with this principle, were unaware of studies performed by other scientists. As a result, the recognition and the use of MEPP by a wider circle of researchers were considerably delayed. The objectives of the present review consist in summation and analysis of studies dealing with MEPP. The first part of the review is concerned with the thermodynamic and statistical basis of the principle (including the relationship of MEPP with the second law of thermodynamics and Prigogine's principle). Various existing applications of the principle to analysis of nonequilibrium systems will be discussed in the second part.
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He who gains time, gains everything.

G.B. Molière

0. Introduction

The notions of entropy and its production in equilibrium and nonequilibrium processes not only form the basis of modern thermodynamics and statistical physics, but have always been at the core of various ideological discussions concerned with the evolution of the world, the course of time, etc. These issues were raised by many outstanding scientists, including Clausius, Boltzmann, Gibbs and Onsager. As a result, today we have thousands of books, reviews and papers dedicated to properties of the entropy in different systems. The present review deals with the entropy production behavior in nonequilibrium processes. This topic is not new. What was the impetus to this study?

Attempts to find some universal function, whose extremum would determine the development of a system, have been made at all times. A certain success was achieved in optics (Fermat's principle), mechanics (the principle of least action), and some other disciplines. Entropy, which was assigned a semimystic significance in the "world management" nearly at the moment it appeared, has been doomed to be a quantity describing the progress of nonequilibrium dissipative process. Great contribution has been done in this respect by two scientists, namely Clausius, who in 1854–1862 introduced the notion of entropy in physics and advanced the concept of the thermal collapse of the Universe, and Prigogine. In 1947 the latter researcher proved the so-called minimum entropy production principle and then spent a number of years developing and popularizing the apparatus of nonequilibrium thermodynamics and his principle as applied to description of various nonequilibrium processes in physics, chemistry and biology. However, applications of this principle are relatively narrow as it was acknowledged by Prigogine himself and his opponents. Nevertheless, two essentially extreme opinions have been formed in the literature. Some scientists glorify the principle and think it is capable of describing various nonequilibrium processes to a certain extent. Other researchers, who observed weak points of the principle and unceasing efforts by Prigogine and his progeny to generalize it, are very skeptic about the possibility to formulate universal entropy principles, which would govern so diverse and dissimilar nonequilibrium processes.

The so-called maximum entropy production principle (MEPP) is known much less (even among specialists in physics of nonequilibrium processes). This antipode, as its name seemingly means, of Prigogine's principle has been overshadowed by its more famous twin. MEPP was independently proposed and used by several scientists throughout the 20th century when they dealt with general theoretical issues of thermodynamics and statistical physics or solved specific

problems. By this principle, a nonequilibrium system develops so as to maximize its entropy production under present constraints. The rigorous formulation, the origin and corollaries of this principle will be analyzed comprehensively in what follows. Here we shall only mention two principal features concerning the relationship between MEPP and the other two known statements about entropy.

1. The second law of thermodynamics, as it was worded by Clausius, states that for an arbitrary adiabatic process entropy (S) of the final state is larger than or equal to entropy of the initial state. In terms of the entropy production (σ), this means that $\sigma \geqslant 0$. In this case, MEPP obviously represents new additional statement meaning that the entropy production is not just positive, but tends to a maximum. Thus, apart from the direction of the evolution, which follows from the Clausius's formulation, we have information about the movement rate of a system. However, if we consider the statistical interpretation of entropy, which follows from studies by Boltzmann and Gibbs, entropy not only tends to increase, but will increase to a maximum value, which is allowed by imposed constraints. Here, the final (equilibrium) state is most probable and is described by a maximum number of microscopic states. On the strength of this statistical interpretation of the second law, MEPP may be viewed as the natural generalization of the Clausius–Boltzmann–Gibbs formulation of the second law and, in some cases, even as a corollary. Indeed, let us take an isolated system in some nonequilibrium state. The system will reach equilibrium with time (of the order of the relaxation time) and, among a great number of possible states, it will be in a state, for which entropy is a maximum. Therefore, the change of entropy within a given time interval will also be a maximum among possible values and, since the system is isolated, the entropy production will be the largest. This relationship between the second law of thermodynamics and MEPP was noted earlier (see, for example [1–3]).

2. The relationship between the minimum entropy production principle and MEPP is not simple. It has been the subject of long-standing discussions and will be considered in p. 1.2.6. Here we shall note the following points. These variation principles are absolutely different. Although the extremum of one and the same function—the entropy production—is sought, these principles include different constraints and different variable parameters. These principles should not be mutually opposed since they are applicable to different stages of the evolution of a nonequilibrium system. It should be noted also that Prigogine [4] (see, [5] too) stated more than once and adduced examples when a nonequilibrium system behaved oppositely to his principle of the minimum (Benard's effect and structure instability during the biochemical evolution). He thought however that this situation is possible only in systems, which are far from the equilibrium.

It will be demonstrated in this review that it is MEPP, rather than Prigogine's principle, can pretend to be a universal principle governing the evolution of nonequilibrium dissipative systems. The present review is the first generalizing treatise on this topic. One more factor, which adds significance to this study, is that publications on this topic are fragmented and different research teams, which are concerned with this principle, are unaware of studies performed by other scientists.[1] Therefore, the recognition and a wider use of MEPP in different fields of science have been considerably delayed.

In the first and second chapters we shall describe in sufficient detail the available thermodynamic and statistical basis of this principle. The third chapter will deal with diverse applications of MEPP. The most interesting and significant thing is that many researchers, who used MEPP, were unaware of general theoretical approaches, which are presented in the first two chapters. They were guided exclusively by the common sense and utility of the principle for settling of some specific problems existing in physics and interdisciplinary sciences. A feature in common of those studies was that MEPP proved to be the missing link, which allowed understanding the evolution of a nonequilibrium system. On account of the diversity of the reading matter and the unwillingness to change traditional well-established designations of quantities, we recommend to read each section attentively so as not to misunderstand a particular symbol. In closing, we shall present conclusions and formulate problems, which, in our opinion, require attention in later studies.

Since one of the objectives of this review was to attract attention of a wide circle of people working in various domains of science, we had to proceed, first and foremost, from a maximum accessibility and a relative simplicity of the presentation of the material. In some cases, therefore, the rigor is impaired and some details were excluded from the review.[2] In our opinion, such presentation of the material, which refers to different areas of knowledge, is most reasonable today.

Notice also that in this review we deliberately concentrated on evolution criteria for nonequilibrium systems, which are directly connected with entropy and MEPP. This is because we wanted to show that the idea about the relationship

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[1] Important results were published not only in English, but also in other languages (Russian, German and French).

[2] These drawbacks can be eliminated if the reader refers to original papers, which are cited in the review.

between entropy and the evolution of nonequilibrium systems, which has been known for over 150 years, still deserves attention and is very useful. We think also that MEPP is relatively simple, elegant and evident as compared to other plentiful hypotheses-criteria, most of which represent just some mathematical structures that are not obvious in physical terms and are not illustrative.

1. MEPP in nonequilibrium thermodynamics

The first part of this section presents necessary notions and some existing variational principles of nonequilibrium thermodynamics, including Prigogine's principle. In the second part we shall consider Ziegler's approach, which is based on the deductive formulation of nonequilibrium thermodynamics using MEPP.

1.1. Fundamentals of linear nonequilibrium thermodynamics

The first law of thermodynamics or the law of conservation of energy states that the heat δQ, which is put into a system, is consumed for the work δW done by the system over external bodies and the change of the internal energy of the system, dU [5,6]:

$$\delta Q = \delta W + dU. \tag{1.1}$$

The second law of thermodynamics, which has many wordings [5,6], states that any equilibrium thermodynamic system has a unique state function or entropy S:

$$T\, dS = \delta Q, \tag{1.2}$$

where T is the temperature.

As applied to nonequilibrium processes in an isolated system, the second law states that entropy cannot decrease. The entropy is one of main notions in thermodynamics and analysis of the behavior of this function or its derivatives is very important as it will be shown below in the text.

Most processes around us are nonequilibrium processes and a local equilibrium is assumed for the use of a relationship like (1.2). This assumption is valid if it is possible to distinguish two characteristic times, that is, the time required to reach the equilibrium in the entire system and the time required to reach the equilibrium in some volume, which is small as compared to the size of a system under study. The first time should be much longer than the second time. A relationship like (1.2) can be applied to each of these small elements. The assumption on the local equilibrium is, of course, very strong, but it holds for many systems [5,6].

The variation of entropy with time t in a local unit volume can be written in the form [5–8]

$$\frac{\partial s}{\partial t} = \sigma - \mathrm{div}(\boldsymbol{j}_s), \tag{1.3}$$

$$\sigma = \sum_i X_i J_i, \tag{1.4}$$

where s is the entropy density; σ is the entropy production density[3] (on the strength of second law of thermodynamics, the entropy production is always larger than or equal to zero); $\boldsymbol{j}_s$ is the entropy flux density, which additively depends on thermodynamic flux densities J_i; X_i is thermodynamic forces (depending on particular problem conditions, the subscript i refers to different fluxes (forces) and vector components).

In 1931–1932 Onsager, who theoretically generalized empirical laws established by Fourier, Ohm, Fick and Navier, proposed a linear relationship between thermodynamic fluxes and forces [5–9] in the form

$$J_i = \sum_k L_{ik} X_k, \tag{1.5}$$

$$L_{ik} = L_{ki}, \tag{1.6}$$

where L_{ik} is the matrix of kinetic coefficients, which are independent of J_i and X_k.

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[3] Further in the text referred to as "the entropy production" for brevity.

The relationships (1.5) and (1.6) form the basis of the apparatus of linear nonequilibrium thermodynamics. They close the system of equations for the transfer of energy, momentum and mass, making it possible to solve the system. It should be emphasized that these expressions are valid only when thermodynamic forces are relatively small (in this case, a nearly linear relationship may be assumed between thermodynamic fluxes and forces). However, the spectrum of problems, which can be solved in terms of this simple formalism, is sufficiently wide. At the same time, examples are known when calculations by the linear relationships (1.5) and (1.6) may prove to be incorrect (specifically when chemical reactions are concerned).

In 1931 Onsager proposed a variational principle, which can yield relationships (1.5) and (1.6) of linear nonequilibrium thermodynamics [6,9]. Thus, he gave the first deductive formulation of linear nonequilibrium thermodynamics. This principle is worded as follows [9]: if values of irreversible forces X_i are assigned, true fluxes J_i maximize the expression $[\sigma(X_i, J_k) - \Phi(J_i, J_k)]$, i.e.,

$$\delta_J[\sigma(X_i, J_k) - \Phi(J_i, J_k)]_X = 0, \tag{1.7}$$

$$\Phi(J_i, J_k) = \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k. \tag{1.8}$$

Here and henceforth $\delta_J[\ldots]_X$ denotes the variation of the expression in square brackets with respect to J at constant X, Φ is the dissipative function (it is postulated that $\Phi > 0$), and R_{ik} is the coefficient matrix (it will be shown later in the text that this matrix is inverse to the L_{ik} matrix).

Let us deduce Eqs. (1.5) and (1.6) from Eqs. (1.7) and (1.8).

We shall show first that the tensor R_{ik} may be viewed as symmetric. Since an arbitrary tensor R_{ik} can be presented at all times as the sum of symmetric S_{ik} and antisymmetric A_{ik} tensors, expression (1.8) takes the form

$$\Phi = \frac{1}{2} \sum_{i,k} (S_{ik} J_i J_k + A_{ik} J_i J_k). \tag{1.9}$$

If we take the second term, rearrange its members, and consider that $A_{ii} = 0$ and $A_{ik} = -A_{ki}$ for the antisymmetric tensor, it is easy to see that the antisymmetric part of the tensor R_{ik} does not contribute to the dissipative function. Therefore, the tensor R_{ik} is symmetric ($R_{ik} = R_{ki}$).

Substituting Eqs. (1.4) and (1.8) into Eq. (1.7) and replacing the variance by the derivative with respect to the corresponding fluxes, we have

$$\frac{\partial}{\partial J_j} \left[\sum_i X_i J_i - \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k \right]_X = 0. \tag{1.10}$$

The differentiation of Eq. (1.10) transforms it to

$$X_j = \frac{1}{2} \sum_k (R_{jk} + R_{kj}) J_k = \sum_k R_{jk} J_k. \tag{1.11}$$

Since Φ is a positively defined quadratic form, the solution to the (1.11) for unknown J_k is existent and unique:

$$J_j = \sum_k R_{jk}^{-1} X_k \equiv \sum_k L_{jk} X_k. \tag{1.12}$$

The designation $R_{jk}^{-1} \equiv L_{jk}$ has been introduced. Since R_{ik} is a symmetric matrix, the matrix R_{jk}^{-1}, which is inverse to it, is symmetric too.

Thus, it was shown that relationships (1.5), (1.6) can be obtained from the variational formulation (1.7), (1.8).

It was demonstrated in the foregoing that the expression $\sigma(X_i, J_k) - \Phi(J_i, J_k)$ has the only extremum point Eq. (1.11) or Eq. (1.12). Since Φ is a homogeneous quadratic positively defined function of fluxes, the obtained point is the maximum point.

Onsager's variational principle was formulated in the space of thermodynamic fluxes. An alternative formulation of this principle in the force space was proposed by Gyarmati [9,10]. His formulation was worded as follows: if values of thermodynamic fluxes J_i are assigned, actual irreversible forces X_i maximize the expression $\sigma(X_i, J_i) - Y(X_i, X_k)$,

i.e.

$$\delta_X[\sigma(X_i, J_i) - Y(X_i, X_k)]_J = 0, \tag{1.13}$$

$$Y(X_i, X_k) = \frac{1}{2} \sum_{i,k} L_{ik} X_i X_k, \tag{1.14}$$

where $Y(X_i, X_k) > 0$ is the dissipative function in the force representation.

Since entropy production is a symmetric bilinear form, then, as Gyarmati demonstrated, the formulations (1.7), (1.8) and (1.13), (1.14) are equivalent.

Let us turn to Prigogine's principle (theorem) (or the minimum entropy production principle), which is formulated as follows [8].

Let Eqs. (1.5) and (1.6) be fulfilled in a system, irreversible forces $X_i(i = 1, \ldots, j; \ j < n, n$ being the number of forces in the system) are kept constant, and entropy production in the system is a minimum. In this case, fluxes having the numbers $i = j + 1, \ldots, n$, which are conjugate to unfixed forces, disappear.

This principle can be proved rather easily [8]. It is necessary to substitute the expressions (1.5) and (1.6) into Eq. (1.4) and differentiate it with respect to unfixed forces. The obtained expressions are equal to within constants to fluxes having the numbers $j + 1, \ldots, n$ and, therefore, are zero, because entropy production is a minimum under the theorem condition.

The corollary of this statement is that Prigogine's system is stationary.

A slightly different formulation of Prigogine's principle is frequently considered and proved [6,10]. It states that in the stationary nonequilibrium state, which is consistent with external restrictions (constant irreversible forces X_i, where $i = 1, \ldots, j; \ j < n, n$ being the number of forces in the system), entropy production in the system is a minimum if Eqs. (1.5) and (1.6) are fulfilled.

It is seen from the above reasoning that Prigogine's theorem is a simple corollary of Onsager–Gyarmati's principle, because this principle is used to deduce the relationships (1.11) and (1.12). Prigogine's result is obtained from these relationships using additional restrictions.

It should be noted that other variational formulations of linear nonequilibrium thermodynamics are available (see, for example, [6,10,11]), which are equivalent to some extent to the aforementioned formulations.

The apparatus of linear nonequilibrium thermodynamics is used extensively for the following reasons:

(1) The relationship (1.5) allow solving a system of equations for the transfer of mass, momentum and energy, because in this case the number of equations is equal to the number of unknowns.

(2) It is possible to describe cross-coupling fluxes (by means of off-diagonal coefficients L_{ik}) of chemical, electrical and other kinetic processes, which are characteristic of a wide range of physical, chemical and biological systems.

(3) Additional information about values of kinetic coefficients can be obtained using, for example, the circumstance that entropy production is a positively defined quadratic form, or reciprocal relation (1.6).

(4) Quantities (for example, entropy production), which have extremum values in the nonequilibrium state, also provide additional information about a system.

Thus, linear nonequilibrium thermodynamics is very useful within its applications. It should be noted that linear nonequilibrium thermodynamics described the majority of engineering problems encountered in the first half of the 20th century and, therefore, the progress and the popularization of nonlinear equilibrium thermodynamics were very slow and were viewed by many researchers as a theoretical whim. As it is known, for a system to be described in terms of linear nonequilibrium thermodynamics, thermodynamic forces should be small. However, sometimes this condition proves to be too rough, specifically, with respect to chemical reactions. As a result, linear nonequilibrium thermodynamics cannot explain and describe many, and often principal, problems encountered today. They include self-organization, oscillation processes, etc.

The possible generalization of Onsager's thermodynamics (linear thermodynamics) to a nonlinear case using the maximum entropy production principle will be discussed in the section below.

1.2. Critical review and development of Ziegler's approach

1.2.1. Formulation of Ziegler's principle

Let us work in the flux space $\{J_k\}$ and assume that we know the form of expression (1.4) for entropy production in this space. Our main task is to find X_k as a function of $\{J_k\}$. A local equilibrium is assumed for the system.
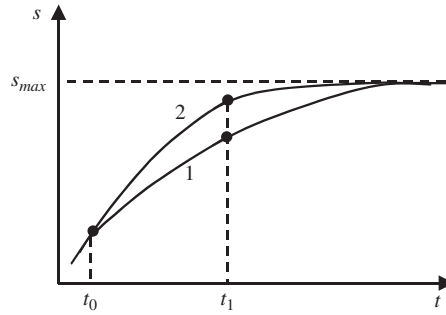
Fig. 1.1. Variation of entropy s with time t for two possible trajectories of the development (two thermodynamic fluxes at a preset force are possible).

In this case, expression (1.4) transforms to

$$\sigma(J_i) = \sum_k X_k(J_i) J_k. \tag{1.15}$$

To find $X_k(J_k)$ in the explicit form, Ziegler [1,12–15] proposed the maximum entropy production principle:

If irreversible force X_i is prescribed, the actual flux J_i, which satisfies the condition $\sigma(J_i) = \sum_i X_i J_i$, maximizes the entropy production (1.15).

A similar principle originally appeared and was widely used in the theory of plasticity where it is called the principle of the maximum dissipation rate of mechanical energy or Mises's principle [12,16,17]. The wording of this principle is that the dissipation rate of mechanical energy in a unit volume during plastic deformation is a maximum in a truly stressed state among all stressed states allowed by the given condition of plasticity (the deformation rate is assumed to be constant) [17]. Ziegler essentially extended this principle of the theory of plasticity to all nonequilibrium thermodynamics [1,13].

In isolated systems $ds/dt = \sigma$ and the maximum entropy production principle reflects the fact that an isolated system tends to the state with maximum entropy along the shortest possible path (by the fastest means). Fig. 1.1 gives an example illustrating the possible behavior of a system.

The maximum entropy production principle can be presented mathematically as

$$\delta_J \left[\sigma(J_k) - \mu \left(\sigma(J_k) - \sum_i X_i J_i \right) \right]_X = 0, \tag{1.16}$$

where μ is a Lagrangean multiplier. It was already mentioned in the foregoing that the subscripts may denote either different thermodynamic forces (fluxes) or their spatial components.

This principle can be also formulated in the force space when entropy production depends only on X_k and fluxes are prescribed, i.e. analogs of expressions (1.15), (1.16) are written simply substituting J for X.

Expression (1.16) is interpreted geometrically as described below. Entropy production in the flux space represents some surface $\sigma(J_k)$. This surface is intersected by the plane $\sum_i X_i J_i$ and fluxes, which maximize $\sigma(J_k)$, are chosen on their intersection line. The simplest form of entropy production is shown in Fig. 1.2 for two thermodynamic fluxes.

Using the formulated principle, we find the explicit expression for the thermodynamic force. For this purpose, transform Eq. (1.16):

$$\begin{cases} \dfrac{\partial}{\partial J_i} \left[\sigma(J_k) - \mu \left(\sigma(J_k) - \sum_i X_i J_i \right) \right]_{X,\mu} = 0, \\[4mm] \dfrac{\partial}{\partial \mu} \left[\sigma(J_k) - \mu \left(\sigma(J_k) - \sum_i X_i J_i \right) \right]_{X,J} = 0. \end{cases} \tag{1.17}$$
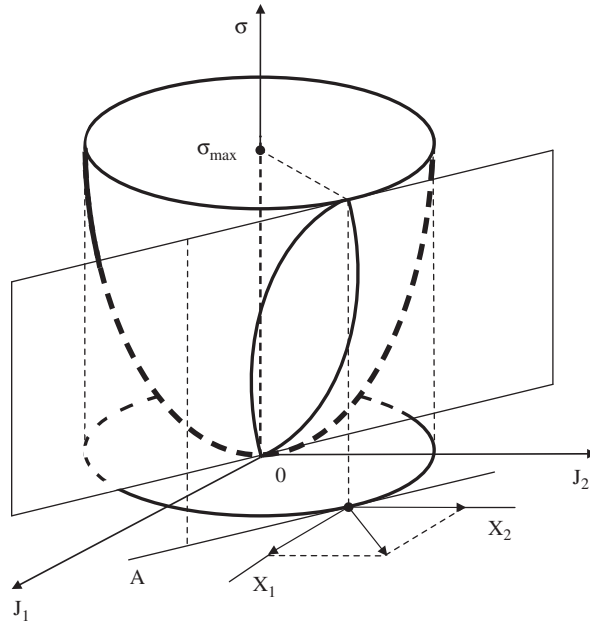
Fig. 1.2. Simplest dissipative surface σ during a linear irreversible process. Here J_1 and J_2 are two thermodynamic fluxes and 0 denotes the point corresponding to the equilibrium state.

Since forces are assumed to be assigned, Eq. (1.17) may be written in the form

$$\begin{cases} \dfrac{\partial \sigma(J_k)}{\partial J_i} - \mu \left(\dfrac{\partial \sigma(J_k)}{\partial J_i} - X_i \right) = 0, \\ \sigma(J_i) = \sum\limits_i X_i J_i. \end{cases} \tag{1.18}$$

Let us denote $\lambda = (\mu - 1)/\mu$ and rearrange the first expression in Eq. (1.18) as

$$X_i = \lambda \partial \sigma / \partial J_i, \tag{1.19}$$

where the proportionality coefficient λ is obtained using the second expression in Eq. (1.18):

$$\lambda = \sigma \left(\sum_i \frac{\partial \sigma}{\partial J_i} J_i \right)^{-1}. \tag{1.20}$$

Expressions (1.19) and (1.20) are known as orthogonality conditions, because their geometrical meaning is that the thermodynamic force X_i, which corresponds to the flux J_i, is orthogonal to the surface $\sigma(J_k) = $ const (the line A in Fig. 1.2). The analog of the orthogonality condition in the theory of the plasticity is called the associated law [17].

The relationship between fluxes and forces, which is given by Eqs. (1.19) and (1.20), is not unique. In a particular case, when Eqs. (1.19) and (1.20) have a unique solution (only one vector $\boldsymbol{J}$ corresponds to a preset vector $\boldsymbol{X}$), the orthogonality condition determines only one extremum point. One can prove that this point corresponds to the maximum of entropy production [1,13]. However, this is clear from geometrical considerations[4] too ($\sigma > 0$ and, if one takes into account the imposed restrictions, entropy production cannot be infinitely large; it is reasonable to expect therefore that the only extremum point corresponds just to the maximum). In this particular case, the maximum entropy production principle and the orthogonality condition are equivalent. In the general case, the orthogonality condition obviously determines all extremum points in the corresponding area of the surface $\sigma(J_k)$, whereas the variational principle selects the point, at which the entropy production has the largest value.

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[4] See, for example, Fig. 1.2.

Although the maximum entropy production principle has been postulated, we shall adduce some arguments for its substantiation.

1.2.2. Some arguments for substantiation of Ziegler's principle

Let entropy production be in the mathematical sense a sufficiently good function of fluxes Eq. (1.15). We shall expand it into a series and restrict ourselves to linear expansion terms:[5]

$$\delta\sigma = \sum_i \frac{\partial\sigma}{\partial J_i}\delta J_i.$$

On the other hand, if thermodynamic forces are assumed to be unchanged during variation, then, according to Eq. (1.4), the change of entropy production can be written as

$$\delta\sigma = \sum_i X_i\delta J_i.$$

In accordance with the last two expressions, forces can be defined as

$$X_i = \lambda\partial\sigma/\partial J_i,$$

where the constant λ can be determined, as before, using Eq. (1.4).

The orthogonality condition can be substantiated more rigorously for a narrower class of functions determining entropy production. Let entropy production $\sigma(J_i)$ be a homogeneous function of degree r. Then, according to Euler's theorem (see, for example, [18]), the expression

$$r\sigma = \sum_i \frac{\partial\sigma}{\partial J_i}J_i$$

or

$$\sigma = \frac{1}{r}\sum_i \frac{\partial\sigma}{\partial J_i}J_i \qquad (1.21)$$

holds.

From the comparison of the last expression and $\sigma(J_i) = \sum_i X_i J_i$ it is reasonable and the simplest to take (define) thermodynamic forces in the form[6]

$$X_i = \frac{1}{r}\frac{\partial\sigma}{\partial J_i}. \qquad (1.22)$$

It is seen that Eqs. (1.21) and (1.22) coincide with Eqs. (1.19) and (1.20), but it should be noted that in this case λ is equal to constant $1/r$.

Let us demonstrate the transition from the orthogonality condition (1.22) to the variational principle (1.16). For this purpose, we shall rearrange the last expression to the form

$$\frac{\partial}{\partial J_i}\left[r\sum_i X_i J_i - \sigma(J_k)\right]_{X,r} = 0. \qquad (1.23)$$

Let $r = \mu/(\mu-1)$, where μ is some number. Then Eqs. (1.23) and (1.4) can be written as

$$\begin{cases} \dfrac{\partial}{\partial J_i}\left[\sigma(J_k) - \mu\left(\sigma(J_k) - \sum_i X_i J_i\right)\right]_{X,\mu} = 0, \\[3mm] \dfrac{\partial}{\partial\mu}\left[\sigma(J_k) - \mu\left(\sigma(J_k) - \sum_i X_i J_i\right)\right]_{X,J} = 0. \end{cases} \qquad (1.24)$$

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[5] This is possible if the described nonequilibrium system is not too far from equilibrium.

[6] In nonequilibrium thermodynamics, the choice of thermodynamic forces and fluxes is not unique (for details see Section 1.2.5).

Expression (1.24) obviously coincides with Eq. (1.16), i.e. the variational principle can be deduced from the orthogonality condition.

Let us consider the simplest type of entropy production as a homogeneous function of degree 2:

$$\sigma = \sum_{i,k} R_{ik} J_i J_k. \tag{1.25}$$

It was shown in the foregoing (see Eqs. (1.8), (1.9)) that the tensor in σ is symmetric, $R_{ik} = R_{ki}$. Using the orthogonality relationship (1.22), we shall obtain the expression for forces,

$$X_k = \frac{1}{2} \sum_i (R_{ik} + R_{ki}) J_i = \sum_i R_{ki} J_i. \tag{1.26}$$

Thus, Eq. (1.26) coincides with Eq. (1.11), i.e. entropy production of the form Eq. (1.25) corresponds, in accordance with Ziegler's principle, to the case of Onsager's linear thermodynamics Eqs. (1.5), (1.6).

So, main relationships of linear nonequilibrium thermodynamics can be deduced from Ziegler's principle if σ is selected as a homogeneous function of degree 2.

Let us note a remarkable feature. In the case at hand, entropy production is a homogeneous function and, as it was demonstrated in the foregoing, the orthogonality condition can be proved rigorously enough using properties of homogeneous functions (rather than deduced from Ziegler's postulate). Since Eq. (1.26) defines a unique set of thermodynamic fluxes, the orthogonality condition and the maximum entropy production principle are equivalent. We have demonstrated therefore that if forces are prescribed, the entropy production is always maximized in a system with nonequilibrium processes described by linear nonequilibrium thermodynamics.

It should be specially emphasized in conclusion that the rigorous substantiation of Ziegler's principle using relatively simple intuitive assumptions and just in terms of thermodynamic representations seems to us very difficult or impossible.

1.2.3. Deduction of Onsager's principle from Ziegler's principle

Let us demonstrate that Onsager's principle can be obtained from Zirgler's principle in the linear case. It was shown in the foregoing that in this case entropy production is a quadratic function of fluxes (Eq. (1.25)). Substituting Eq. (1.25) into Eq. (1.17), rearrange Ziegler's principle to the form

$$\begin{cases} \dfrac{\partial}{\partial J_i} \left[\sum_{i,k} R_{ik} J_i J_k - \mu \left(\sum_{i,k} R_{ik} J_i J_k - \sum_i X_i J_i \right) \right]_{X,\mu} = 0, \\ \sum_{i,k} R_{ik} J_i J_k = \sum_i X_i J_i. \end{cases} \tag{1.27}$$

The first relationship (1.27) gives

$$X_i = \frac{2(\mu - 1)}{\mu} \sum_k R_{ik} J_k. \tag{1.28}$$

Substituting Eq. (1.28) into the second relationship (1.27), we have $2(\mu - 1)/\mu = 1$, i.e. $\mu = 2$. Therefore, Eq. (1.27) can be written as

$$\delta_J \left[\sum_{i,k} R_{ik} J_i J_k - 2 \left(\sum_{i,k} R_{ik} J_i J_k - \sum_i X_i J_i \right) \right]_X = 0. \tag{1.29}$$

Collecting terms and considering Eq. (1.4), recast Eq. (1.29) as

$$\delta_J \left[\sigma(X_i, J_k) - \frac{1}{2} \sum_{i,k} R_{ik} J_i J_k \right]_X = 0. \tag{1.30}$$

Here the second term coincides with the dissipative function in the flux representation (Eq. (1.8)):

$$\delta_J [\sigma(X_i, J_k) - \Phi(J_i, J_k)]_X = 0. \tag{1.31}$$

Thus, Onsager's variational principle can be obtained from Ziegler's principle.

1.2.4. MEPP and the second law of thermodynamics

The relationship between MEPP and the second law of thermodynamics, which is supplemented with statistical arguments due to Boltzmann and Gibbs, has been already mentioned in the Introduction. We shall only consider if the second law can be deduced from MEPP. In doing so, we shall use exclusively the thermodynamic interpretation of the entropy and its production.

The second law of thermodynamics was used to prove that entropy production, which was determined from orthogonality conditions, was not a minimum, but a maximum (Section 1.2.1). However, if the maximum entropy production principle is postulated ab initio, the second law of thermodynamics can be obtained as a corollary.

We shall assume in line with [13] that entropy production is convex as a function of fluxes and the maximum principle must provide the biunique correspondence between fluxes and forces. The geometrical interpretation of the principle (see Section 1.2.1 and Fig. 1.2) will be used. Since entropy production is a convex function and tends to zero as fluxes tend to zero, all the surface $\sigma(J_i)$ will be located above or below the plane $\sigma(J_i) = 0$, i.e. the sign of $\sigma(J_i)$ is fixed. Let us assume that $\sigma(J_i) \leqslant 0$. If forces have arbitrary values, the line of intersection between the surface $\sigma(J_i)$ and the plane $\sum_i X_i J_i$ will be located in the negative region and the entropy production maximum corresponding to this line will be zero. However, the unique correspondence between fluxes and forces is disturbed at this point (a zero flux corresponds to any force). Thus, the assumption on the negative value of entropy production leads to contradiction. It is proved therefore that $\sigma(J_i) > 0$.

It is remarkable that even if convexity and uniqueness, which were used by Ziegler, are not assumed, the second law of thermodynamics can be obtained as a corollary of MEPP. Indeed, let the entropy production in some imaginary system take the negative values at some preset force. Then, on the strength of the postulated principle, the physically realizable flux will be such that entropy production is the largest, i.e. entropy production in the system will be equal to a maximum positive value out of those possible. If it is assumed that the system cannot find any flux satisfying the preset force such that entropy production is greater than zero, then in any case the system has the variant to take the flux equal to zero, since this value is a maximum in this extravagant example. Therefore, from the maximum entropy production principle it follows that physically realizable states with negative entropy production are impossible whatsoever.

1.2.5. On the possible "paradox" of the use of the variational approach

Some type of entropy production is postulated in the variational construction of nonequilibrium thermodynamics. However, fluxes and forces are chosen arbitrarily to a certain extent. We shall illustrate this arbitrariness for the case when two forces X_1 and X_2, which are known functions of fluxes J_1 and J_2, are present in a system.

By the definition (Eq. (1.15)), entropy production in this system is written as

$$\sigma(J_1, J_2) = X_1(J_1, J_2)J_1 + X_2(J_1, J_2)J_2. \tag{1.32}$$

Let us determine the forces using the orthogonality condition (1.19), (1.20) and designate them as X_1^* and X_2^*:

$$X_k^* = \lambda \partial\sigma/\partial J_k; \quad k = 1, 2. \tag{1.33}$$

$$\lambda = \sigma \left(\sum_{k=1}^{2} \frac{\partial\sigma}{\partial J_k} J_k \right)^{-1}. \tag{1.34}$$

Rearranging Eqs. (1.33), (1.34) and taking into account Eq. (1.32), we have correspondingly

$$X_1^* = X_1 + \Delta/J_1, \tag{1.35}$$

$$X_2^* = X_2 - \Delta/J_2, \tag{1.36}$$

$$\Delta = -\frac{\lambda J_1 J_2}{\sigma} \left(X_1 J_1 \frac{\partial X_1}{\partial J_2} - X_2 J_2 \frac{\partial X_2}{\partial J_1} + X_1 J_2 \frac{\partial X_2}{\partial J_2} - X_2 J_1 \frac{\partial X_1}{\partial J_1} \right). \tag{1.37}$$

The forces X_1 and X_2 in expression (1.32) and the forces X_1^* and X_2^*, which are determined from the orthogonality condition, differ by Δ (the discrepancy) divided by the corresponding flux. It is seen that both sets of forces satisfy the entropy production (1.32).

If the discrepancy is equated to zero, it is possible to determine the condition when the set of forces is uniquely determined by known entropy production:

$$X_2(J_1, J_2)\frac{\partial\sigma(J_1, J_2)}{\partial J_1} = X_1(J_1, J_2)\frac{\partial\sigma(J_1, J_2)}{\partial J_2}. \tag{1.38}$$

Eq. (1.38) defines the class of entropy production functions when forces, which are determined using Eq. (1.32) and orthogonality conditions, coincide. The search for and analysis of these functions represent a separate very interesting problem. We shall only note that for the quadratic function of entropy production (1.25) condition (1.38) is fulfilled if Onsager's reciprocity relations hold.

This feature was also noted in [19]. The conclusion, which is drawn herein, is not a drawback or even a refutation of Ziegler's approach. It is rather a specific feature of all nonequilibrium thermodynamics, which ab initio is based on the equation of balance of entropy, energy, momentum and matter, and also on the first two laws of thermodynamics.

1.2.6. The relation of Ziegler's maximum entropy production principle and Prigogine's minimum entropy production principle

If one casts a glance at the heading, he may think that the two principles are absolutely contradictory. This is not the case. It follows from the above discussion that both linear and nonlinear thermodynamics can be constructed deductively using Ziegler's principle. This principle yields, as a particular case (Section 1.2.3), Onsager's variational principle, which holds only for linear nonequilibrium thermodynamics. Prigogine's minimum entropy production principle (see Section 1.1) follows already from Onsager–Gyarmati's principle as a particular statement, which is valid for stationary processes in the presence of free forces. Thus, applicability of Prigogine's principle is much narrower than applicability of Ziegler's principle.[7]

These differences can be also explained in terms of a less formalized language. Let us consider a system with known entropy production as a function of fluxes (forces). If thermodynamic forces (fluxes) are assigned, the system will adjust, in accordance with Ziegler's principle, its thermodynamic fluxes (forces) such that entropy production is a maximum. If entropy production is a quadratic function, the relation between fluxes and forces takes the form (1.5) as a result of this adjustment (Section 1.2.2). Further, if the system acquires a stationary weakly nonequilibrium state, but some thermodynamic forces remain free, fluxes, which are formed under Ziegler's principle (relationships (1.5)), will decrease thermodynamic forces and these forces will decrease, in turn, fluxes to a minimum of entropy production. Thus, some hierarchy of the processes is observed. If the time is short, the system maximizes entropy production at preset fixed forces at a given moment. As a result, linear relationships (1.5) are valid. If the time is long, the system changes free thermodynamic forces so as to decrease entropy production.

Let us dwell on one more important issue relevant to this problem. What is the rate at which a nonequilibrium system tends to its final state? As it was discussed in Section 1.2.1 (Fig. 1.1), the maximum entropy production principle suggests that a system tends to its state with maximum entropy at the largest rate. At each moment of time the system chooses its flux at fixed forces such that the change of entropy is the largest and, hence, the tendency to the final state is the fastest. This adjustment of parameters may be continuous or stepwise (at bifurcation points) depending on specific features of the system. In the last case, one force may correspond simultaneously to several fluxes and the flux satisfying the principle is chosen out of these fluxes. This circumstance does not contradict the principle in mathematical terms, because the relation between fluxes and forces is ambiguous in the general case (see Eqs. (1.19), (1.20)). How the choice is made from different states satisfying Eqs. (1.19), (1.20) requires more studies.[8] Notice that the consequence of this ambiguity of fluxes and forces was not considered by Ziegler (who only discussed a biunique case).

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[7] Considering what has been said above, MEPP is applicable to both linear and nonlinear systems. The popular opinion (see, for example, [20]) that Prigogine's principle is valid for linear systems and MEPP holds for nonlinear systems is wrong. Of course, the application of MEPP to nonlinear systems presents the greatest interest.

[8] Studies by Sawada (1981–1984) [3,21–23] present interest in this respect. He independently advanced a hypothesis that the most stable state against perturbation among the possible (metastable) states should correspond to the state of the maximum entropy production. To support his postulate, Sawada reported results of computation of the dissipative structure in charged-fluid layer systems (electroconvection), a nonlinear chemical reaction system (Brusselator), and a growing random pattern. Similar conclusions were drawn by Shimokawa et al. [24], who made calculations using the oceanic general-circulation model. The use of MEPP for selection of the most stable state among several possible states in nonequilibrium processes will be discussed in Section 3.2.

1.3. Brief conclusion

When Ziegler formulated his principle, he aimed mainly at the deductive foundation of nonequilibrium thermodynamics, which would hold in both linear and nonlinear cases. The main idea of his approach was that the nature disposes of its freedom at preset thermodynamic forces and the dissipation law so as to maximize the entropy production. The principal result is that he obtained, as a corollary of the principle, all results, which were known for the linear case, and the second law of thermodynamics.

It should be acknowledged that Ziegler presented his material in a formalized theoretical manner and applications of his principle were exemplified by some problems of the theory of plasticity and chemical kinetics [1,13–15], which could be solved by alternative methods. This factor, imperfect understanding of nonlinear phenomena, and other variational formulations in thermodynamics, which are valid for nonlinear cases (for example, Biot's principle [10,11]), had the result that Ziegler's principle was overlooked and did not receive wide acceptance. However, as compared to other variational formulations of thermodynamics, which are applicable to the nonlinear region, Ziegler's formulation is most evident and simplest in our opinion. This is confirmed by the fact that many researchers intuitively advanced similar statements both before and after Ziegler's publications. However, their formulations were not so complete and general as in studies by Ziegler and represented just statements, which could help solve a specific problem. The principles themselves were formulated proceeding from the common sense and practicability for solution of particular problems, rather than the general logic of formation of nonequilibrium thermodynamics (for more details see Section 3).

The thermodynamic discussion of MEPP raises the question as to how this principle shows itself at the microscopic level. The second section of the present study deals with this question.

2. The MEPP in nonequilibrium statistical physics

In this section we shall consider MEPP from the viewpoint of different directions in modern nonequilibrium statistical physics, such as the kinetic theory of gases, the theory of random processes, the linear response theory, etc.

2.1. MEPP and kinetic theory of gas

The kinetic theory of gases deals with determination of the one-particle velocity distribution function and calculation of all necessary characteristics of a system (kinetic coefficients, fluxes, etc.) using this function. We shall briefly recall this theory foundation.

Let us consider a sufficiently rarefied monatomic gas in a nonequilibrium state, whose properties can be expressed as the one-particle distribution function $f(\boldsymbol{r}, \boldsymbol{c}, t)$, where $\boldsymbol{r}$ is the particle radius-vector, $\boldsymbol{c}$ is the particle velocity vector, and t is the time. The full change of $f(\boldsymbol{r}, \boldsymbol{c}, t)$ with time can be written as [25–28]

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \left(\boldsymbol{c}\frac{\partial f}{\partial \boldsymbol{r}}\right) + \frac{1}{m}\left(\boldsymbol{F}\frac{\partial f}{\partial \boldsymbol{c}}\right) = I(f), \tag{2.1}$$

where $(\boldsymbol{c}\,\partial f/\partial \boldsymbol{r}) + 1/m(\boldsymbol{F}\partial f/\partial \boldsymbol{c})$ is the change of the distribution function, which is caused by collisionless motion of particles in the field of external forces (m being the molecule mass and $\boldsymbol{F}$ the external force acting on molecules); $I(f)$ is the collision integral characterizing the change of the distribution function resulting from collisions of molecules.

If the mean free path of particles is much larger than the effective radius of intermolecular forces, then, on the one hand, only binary collisions may be considered and, on the other hand, the hypothesis of molecular chaos can be used. If it is assumed further that collisions represent instantaneous events occurring at a single point in the space, the collision integral can be written in the form [25–28]

$$I(f) = \int\int\int \left(f'f'_* - ff_*\right) gb\,\mathrm{d}b\,\mathrm{d}\varepsilon\,\mathrm{d}\boldsymbol{c}^*, \tag{2.2}$$

where $f = f(\boldsymbol{r}, \boldsymbol{c}, t)$ and $f_* = f(\boldsymbol{r}, \boldsymbol{c}^*, t)$ are distribution functions of particles having velocities $\boldsymbol{c}$ and $\boldsymbol{c}^*$ before the collision; $f' = f(\boldsymbol{r}, \boldsymbol{c}', t)$ and $f'_* = f(r, \boldsymbol{c}'^*, t)$ are distribution functions of particles having velocities $\boldsymbol{c}'$ and $\boldsymbol{c}'^*$ after the collision (these velocities can be expressed as velocities of particles before the collision in terms of the collision

law); $g = |c - c^*|$ is the relative velocity of colliding molecules. The integration in Eq. (2.2) is taken over the impact parameter b, the azimuth angle ε, and all possible velocities of one of the colliding molecules.

Eq. (2.1) and the collision integral (2.2) are called the Boltzmann equation.

If the gas approaches the locally equilibrium state and the ratio between the mean free path and the characteristic size of the system is small, Eq. (2.2) is often simplified [25–27]. It is assumed that in this case the sought-for distribution function is nearly equal to the Maxwell local equilibrium function f_0:

$$f = f_0(1 + \Phi(c)), \quad |\Phi| \ll 1, \tag{2.3}$$

where

$$f_0 = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mC^2}{2kT}\right)$$

is a locally equilibrium distribution function of particles having the mass m, the temperature $T(r, t)$, the peculiar velocity $C(r, t)$, and the number density $n(r, t)$. The function $\Phi(c)$ should meet the normalization conditions, which follow from the assumption on the local equilibrium. As a result, this function should not contribute to the density, the mean velocity and the temperature:

$$\int f_0\Phi \, dc = \int f_0\Phi C \, dc = \int f_0\Phi\frac{mC^2}{2} \, dc = 0, \tag{2.4}$$

where $C = c - u$, u is the local hydrodynamic velocity.

In this case, using Eqs. (2.3) and (2.4), the collision integral (2.2) can be written in the form [25–27]

$$I(f) = \int \int \int f_0 f_{0*}(\Phi' + \Phi'_* - \Phi - \Phi_*)gb \, db \, d\varepsilon \, dc^* = -\hat{\Omega}\Phi, \tag{2.5}$$

where designations of the functions Φ are similar to those of f above. The integral operator $\hat{\Omega}$ is introduced for compactness of subsequent transformations.

Using Eq. (2.5), it is possible to obtain the following properties of the operator $\hat{\Omega}$ [25–27,29]:

(1) the operator $\hat{\Omega}$ is linear, i.e.

$$\hat{\Omega}(\lambda F + \mu G) = \lambda\hat{\Omega}F + \mu\hat{\Omega}G, \tag{2.6}$$

where λ and μ are some numbers, while F and G are some functions of the same variables as Φ is.

(2) the operator $\hat{\Omega}$ is self-adjoint, i.e. $\int F\hat{\Omega}G \, dc = \int G\hat{\Omega}F \, dc$.

Introducing the so-called integral brackets as $\int F\hat{\Omega}G \, dc \equiv [F, \hat{\Omega}G]$, the reduced property can be recast to the form

$$[F, \hat{\Omega}G] = [G, \hat{\Omega}F]. \tag{2.7}$$

(3) $[G, \hat{\Omega}G] \geqslant 0$. \hfill (2.8)

Eq. (2.1) with the collision integral (2.5) can be written as

$$Z = -\hat{\Omega}\Phi, \tag{2.9}$$

where the symbol Z denotes the left-hand side of the linearized Eq. (2.1).

Multiply the left- and right-hand sides of Eq. (2.9) by Φ and integrate it over c. Then, using the designations introduced above, we can write

$$[\Phi, Z] = -[\Phi, \hat{\Omega}\Phi]. \tag{2.10}$$

Let us prove the following variational principle (see, for example, [25–27,29–33]). Amongst all the functions satisfying the condition (2.10), the function Φ, which maximizes $[\Phi, \hat{\Omega}\Phi]$, is the solution to Eq. (2.9).

Proof. Let there be another function Y, which is not a solution to Eq. (2.9), but satisfies condition (2.10):

$$-[Y, \hat{\Omega}Y] = [Y, Z]. \tag{2.11}$$

Then, considering Eq. (2.8), one can write for the function $\Phi - Y$:

$$[\Phi - Y, \hat{\Omega}(\Phi - Y)] \geqslant 0. \tag{2.12}$$

Since the operator $\hat{\Omega}$ is linear and self-adjoint (Eqs. (2.6), (2.7)), then Eq. (2.12) can be transformed to

$$[\Phi, \hat{\Omega}\Phi] + [Y, \hat{\Omega}Y] - [\Phi, \hat{\Omega}Y] - [Y, \hat{\Omega}\Phi] = [\Phi, \hat{\Omega}\Phi] + [Y, \hat{\Omega}Y] - 2[Y, \hat{\Omega}\Phi] \geqslant 0 \tag{2.13}$$

Using Eqs. (2.9) and (2.11), inequality (2.13) takes the form

$$[\Phi, \hat{\Omega}\Phi] + [Y, \hat{\Omega}Y] + 2[Y, Z] = [\Phi, \hat{\Omega}\Phi] + [Y, \hat{\Omega}Y] - 2[Y, \hat{\Omega}Y] = [\Phi, \hat{\Omega}\Phi] - [Y, \hat{\Omega}Y] \geqslant 0 \tag{2.14}$$

Thus, it is proved that the inequality

$$[\Phi, \hat{\Omega}\Phi] \geqslant [Y, \hat{\Omega}Y] \tag{2.15}$$

holds for any trial function Y, which satisfies condition (2.10).

The proved variational principle is widely used to solve the linearized Boltzmann equation [25–27]. The calculation algorithm is as follows:

1. Introduce a trial function Y constructed of known functions φ_i, which include some number of arbitrary variation parameters a_i:

$$Y = \sum_i a_i \varphi_i. \tag{2.16}$$

Hermite polynomials, etc. are chosen as φ_i. However, associated Legendre polynomials (or Sonine polynomials) are most convenient since they provide the best efficiency from the viewpoint of the algebraic manipulation simplicity [27].

2. Substituting Eq. (2.16) into the functionals $[Y, \hat{\Omega}Y]$ and $[Y, Z]$ and finding the extremum of $[Y, \hat{\Omega}Y]$ subject to condition (2.10), we obtain a_i values.

3. Considering the proved variational principle, the function Y, which is determined by this means, approaches best the true solution of the Boltzmann equation.

The solution of the linearized Boltzmann equation, which was obtained by this method, can be used for calculation of kinetic coefficients by standard methods [25–27].

The variational principle in the above-discussed form represents just some mathematical tool for the approximate solution of the linearized Boltzmann equation. Since this equation can be solved by other methods as well, one may get an impression of the secondary importance and physical insignificance of this principle. But this is not the case [29–31]. Let us multiply Eq. (2.1), which includes the linearized collision integral (2.5), by $-k \cdot \ln f$ and integrate over the whole space of velocities. Then we have

$$\frac{\partial s}{\partial t} + \text{div } j_s = k[\Phi, \hat{\Omega}\Phi], \tag{2.17}$$

where $s = -k \int f \ln f \, d\mathbf{c}$ is the local density of the entropy, $j_s = -k \int \mathbf{c} f \ln f \, d\mathbf{c}$ is the entropy flow density, and k is the Boltzmann constant.

If we use the nomenclature adopted in nonequilibrium thermodynamics, the right side of Eq. (2.17) may be called the density of the local entropy production σ, i.e.

$$\sigma = k[\Phi, \hat{\Omega}\Phi]. \tag{2.18}$$

Thus, the above principle can be worded as follows [26,29–32]: *the velocity distribution function for nonequilibrium gas systems is such that the entropy production density is a maximum at preset gradients of the temperature, the concentration and the mean velocity.*

This principle can be formulated in terms of the thermodynamic formalism when the entropy production $\sigma(J_i)$ equals $\sum_k X_k J_k$ [29–32]. Since the temperature, the concentration, etc. are preset at each point of the system, the

corresponding thermodynamic forces X_k (gradients of the temperature, the concentration, etc.) are known. Therefore, the entropy production (2.18) is maximized at constant forces. Then the thermodynamic formulation of the principle is

$$\delta_{\Phi,\mu}\left\{\sigma(\Phi) + \mu\left(\sigma(\Phi) - \sum_k X_k J_k(\Phi)\right)\right\}_X = 0, \tag{2.19}$$

where the Lagrange multiplier μ is introduced to take into account the additional restriction on the sought-for function Φ in accordance with Eq. (2.10).

It is seen that the mathematical notation of this principle formally is analogous to Ziegler's principle (see the previous chapter), but the variation in Eq. (2.19) actually is not over fluxes J_k, as it is in Ziegler's principle, but over the distribution function.

Let us note one corollary of Eq. (2.19). It is known that if forces are fixed, the entropy production in the linear approximation proves to be only a function of the kinetic coefficients L_{ik}: $\sigma = L_{ik} X_i X_k$. Therefore, by finding the velocity distribution function, which maximizes the entropy production, we actually maximize the kinetic coefficients L_{ik}.

Enskog [32] and Hellund and Uehling [33] were the first to propose and use the variational principle for the solution of the Boltzmann equation. In 1948 Kohler [31] formulated another principle, which is similar to the principle discussed above, but contains slightly different additional conditions, which, in his opinion, are more illustrative from the physical viewpoint. According to his calculations, both principles yielded the same results for the kinetic coefficients. Kohler probably was among those who first used the variational approach for description of the transport of electrons in metals (a study by Sondheimer [34] should be mentioned too). Ziman [30] was the first to give a thermodynamic interpretation of the variational principle and assign it the status of a physical law, rather than just a mathematical method for the solution of the Boltzmann equation. He voiced an idea that Boltzmann's H-theorem represented a kind of a proof (or demonstration) of the second law of thermodynamics. By analogy, the variational theorem under consideration points to some additional rather general statement about the behavior of the entropy production in nonequilibrium systems (the maximum entropy production principle). He also pointed out that similar, but more particular, propositions were made by Rayleigh [35] for mechanical systems and by Jeans [36] for electrical systems.

Today this variational principle is viewed as one of the main efficient methods for solving the Boltzmann equation not only in classical gas systems [25–27], but also for the study of the electron and phonon transport in solids [29–31,37–39].[9] Different generalizations of this principle (beyond the region of linear response, etc.) are available, but they are not used widely since they represent some mathematical structures and are less intuitively understood in physical terms.[10] The discussion of those principles is beyond the scope of the present review.

We conclude this section by emphasizing the following point. The kinetic approach and, specifically, results of analysis of the Boltzmann equation represent the basis for the microscopic argumentation of the second law of thermodynamics. However, as it was shown above, this equation has one more feature, which received little attention. The solution to the Boltzmann equation obeys MEPP—a thermodynamic principle, which was introduced independently in the most complete form by Ziegler. One may expect therefore that MEPP is not just a "freak of mind" of theoreticians, who need it for a generalized formulation of thermodynamics or the variational solution to the Boltzmann equation, but is a regularity inherent in the nature.

2.2. MEPP and general statistical theory of nonequilibrium processes (linear response theory, etc.)

The classical kinetic theory, which is briefly described in the foregoing, proves to be inapplicable to relatively dense systems with a strong interparticle interaction. Therefore, it is necessary to develop a nonequilibrium microscopic theory capable of describing such systems. One of the main tasks of this theory consists in deduction of equations for the transfer of energy, momentum, mass, etc. and calculation of kinetic coefficients for various systems (gases,

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[9] The authors hold to the opinion that the further expansion of applications of this approach (for example, solution of the Boltzmann equation taking into account the gas–surface interaction) is interesting and fruitful [40].

[10] By way of example, the reader is referred to studies by Kikuchi [41] and Blount [42]. The last author also holds to the opinion that the relationship between the entropy production and the variational principle in the solution to the kinetic equation in the general case is not sufficiently close to justify Ziman's interpretation.

liquids, solids) directly from equations of classical and quantum mechanics. Such statistical theory has been developing vigorously starting from the middle of the 20th century (see reviews [43–47]).

Onsager may be reputed as one of the initiators of this general approach. He made the following statement: *the time evolution of the fluctuation of a given physical value in an equilibrium system obeys the same laws on the average as the change of the corresponding macroscopic variable in a nonequilibrium system* [47–51]. The essence of this assumption is that, being in a nonequilibrium state, a system "does not know" how it got to this state: thanks to a fluctuation or an external effect. Therefore, its subsequent response should be the same. As a consequence, relaxation of the nonequilibrium system near the equilibrium and dissipation of fluctuations obey the same laws.

If we assume that fluctuations of a_i dissipate near the equilibrium state by linear laws (in proportion to thermodynamic forces) and fluctuations arising in the system are ergodic, it is possible not only to obtain reciprocity relations, but also express kinetic coefficients L_{ij} as time correlation functions for time variation of the corresponding values $\overset{\bullet}{a}_i$ [48–50]:

$$L_{ij} \sim \int_0^\infty \left\langle \overset{\bullet}{a}_i(t)\, \overset{\bullet}{a}_j(0) \right\rangle \mathrm{d}t, \tag{2.20}$$

where $\langle \cdots \rangle$ means averaging over an equilibrium ensemble of fluctuations having the distribution function $P(\boldsymbol{a})$:

$$P(\boldsymbol{a}) \sim \exp\left(-\frac{\Delta S(\boldsymbol{a})}{k}\right), \tag{2.21}$$

where k is the Boltzmann constant, $\Delta S(\boldsymbol{a}) = S_{\mathrm{eq}} - S$ is the change of entropy during a fluctuation, S_{eq} is entropy of the system in the equilibrium, and $\boldsymbol{a}(a_1, \ldots, a_i, \ldots, a_j \ldots)$ is a set of values characterizing the system.

Formula (2.20) has the following physical meaning: the longer a fluctuation exists (the slower the correlation function decays), the larger the kinetic coefficient is [46].

Let us use Onsager's hypothesis and show how we can obtain the statement about the maximum entropy production when a nonequilibrium isolated system is relaxed to the equilibrium [52].[11] Let a system be in a nonequilibrium state with entropy S_0 at a moment of time t_0. Assume that during the next time interval t (which is much longer than the time between two collisions, but is shorter than the relaxation time) the system can change to one of states with entropies $S_1, \ldots, S_N$ $(S_1 < \cdots < S_N < S_{\mathrm{eq}})$[12] and, since the process is spontaneous, part of S_i will be larger than S_0. In accordance with the ideology of Onsager's approach and formula (2.21), the most probable transition of the system at hand is the transition to the state with S_N. The point is that each of the states $S_1, \ldots, S_N$ may be also viewed as a fluctuation,[13] but the probability of its occurrence is the larger, the closer is entropy of the system to the equilibrium ($S_{\mathrm{eq}} - S_N$ is a minimum). Therefore, $(S_N - S_0)/(t - t_0)$ will have a maximum possible value and, hence, the system will evolve following the principle of maximum entropy production.

The modern theory of nonequilibrium processes is characterized by a variety of approaches, but basic ideas underlying these approaches are similar (see reviews [43–47]). Let us dwell on one of those approaches (the method of nonequilibrium statistical operator), which is widely used currently. In doing so, we shall focus on issues directly related to the topic of the present review. The Liouville equation [43–46], which was deduced for classical systems,[14] is chosen as the basis:

$$\frac{\partial \rho}{\partial t} + \mathrm{i}L\rho = 0, \tag{2.22}$$

where $\rho(q, p, t)$ is the distribution function of many particles, q and p denote the coordinate and the momentum of the system in the $6N$-dimensional phase space, t is the time, i is an imaginary unit, L is the Liouville linear operator, which

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[11] Woo [53] proposed a little different procedure for deduction of MEPP basing on Eq. (2.21). He supposed that the probability of transition from one state to another in an arbitrary (nonlinear) case has a slightly more complicated form than Eq. (2.21). The goal was to substantiate that Onsager's variational principle (see Eqs. (1.7) and (1.8)) can be used in cases when instability and pattern formation can occur. According to Woo, the so-called generalized entropy production is maximized and it is reduced to the ordinary (thermodynamic) entropy production at a linear constitutive relation.

[12] The number of these states and their entropy values are naturally determined by both the initial state and the time interval t.

[13] Rigorously speaking, the validity of this statement requires additional verification.

[14] Only classical systems will be considered below, but the given equations can be easily generalized to quantum systems [43–46].

is defined in terms of the Poisson brackets as

$$iL\varphi = \{\varphi, H\} = \sum_k \left(\frac{\partial \varphi}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial \varphi}{\partial p_k} \frac{\partial H}{\partial q_k} \right), \tag{2.23}$$

where φ is some function and $H = H(q, p, t)$ is the Hamiltonian of the system.

A considerable problem encountered in nonequilibrium statistical mechanics constructed on the basis of Eq. (2.22) is the deduction of time-irreversible transfer equations from the reversible Liouville equation. A detailed discussion of this principal issue is beyond the scope of this review. We shall note only that this is achieved by sacrificing completeness of the description inherent in the distribution function and converting to a more concise description of nonequilibrium states [43–46]. We shall assume therefore that the nonequilibrium macroscopic state is only described by a set of observed values $\langle P_m \rangle^t$ representing averages of the corresponding basis dynamic variables P_m (for example, energy, number of particles and momentum). Further we shall seek for such solutions ρ of Eq. (2.22), which only depend on these observed values. Obviously, values $\langle P_m \rangle^t$ do not uniquely define ρ. Amongst the whole multitude, we shall choose the distribution function, which corresponds to the principle of maximum information entropy (naturally at preset $\langle P_m \rangle^t$).[15] As a result, it is possible to find the so-called quasi-equilibrium distribution function ρ_q in the form

$$\rho_q(t) = \exp\left(-\Phi(t) - \sum_m F_m(t) P_m \right), \tag{2.24}$$

where $\Phi(t)$ is the Massieu–Planck function, which is determined from normalization conditions:

$$\Phi(t) = \ln\left(\int \exp\left\{ -\sum_m F_m(t) P_m \right\} \mathrm{d}\Gamma \right), \tag{2.25}$$

while the Lagrange multipliers $F_m(t)$ are chosen considering the so-called self-consistency condition, according to which true averages of the set of values P_m should be equal to their quasi-equilibrium averages:

$$\langle P_m \rangle^t = \langle P_m \rangle_q^t \equiv \int \rho_q P_m \, \mathrm{d}\Gamma. \tag{2.26}$$

The integration is taken over the whole phase volume and $\mathrm{d}\Gamma = \mathrm{d}q \, \mathrm{d}p / (N! h^{3N})$ (N being the number of particles and h the Planck constant).

Thus, considering Eq. (2.26), averages over the quasi-equilibrium ensemble (Eq. (2.24)) coincide with true values of the observed macroscopic values.

We shall assume further that the equality

$$\rho(t') = \rho_q(t') \tag{2.27}$$

is fulfilled at some initial moment of time t'. Then the formal solution of Eq. (2.22) becomes [44,45]

$$\rho(t) = \mathrm{e}^{-\mathrm{i}(t-t')L} \rho_q(t'). \tag{2.28}$$

Since classical phase trajectories are considerably unstable, the behavior of a macroscopic system over time intervals, which are not too short, should be independent of microscopic details of its initial state. It is necessary therefore to exclude the considerable dependence of Eq. (2.28) on initial conditions. In line with [44,45] we shall assume that the evolution can begin with an equal probability from any state $\rho_q(t')$ over the interval from t_0 to t and the true nonequilibrium distribution $\rho(t)$ is equal to the average taken over initial moments of time t' with respect to the distribution (2.28):

$$\rho(t) = \frac{1}{t - t_0} \int_{t_0}^{t} \mathrm{e}^{-\mathrm{i}(t-t')L} \rho_q(t') \, \mathrm{d}t'. \tag{2.29}$$

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[15] This principle will be discussed in detail in Section 2.3.2. Here we shall only note in advance that the maximum entropy production principle can be directly obtained from the principle of maximum information entropy (see Sections 2.3.3–2.3.4).

It should be noted that $\rho(t)$ enters both sides of Eq. (2.29), because parameters of the quasi-equilibrium distribution on the right are determined from the self-consistency condition (2.26). Expression (2.29) can be rearranged [44,45] to the form

$$\rho(t) = \lim_{\varepsilon \to +0} \varepsilon \int_{-\infty}^{t} e^{-\varepsilon(t-t')} e^{-i(t-t')L} \rho_q(t') \, dt'. \tag{2.30}$$

It is remarkable [44,45] that the pre-limit statistical distribution $\varepsilon \int_{-\infty}^{t} e^{-\varepsilon(t-t')} e^{-i(t-t')L} \rho_q(t') \, dt'$ satisfies the Liouville equation with an infinitely small source on the right, which disturbs the symmetry of Eq. (2.22) relative to the time reversal:

$$\frac{\partial \rho}{\partial t} + iL\rho = -\varepsilon\{\rho(t) - \rho_q(t)\}. \tag{2.31}$$

Although the source tends to zero ($\varepsilon \to 0$), it selects "delayed solutions" of the Liouville equation, which describe the irreversible evolution of a system.

Relations (2.30), (2.31) form the basis of the so-called nonequilibrium statistical operator method, which can help, depending on selection of basic variables, derive kinetic, hydrodynamic or relaxation equations for description of the evolution of a nonequilibrium system on different time scales [43–46]. It should be also emphasized that ideas forming the basis of this approach and the majority of derived equations are much like ideas and results of other existing approaches to the construction of the general theory of nonequilibrium processes using first principles [43–46].

When the equilibrium-disrupting perturbation is sufficiently weak, general equations derived from Eqs. (2.30), (2.31) [43–46] can be simplified if we only find linear corrections to equilibrium values (the so-called linear response theory).[16] Assume that a perturbation (an additional term in the Hamiltonian of an unperturbed system) can be written as:[17]

$$-\sum_j h_j B_j, \tag{2.32}$$

where h_j denotes some stationary (to be selected exclusively for more simplicity) external fields and B_j stands for their conjugate dynamic variables. For example, if a system in a magnetic field is considered, components of the magnetizing force may be taken as h_j and projections of the magnetic moment as B_j. In this case, using Eqs. (2.24)–(2.26) and (2.30), (2.31), it is possible to obtain [45] stationary equations for response parameters of the system F_n to the disturbance (2.32) in the form

$$\psi_m = \sum_n D_{mn} F_n, \tag{2.33}$$

where D_{mn} is the generalized probability of the transition (an analog of the collision integral) and ψ_m is the so-called drift term. Here

$$D_{mn} = \langle P_m; \dot{P}_n \rangle_{i\varepsilon}, \quad \psi_m = \sum_j \langle P_m; \dot{B}_j \rangle_{i\varepsilon} h_j. \tag{2.34}$$

The last expression includes the following designations:

$$\langle A; B \rangle_{i\varepsilon} = \int_0^\infty e^{-\varepsilon t} (A(t), B) \, dt, \quad \varepsilon \to +0; \quad (A, B) = \langle \Delta A \Delta B \rangle_{eq};$$

$$A(t) = e^{itL} A; \quad \Delta A = A - \langle A \rangle_{eq}; \quad \Delta B = B - \langle B \rangle_{eq}; \quad \langle \varphi \rangle_{eq} = \int \varphi \rho_{eq} \, d\Gamma,$$

where ρ_{eq} is the equilibrium distribution function.

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[16] It was shown [43–45] that the Kubo method, which is widely used in the linear response theory, and the method of nonequilibrium statistical operator yield similar expressions for the corresponding nonequilibrium values, but the second method is more convenient for solution of specific problems.

[17] We only deal with so-called mechanical disturbances. However, the approach can be generalized to so-called thermal disturbances [43–45].

The derived Eq. (2.33) can be solved using the variational principle, which is very much like the principle described in Section 2.1 for solving the linearized Boltzmann equation. Indeed, let $\{F'_m\}$ be a trial set of response parameters satisfying the condition (see Eq. (2.33))

$$\sum_m F'_m \psi_m = \sum_{mn} F'_m D_{mn} F_n. \tag{2.35}$$

Then it is possible to formulate and prove the following principle [45]: *response parameters*, *which represent solutions of Eq.* (2.33), *maximize, amongst all functions* $\{F'_m\}$ *obeying the condition* (2.35), *the entropy production of a system.*[19]

This principle considerably generalizes the results under Section 2.1 since the selected fluxes (response parameters) maximize the entropy production at preset forces, but no assumptions are made with respect to the rarefaction of the system. This generalization was first made by Nakano in 1959–1960, who noted not only the maximum entropy production, but also the accompanying maximization of transfer coefficients, which are calculated in terms of the linear response theory [54–56]. A similar generalization of the variational method for solving the Boltzmann equation was performed by Christoph and Röpke [57] too.

Thus, methods of solving some statistical model equations by means of MEPP are described in Sections 2.1, 2.2. Although these results adduce microscopic arguments in favor of the given principle, the reasons for this regularity are still not clear. For example, microscopic reasons for the second law of thermodynamics are instability of the motion in a system with many particles. As a result, the system realizes all possible (a maximum number) microstates with time. A question arises if MEPP is based on a similar logic? In the next section we shall present attempts to answer this question.

2.3. The most probable trajectory of the evolution and the information theory

Since nonequilibrium evolution of a system is too complex and, as a rule, unstable, its microscopic characteristics may be viewed as random variables. The maximum entropy principle is used in statistical physics to find the distribution of these variables in equilibrium. If nonequilibrium processes are described, the knowledge of distributions of random variables at a given moment of time is insufficient, because it is important to know additionally the rate (the probability) at which a system passes from one state to another. One more postulate is needed to determine this quantity. Is it possible to use some analog of the second law of thermodynamics by introducing, similarly to the Boltzmann entropy, some quantity (for example, entropy of the evolution (trajectory probabilities) or entropy production) and determine probabilities of the transition from the maximum of this quantity? We shall dwell on this issue in more detail below.

2.3.1. The method of the most probable path of the evolution

Filyukov and Karpov [58–60] proposed the method of the most probable path of the evolution for description of nonequilibrium stationary systems. This approach is very interesting and is intimately connected with the topic of the present review. The studies by Filyukov and Karpov did not attract attention at their time, but the method, which was proposed and developed by these researchers, has much in common with approaches, which were advanced much later, and evoked great interest (for details see Section 2.3.4).

In what follows we shall describe the essence of their approach. Let us have a nonequilibrium system, in which a stationary flux is established. It is assumed for simplicity that the evolution of the system can be described by the Markovian chain with a discrete time and a finite number of the system states. The symbol $p_{ij}(\tau)$ means the conditional probability of the transition during the time step τ from the state i to the state j and the symbol p_i denotes the stationary probability of the state i. In the case of stationary Markovian chains, these probabilities should satisfy the following

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[18] It holds not only in the classical stationary case under consideration, but also in quantum nonstationary case.

[19] Here it equals $\sum_j \langle \dot{B}_j \rangle^t h_j$ to within the positive constant multiplier.

equalities:

$$\sum_i p_i p_{ij} = p_j, \tag{2.36}$$

$$\sum_j p_{ij} = 1; \quad \sum_i p_i = 1. \tag{2.37}$$

Hinchin [61] demonstrated[20] that sufficiently long trajectories can always be divided into two classes. All trajectories of the first class have equal probabilities P of the form

$$P = \exp(-sH), \tag{2.38}$$

where s is the length of the Markovian chain (the number of steps) and H is the so-called evolution entropy per one step, which is equal to

$$H = -\sum_i \sum_j p_i p_{ij} \ln(p_{ij}). \tag{2.39}$$

The number of these trajectories is $\exp(sH)$. It is known about the second class of trajectories that the sum of probabilities of these trajectories can be made arbitrarily small by selecting a sufficiently large s.

The knowledge of the vector $\{p_i\}$ is insufficient for description of nonequilibrium systems. It is necessary to know the whole matrix of $\{p_{ij}\}$. As is well known, if a system is in the thermodynamic equilibrium, $\{p_i\}$ is found from the maximum of equilibrium entropy of the system. A question arises if there is some function, whose extremum can be used for determination of $\{p_{ij}\}$? The researchers give the affirmative answer and adduce the following arguments.

Let k average values (average energy, average heat flux, etc.) F_l, $l = 1 \cdots k$, are known from measurements. The observed evolution of the system corresponds to some trajectory of the Markovian chain. The performed measurements satisfy equations of the form

$$f_l(\{p_i\}, \{p_{ij}\}) = F_l. \tag{2.40}$$

Let us take another trajectory of the Markovian chain having the same time averages. From the macroscopic viewpoint, these systems are indistinguishable since experimental results (Eq. (2.40)) coincide for the systems. We shall refer to trajectories of this kind as adequate and to other trajectories as inadequate.

Let us select some stochastic matrix, which satisfies Eq. (2.40), but is arbitrary in other respects. This matrix determines the multitude of trajectories, which, as it was mentioned above, are divided into two classes. All trajectories of the first class are almost equiprobable if they are sufficiently long. For these trajectories, the time (trajectory) average coincides with the ensemble average and, since Eq. (2.40) holds for the matrix elements $\{p_{ij}\}$, all trajectories of the first class are adequate. Both adequate and inadequate trajectories are in the second class of trajectories. If we select another stochastic matrix, which also satisfies Eq. (2.40), but has larger H, the number of trajectories of the first class grows and, consequently, the proportion of adequate trajectories increases (part of adequate trajectories pass from the second to the first class). All adequate trajectories are alike for an observer. For them to be equivalent for the process as well, the stochastic matrix should be chosen such that all adequate trajectories fall within the first class. *This is achieved by maximizing Eq.* (2.39) *subject to conditions* (2.40). Of course, this statement is only valid for stationary systems, in which τ is much shorter than the observation time.

Filyukov and Karpov also demonstrated that in the limit equilibrium case the maximum conventional entropy follows from their proposed criterion and determined the explicit form of the stochastic probability matrix in quasi-equilibrium conditions and conditions far from equilibrium for a system connected with two thermostats. It should be noted that these researchers did not discuss directly MEPP in their study and they even did not pose themselves this task. Nevertheless, an intimate connection may be traced between the evolution entropy per one step, which was introduced by them, and the entropy production. This fact makes their study extremely interesting and useful for the topic discussed in the present review.

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[20] Actually, Hinchin generalized and rigorously reproduced in mathematical terms results reported by Shannon [62].

2.3.2. Introduction to Jaynes' method

In what follows we shall present basic ideas for construction of statistical physics on the basis of informational entropy in line with the approach, which was proposed in the most complete form by Jaynes [2,63–67].[21] This approach is widely used currently for MEPP substantiation.

Let $p(x)$ be a distribution function of a multidimensional random variable x. This function is unknown so far and the main task is to determine it using available information about a given system. Assume that we only have information about some average values $\langle A_m \rangle$:

$$\langle A_m \rangle = \int A_m(x) p(x)\, \mathrm{d}x, \quad m = 1, \dots, M. \tag{2.41}$$

Considering the normalization condition, we can also write for the distribution function:

$$\int p(x)\, \mathrm{d}x = 1. \tag{2.42}$$

Obviously, in the general case the conditions (2.41) and (2.42) may be insufficient for determination of $p(x)$. Therefore, according to Jaynes, the most objective (unprejudiced)[23] method consists in determination of the distribution function by maximizing the so-called informational entropy S_I:

$$S_I = -\int p(x) \ln p(x)\, \mathrm{d}x. \tag{2.43}$$

Informational entropy S_I is maximized by a standard method using the additional conditions (2.41) and (2.42) and Lagrange multipliers λ_m. The maximization procedure leads to the following results:

$$p(x) = \frac{1}{Z} \exp\left\{ -\sum_{m=1}^{M} \lambda_m A_m(x) \right\}, \tag{2.44}$$

$$Z = \int \exp\left(-\sum_{m=1}^{M} \lambda_m A_m(x) \right) \mathrm{d}x, \tag{2.45}$$

where the parameters λ_m can be determined from conditions (2.41).

The obtained formulas fully solve the posed task and provide a very easy means of finding distribution functions for microcanonical, canonical and other ensembles[25] when Eq. (2.41) is used as conditions characterizing each of these equilibrium ensembles (see, for example, [45,63]).[26] It is shown also that in the equilibrium case, when random variables x are chosen appropriately, the maximum of informational entropy coincides with the Gibbs entropy and may be equated to the thermodynamic entropy.

Elsasser [68] probably was the first to advance the idea to construct distribution functions using an algorithm, which resembles the one described above. However, the most rigorous, substantiated and complete theory of this method was developed by Jaynes twenty years later (Shannon's studies, which are of principal importance for this formalism, appeared only in 1948 [62,69]). He also demonstrated a profound relation and succession of his approach to both classical studies by Bernoulli, Laplace and other researchers concerning the probability theory and statistics and treatises on physics and information theory (especially those by Gibbs and Shannon) [65,66].

Let us make some comments on this approach.

1. The approach in question is viewed as the simplest and most convenient method for construction of equilibrium statistical (classical and quantum) thermodynamics, which is based essentially on one hypothesis and is devoid of some complexities (the ergodic hypothesis, etc.) [2,45,63–67,70].

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[21] Most of Jaynes' papers can be found at http://bayes.wustl.edu/etj.

[22] For example, the average energy of the system or the number of particles.

[23] This estimate will be free of additional information, which does not follow from available data.

[24] Obviously, the Gibbs entropy is a particular case of informational entropy for classical (quantum) ensembles representing the macroscopic state of a many-particle system.

[25] They may be used to determine other characteristics of a system, which are not known ab initio.

[26] In this case, Eq. (2.45) represents nothing else than an expression for the statistical sum.

2. Although the information theory was primordially constructed using some notions of statistical physics, at present it is possible, according to Jaynes, to take its principles as initial and use them for construction of statistical physics. In this case, the formalism of statistical mechanics proves to be some sequence of actions, which provides the best objective estimate while we know very little about the microworld (this is a statistical method for avoidance of possible errors) [45,70].

3. The Jaynes approach has both its adherents and opponents. The critical analysis of those papers is beyond the scope of this review (the analysis can be partly found in [66,71–73]). We shall mention here just one point [63,73]. If average values[27] are found using the distribution function (2.44), one can make predictions, which allow comparison with experiment. If predictions are vague or do not come true, then the restrictions (2.41) are either insufficient or their selection was partially or completely wrong. This may be due, in the final analysis, to the existence of some new law governing the system under consideration.

4. A considerable virtue of the Jaynes formalism is that it can be extended to nonequilibrium systems.[28] The literature reports various applications of this formalism starting with description of relaxation processes (related to thermodynamics of irreversible processes, Green–Kubo formulas, etc.) [2,65–67,71,74,75] and ending with description of self-organization and nonequilibrium phase transformations [73]. In view of the versatility of the principle of maximum informational entropy, Haken "awarded it the title" of the second law of synergetics.[29]

In line with the objectives of this review, we shall consider two studies [76,77], in which the Jaynes formalism was used to substantiate the maximum entropy production principle.

2.3.3. The variational principle for the most probable state

In 1983 Jones [76] interpreted, in terms of the Jaynes formalism, the relationship between Prigogine's minimum entropy production principle and Kohler's maximum entropy production principle (see Section 2.1). The conclusion drawn by Jones that Prigogine's principle represents a particular case of the maximum entropy production principle is of secondary importance (we considered it in Section 1.2.6). But the relationship between the approaches due to Jaynes and Kohler, which was noted by Jones, presents interest and will be discussed below. From the very start we should make a reservation that this part of the study [76] is very laconic and too short and, therefore, its ambiguous interpretation cannot be excluded. In what follows we shall try to convey the main idea expressed by Jones, as we view it.

Let us determine the external entropy production[30] σ_e using the standard macroscopic method $\sigma_e = \sum_i X_i J_i$ (X_i and J_i being conjugate thermodynamic forces and fluxes). We shall also determine the so-called internal entropy production $\sigma_i(\theta)$, where θ denotes microscopic parameters describing the internal state of a system (for example, the distribution function of molecules in a system). Let X_i be fixed and maintained constant. The system evolves from some initial state Σ_0 to the stationary state with parameters θ^* in a time of the order of the system relaxation time τ. It should be noted also that the internal and external entropy productions should be equal, i.e. $\sigma_i(\theta^*) = \sum_i X_i J_i(\theta^*)$, in any nonequilibrium stationary state. Let us consider now this process in terms of Jaynes' "informational philosophy". Some information is available about a system (values X_i characterizing external conditions, the equality $\sigma_i(\theta^*) = \sum_i X_i J_i(\theta^*)$, and the initial state Σ_0), which is obviously insufficient for unambiguous determination of the stationary state characteristics as the time τ. Therefore, amongst all possible states, including Σ_0, it is most preferable to choose the state having the largest informational entropy (we shall make the least mistake on the basis of the available knowledge). As a result, the system will be in the state with the largest entropy in the time τ or, which is the same, its entropy production will be as large as possible. Jones held to the opinion that from this reasoning it was possible to obtain Kohler's principle without the assumption on the system rarefaction.

Obviously, the arguments adduced by Jones cannot be viewed as rigorous at least for the following reasons. Firstly, the distribution, which maximizes informational entropy, is "true" only if the whole set of restrictions on variable parameters is taken into account. However, the question concerning completeness of the restrictions in passing from the state Σ_0 was not discussed altogether. Secondly, it is not clear why the maximum of usual thermodynamic entropy,

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[27] What is meant here are "new" average values, which are different from Eq. (2.41).

[28] One of these possibilities was shown in Section 2.2.

[29] Most likely, he meant some similitude to the second law of thermodynamics.

[30] The term "external entropy production" is due probably to the fact that σ_e is obtained when one considers the entropy flux through the boundary of the system at hand.

i.e. $\tau\sigma_i(\theta^*)$, follows from the maximum informational entropy. Thirdly, it should be noted that placement of Σ_0 among possible states and selection of the state having the maximum entropy among them is highly questionable (new boundary conditions X_i are imposed on the system), but the exclusion of Σ_0 may have the result that entropy in the state, which is chosen after maximization, is smaller than in Σ_0.

2.3.4. The second derivation of MEPP using Jaynes' method

Twenty years after Jones' paper (Section 2.3.3), Dewar [77] made public one more derivation of the maximum entropy production principle using the Jaynes formalism. Remarkably, his study was published in the same journal as Jones' paper, but, most probably, Dewar was unaware of its existence. Investigations performed by Paltridge in atmosphere physics (for detailed analysis see Section 3.1.1) gave Dewar an impetus to substantiate the maximum entropy production principle. His derivation seems to be more rigorous and mathematically formalized as compared to the approach described in the previous subsection. Let us dwell on it.

Assume we have a nonequilibrium stationary open system (the volume V and the boundary Ω). Let the vectors $d(x, t)$ and $F^n(x, t)$ characterize, respectively, internal macroparameters of the system (for example, the internal energy and the mass) and their fluxes (normal components) across the boundary Ω (x and t being, respectively, a coordinate of the system element at hand and the time). By analogy with the equilibrium case, in which the notion of microstate is used, we shall use the notion "microscopic path", which means the change of the microstate with time. Assume a discrete spectrum of possible paths Γ whose number is limited due to the boundary conditions imposed on the system, conservation laws, etc. In accordance with the procedure proposed by Jaynes, the most probable macroscopic behavior (which is realized by the largest number of microscopic paths) is determined by maximization of informational (path) entropy of the form

$$S_I = -\sum_\Gamma p_\Gamma \ln p_\Gamma, \tag{2.46}$$

where p_Γ is the probability of the microscopic path Γ.

Designate the average value of X over the time interval τ as $\bar{X} = 1/\tau \int_0^\tau X(t)\mathrm{d}t$ and the average in the space of possible microscopic paths as $\langle X \rangle = \sum_\Gamma p_\Gamma X_\Gamma$, where X_Γ is the value X for the path Γ.

In line with [77], Eq. (2.46) is maximized over the time interval from the initial moment (label it as 0) till τ as follows.

Assume that the initial distribution $\langle d(x, 0) \rangle$ and average fluxes across the boundary, $\langle \bar{F}^n \rangle$, over the time interval τ are fixed.[31] Using local conservation laws relating $d(x, t)$ and $F^n(x, t)$, the maximization of Eq. (2.46) yields p_Γ, which in the general case is a function of Lagrange multipliers $\lambda(x)$ (for details see [77]):

$$p_\Gamma = \frac{1}{Z} \exp(A_\Gamma), \tag{2.47}$$

$$Z = \sum_\Gamma \exp(A_\Gamma), \tag{2.48}$$

where A_Γ is the so-called action along the path Γ, which can be transformed to

$$A_\Gamma(\lambda) = \frac{1}{2} \int_V \lambda(d_{\Gamma(0)} + d_{\Gamma(\tau)}) \, \mathrm{d}x + \frac{\tau\sigma_\Gamma}{2}, \tag{2.49}$$

where $d_{\Gamma(0)}$ and $d_{\Gamma(\tau)}$ denote d at the beginning and the end of the trajectory Γ and σ_Γ is τ-averaged function of λ, which, if the local temperature and the chemical potential are introduced, means time-averaged entropy production in the trajectory Γ [77].

The maximization (so far incomplete) allows writing

$$S_{I,\text{max}}(\lambda) = -\sum_\Gamma p_\Gamma \ln p_\Gamma = \ln Z(\lambda) - \langle A(\lambda) \rangle. \tag{2.50}$$

The expressions (2.46) and (2.47) and, also, $\sum_\Gamma p_\Gamma = 1$ were used in the derivation procedure above.

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[31] Since the system under consideration is in the stationary state, these quantities should be sufficient for description of the macroscopic behavior of the system during the whole time τ.

Let us transform the relationship (2.48), for which purpose substitute the sum over all paths from $\exp(A_\Gamma)$ as the product of $W(\langle A \rangle)$ (the number of paths contributing to the calculation of the average $\langle A \rangle$) by $\exp(\langle A \rangle)$.[32] Hence,

$$Z = \sum_\Gamma \exp(A_\Gamma) \approx W \exp(\langle A \rangle). \tag{2.51}$$

Using Eqs. (2.50) and (2.51), we have

$$S_{I,\max}(\lambda) \approx \ln W(\langle A(\lambda) \rangle). \tag{2.52}$$

According to Eq. (2.49), the action A_Γ represents the sum of two parts: reversible A_Γ^{rev} (symmetric relative to the reverse direction of the path Γ) and irreversible A_Γ^{irr} (asymmetric relative to the reverse direction; in this case, $\tau \sigma_\Gamma / 2$ reverses sign). Among all possible trajectories, trajectories with the irreversible action should be considered in calculations of the average A_Γ (because, for example, in the presence of cyclic trajectories, which make the point of the phase space fixed, trajectories with A_Γ^{rev}, if they are taken into account, lead to a considerable error in calculation of the average).[33] Therefore,

$$S_{I,\max}(\lambda) \approx \ln W(\langle A^{\text{irr}}(\lambda) \rangle). \tag{2.53}$$

Then Dewar maximized $S_{I,\max}(\lambda)$ with respect to λ,[34] which, in accordance with Eq. (2.53), was equivalent to the maximization $W(\langle A^{\text{irr}}(\lambda) \rangle)$. Assuming further[35] that $W(\langle A^{\text{irr}}(\lambda) \rangle)$ was an increasing function of A^{irr}, it was inferred that $\langle \sigma(\lambda) \rangle$ was also maximized ($A_\Gamma^{\text{irr}} = \tau \sigma_\Gamma / 2$) [77]. Thus, Dewar demonstrated how the maximum entropy production principle could be obtained from the Jaynes maximization procedure.

The study by Dewar, when he tried to relate the maximum informational entropy of trajectories to MEPP, is undoubtedly useful. However, it cannot be acknowledged as the work, in which this problem was solved. Indeed, as is seen from the foregoing discussion, the derivation procedure due to Dewar cannot be viewed as rigorous.[36] Moreover, the adopted assumptions, especially the last ones, may be taken as additional considerable hypotheses.

2.4. Brief conclusion

The maximum entropy production principle, which was phenomenologically introduced by Ziegler both near and far from equilibrium, has its statistical substantiation only if the deviation from equilibrium is small (linear disturbance). This was done most rigorously for rarefied systems described by the Boltzmann equation. In the literature this approach is generalized to arbitrary condensed systems (e.g., the method of nonequilibrium statistical operator) too. A point of special significance is that mathematical formulations of MEPP nearly coincide both at thermodynamic (Ziegler) and kinetic (Kohler) levels.

A series of studies is available, in which attempts are made to elucidate the microscopic origin of the principle. A hypothesis was advanced that this principle is a generalization of the maximum entropy principle and is connected with maximization of trajectory entropy. However, attempts to derive the principle under discussion are so far unconvincing since they often require introduction of additional hypotheses, which by themselves are less evident than the proved statement.[37]

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[32] Probably, Dewar used an analog of the mean-value theorem for calculation of definite integrals. In this case however, $\langle \exp(A) \rangle$ should be used rather than $\exp(\langle A \rangle)$.

[33] The explanation in parentheses is added by us. No comments are given in the original study.

[34] This corresponds essentially to the variation of $\langle d(x, 0) \rangle$ and $\overline{\langle F^n \rangle}$.

[35] No substantiation was given.

[36] Quite recently Dewar presented a new more rigorous derivation of MEPP also proceeding from the Jaynes formalism and using so-called anti-symmetric constraints [78]. He showed the relation of this principle with the fluctuation theorem and orthogonality conditions (resembling those introduced earlier by Ziegler (see Section 1.2.1)).

[37] In this connection, useful studies were performed by Wang [79,80] and Woo [53] who, independently of the aforementioned researchers, considered MEPP from the viewpoint of the Jaynes formalism and the trajectory entropy.

3. The use of MEPP in different sciences

Some thermodynamic and statistical arguments in favor of MEPP have been adduced above. Basic problems and relatively simple systems are considered in Sections 1 and 2. Obviously, the construction of the general foundation of this principle and the analysis of all its corollaries are far from being complete. However, a lot of papers are available now dealing with the application of this principle to specific complex systems having the physical, chemical or biological origin. Therefore, those papers adduce an independent proof of the general approach considered above. But their analysis is very useful for understanding the possible range of the MEPP validity, that is, its scope and universality. Indeed, it was demonstrated earlier that the principle determines the relation between thermodynamic fluxes and forces in the thermodynamic description and selects the real distribution function of the corresponding values in kinetic terms. It will be shown in this section that at higher organization levels MEPP also removes the ambiguity and selects the correct solution. Therefore, MEPP is used in problems concerned with the hydrodynamic/morphological instability, the choice of the direction of chemical reactions and the biological evolution, etc. Let us dwell on those studies in more detail.

3.1. MEPP in hydrodynamics. Transfer in the atmosphere and oceans

3.1.1. Convective transfer. Paltridge's method

In 1975 Paltridge [81–85] proposed the climatic thermodynamic zone model supplemented with the maximum entropy production principle. He formulated this principle as follows: the Earth—atmosphere system should have such an average annual climate that the thermodynamic dissipation, which is connected with horizontal energy fluxes in the atmosphere and the ocean, is a maximum (or, among the great variety of stable states, the system will choose the one with the maximum entropy production) [82–85]. Let us dwell on this model and the introduced principle in more detail.

The climatic model of the Earth—atmosphere system represents a set of cells. Each cell is characterized by some average parameters determining the atmosphere—ocean: the surface temperature, cloud cover, horizontal energy fluxes across the boundaries in the atmosphere and the ocean, and the total heat (the latent and sensible heat). It is assumed that the system at hand is in the stationary state. Two energy balance equations are written for each cell. The first one is the equation for the complete energy balance in a cell, which depends (a) on meridional fluxes of energy across boundaries of adjacent cells in the atmosphere and the ocean and (b) on the flux of energy arriving from the Sun into the cell and leaving it (to the outer space). The second one is the balance equation for the ocean energy, which depends (a) on meridional fluxes of energy across boundaries of adjacent cells in the ocean, (b) on the flux of energy arriving from the Sun to the ocean surface (taking into account the energy absorption by liquid water in clouds and the water vapor in the atmosphere), and (c) on the flux of energy from the ocean surface (thanks to radiation in accordance with the Stefan–Boltzmann law and evaporated water). Explicit expressions for these fluxes, which depend on some geophysical parameters, are given in the original papers [81,82,84] and are not reproduced here for their awkwardness. Since the written balance equations are insufficient for determination of all characteristics of a cell (the temperature, cloudiness, etc., see above), it was necessary to make some additional assumptions. The main assumption is the requirement that total (in the atmosphere and the ocean) horizontal heat fluxes in each cell are established so as to maximize the entropy production:[38]

$$\sigma = -\sum_i (F_{S,i} - F_{L,i})/T_i^*, \tag{3.1}$$

where $F_{S,i}$ and $F_{L,i}$ denote the energy flux arriving into the ith cell from the Sun and the flux leaving the ith cell and T_i^* is some average temperature in the ith cell [82]. The summation is over all cells. The expression (3.1) follows from the assumption on the stationary state of the system (the total flux of entropy across the boundaries equals entropy produced in the system).

Using this relatively simple model, Paltridge determined global average annual distributions of the temperature, heat fluxes and cloud cover on the Earth, which agreed well with observations [81–84]. Therefore, Paltridge's approach to

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[38] Here σ means, unlike in the rest of the paper, the integral, rather than local, entropy production.

the entropy production maximization has received wide acceptance in studies of the climate on the Earth and other planets of the solar system. References to those studies and their discussion can be found in recent reviews [20,86].[39]

One of the problems facing Paltridge and his followers was the substantiation of the maximum entropy production principle, which was established empirically per se. Studies performed by Malkus and Veronis (1954, 1958) [89,90] and a study by Lorenz [91][40] were initially cited as arguments. Considering data on the convective transfer of heat in a liquid between surfaces having different temperatures (the Rayleigh–Benard convection), it was supposed in the first study that if the Rayleigh number is preset, the regime providing the maximum heat transfer is realized among the multitude of possible stationary regimes of the transfer. Clearly, if a system is stationary (temperatures are fixed at the boundaries), the entropy production is directly proportional to the heat transfer and the relationship between the principles of Paltridge and Malkus and Veronis is obvious [20]. It should be noted however that the attitude to the principle of Malkus and Veronis is different in the literature: either positive or negative [93–96]. As a result, the "grave heritage" of Malkus and Vernis' principle weighed on the maximum entropy production principle. For example, researchers [97] performed a numerical study into specific features of the Rayleigh–Bernard convection and found that structures having a large entropy production (the heat transfer) were more immune to perturbations. However, this was not true at large Rayleigh numbers ($Ra \approx 5 \times 10^4$). Performing numerical calculations of transfer equations in another model, it was found [98] that at $Ra \approx (1.5–2.5) \times 10^5$ lamellar-like harmonic and turbulent-like chaotic flow morphologies coexisted and the latter was more stable and had a smaller entropy production. The same paper reported an experimental proof of the calculation results. The cited examples are enough to doubt the universality of Malkus and Veronis' principle and, hence, MEPP at least for considerably nonequilibrium systems (large Rayleigh numbers). We shall make several comments in defense of the principle under discussion. (1) Calculations of convective turbulent flows, especially developed ones, involve a great variety of computational difficulties, which have not been removed completely so far.[41] Consequently, it is difficult to interpret and analyze results of each of the studies.[42] (2) Criteria of stability and the coexistence of different flows in the presence of perturbations, which are not infinitely small, are sufficiently subjective both in numerical and physical experiments. (3) The heat flux or the entropy production is calculated for the whole volume of the system (the integral value is found) as an average over a considerable interval of time. Referring to the theoretical discussion of MEPP performed in the foregoing (Sections 1 and 2), it is more correct to perform local calculations of the entropy production for individual vortices (or sections thereof) without averaging over considerable time intervals. This is especially important just for strongly nonequilibrium and unsteady-state processes (when the choice of the evolution path[43] depends on both the presence of several states with different entropy productions and the occurrence of a fluctuation at the moment the choice is made). This issue will be discussed in more detail in Section 3.2, which deals with a nonequilibrium growth of crystals.

One more principle, which was noted by Paltridge when he initially introduced MEPP, was formulated by Lorenz for the energy transfer in the atmosphere. According to one of his statements, atmospheric processes have a maximum efficiency, i.e. the efficiency of an atmospheric energy cycle is the largest [91].[44] The relation between the principles due to Lorenz and Paltridge is comprehensively discussed in Ref. [20] and we shall not dwell on this relation herein.[45] It should be noted that there are many statements in geophysics, which are essentially similar to the principle at hand. For example, in 1980 Golitsyn formulated the fastest reaction rule for phenomena, which are described in hydrodynamic terms: the scale of kinetic energy is equal by its order of magnitude to the rate of the energy input to the system multiplied into the least time scale inherent in the system [99,100].

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[39] We shall also mention the studies [87,88], which are not cited in the reviews.

[40] Notice that studies by Malkus and Veronis also influenced investigations by Sawada (see Section 1.2.6) and Woo [92]. The last researcher independently proposed to use the entropy production maximization principle for selection of the real nonequilibrium stationary state from multiple solutions (hydrodynamic pattern formations). Woo surmised that Onsager's variational principle (see Section 1.1) can be used for description of such systems (if a system is linear, the entropy production is obviously a maximum from this principle (see Eqs. (1.7) and (1.8)). Strictly speaking, such an extension involves an assumption, which goes beyond Onsager's principle. The author himself rightly noted this circumstance.

[41] One of such difficulties will be described below in Section 3.1.2.

[42] Calculation details are often covered little in papers.

[43] This choice may be irreversible in the general case.

[44] The atmosphere is viewed as some heat engine, which receives energy from the Sun and performs an analog of work related to kinetic energy of the motion of air and water masses.

[45] These problems are very specific and would lead us far from the main topic of this review, deep into atmosphere physics.
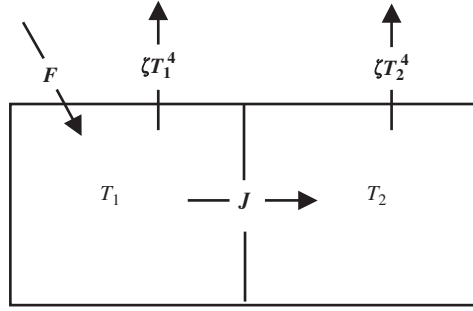
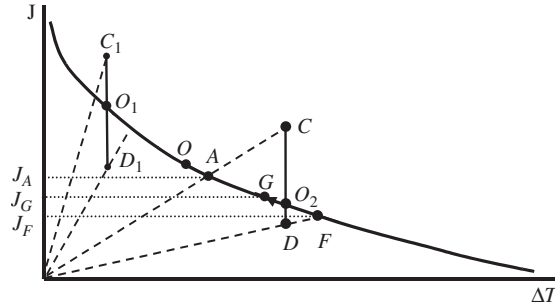Fig. 3.1. Paltridge's idealized model based on two cells [85].

Fig. 3.2. Dissipation of fluctuations by a linear law. The point O is the point of the maximum entropy production. The thick solid line denotes stationary states (Eq. (3.5)). The dashed line marks the fluctuation evolution direction [85]. $J_G = (J_A + J_F)/2$.

The adduced arguments were obviously insufficient to understand that a turbulent system tends to a state with a maximum entropy production. For this reason, Paltridge used the simplest model of the energy transfer in a system of two cells [85] and tried to show why his principle holds. Let us consider this example.

We shall discuss a model (Fig. 3.1) of two cells where T_1 and T_2 are their temperatures, F is the solar energy flux, J is the energy flux from one cell to another, and ζT_1^4 and ζT_2^4 denote heat radiation energy fluxes (ζ being the Stefan–Boltzmann constant).

The change of the heat in each cell can be written as

$$dQ_1 = c_1\, dT_1 \quad \text{and} \quad dQ_2 = c_2\, dT_2. \tag{3.2}$$

If the heat capacity c_i of each cell is assumed to be 1, the energy balance equation is written as

$$dT_1/dt = F - \zeta T_1^4 - J, \tag{3.3}$$

$$dT_2/dt = J - \zeta T_2^4. \tag{3.4}$$

To simplify the further analysis, in accordance with [85] we shall assume that ζ and F are equal to unity. Then for the stationary state it follows from the last equations that $J = 1 - T_1^4$, $J = T_2^4$ and

$$\Delta T = (1 - J)^{1/4} - J^{1/4}, \tag{3.5}$$

where $\Delta T = T_1 - T_2$.

Eq. (3.5) defines the curve of stationary states in variables of the thermodynamic forces ΔT and the flux J (Fig. 3.2). Notice also that the difference of energies coming into and going out of a system of two cells is zero in the stationary state $(1 - T_1^4 - T_2^4 = 0)$.
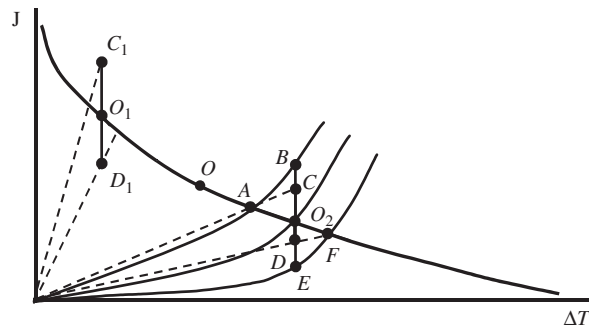
Fig. 3.3. Dissipation of fluctuations by a nonlinear law. O denotes the point corresponding to the maximum entropy production. The thick solid line is the curve of stationary states (Eq. (3.5)). The dashed and thin solid lines show the evolution direction of a fluctuation for linear and nonlinear relationships between fluxes and forces, respectively.

The entropy production in the stationary model at hand can be easily determined using methods of nonequilibrium thermodynamics [8]:

$$\sigma = J \cdot \Delta T / T_1 T_2. \qquad (3.6)$$

According to Paltridge's principle, among an infinite number of possible stationary states (Eq. (3.5)), a system selects the state with the maximum entropy production (the maximum entropy production is achieved at the point O (Fig. 3.2) in accordance with calculations from Eqs. (3.5) and (3.6)). Paltridge explained this situation as follows [85].

Let a system be in some stationary state (for example, at the point O_2, Fig. 3.2) and a fluctuation of the energy flux between cells arise. It is most reasonable to assume that fluctuations both responsible for the increase, CO_2, and the decrease, DO_2, in the energy J are possible. Paltridge supposed that fluctuations dissipate by a linear law (the line AC or DF), leading to a new stationary state (the point A or F). If one considers the behavior of the system over time intervals much larger than the lifetime of one fluctuation, then, on the assumption of the nearly equal number of increasing and decreasing fluctuations, he may conclude that the resulting point (the point G if averaging is taken only over two fluctuations CO_2 and DO_2) shifts to the left towards the point O. According to Paltridge, the shift of the system towards the point O can be explained by different amplitudes of the decreasing and increasing fluctuations. Increasing fluctuations are larger than decreasing ones ($CO_2 > DO_2$) at large temperature gradients and vice versa ($C_1O_1 < D_1O_1$) at small temperature gradients. Few arguments were adduced [85] why the fluctuations should have different amplitudes[46] (if they are equal, the numerical analysis (Eqs. (3.5), (3.6)) demonstrates that the resulting stationary state would shift constantly towards the larger temperature gradient).

In our opinion, it would be more correct to think that the increasing and decreasing fluctuations have equal amplitudes, but dissipate by a nonlinear law (see Fig. 3.3). When the temperature gradient is small (on the left of the point O), the fluxes and the forces are coupled linearly and the fluctuations dissipate by a linear law, as Paltridge supposed. According to numerical calculations, the system moves to the right after averaging, which is described above. When the temperature gradient is large (on the right of the point O), the relationship between the fluxes and the forces is nonlinear in the general case. We shall explain what the result will be. Let the increasing and decreasing fluctuations have an equal amplitude ($BO_2 = EO_2$). After the fluctuations dissipate by a nonlinear law, the system gets to the point A or F, respectively. If the system dissipated by a linear law, as Paltridge proposed, it would get to these points if the initial fluctuations had different amplitudes ($CO_2 > DO_2$). Thus, if Paltridge's supposition about different amplitudes of the fluctuations is replaced by the supposition of their dissipation by a nonlinear law, it is possible to explain the shift of the system to the region of the maximum entropy production.

Obviously, this deduction cannot be viewed as a proof of MEPP. It is rather some very simple model, for which the principle is approximately fulfilled (it is not excluded that by chance). The sampling point O_2 may not tend to O if more plausible models are taken or the coefficients are changed (for example, ζ or F). A too large number of additional assumptions and hypotheses, which are introduced into the model, essentially "fit" it to the required result. Therefore,

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[46] His considerations had not any reliable theoretical basis and mistook the wish for the reality.

it is necessary to deduce the principle, which was empirically revealed from climatic studies, on the basis of general laws of nonequilibrium statistical physics and thermodynamics. Paltridge and his followers understood this well and they met with approval Dewar's statistical substantiation[47] of MEPP, which was only known to them. However the hydrodynamic instability, which is of principal significance in this case, was not taken into account directly in Dewar's paper. In our opinion, the development of Ziegler's method (see Section 1) is more relevant to the substantiation of results obtained by Paltridge. If statistical reasoning matters, of special interest is the series of papers discussed in the next paragraph.[48]

In closing we shall note that one cannot but admire the intuition of Paltridge who used MEPP in climate models and pointed to the relation between this principle and fluctuations in a system (for details see Section 2.2–2.4).

3.1.2. Statistical model of turbulence

From the discussion in Section 3.1.1 it is clear that the study of turbulent flows is very important for atmosphere and ocean physics and represents a very complicated task. One of the problems is that understanding of a developed turbulent flow on some scale requires the knowledge of much smaller scales since a large vortex can break up to a multitude of small vortices. Thus, the choice of the mesh size for numerical calculations imposes constraints on achievable Reynolds numbers. This problem can be avoided by decreasing the mesh scale. However, sufficiently large- scale processes present the greatest practical interest and the use of small-scale meshes leads to consumption of a considerable machine time even for modern computers. For this reason, researchers try to limit calculations to relatively large meshes and, to this end, approximate the effect of small scales by introducing additional hypotheses and coefficients. One of such approaches, which is closely related to the topic of this review, is briefly described below.

Let the velocity (the vorticity) of a turbulent flow has some distribution function for a region Ω at the initial moment of time. This distribution will evolve to some state in a very complicated manner. It is shown (see, for example, [101–105]) that this state can be determined by maximizing the mixing entropy S:

$$S(p_i) = - \int_\Omega \sum_{i=1}^n p_i \ln p_i \, d\boldsymbol{r}, \tag{3.7}$$

where p_i is the probability that the ith value of the velocity (the vorticity) is at the point having the coordinate $\boldsymbol{r}$ in the region Ω.[49]

Of course, the mixing entropy S is maximized taking into account the constraints, which are determined by laws of conservation, boundary and initial conditions, and the standard requirement on the distribution probability: $\sum_i p_i(\boldsymbol{r}) = 1$.

Thus, the transition from the dynamic to statistical description of a continuum is realized in this approach and the formed turbulent structure is viewed as the state with the maximum entropy. Therefore, the obtained structure can be conditionally referred to as an equilibrium structure. This approach is obviously similar to ideas expressed by Jaynes (see Section 2.3) and this similarity was noted by the authors themselves [103,104].

An important point is the description of the system relaxation to the equilibrium state.[50] It is necessary to describe a complicated evolution of flows in the absence of detailed information about small scales, which undoubtedly have a considerable effect. Small-scale fluctuations make the local probability p_i change with the time t according to the diffusion-convection equation of the form [103–107]:

$$\frac{\partial p_i}{\partial t} + \operatorname{div} \boldsymbol{P}_i = 0, \tag{3.8}$$

where $\boldsymbol{P}_i$ is the probability flow density, which depends on the local average transport velocity $\boldsymbol{u}$ (it can be calculated using probabilities p_i [103–107]), the diffusion flow of the ith value of the velocity (the vorticity) J_i, etc. Eq. (3.8) and the explicit expression for $\boldsymbol{P}_i$ can be derived as a corollary of the mass conservation law (in the case of an incompressible fluid, which is defined by the Euler equation, $\boldsymbol{P}_i = p_i \boldsymbol{u} + \boldsymbol{J}_i$ [103,104]).

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[47] This study (for details see Section 2.3.4) was largely influenced by Paltridge's ideas.

[48] A study by Woo [53] is also recommended.

[49] The assumption on the discreteness of the velocity distribution is not of principle significance and the distribution can be viewed as continuous.

[50] Observations (for example, of the motion in the ocean) and experiments demonstrate that this state is sufficiently resistant to perturbations (the wind, etc.)

To obtain a closed set of equations, it is necessary to find the relation between J_i and p_i. It was proposed to use the maximum entropy production principle [51] as this relation (maximization is performed subject to the corresponding dynamic constraints that follow from the laws of conservation and boundary conditions [103,104]). This principle was advanced by the authors as a plausible hypothesis whose corollaries had to be carefully verified. The equation relating J_i and p_i was obtained from the entropy production variation using the Lagrange multiplier. In this case, the flow proves to be linearly dependent on ∇p_i. It should be noted that this relationship followed only from the variational principle and no other hypotheses, including those about the local equilibrium, were introduced. The obtained equations (in combination with equations of a specific model of the transport, which are written for average values)[52] can be used to calculate the time evolution of a turbulent flow. A remarkable feature of these equations is that they take into account the small-scale motion and, simultaneously, satisfy the energy conservation law and other integrals of motion. [53]

The maximum entropy production principle as a useful tool for calculation of turbulent flows was proposed recently by Robert and Sommeria [103]. This hypothesis was primordially verified on the model of a two-dimensional ideal liquid (using the Euler equation)[54] by comparing numerical results, which were obtained in the model, with results of the direct numerical solution of the Navier–Stokes at large Reynolds numbers (and, as a consequence, on meshes with a large spatial resolution) [103,104]). The comparison was in favor of the introduced principle. This approach was developed further in Refs. [105–107] when it was used to analyze various hydrodynamic phenomena, including those in the ocean, and was compared with other calculation models. Notice that the approach at hand is applicable only to the two-dimensional case so far. This is not connected with principal considerations, but is due just to some problems encountered in the choice of constraints during variation [106,107]. A very interesting application and the extension of the aforementioned ideas to the evolution of stellar systems can be found in studies by Chavanis [108–111]. He also used the maximum entropy production principle to derive the generalized Fokker–Planck equation. Chavanis made an interesting remark that although the principle introduced by Robert and Sommeria had practical significance, its drawback was the lack of any theoretical substantiation ("ad hoc nature") [111].

It should be remembered in the future that the principle (R. Robert and J. Sommeria) could be a statistical basis of the Paltridge method, because it explicitly interprets the hydrodynamic instability and has an integral formulation, which helps determine the spatial distribution of system parameters.

There is one more type of the evolution instability of nonequilibrium systems, which is connected with the unstable form of the moving phase boundary. The need of selecting the evolution trajectory again turns researchers to MEPP. This problem will be covered in the next section.

3.2. MEPP in a crystal growth and other solid state transformations

The maximum entropy production principle (or, in a particular case, the principle of the maximum growth rate)[55] has been used for a long time in solid-state physics [112–114]. Zener probably was the first to use it [112,113,115]. When Zener analyzed the pearlite velocity-spacing problem, he supposed that among the great variety of possible spacings satisfying his model, stable pearlite has spacings that maximize its growth rate. Analyzing Zener's results, Kirkaldy [112,113,116,117] noted that the experimental and theoretical results suggested the maximum entropy production principle[56] rather than the principle of the maximum growth rate (in this case, the entropy production should vary by order parameters, which characterize the system at hand, for example, the spacing). Kirkaldy believes that this principle holds for steady-state systems, which are highly degenerate.[57] A wide class of pattern formations in solid materials

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[51] The entropy production is defined as the derivative of the entropy with respect to time: $dS/dt = -\int_\Omega \sum_i \nabla \ln p_i \cdot J_i \, dr$.

[52] To this end, it is necessary to substitute the local velocity as the sum of u and the fluctuating part into these equations.

[53] When the motion of a nonviscous liquid is calculated from the Navier–Stokes equation, one has to introduce the artificial turbulent viscosity to avoid numerical instability. This technique leads to violation of the laws of conservation [103,104].

[54] Structures are often two-dimensional or quasi-two-dimensional in the case of a developed turbulence. Therefore, it is possible to describe them in terms of two-dimensional hydrodynamics. Since the structures are observed at arbitrary large Reynolds numbers, the viscosity may be assumed to be zero as the first approximation.

[55] Indeed, the entropy production during the isothermal–isobaric crystallization is proportional to $v\nabla\mu$, where v is the local growth rate of crystal and $\nabla\mu$ is the chemical potential gradient of the crystallizing component [8,114].

[56] The paper [118] also deserves mentioning where the author state in conclusion: "The assumption that the system chooses to maximize the free energy decrease proved to be useful, and it is felt that such an assumption should be drivable from more basic kinetics assumptions". The relation between this statement and MEPP will be shown in Section 3.4.1.

[57] There is a finite or infinite number of solutions to steady-state differential equations, which satisfy boundary conditions [116].

(eutectoid(is)s, forced velocity cell, etc.) may be referred to these systems. In an effort to eliminate the contradiction[58] between the known Prigogine's principle and results of his studies and studies by other authors, Kirkaldy proposed the so called minimax theorem: the entropy production is a maximum or a minimum (or both) over one or more order parameters. His proof is rather confused and has many unobvious assumptions [113,116]. The relation of the maximum and minimum principles was discussed in the foregoing (see Section 1.2.6) and, therefore, we shall not dwell on this issue here.

Independently of Zener, Temkin [119] proposed to maximize the growth rate of crystals. He examined the problem of a steady growth of a needle-shaped crystal (a dendrite) from a melt. Developing a mathematical model and solving some equations, he found that at preset supercooling the dendrite could have a continuous range of sizes (the tip radii) and the corresponding rates (a dome-shaped dependence of the rate on the dendrite radius was obtained). It followed from the experiment however that the dendrite had quite definite growth rate and size at preset supercooling. Temkin assumed therefore that the most probable radius of the dendrite tip would be such when the dendrite growth rate would be a maximum. The comparison of the obtained results with experimental data on the solidification of tin was in favor of the proposed principle. Independently of Temkin, a little later Bolling and Tiller [120] also studied the dendrite growth from pure and alloy liquids using a slightly different model. To specify the problem completely, they selected the condition of a "maximum velocity". The authors noted that they selected this optimization condition for the following reasons, in addition to the study [115]: (1) it was the only tractable method available, and (2) it provided a reasonable agreement with experimental observations (for pure nickel, tin, ice, KCl and an acetic acid solution). They did not pass over the minimum entropy production principle either and dedicated a section of their study to this principle. The authors found that their solutions did not satisfy the minimum and, therefore, concluded that "either the minimum entropy production was not the proper optimization condition or we neglected an important, but not obvious contribution to the entropy production during the dendritic growth process".[59] The validity of the maximum growth rate principle for the free dendritic growth was called in question after specially staged experiments [121]. The dendrite tip radius and the growth rate during solidification of succinonitrile were measured in those experiments. It was found that the steady growth of the dendrites proceeded at a smaller rate and the dendrites had a larger radius than it was predicted from the maximum growth rate principle. At the same time, theoretical studies [122,123], which included the linear analysis for the morphological stability of a growing paraboloid on the assumption of the isotropic surface tension, gave, on the contrary, a good fit to the experiment. As a result, the last theory [122,123], which was called the marginal stability theory, was opposed to the maximum growth rate principle and, hence, this principle was assumed to beincorrect.[60] New theoretical studies, which pointed to contradictions (the absence of the steady-state solution for a needle-shaped dendrite) arising in the marginal stability theory itself, appeared eight years later. A modernized theory was created by introducing a weak anisotropy of the surface tension (see the reviews [126,127]). The new approach, which is known as the microscopic solvability theory, was also based on the stability analysis. One of its inferences was the statement that the solution with a maximum growth rate was the only stable one amongst the discrete spectrum of stationary needle-shaped solutions.

It might seem that the microscopic solvability theory proved to be the consistent theory, which was capable to explain results of experiments on the steady growth of the needle-shape dendrite. However, the Hele–Shaw anisotropic experiment[61] and calculations using the boundary-layer model revealed a new problem: the dendrite tip split if the anisotropy was weak and supercooling/supersaturation was below some critical value [129–131]. To resolve this

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[58] As was noted in the foregoing (see Section 1.2.6), this contradiction is apparent and principles work in different situations (see also [114]). Naturally, the general formalism of MEPP, which was introduced in Section 1.2, is also applicable to the problem under consideration. For crystallization, e.g., from solution, the thermodynamic force is the concentration gradient (the chemical potential), which may be assumed as preset at each moment, while the crystal surface changes itself. The change of the surface is connected with the flow of matter to this surface. According to MEPP, if supersaturation is fixed, a crystal grows and changes its surface so as to select a flow, which maximizes the entropy production.

[59] Notice also that in some cases (for example, the directional solidification), which filly satisfy conditions for applicability of Prigogine's principle, the minimum entropy production principle is fulfilled and can be used.

[60] In this connection, it is very interesting to compare the first [124] and the next [125] editions of the classical book "Physical Metallurgy" (edited by Cahn et al.). In our opinion, the discrepancy between the theory, which used the maximum principle for selection of a definite solution, and the experiment might suggest, first of all, crudeness of the model [119,120] forming the basis of the theory.

[61] The phenomena, which take place during crystallization and in the Hele–Shaw experiment, are similar mathematically and morphologically. We cannot but mention a study by Ametov (1999) [128], who analyzed the stability of displacement of one liquid (oil) by another (water) in a porous medium (an analog of the Hele–Shaw experiment) and found that the entropy production considerably accelerated when the displacement front became unstable and fractal structures were formed.

contradiction, Ben-Jacob et al. proposed to replace the solvability criterion by a more general criterion: the dynamically selected morphology is the one that grows fastest. In other words, if more than one morphology exists, then the fastest growing morphology is nonlinearly stable and, therefore, observable. Thus, after a 30-year intensive development of the theory of the dendrite growth, researchers again returned to the maximum growth rate principle.

It should be noted that Ben-Jacob and Garik also hypothesized [130] that in the general case the criterion of the morphology selection during crystallization was not the crystal growth rate, but the entropy production. This idea was not overlooked. Let us dwell briefly on some studies. Wang and Ming [132] analyzed the transition between a dendrite and a dense-branching morphology during electrochemical deposition of an aqueous $FeSO_4$ film. Measuring the interfacial growth rate and the mass deposition rate as a function of time for a single branch, they concluded that the selection of the fastest growth rate was a one-dimensional approximation of a more general principle, that is, the largest mass deposition rate. The researchers noted that this principle probably could be generalized by introducing the entropy production. Hutter and Bechhoefer [133] studied the growth morphology during rapid solidification in a liquid crystal (the smectic-to-crystal phase transition). They observed several different solidification modes, each characterized by a distinct morphology and velocity as undercooling changed. According to their measurements, one morphology transition (between the E and F modes) out of five transitions did not follow both the fastest growth rate principle and the largest mass deposition rate principle. Hill's study [134] presents great interest in the context of the topic at hand. The author used literature experimental data concerning a discontinuous change from the ⟨110⟩ to ⟨100⟩ orientations in dendritic forms of NH_4Cl crystallizing from a solution. He analyzed the rate of the main dendrite axis as a function of supersaturation before and after the morphology transition. Using these experimental data, he determined the supersaturation dependence of the entropy production for ⟨110⟩ and ⟨100⟩ dendrites. The point of intersection of these curves was shifted by less than 3% from the observed transition and the direction of the transition was exactly from the structure with a smaller entropy production to the one with a larger entropy production. In view of this remarkable agreement between the MEPP-based theory and relevant experimental results, Hill concluded that the dynamic morphological selection based on the entropy production, rather than energy or entropy calculations. Assuming the principle also worked for many other dissipative systems [134,135], Hill, being in the grip of his method for calculation of the entropy production during a morphological transition [134], believed the principle would not hold for chemical systems with only one force (the affinity).

Let us dwell on one more direction of research [114,136,137]. These studies assume ab initio the validity of MEPP (on the strength of reasoning adduced in Sections 1 and 2, and this section) and consider the relation of existing approaches to the problem of morphology selection, that is, the linear analysis for stability[62] and MEPP calculations. In the majority of cases each of the approaches will give instability points, which differ at least quantitatively if not qualitatively. What is the way out and which point is correct?

The following outlet is proposed. Transitions between different morphologies during nonequilibrium crystallization are often described in the language of the classical theory of phase transitions. This is because the processes are similar. For example, the growth rate of a crystal can change sharply during a morphological transition and this morphological transition is referred to transitions of the first order, etc. (see, e.g. [130]). An important feature of many morphological transitions is that different forms of crystals can be observed over some region near the transition under the same conditions—the so-called coexistence of morphological phases (see references in [114], and also [138,139]). It is well known that a similar situation takes place during classical equilibrium phase transitions when several phases can coexist between the binodal (the line of equilibrium between two phases, which is found from the equality of chemical potentials) and the spinodal (the boundary, beyond which a phase is unstable relative to any infinitely small fluctuations). This is the so-called metastable region. Analytical calculations of some problems of the nonequilibrium free growth of crystals from a solution demonstrated that the critical size of instability, which was determined using MEPP, was always smaller than the size determined from the linear stability theory. This fact and the fundamental character of the notion of the entropy production and MEPP in nonequilibrium thermodynamics led to the conclusion that MEPP allowed determining the binodal of the nonequilibrium morphological transition, while the linear analysis for stability determined the transition spinodal. In this case, MEPP proved to be not an alternative, as it was supposed earlier, but an addition to the traditional theory of perturbations, making its contribution to the solution of the problem of morphological selection. This idea was used for analytical calculation of full morphological diagrams (regions of

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[62] An infinitely small perturbation is applied to the crystal surface and the behavior of this perturbation during the crystal growth is analyzed (whether the perturbation increases or decreases).

stable, metastable and unstable growth) for several problems of free nonequilibrium crystallization from a solution. The results obtained in [114,136,137] are sufficiently interesting, but require independent both numerical and experimental verification.

Now we shall mention some more papers, whose authors analyzed specific problems relating to solids and nearly independently formulated statements, which were actually analogous to MEPP.

Bene [140] presented a model for solid-state silicide nucleation at the interface of a thin metal film and a silicon substrate, starting with the assumption that compound nucleation in these systems was a kinetically controlled process. One of the principal statements of his research sounds as follows: "The Si–metal interface region, which is at a high free-energy state compared to the mixed state, will undergo kinetic transition(s) to structure(s) that maximize the energy degradation rate[63] (locally) after successive small increments of time". Analyzing properties of his system, Bene also concluded that the process was not determined only by the interface growth rate or the free energy of the structures. The kinetic structure is selected as the one with the maximum rate of energy degradation accessible by small fluctuations from the previous structure.

Tu et al. [141] explained the phenomenon of slow amorphization during a constant-temperature and constant-pressure thin-film reaction by a kinetic model emphasizing the rate of transition. He supposed that the reaction was determined by a maximum time-dependent rather than time-independent negative Gibbs free energy change.

Kornienko and Gusak [142] analytically considered different paths of the reactive diffusion in a model ternary system with two quasi-binary intermediate phases and full solubility on one side of the concentration triangle. It was shown that the problem was ambiguous and required an additional criterion for selection. Referring to the study by Tu et al. (see above), they also proposed a criterion including the highest rate of the Gibbs potential change. Later Radchenko [143] took a simpler two-component system and used this principle to calculate the reactive–diffusion path of evolution to the thermodynamic equilibrium.

Lyashenko [144] constructed a model of discontinuous precipitation in supercooled binary polycrystalline alloys at reduced temperatures, resulting from the diffusion-induced grain boundary migration. He determined independently the interlamellar distance, the maximum velocity of the phase transformation front, the concentration jump at this boundary, etc. This was done thanks to a set of equations for (i) the mass transfer in a moving interphase boundary, (ii) the balance of entropy fluxes at the phase transformation front, and (iii) the maximum rate of the free energy release (the maximum entropy production). The theoretical results agreed well with available experimental data. It was noted that the model required minimum thermodynamic information about a binary two-phase system and was free of the assumption [118] on a linear relationship between the change of the energy (the motive force) and the boundary velocity. The form of the dependence could be derived.

Ford and Lee [145] considered the evaporation of materials from a heated substrate into a vacuum. They did not solve directly the Boltzmann equation in numerical terms, but applied a simple parameterization (half-Maxwellian form) of the velocity distribution function of vapor at the surface and then used the conservation of mass, momentum and energy fluxes to characterize the flow. However, the mean velocity of the vapor was undetermined in this approach. As a way out, they proposed to determine this parameter from maximization of the entropy production. It turned out in this case that the generation of vapor, whose speed was nearly equal to the sound velocity, corresponded to the maximum rate of the entropy production. This result can be interpreted doubly. On the one hand, it adduces some additional physical arguments why the evaporation rate into a vacuum approaches the sound velocity (this result was obtained more than once by experimental and other analytical methods as well, but still is not perfectly understood). On the other hand, it may be viewed as evidence in support of MEPP. The result obtained by Ford and Lee is important and interesting for the following reasons. Firstly, Ford and Lee most likely were unaware of studies concerned with the solution of the Boltzmann equation (Section 2.1) and came to MEPP independently. Secondly, unlike most of the aforementioned studies (including those cited in Sections 1 and 2), which assumed the presence of the local equilibrium, their study was the first to deal with a system without the local equilibrium (near the heated substrate boundary).

We conclude this section by making some important notes.

1. The dendrite growth has two well pronounced stages (see, for example, [146,147]). A rapidly growing needle appears first and then branches to different sides nearly at regular intervals and the same angle. This crystalline "tree" grows up in a relatively short time (about several tens of seconds when NH_4Cl crystallizes from an aqueous

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[63] What is meant here is rate at which the Gibbs free energy decreases. It will be shown in Section 3.4.1 that this principle fully corresponds to MEPP.

solution [147]). As soon as a dendrite crystal takes its final shape and removes most of supersaturation/supercooling of the medium, it slowly modifies its shape, minimizing the surface energy (this process lasts for several hours in the aforementioned system [147]). As a result, the crystal turns to a sphere or a regular polyhedron. In some cases however, the second stage is almost absent or is extremely slow (a very high viscosity, all the solvent evaporates, etc.) and the system remains in this, generally, metastable state. Both the first and second stages are directed to the decrease in the thermodynamic potential, which characterizes the system[64] (according to the laws of equilibrium thermodynamics), and progress as fast as possible (according to MEPP). This example is important since it vividly demonstrates that a crystal, while it tends to the equilibrium, develops so that the largest dissipation of energy takes place *at a given moment and in a given local place*. The crystal "does not care" about consequences of this "behavior" from the viewpoint of achievement of the global minimum in the long run. The fact that it will have to get rid of the branches (they will be a hindrance to achievement of the global minimum) is of secondary importance for the growing dendrite at the first stage—the main task is to increase the surface so as to remove the nonequilibrium at the given moment as quickly as possible.

2. It is stated in some papers dedicated to the crystal growth that a crystal is faceted with most slowly growing faces during its stationary growth [148]. This is because a face, which grows most rapidly, degenerates as a result of its growth and, consequently, two adjacent faces, which grow slowly, are left. Of course, this fact does not refute MEPP. A disproof of the principle at hand might be just the reverse—development of most slowly growing faces at the initial stage of the crystal growth in the presence of faces capable of fast growth.

3. The so-called phase field modeling (see, for example, [149,150]) has become very popular recently for numerical calculations of structures, which are obtained during nonequilibrium crystallization. The sharp solid-liquid interface of the classical model is replaced by a diffuse interface through introduction of an auxiliary variable φ (the order parameter or the phase field) indicating the phase. The order parameter varies from 0 in the solid to 1 in the liquid. It changes continuously from 0 to 1 over a thin region of space—the diffuse interface. By writing an equation for the order parameter and solving it numerically, it is possible to describe well (qualitatively and quantitatively) the time variation of the phase boundary during cellular and dendrite growth for different systems (alloys, etc.). One of fundamental problems of this kind of modeling is a strict deduction of dynamic equations for the order parameter. It is customary to take the simplest equation: $\partial \varphi / \partial t = -\gamma \delta F / \delta \varphi$ (where γ is a positive constant and F is a free-energy functional [149,150]). This equation is accepted without proof (as a hypothesis yielding sufficiently plausible results) (see, for example, [150]) or some unsubstantiated arguments are adduced (for example, the assumption on the linear constitution law: $\partial \varphi / \partial t \sim \nabla^2 \varphi$ [149]). Dynamic equations for the order parameter can be deduced as a direct consequence of MEPP by varying the expression for the entropy production with respect to the order parameter at preset constraints.

4. Ideas and methods, which were advanced in the crystal growth theory, are also used in studies of the crack propagation (for example, the phase field model [151,152]). This fact is due to similarity of many problems encountered when one analyzes development of dendrites and cracks (specifically, prediction of instabilities of the tip dynamics, morphology, etc.). Therefore, we cannot but mention the variational principle, which was proposed independently by Fridman and Morozov [153–155] for description of crack development in solids.[65] This principle is worded as follows: a crack propagates in the direction of the largest difference between released and absorbed energies.[66] The released energy is consumed primarily for formation of a crack (the absorption energy) and only after a crack element appears, the excess energy can dissipate as heat. Therefore, considering Fridman and Morozov's principle, one may talk about the maximum value of the dissipation energy and the relationship of the principle to MEPP is obvious. Fridman and Morozov showed that their principle did not contradict some other known theories (specifically, Griffith) and its consequences were confirmed by experimental observations. It should be noted that in an attempt to additionally substantiate their principle, later the authors attracted [154] Prigogine's principle. This was not only incorrect in their case, but also caused unnecessary confusion and the loss of the physical clarity present in their initial interpretation.

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[64] For example, the Gibbs potential if one considers crystallization in isothermal–isobaric conditions.

[65] It is remarkable that one of impetuses to the formulation of this principle was the fact that extremum principles were widely and successfully used in the theory of elasticity and plasticity, whereas the theory of failure did not use these principles. Let us recall that Ziegler (see Section 1.2) also formulated his principle largely under the influence of principles available in the theory of plasticity.

[66] The released energy is supplied either from the loading system or volumes adjacent to the crack. Absorption of the energy is connected with formation of new surfaces, structural changes near the ruptured zone, etc. [153].

Thus, it was shown in this section that MEPP is widely used in studies of various nonequilibrium processes taking place in solids. It should be noted that while in hydrodynamic applications (Section 3.1) this principle is frequently used for selection of a particular regime of the heat or mass transfer, in this case it serves most frequently for determination of morphological and kinetic features of the evolution of phase boundaries.

3.3. MEPP and transfer of electrical charge, radiation, etc.

In what follows we shall consider some interesting applications of MEPP to problems, which earlier were solved on rare occasions by calculating the entropy production.

Županović et al. [156] deduced the Kirchhoff law for an electric circuit using MEPP and not the standard approach, which is described in the general course of physics. It reduces to the following. Let we have an electrical network. Simple loops (meshes) in the network are defined as those having no loop within them. Equivalent electromotive forces (EMFs) and resistances are introduced. An equivalent EMF equals the algebraic sum of EMF's in a simple loop, while an equivalent resistance is the sum of resistances in this loop. Loops and the corresponding currents are numbered by single indices, while double indices are used for equivalent EMF's and for equivalent resistances. Different indices in the double index notation appear when circuit section is common for two loops.

The system of equations, which includes both Kirchhoff's laws, is

$$\sum_j E_{ij} = R_{ii} I_i + \sum_j R_{ij} (I_i - I_j), \tag{3.9}$$

where I_i is the current in the ith loop; R_{ij} and E_{ij} are resistances and electromotive forces respectively. Obviously, $R_{ij} = R_{ji}$ and $E_{ij} = -E_{ji}$.

The temperature T is assumed to be constant. In this case, the entropy production σ of an electric circuit can be written as[67]

$$\sigma = \frac{1}{T} \frac{dQ}{dt}, \tag{3.10}$$

where dQ/dt is the heat release per unit time.

Expand the entropy production into a Taylor series:

$$\sigma = cI^2 + O(I^4). \tag{3.11}$$

The free term vanishes since it corresponds to the entropy production in the equilibrium state. The terms with all odd powers also vanish since the current direction cannot influence the entropy production. The coefficient c is greater than zero ($\sigma > 0$) and it may be assumed to be equal to R/T on the strength of the Joule law and Eq. (3.10).

Relation (3.11) can be generalized to the circuit under discussion, which comprises many loops, as[68]

$$\frac{dQ}{dt} = \sum_i R_{ii} I_i^2 + \frac{1}{2} \sum_j R_{ij} (I_i - I_j)^2. \tag{3.12}$$

On the other hand, the energy released by all sources (EMF) per unit time is

$$\frac{dW}{dt} = \sum_i E_{ii} I_i + \frac{1}{2} \sum_j E_{ij} (I_i - I_j). \tag{3.13}$$

The multiplier 1/2 in these equations takes into account double calculations for internal branches.

In accordance with the first law of thermodynamics,

$$\Psi \equiv \frac{dQ}{dt} - \frac{dW}{dt} = 0. \tag{3.14}$$

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[67] See footnote 38.

[68] In what follows we shall take the heat release per unit time instead of the entropy production for the sake of convenience only. According to Eq. (3.10), the behavior of these functions in the isothermal case is fully identical.

We shall assume further that the electric current is established in the system according to the maximum full entropy production (since T is constant, the maximum entropy production is achieved at the same point as the maximum of the generated heat) if Eq. (3.14) is fulfilled, i.e.[69]

$$\text{Max} \left(\frac{\mathrm{d}Q}{\mathrm{d}t} + \lambda \Psi \right). \tag{3.15}$$

It was shown [156] that expression (3.15) directly yields Eq. (3.9) and this solution satisfies the maximum rather than minimum entropy production.

It is obvious therefore that MEPP is also useful for problems encountered in complicated networks of various kinds of resistances (electric, diffusion, hydrodynamic, etc.) when it is necessary to find a relationship between numerous flows and forces in the presence of external forces. These tasks should not be confused with those when the linear relation between flows and forces is postulated and it is necessary to determine the distribution of a preset external voltage over resistances of a circuit in steady-state conditions. The last task probably can be solved using Prigogine's theorem (see Section 1.1).[70]

Let us mention briefly other papers relating to the topic under consideration. Würfel and Ruppel [159] analyzed steady-state processes in a body absorbing incident radiation of an arbitrary frequency distribution and emitting either temperature or luminescent radiation. The objective of the study was to determine the emitted spectral intensity. Unlike other researchers of this problem, which determined limits of the conversion of incident radiation to luminescent radiation by applying known spectrum intensity distributions, they obtained necessary information from the variation of the entropy production with respect to the chemical potential of electron excitations. It turned out that the behavior of a body in a radiation field was characterized by a maximum of the entropy production. Two important cases were considered. (1) If no constrains are imposed on the emission process, the body is a temperature radiator in accordance with Planck's law. (2) If a constraint is applied exclusively with respect to the number of absorbed and emitted photons, the body becomes a luminescent radiator, which is characterized by a non-zero chemical potential independent of the photon energy. This study is a good example of a possible application of the model proposed by Filyukov and Karpov (Section 2.3.1).

Hayashi and Sato [160] and Sato [161] studied the evolution of a twisting magnetic flux and other structures in a plasma by the magnetohydrodynamic simulation. Analyzing their results, they concluded that when a new structure appeared, the entropy production rate increased anomalously and then minimized after the new structure was formed. Considering results of numerical experiments on self-organization in plasmas and some other systems, the researchers suggested, as the working hypothesis, that the entropy production was maximized during a structural (nonequilibrium) transition. They held to the opinion that this was a sufficiently universal law for open nonequilibrium systems. Their study considerably supplements the results described in Section 3.1 and shows usefulness of MEPP also for analysis of complicated magnetohydrodynamic instabilities in conditions of a strong chaos.

Ivanchenko [162] analyzed the electrodynamic behavior of a periodic array of Josephson junctions. MEPP was applied to find the value of the synchronization parameter (the difference in phase between adjacent junctions). This principle led to appearance of bands inherent to one-dimensional periodicity of the system. The author introduced MEPP by a formal analogy. In his opinion, this principle in a nonequilibrium situation should replace the maximum entropy principle in an equilibrium state.

3.4. MEPP in chemistry and biology

3.4.1. Berthelot and Shahparonov's principles

In chemistry, analyzing a great variety of empirical data, Berthelot formulated the following principle[71] [163–166]: "If several chemical reactions can take place in a system without exposure to an external energy, the reaction, which is accompanied by the release of the largest heat, is realized". An external energy implies heat, electricity, light, etc.

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[69] It is easy to show that this formulation of the principle is readily reduced to the formulation proposed by Ziegler (see Section 1.2).

[70] A sharp criticism of usefulness and correctness of Prigogine's minimum entropy production principle (including problems of the charge transfer) can be found in [2,156–158].

[71] Sometimes it is called the Berthelot–Thomsen principle.

At present this principle is often criticized from the viewpoint that the thermodynamic potential (for example, the Gibbs potential), rather than heat, determines the direction of a chemical reaction. It is commonly accepted that this principle fully lost its significance, representing a particular consequence of the second law of thermodynamics. In our opinion, the Berthelot principle may be viewed as one of the first, even if not quite correct, formulations of MEPP as applied to chemical reactions. It somewhat resembles Malkus and Veronis's principle, which was considered in Section 3.1.1.

First, we shall quote a study by Luginin [166], who was a disciple and a colleague of Berthelot: the second law does not imply that a reaction should be accompanied by a *maximum* release of heat, i.e. if a reaction has several paths, all of which are accompanied by the release of heat, the reaction will inevitably choose the path leading to the maximum release of heat according to the Berthelot principle rather than the second law of thermodynamics.[72]

To understand the relation between the Berthelot principle and the maximum entropy production principle, we shall consider an arbitrary chemical reaction having the chemical affinity A, which takes place under isobaric-isothermal conditions (these conditions are often realized in chemical processes).

Let us use an equation for the affinity expressed as the Gibbs potential ($G = H - TS$), which is known from thermodynamic [8]:

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = -\left(\frac{\partial H}{\partial \xi}\right)_{P,T} + T\left(\frac{\partial S}{\partial \xi}\right)_{P,T}, \tag{3.16}$$

where H is the enthalpy, ξ is the reaction completeness, P is the pressure and T is the temperature.

In the system under consideration the change of the enthalpy per one event of the reaction represents the reaction thermal effect $r_{P,T}$. Therefore, Eq. (3.16) can be written as

$$A = r_{P,T} + T\left(\frac{\partial S}{\partial \xi}\right)_{P,T}. \tag{3.17}$$

If the second term in Eq. (3.17) is disregarded, the entropy production, which is due to the chemical reaction, is written as [8]

$$\sigma = AJ \cong r_{P,T}J, \tag{3.18}$$

where $J = v(1 - \exp(-A/RT))/T$ is the chemical reaction rate, v is the direct reaction rate [8], R is universal gas constant, and $r_{P,T}J$ is the released heat.

It follows from Eq. (3.18) that the entropy production in this approximation is connected with the reaction thermal effect and, therefore, the larger the thermal effect of the reaction, the higher the entropy production. Thus, a relationship between MEPP and Berthelot's formulation is obvious.

Of course, $T(\partial S/\partial \xi)_{P,T}$ turns to zero only at $T = 0$. Experiments demonstrated however that this assumption is often sufficiently accurate even at usual (room) temperatures, especially for chemical reactions between solids and liquids [163]. Therefore this law, which was deduced from a great variety of experimental data, may be viewed as a kind of substantiation of MEPP for chemical processes.[73]

Let us consider one more principle, which was formulated by Shahparonov [167] (see also [168,169]) from the analysis of experimental data on chemical reaction rates, diffusion, etc. By this principle, in a macroscopic nonequilibrium system only processes, which bring the system to a thermodynamic equilibrium most quickly at preset external conditions, occur spontaneously.

The author called this statement "the principle of the maximum rate of irreversible processes". In his opinion, it pretended to the role of a new principle of nonequilibrium thermodynamics. In terms of thermodynamic potentials this principle is written as $dG/dt \to \min$ (at P, $T = $const) or $dF/dt \to \min$ (at $T = $const and the volume ($V$) is constant). Let us show that Shahparonov's principle is identical to MEPP.

It is known that the change of the system entropy equals the difference between the entropy production and the entropy flow across boundaries of the system (see Eq. (1.3)). For simplicity we shall consider an isobaric-isothermal

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[72] Notice that this interpretation is very similar to the one considered in Section 3.2 (especially Bene and Tu).

[73] The analysis of experimental data in cases when the term $T(\partial S/\partial \xi)_{P,T}$ cannot be neglected presents considerable interest for substantiation of MEPP.

system, which only exchanges heat with the environment. In this case,

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sigma + \frac{1}{T}\frac{\mathrm{d}Q}{\mathrm{d}t}. \tag{3.19}$$

Using the first law of thermodynamics (Eq. (1.1)) and assuming the work δW to be equal to $P\,\mathrm{d}V$, rearrange Eq. (3.19) to

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sigma + \frac{1}{T}\left(\frac{\mathrm{d}U}{\mathrm{d}t} + P\frac{\mathrm{d}V}{\mathrm{d}t}\right) \text{ or } \sigma = \frac{\mathrm{d}S}{\mathrm{d}t} - \frac{1}{T}\left(\frac{\mathrm{d}U}{\mathrm{d}t} + P\frac{\mathrm{d}V}{\mathrm{d}t}\right). \tag{3.20}$$

The variation of the Gibbs potential ($G = U - TS + PV$) at $P, T = $ const. can be written as

$$\frac{\mathrm{d}G}{\mathrm{d}t} = -T\frac{\mathrm{d}S}{\mathrm{d}t} + \frac{\mathrm{d}U}{\mathrm{d}t} + P\frac{\mathrm{d}V}{\mathrm{d}t}. \tag{3.21}$$

Then Eq. (3.20) transforms to

$$\sigma = -\frac{1}{T}\frac{\mathrm{d}G}{\mathrm{d}t}. \tag{3.22}$$

Thus, in an isobaric–isothermal system the maximum entropy production corresponds to the minimum time variation of the Gibbs potential. It may be shown similarly that in an isochoric–isothermal system MEPP corresponds to the minimum time variation of the free energy (F).

Shahparonov noted also [167] an interesting consequence of the introduced principle, which consisted in an extremum character of the transfer coefficients.[74]

3.4.2. Laws of biological evolution

Principles similar to MEPP appeared in theoretical biology a long time ago too. In 1922 Lotka made the following proposal [170,171]: evolution proceeds in such direction as to make the total energy flux through the system a maximum compatible with the constraints. One more formulation may be quoted: species, which utilize portions of the flow of available energy most efficiently (all other things being equal) for their growth and existence will increase their population and, therefore, the flow of energy through the system will increase.

Let us explain the relation between the above statement and MEPP. Let us take two biological systems having access to one and the same kind of energy (for example, solar energy). Assume that the first system does not absorb the available energy (for example, fully reflects it), while the second system is capable of absorbing part of the energy Q. Only part of this energy $Q - Q_{\text{diss}}$ (here Q_{diss} is the dissipation energy released as heat as Q transforms to the useful energy) is consumed to maintain vital activities, growth, development, and so on. Since a flow across the boundary is absent altogether in the first system, the biological evolution will progress, according to Lotka, towards systems of the second type. They will increase in number (thanks to $Q - Q_{\text{diss}}$) and, therefore, the energy flow through the system will inevitably rise with time (a kind of a positive feedback is observed). It is reasonable to think that at the first stage, when the available energy is abundant, the development will progress towards the increase in the number of individuals of the second type of species. Individuals, which are capable of absorbing most of the available energy (increasing Q) will have an advantage again. Obviously, Q_{diss} and, hence, the entropy production will increase.[75] Thus, as long as the store of the available energy is not exhausted, the evolution will follow the path of the entropy production maximization.

As soon as all available energy is consumed, relatively fast (stepwise) evolutionary changes will be replaced by relatively slow processes of optimization of the formed structures. These processes will be oriented at reducing the loss due to conversion of Q into the useful energy.[76] Correspondingly, Q_{diss} and, hence, the entropy production will be minimized. The flow through the system will rise again ($Q - Q_{\text{diss}}$) and Lotka's principle holds. One cannot say that MEPP will be violated in these evolutionary processes. In this case, at the forefront will be its particular case, that is, Prigogine's principle of the minimum entropy production (for details see Section 1.2.6).

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[74] This conclusion has something in common with conclusions in Section 2.1.

[75] According to the second law of thermodynamics, the increase in conversion of the available energy Q to the useful work will inevitably lead to the increase in the released heat. It is assumed that efficiency changes little at this stage of evolution of the species.

[76] The situation largely resembles the development of a dendrite crystal, which is described in Section 3.2 (see the first note in the conclusion).

Ideas similar to those of Lotka were expressed more than once later by other researchers either independently or as elaboration of his ideas. The principle of the maximum total rate of a biochemical reaction[77] [172] and the principle of the maximum sum respiration[78] [173] are known in particular. The elaboration and the use of ideas expressed by Lotka can be found, for example, in studies by Odum[79] [174] or the so-called principle of optimizing ascendancy introduced by Ulanowicz [175]. Reviews of similar principles can be found in [86,175–178].

The production of entropy, rather than energy, came into wide use for formulation of development criteria in biology after a study by Prigogine and Wiame [8,179,180]. They supposed that relations of linear nonequilibrium thermodynamics and, specifically, the minimum entropy production principle (for details refer to Section 1) are applicable to description of the development and growth of organisms. It was also proposed to estimate the entropy production from the heat release, which, in turn, is connected with the oxygen consumption intensity. The discussion of this principle as applied to biological systems and results of numerous measurements can be found in papers by Zotin [180–183] (they are critically reviewed in [86]). The main conclusion of those studies is that the heat production indeed decreases at separate stages of the ontogenesis (if early stages of development are excluded), but a sharp increase in the heat production is observed during the biological evolution (phylogenesis) and development of a civilization. Studies by Zotin represent a good illustration and extension of Lotka's principle and, therefore, we shall briefly describe some interesting results. According to Zotin, the temperature inevitably rises as the energy exchange increases, leading to denaturation of proteins. The nature copes with this problem first by appearance of heat regulation in animals and then by the coming of the man. The man began to use energy sources not only inside, but also outside the organism, such as combustible materials and fire, and, lately, the atomic energy (i.e. Q increases permanently). Thus, the appearance of the man and the development of the civilization may be viewed as a consequence of Lotka's principle and MEPP. If the man did not appear during the evolution, some species would occupy his place sooner or later. The development of the civilization is accompanied by the exponential increase in the energy production [184], which should certainly lead to an ecological catastrophe on the Earth. The increase in the energy consumption cannot be stopped (since it is an objective law of the nature) and, therefore, the mankind will have, in order to survive, to place the energy production and consumption to the outer space [182,183].

Not only the evolution of biological creatures, but their appearance, is the consequence of MEPP. For example, Ulanowicz and Hannon [185] showed that living communities serve to augment the rate of the entropy production over what it would be in the absence of biota. They adduced several arguments in support of their hypothesis, specifically, the comparison of the spectra of electromagnetic fluxes incident to and emanating from the surface of the Earth.

Swenson [186,187] independently, although a little later, came to the ideas discussed here. His arguments cannot be viewed as rigorous, but they are sufficiently interesting and, for this reason, we shall present them below. Swenson thought that the laws of thermodynamics should be supplemented with some statements in order to describe the development of ecosystems. These statements are two: (1) the universe develops such as to achieve the final state as quickly as possible and (2) the appearance of ordered subsystems is more efficient for realization of the former. As proof, R. Swenson essentially gave two examples, namely the Benard effect and the change of the temperature in a house. The Benard effect is considered as one of examples when a structure is formed in a liquid layer heated from beneath and, as is known, the heat transfer sharply increases. The latter circumstance has a consequence, if an established steady-state regime is concerned, that the entropy production and the entropy flux from the system increase sharply. Correspondingly, the entropy increases much larger in the medium surrounding the system during the structure formation. As an example, R. Swenson considered further the change of the temperature in a house in winter. If all doors and windows are closed, the street and room temperatures equalize through heat conduction, i.e. relatively slowly. Opening of a door or a window provides a new opportunity for equalization of the temperatures through the convective transfer. This mechanism will bring the "house-street" system to the thermal equilibrium faster. As is known from experiments, the system "seizes" this opportunity. According to Swenson, this fact adduces evidence that a system moves to its final state at a maximum possible speed. On the strength of the two formulated statements,

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[77] In the case of a steady-state process, the total reaction rate is a maximum if a constraint is imposed on the rate of elementary reactions and the reaction equilibrium constant is preset.

[78] An ecosystem develops such as to achieve the configuration, in which respiration is a maximum, as quickly as possible. Since oxygen is responsible for the heat release in an organism, the relation to Lotka's principle and MEPP is evident.

[79] In this study Lotka's principle essentially was raised to the basic (third) law of development of systems along with the two other known laws of thermodynamics and was illustrated for both developing biological and economic systems.

R. Swenson drew the following conclusion [186,187]: the environment produces order (more ordered systems appear, e.g., convective currents, the man, etc. are organized) as soon as it gets a chance, because order produces entropy faster. Thus, Swenson came to statements similar to those described above. One cannot but admire his intuition.

The studies, which are discussed above, and studies by Paltridge (see Section 3.1.1) had a considerable effect on the use of MEPP for solution of biological and ecological problems. For example, Kleidon [188] used MEPP to analyze the role of biota in the exchange of carbon dioxide and partitioning of energy at the land surface. It was argued that biota add the degree of freedom to these processes and, therefore, can be expected to evolve to the state of the maximum entropy production. It was shown that this leads to the near-homeostatic behavior of the Earth system on the long time scale (earlier one had to postulate this in similar ecological models). Juretić and Županović [189] modeled the steady-state bacterial photosynthesis as a cyclic chemical reaction (a nonlinear flux–force relationship was assumed) and concluded that photosynthetic proton pumps operate close to the maximum entropy production mode. Other examples of the use of MEPP in biology can be found in [190,191].

4. Conclusion

Let us formulate main conclusions that follow from the review.

1. MEPP is a logical generalization of the second law of thermodynamics to nonequilibrium processes. Its thermodynamic formulation goes back to studies by Onsager and Ziegler and the microscopic formulation is due Enskog and Kohler. This principle probably originates from maximization of the number of possible trajectories of a nonequilibrium system in the phase space.

2. MEPP is confirmed in studies of various systems of the physical, chemical or biological origin on different observation scales (both microscopic and macroscopic). In the case of weakly nonequilibrium systems, the principle is substantiated in theoretical terms relatively well.

3. MEPP and the minimum entropy production principle do not contradict one the other. The latter is a consequence of the former.

4. Being simple and physically obvious, MEPP is used by many researchers, who guide themselves by their intuition and are often unaware of the general formalism supporting the validity of MEPP.

5. When a study is concerned with the evolution (especially with nonequilibrium phase transitions) or relaxation of a nonequilibrium macroscopic/microscopic system, researchers almost at all times are unable to describe events in sufficiently rigorous terms using the first principles and have to roughen or average a process. The principle is just necessary for acquisition of lacking information or selection of the development regime. As a result, this principle proves to be very useful and this statement is illustrated by numerous examples given in the review.

6. This principle can be used most correctly in its differential form. The maximum entropy production should be chosen from different possible values for some element of the system volume over a preset small interval of time. Various integral formulations of MEPP probably cannot always lead to the correct answer.

7. MEPP determines just the most probable state. A system may choose a development trajectory with a smaller production, but it will be metastable.

Let us briefly enumerate some important, as they viewed by the authors, directions of development of the aforementioned ideas and problems encountered.

1. MEPP shows greatest promise in biology (the theory of evolution, ecology, etc.) and astrophysics (problems of the origin of the Universe, the evolution of galaxies, etc.),[80] and also in fields where this principle was not used earlier, such as nuclear physics and physics of elementary particles.

2. Some researchers [77,192,193] point to an intimate relation between MEPP and such frequent manifestations of a nonequilibrium development of a system as self-organized critical phenomena, dendrite/fractal growth, sigmoidal kinetic growth curves and relaxation laws (Exponential, Kohlrausch). The development of these ideas is very promising from the viewpoint of both the substantiation of the principle and better understanding of laws underlying the evolution of systems far from the equilibrium.

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[80] Of course, the development of the other applications of MEPP, which are described in Section 3, is interesting and reasonable. The emphasis on the two directions is explained exclusively by the subjective opinion of the authors.

3. What is the importance of the principle from the viewpoint of the general apparatus of nonequilibrium statistical physics? Does it add or is it redundant to the existing fundamentals of this theory (for example, those using the maximum information entropy or maximization of the number of possible trajectories of a nonequilibrium system as the basis)? Can it help deduce main kinetic equations, which are currently in use (including equations that hold in the absence of local equilibrium or those for systems with memory) and how simple and logically consistent the deduction will be?[81] Answers to these questions will help draw the final conclusion about universality and fundamentality of MEPP.

4. This principle relates two values, which currently represent the corner stone of the modern science: entropy-information and time. Did it happen by chance and, if not, what the origin of the principle is?

We conclude our review with this intriguing question.

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[81] Just first steps have been taken in this direction so far. For example, Chavanis [110] used MEPP to obtain relaxation equations of a generalized Fokker–Planck type. Gheorghiu–Svirschevski [194] presented an interesting study dealing with a nonlinear extension of the nonrelativistic Liouville-von Neumann dynamics driven by the maximum entropy production with conservation of energy and probability.

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