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Maximum entropy production principle: history and current status

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Contents

Abstract. The maximum entropy production principle (MEPP) was repeatedly and independently proposed in the mid-20th century in various fields of physics and proved to be extremely effective in various nonequilibrium problems. We describe the main areas of research that laid the foundations for this principle and discuss its modern form and limitations. We give special attention to a discussion of nonequilibrium phase transitions based on the MEPP and to the relation between the MEPP and other known assertions about the behavior of entropy. We discuss the role of this principle in the analysis of various modern problems in both physics and biology, including the laws of evolution and the definition of life.

Keywords: entropy production, nonequilibrium thermodynamics, nonequilibrium phase transitions, evolution

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One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.
J W Gibbs (1881)

1. Introduction

A hypothesis that emerged in the mid-20th century states that the second law of thermodynamics can be supplemented with the assertion that the value of entropy production not only remains positive but is also maximized in the course of the evolution of a nonequilibrium system. This hypothesis or some other assertions very close to it appeared independently in different branches of theoretical physics, as well as in applied hydrodynamics, materials science, chemistry, and biology. As a result of its simplicity, profundity, and consistency, as well as its usefulness in solving many theoretical and applied problems, it came to be known as the maximum entropy production principle (MEPP) and is regarded as an important principle in modern nonequilibrium physics. There was great interest in this subject in the early 21st century, which resulted in numerous dedicated seminars and conferences, including those in Bordeaux (France) (2003–2005), Split (Croatia) (2006), Jena (Germany) (2007–2010), Kyoto (Japan) (2008), and Canberra (Australia) (2011). Publications of collected papers, special journal issues, and reviews in leading journals resulted from this fruitful work (see, e.g., [1–7]).

The avalanche-like increase in the number of publications associated with the MEPP has started slowing down in the last five to ten years. This means that this area of research

has completed a prolonged initial phase of formation and explosive growth and entered the maturation stage. This is the time to once again discuss the principle, recall those responsible for its inception, refine the formulation of the MEPP, and highlight its limitations, which have not been given due attention previously.[1] This is also the time to consider the relation of the principle to other known statements about entropy and to discuss modern studies and prospects of applying the principle. Almost 15 years has passed since our first review dedicated to the MEPP [4]; at that time, much was unknown or not fully understood. Reviews that have been occasionally appearing recently, related to the MEPP in one way or another, are focused on very specific MEPP-related problems, such as hydrodynamics or materials science. Understandably, these studies do not provide a coherent picture of the MEPP, of the place it occupies in science, or of the influence that it exerts on various applications. All this was the motivation in writing this review. The main attention is here focused on work that appeared in the last 10 to 15 years and is arguably important for the development of MEPP studies.

An important goal addressed in this review is to have a broader circle of researchers working not only in different domains of physics but also in related areas, from materials science to biology, become acquainted with the MEPP. This determined our desire to make the presentation broadly accessible by making a choice in favor of the relative simplicity of the material. This explains why formulas are scarce and specialized terms are not abundant.[2] At the same, naturally, we try to maintain a due level of rigor. If the reader is for some reason not satisfied with the resulting compromise between accessibility and rigor, a reasonable course of action would be to address the original papers following the references given throughout this review.

2. First formulations of the maximum entropy production principle

We discus the main areas of the work that laid the foundation of the MEPP. We follow the chronological order and attempt to be concise, limiting ourself to only the highlights, because this theme was covered in sufficient detail in our review [4]. But in discussing the MEPP in this section, we also give some new information that was largely overlooked previously.

2.1 Maximum entropy production principle in theoretical physics

2.1.1 Work of M Kohler and J Ziman (1948–1956). It is well known that a popular strategy to solve the linearized Boltzmann kinetic equation is to use the variational method proposed by Enskog [12] (1917) and Hellund [13] (1939). This is a valid strategy for gases in which (1) the mean free path of a molecule is much longer than that range of intermolecular forces and at the same time less than the characteristic size of the problem; (2) the properties of the gas slightly deviate from equilibrium ones. In 1948, Kohler [14] reformulated this variational method by adopting the entropy production extremization, together with some other constraints, as a basic requirement. Kohler was apparently among the pioneers to use this method to describe the transport of electrons in metals. Ziman [15, 16] (1956) was a pioneer in reformulating Kohler's principle in essentially the modern form and in giving it the status of a physical law (principle), rather than a simple mathematical trick used to solve the Boltzmann equation. The Kohler–Ziman principle is stated as follows: *in nonequilibrium gaseous systems, the distribution function of molecules over velocities is such that, at fixed gradients of the temperature, concentration, and mean velocity, the entropy production density is maximal*. In [15], Ziman noted that Boltzmann's H-theorem is often regarded as a kind of molecular–kinetic proof of the second law of thermodynamics and suggested that, by extension, the variational method for solving the Boltzmann equation can give proof at the molecular level of a sufficiently general statement on the behavior of entropy production in nonequilibrium systems (the MEPP).

These ideas were generalized to dense (including quantum) systems with strong interparticle interaction by Nakano (1959–1960), who noted not only the maximum entropy production but also the maximization of transport coefficients evaluated in the framework of the linear response theory [17–19]. Independently of Nakano, such a generalization was given by Christoph and Röpke [20] in 1985. In the framework of the so-called method of a nonequilibrium statistical operator, the entropy production maximization principle was considered in detail by Zubarev [21] (2002) in discussing variations in the system response parameters in fixed external fields.

2.1.2 Work of H Ziegler (1957–1987). The area to which Ziegler's work belongs is classical nonequilibrium thermodynamics, with the postulated existence of local equilibrium in the system. In this case, the local entropy s of the system depends on local thermodynamic parameters α_i, as is the case in full equilibrium, and the rate of entropy emergence in a local element of the volume (entropy production σ) as time t progresses is expressed as [22]

$$\sigma = \sum_i \frac{\partial s}{\partial \alpha_i} \frac{\mathrm{d}\alpha_i}{\mathrm{d}t} \,. \tag{2.1}$$

We regard the variation in entropy due to a variation in α_i as the cause of an irreversible process, and call X_i the thermodynamic force. We say that the rate of change of α_i with time (response of the system) is the thermodynamic flux J_i. Relation (2.1) then becomes

$$\sigma = \sum_i X_i J_i \,. \tag{2.2}$$

The relation between thermodynamic fluxes and forces can be arbitrary (and in a particular case, the simplest one, is linear) [22].

Working in plasticity theory, Ziegler noted that the principle of the maximum rate of mechanical energy dissipation due to R Mises (1913) was applicable there. In 1963, Ziegler generalized Mises's approach by proposing an original version of a deductive construction of nonequilibrium thermodynamics (both linear and nonlinear) based on a variational principle [22–25]. Ziegler's principle can be stated as follows [22]: *if thermodynamic forces X_i are preset, the true thermodynamic fluxes J_i satisfying auxiliary equation* (2.2) *give the*

[1] This has given rise to a number of critical studies (see, e.g., [8–11]).

[2] Another reason is the extreme diversity of the material that has to be considered (ranging from different branches of theoretical physics to materials science, biology, and medicine). Had another approach been adopted in this review, it would have become a multivolume encyclopedia with its own notation and special terms.

maximum entropy production density $\sigma(J)$. Mathematically, this principle can be written with the use of a Lagrange multiplier μ as

$$\delta_J\left[\sigma(J_k)-\mu\left(\sigma(J_k)-\sum_i X_i J_i\right)\right]_X = 0\,. \tag{2.3}$$

Taking the variation in (2.3) with respect to thermodynamic fluxes at constant forces yields a relation between fluxes and forces:

$$X_i = \frac{\sigma(J)}{\sum\limits_i (J_i\,\partial\sigma/\partial J_i)}\,\frac{\partial\sigma}{\partial J_i}\,. \tag{2.4}$$

It follows from (2.4) that the relation between thermodynamic fluxes and forces can be both linear and *nonlinear*. This is an important corollary of Ziegler's principle. Relation (2.4) was called the orthogonality condition (because geometrically it means that the thermodynamic force X_i corresponding to the flux J_i is orthogonal to the surface $\sigma(J_i) = \text{const}$).

If $\sigma = \sum_{i,k} R_{ik}\,J_i\,J_k$ (where R_{ik} is a matrix of coefficients), then (2.4) readily implies the basic relations of Onsager's linear nonequilibrium thermodynamics (1931), including the reciprocity relation for kinetic coefficients L_{ik} $(= R_{ik}^{-1})$ [4, 22]:

$$J_i = \sum_k L_{ik} X_k\,, \tag{2.5}$$

$$L_{ik} = L_{ki}\,. \tag{2.6}$$

Relations (2.5) and (2.6) close the system of energy, momentum, and mass transfer equations, which then allows solving that system.

Ziegler's principle can also be stated in the space of forces in the case where entropy production depends only on X_k and thermodynamic fluxes are fixed. According to Ziegler, entropy production as a function of fluxes (or forces) must be known and must also be convex (which ensures a single-valued relation between flows and forces).

Admittedly, Ziegler's presentation was quite formal in nature, and the examples of the application of the principle that he discussed were limited to some problems in plasticity theory and chemical kinetics [22–25], which could also be solved by alternative methods. This, together with the existence in nonequilibrium thermodynamics of other variational formulations applicable to the nonlinear case, led to little interest in Ziegler's principle at the time; it remained largely unknown.

2.1.3 Work of G Beretta and S Gheorghiu-Svirschevski (1987–2001). In dealing with the challenge of combining two successful theories, thermodynamics (including the irreversible one) and quantum theory, several researchers — Hatsopoulos, Gyftopoulos, and Beretta — proposed so-called quantum thermodynamics (see, e.g., [26–31]). Quantum thermodynamics posits that a system has a much vaster collection of states than that considered in traditional quantum mechanics and is based on a certain new nonlinear equation of motion. This dynamics reduces to the standard quantum dynamics of Schrödinger–von Neumann only in special conditions, as follows from the natural tendency of an isolated system to move from any nonequilibrium state into an equilibrium, higher-entropy state. On the other hand, in quantum thermodynamics, the laws of thermodynamics and irreversibility emerge as consequences of the quantum-dynamics behavior of elementary constituents of a given material system, microscopic or macroscopic, simple or complex.

The theory developed along these lines faced several difficulties. An important step in this direction from the standpoint of this review was made by Beretta [32] (1987), who showed that the proposed nonlinear evolution occurs along the direction corresponding to the steepest entropy ascent at given constraints in the system. Initially, no particular importance was assigned to the fastest increase in entropy, which was considered merely a mathematical method (ansatz) of gradient extremization based on the good old effective method for minimizing nonlinear functions. But in about 14 years, Gheorghiu-Svirschevski [33, 34] (2001), who was unaware of [26–32], independently arrived at the dynamic equation and a number of conclusions similar to those reached by Beretta. Gheorghiu-Svirschevski used an explicit variational principle based on maximizing the entropy production under certain constraints imposed on energy and probability. At the same time, it was stipulated in [33] that the new principle does not contradict the known principle of Prigogine, because, according to Prigogine, entropy production evolves towards a minimum of the maximum values at each moment. This conclusion, as we show below, is somewhat closer to modern concepts.

Papers [33, 34] rekindled Beretta's interest in the subject. In [35], he analyzed the results of Gheorghiu-Svirschevski and gave a more explicit derivation of the equation of motion in the spirit of the fastest increase in entropy. We also note Beretta's very interesting results on the maximum possible quantity of entropy production and the relation of this quantity to Heisenberg's energy–time uncertainty principle [35, 36]. After an avalanche of papers related to the MEPP and largely initiated by review [4], Beretta started considering his method of the fastest increase in entropy to be a version of the MEPP [36] and obtained a number of interesting corollaries of this principle in the framework of classical approaches to nonequilibrium physics, going beyond the limits of his preceding work on quantum thermodynamics (see, e.g., [37]).

2.2 Maximum entropy production principle in physics applications

We briefly discuss only the most prominent work where the MEPP (or similar principles) is introduced to solve specific problems. Other examples can be found, e.g., in [1–7].

2.2.1 Work by G Paltridge in geophysics (1975–2001) and investigations of hydrodynamics by W Malkus (1954–2003). Starting in 1975, a series of publications appeared in which Paltridge calculated global climate using a certain zone model augmented with the MEPP [38–42]. The idea of the approach was as follows. The climate model was based on a collection of cells, characterized by parameters providing an averaged description of the atmosphere and ocean: surface temperature, cloud coverage, horizontal energy fluxes through boundary zones in the atmosphere and ocean, etc. Energy balance equations are written for each cell. Because these balance equations are not sufficient for finding all the characteristics of the cell, it was necessary to introduce an additional assumption that overall (atmospheric and oceanic) horizontal heat fluxes are established in each cell such that the integral entropy production over the cells is maximal [39–41]. Using this model, Paltridge derived annual average distribu-

tions of the temperature, heat fluxes, and cloud coverage on Earth, which agreed well with the observed ones. As a result, Paltridge's approach to maximize entropy production became quite popular in studies of Earth's climate and that of other planets of the Solar System [1–3]. An essential problem faced by Paltridge and others working in the same vein was the justification of the postulated MEPP. The most important supporting argument was provided by Malkus's studies. We describe them briefly.

Starting with his first work in 1954–1958, for nearly half a century, Malkus theoretically and experimentally defended the hypothesis that, when becoming turbulent, a fluid flow maximizes some functional under given constraints on the flow [43–47]. Turbulent flows under both heat convection and a pressure gradient were studied, demonstrating the fruitfulness of the assertion that at a given Rayleigh (Reynolds) number, the turbulent mode is realized, ensuring the maximum heat transfer (dissipation) among all possible stationary modes of the flow. In the conclusion of [47], Malkus, in particular, writes: "...the observed solutions of the Navier–Stokes equation will be those solutions whose mean flows have the maximum dissipation rate." In that same paper, Malkus identifies the average dissipation rate of mean flows with entropy production. These ideas have had considerable impact on the development of the theory of turbulent motion, stimulating new research strategies, in particular, Howard's variational method for obtaining upper bounds of dissipative functionals [48–50].

2.2.2 Work on nonequilibrium crystallization (1946–1990). In the physics of nonequilibrium crystallization, the MEPP occurred naturally from the principle of the maximum crystallization rate. Apparently, the first to use the principle of maximal growth rate of a crystal was Zener [51] (1946). In studying the problem of selecting the rate and characteristic size in the formation of perlite, Zener hypothesized that, among the possible values satisfying his model, stable perlite has the structure that maximizes its formation rate. Studying similar problems, Cahn [52] (1959) arrived at the following 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." It is easy to show (see, e.g., [4]) that this assertion is identical to the MEPP.

Subsequently, maximization of the rate of nonequilibrium dendritic crystallization was proposed independently by Temkin [53] (1960) and Tiller and collaborators [54] (1961). In the latter study, the relation among the rate maximization and entropy production and, importantly, Prigogine's principle is discussed. Having found that their solutions do not satisfy this principle, the authors of [54] write: "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." Starting in 1964, Kirkaldy [55–57], in analyzing the data of Zener and Cahn, noted that experimental and theoretical results tend to be in favor not of the principle of the maximal rate but of the maximization of entropy production under variations of free characteristics of the system (those not fixed by external conditions, for example, the characteristic size).

A milestone in work on this subject was provided by studies and conclusions by Ben-Jacob [58, 59] (1989–1990), who put forward the following principle: the dynamically selected morphology in nonequilibrium crystallization is the one with the fastest growth. In other words, whenever more than one morphology can exist, only the fastest-growing one is nonlinearly stable and therefore observable. We note that Ben-Jacob in [58, 59] proposed the hypothesis that the criterion for morphology selection under crystallization is in the general case not the crystal growth rate but entropy production. This idea did not go unnoticed.

Of interest in the context discussed here was Hill's work [60], where he used experimental data on jump-like changes in the growth direction (from $\langle 110\rangle$ and $\langle 100\rangle$) of ammonium chloride dendrite branches in crystallization from solution at a change in supersaturation. Hill used linear functions to approximate the dependence of the growth rate of the main branch of the dendrite on supersaturation before and after the morphological transition. Using these data, he constructed a dependence of the entropy production on supersaturation for $\langle 110\rangle$ and $\langle 100\rangle$ dendrites. Supersaturation corresponding to the intersection point of these curves differed by no more that 3% from the observed supersaturation at which the transition occurred, in the direction from the structure with lower to the structure with greater entropy production. With such a remarkable agreement between theoretical and experimental results, Hill substantiated Ben-Jacob's hypothesis that entropy production governs the selection of structures undergoing nonequilibrium crystallization.

3. Current generalized formulation of the maximum entropy production principle. Justification and limitations of the principle

A unified principle derived by generalizing the information about the MEPP available from various applications originated from the work by Sawada [61]. Back in 1981, unaware of the existing thermodynamic and kinetic formulations of the MEPP (see Section 2.1), Sawada proposed an original particular thermodynamic formulation of the MEPP. Today, this formulation and Sawada's arguments, partially based on the second law of thermodynamics, are only of historic interest. But the indisputable value of Sawada's work is that he related the MEPP to the experimental data, available at the time, on crystallization and hydrodynamics (see Section 2.2) and also to the Lotka principle in biology (see Section 6.2). In addition, Sawada emphasized that the maximal entropy production state is most stable to perturbations among all possible (metastable) states. To substantiate this conclusion, he performed numerical computations of dissipative structures under electroconvection, in nonlinear chemical reactions (Brusselator), and during crystal growth [62–64]. Sawada was among the first of those who had to reconcile their formulation of the MEPP with Prigogine's assertion of a minimum of the same quantity to consider the applicability domain of the principle and to engage in the debate in print with the critics of the MEPP from the standpoint of chemistry [65].

From the history of the subject, we now turn to modern concepts. It follows from the information given in Section 2 that assertions on the entropy production maximization have occurred in different branches of science independently and were used in discussing diverse systems and different scales (modes) of description. These assertions were instrumental in problem solving. All this resulted in 2010 in the modern generalized formulation of the MEPP [6, 66, 67]: *at every level of description with preset external constraints, the local*

relationship between a cause and the response of a nonequilibrium system is established such that the entropy production density maximizes.

We clarify this generalized formulation with the example of nonequilibrium crystallization from solution. Let supersaturation (the concentration gradient) be fixed. At the kinetic level of the description of the system, the distribution function of molecules over velocities, and hence the diffusion coefficient, are established, such that the entropy production density is maximized. At the thermodynamic level of the description, the relation between the flow of matter and concentration gradient (thermodynamic force) is established, such that the corresponding production entropy density is maximized. In the course of nonequilibrium growth, a crystal whose size exceeds a certain critical value can lose morphological stability. As a result, the shape of the crystal essentially changes, for example, a transition from a regular polygon to a dendrite occurs. The cause of this transition lies in different local supersaturation levels in the solution near the crystallization front. The system responds to this action by an increase in the flow of particles from the solution to the crystal due to the increasing area of the crystal (and hence the added complexity of its shape). Such a bifurcation transformation is also consistent with the maximization of local entropy production. Thus, in this simplest example, there are at least three levels of description to which the generalized MEPP is applicable.

As can be seen from the material in Section 2, the principle emerged as a useful hypothesis that served to either concisely generalize the known regularities or to successfully solve some problems. Naturally, the question arises as to whether a justification of this principle is possible. As is well known, a rigorous theoretical proof of any fundamental principle is impossible by definition: the principle itself lies at the foundation of the theory being constructed. Therefore, any proof of a principle can be only somewhat conventional. In particular, a principle that allows arriving at sufficiently many successful generalizations and predictions is often considered substantiated. Another possible substantiation of a principle can consist of establishing its relation to other principles and laws. We now discuss the MEPP from this standpoint.

From the standpoint of nonequilibrium thermodynamics, Ziegler showed that, in a number of cases (in particular, when entropy production is a homogeneous function of thermodynamic fluxes or forces), it is easy to obtain the orthogonality condition and then the extremality principle itself [4, 22, 23]. Another possible thermodynamic justification of the MEPP was given in [68]. Its essence is as follows. We assume that the second law of thermodynamics is valid (i.e., entropy production is positive, $\sigma \geqslant 0$). Let one thermodynamic force $X = \text{const} \geqslant 0$ be given and the task consist of proving that the system selects the maximum possible thermodynamic flux J (and hence σ, which is known to equal XJ; see (2.2)). We assume that there are several different fluxes. All of them must be nonnegative because $\sigma \geqslant 0$ (the flows are directed toward the decrease in the thermodynamic force). The choice of the zero level of fluxes for an observer inside the system under consideration is arbitrary in the general case; we choose it such that the maximum flux among all those possible in the system is equal to zero. In the chosen frame, all the other fluxes are then negative and hence the entropy production corresponding to each of them is negative. But this contradicts the second law of thermodynamics. Assuming that the second law is a universal law of nature and is independent of the transformations described (which can in fact be adopted here as a postulate, a kind of generalized Galilei transformation), we conclude that, at a fixed thermodynamic force, only the maximal possible flux, and therefore the maximal entropy production, is realized.

Justifications of the MEPP from the standpoint of statistical physics are mainly constructed based on the information entropy and the related approach proposed by Jaynes [69, 70] (1957). The most cited papers in this area are by Dewar [71, 72] (2003, 2005) (references to other works can be found in [4]). In [71, 72], Dewar tried to relate the maximum information trajectory entropy and the MEPP. These studies are useful and interesting without a doubt, but they hardly belong to the class of studies where this problem is solved. Indeed, as can be seen from their critical analysis (see, e.g., [4, 73]), Dewar's argument not only involves a number of nonobvious fundamental assumptions but also is nonrigorous and erroneous in a number of points. The general methodological weaknesses of Jaynes's approach to the justification of principles are discussed in Section 4.3.

Like any other principle, the MEPP has its own applicability domain and a number of limitations. There are two main limitations [6, 74, 75] which, as an analysis of the literature suggests, are most frequently ignored in work devoted to applications of the principle. This leads to errors in its justification and to confusion [8–11]. We discuss these two main limitations of the MEPP in Sections 3.1 and 3.2.

3.1 Locality

Mathematical formalization of phenomena occurring at the minimal possible scale of a chosen level of description is the most complicated in theoretical analysis. This is because, when artificially coarse-graining space and/or time (discretizing it to indivisible elements), we must somehow take the existence of the underlying levels of the description into account. The accepted smallest scale (element) is the most important for the entire description, because it is located at its base. It is on this scale that the MEPP is valid and its use is most effective and error-free. With the MEPP used to find linear or nonlinear relations between cause and response in the system on this lowest scale, we can then go up the 'ladder of scales,' taking the conservation laws relevant to the system, the imposed constraints, the boundary conditions, etc. into account. On 'higher' scales, entropy production can behave arbitrarily, depending on the specific features of a given problem. The simplest example is provided by heat transfer in a rod: at the thermodynamic level of description, we first use the MEPP to determine a linear local relation between the heat flux and the temperature gradient (the Fourier law). Next, invoking the heat balance equation and integrating, we can calculate the temporal and spatial distributions of temperature in the rod for the given constraints. The constraints and initial conditions can be diverse, and therefore any behavior of entropy production can in general be obtained at this second stage [76]. No conclusions follow from the MEPP as regards the properties of the solutions of those equations.

In this sense, the MEPP is a local rather than an integral principle. We emphasize once again that entropy production is maximized and the resulting cause-and-response relations are established for a certain lowest level of the description of a spatial/temporal element. Obviously, the characteristic size of the element can be different in various problems, being directly related to the level of description. The MEPP may

well be *not satisfied* in the integral case, i.e., in the analysis of the integral (over space and time) entropy production. For such systems, the MEPP can turn out to be valid only in some special cases (in particular, for relatively small deviations from equilibrium).

3.2 Complexity

The principle holds for complex systems. This limitation was already discussed in detail by Ziegler [23]. The notion of complexity can be formalized in terms of a special property of the system: entropy production of the full system (process) *is not* an additive function of entropy production of the subsystems (subprocesses). For example, in the linear thermodynamic approximation, entropy production in a complex process consisting of two subprocesses characterized by the fluxes J_1 and J_2 is known to have the form $J_1^2 + J_2^2 + 2J_1J_2$ up to some factors. The last term here is precisely responsible for the nonadditivity.

Systems can exist in nature that preserve the additivity 'in the making' from subsystems. Such systems are called compound [23]. For compound systems, the MEPP is not valid in general. An example of a compound system is a system of chemical reactions proceeding independently. It is obvious that in this case the entropy production due to independent reactions in the system is the sum of independent terms pertaining to different reactions. Each reaction separately obeys the MEPP [75, 77–79], but, taken together, they make up a compound system and do not necessarily obey the MEPP. This is somewhat similar to the locality discussed in Section 3.1: the MEPP is applicable to each local element (reaction), but when the sum over local elements is taken, the MEPP may be invalid for the integral (compound) system.

This shows that systems of reactions that are sometimes discussed in the literature (Schlögl model, etc.) and which allegedly disprove the MEPP [9, 10] are nothing new. Such models represent a small collection of consecutive or parallel chemical reactions, which *have no influence* on one another. If the properties of individual reactions (in particular, their rate constants of reactions) are known, then the behavior of the chemical process made up of them can be completely described (calculated); if the entropy production values are known for individual reactions, then the entropy production of the total process is completely determined (because the overall entropy production is just the sum of entropy productions of separate processes). From the standpoint described in the foregoing, this system is obviously not complex. Therefore, the behavior of entropy production for such a compound (not complex) system cannot obey the MEPP. It is unlikely, moreover, that any general law or principle can be found to govern such systems, in view of their being totally deterministic. We here fully agree with Landauer's conclusions in [80, 81]. Indeed, any accomplished chemist or radio engineer can build a system from elements (with known properties that remain unchanged when combined into a system) such that entropy production or any other quantity behaves in any prescribed way in that system. We note that the assumption that the reactions are independent, which turned out to be very productive in chemical kinetics, is not general: numerous violations are known. Abundant examples can be found among such reactions as coupled, chain, photochemical, and catalytic [82, 83]. Evidently, whenever the assumption of the independence of reactions is violated, the system of chemical reactions becomes complex, with the MEPP applicable to its description.

The notion of a complex system means much more. As is known [84–86], a system consisting of a large number of diverse elements coupled to each other nonlinearly acquires new, sometimes quite unexpected, properties, which are difficult (or impossible) to deduce from the study of individual elements or constraints. This property is generally called emergence and is the most important property of truly complex systems. Aristotle's adage that the whole exceeds the sum of its parts applies here. For example, the properties of a large collection of molecules (of the order of Avogadro's number) of a sufficient density are not additive with respect to the properties of individual molecules,[3] and the properties of a biological population are not reducible to only the properties of individual creatures. From the standpoint of entropy production, the complexity (emergence) of a system manifests itself in the nonadditivity of this quantity under system formation from its constituent subsystems.

4. Maximum entropy production principle and other known assertions on the behavior of entropy

4.1 Nonnegativity of entropy production

If we postulate the MEPP, then the assertion of the nonnegativity of entropy production (the most important part of the second law of thermodynamics for nonequilibrium processes) can be obtained as a corollary [4]. Indeed, we suppose that entropy production can be negative in some hypothetical thermodynamic system. In accordance with the thermodynamic formulation of the MEPP, the physically realized flux is the one that ensures maximum entropy production. In other words, entropy production in the system is equal to the maximum positive value among all possible ones. If we assume that there are no thermodynamic fluxes associated with a given thermodynamic force with positive entropy production, then it is *always* possible to choose a flux equal to zero (Fig. 1a). Therefore, entropy production is also zero, and this value is maximal in this exotic example. Hence, in accordance with the MEPP, no physically realizable states with negative entropy production can exist.

4.2 Minimum entropy production principle

The minimum entropy production principle was formulated by Prigogine in 1945–1947. It can be stated as follows [76–78]: let the basic relations of *linear* nonequilibrium thermodynamics (2.5) and (2.6) be satisfied in a system and let some of the total number of thermodynamic forces X_i be kept constant; then, the necessary and sufficient condition for the *stationarity* of the nonequilibrium system is the minimum of the entropy production density.

Two points are typically considered the main drawbacks of this principle (see, e.g., [6, 76]). The first is that the principle is valid only for *linear* nonequilibrium thermodynamics. The second, and more significant one, is that the principle is not constructive, because the information necessary for its use must be so comprehensive that the principle adds nothing new, and solving the problem directly with the use of conservation laws and Eqns (2.5) and (2.6) is typically easier than using Prigogine's principle. The principle of a minimum,

[3] This, notably, is the origin of some known complications when solving the Bogoliubov–Born–Green–Kirkwood–Yvon equations in the physics of liquids.

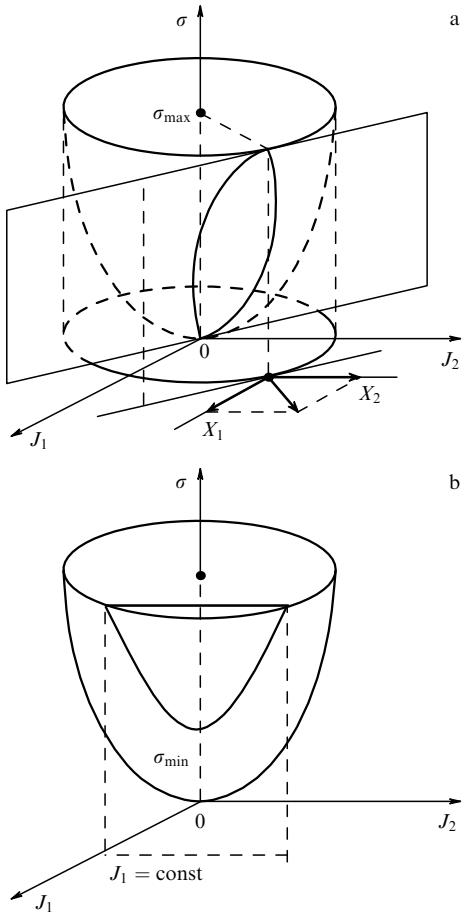

Figure 1. Geometric interpretation of the (a) maximum and (b) minimum entropy production principles in a system with two thermodynamic fluxes (forces) [6].

introduced and proved as a local (differential) one, has been used in attempts to find the spatial distribution of physical quantities, i.e., in attempts to extend the principle to the integral case (see, e.g., [77]). But it has been shown (see, e.g., [76]) that such an extended reading of the principle is mostly erroneous.

Prigogine's principle can be considered a corollary of the MEPP. Indeed, as noted in Section 2.1, the basic relations of linear nonequilibrium thermodynamics, Eqns (2.5) and (2.6), can be obtained from the MEPP. Therefore, with several additional constraints, we can prove the minimum entropy production principle following Prigogine. That the same quantity (entropy production) can be both maximal and minimal may cause misunderstanding. The resolution lies in the extra conditions that are used in problems in varying the entropy production, and these are essentially different. The geometric interpretation in the case of two fluxes and $\sigma = R_{11}J_1^2 + 2R_{12}J_1J_2 + R_{22}J_2^2$ is illustrated in Fig. 1. According to the MEPP (Fig. 1a), the maximum entropy production density is sought with respect to J_1 and J_2 on a cross section of the paraboloid $\sigma = R_{11}J_1^2 + 2R_{12}J_1J_2 + R_{22}J_2^2$ by the plane perpendicular to vectors with the components $X_1 = \text{const}$ and $X_2 = \text{const}$ (this plane is located at an angle to the vertical axis). In Prigogine's method (Fig. 1b), the extremum is sought with respect to J_2 on the cross section of the same paraboloid by the plane $J_1 = \text{const}$.

The result of maximizing by Ziegler's method gives the relation between thermodynamic fluxes and forces, Eqn (2.4) (or (2.5) and (2.6) for the particular form of $\sigma(J)$ considered in the above example), whereas, in applying Prigogine's method (with Eqns (2.5) and (2.6) postulated), it turns out that $J_2 = 0$ corresponds to the minimum entropy production density.

Because of the difference between the characteristic times of the processes, extremizations can be done consecutively in time in a single system [6]. Indeed, let thermodynamic forces be constant within some interval of time τ_0. According to the maximum principle, the system then arranges its thermodynamic fluxes such that entropy production is maximal. If entropy production is a quadratic function, then, as a result of such an arrangement, a linear relation between fluxes and forces sets in and the system passes into a stationary nonequilibrium state on time scales τ longer than τ_0.

As an example, we consider a local element of size L in a sufficiently dense medium, and assume that diffusion and heat transfer can occur in it. As is known, transport coefficients are proportional to the mean free path λ of a molecule times the mean velocity v. The characteristic time needed for fluxes to be tuned to forces is then $\tau_0 \propto \lambda/v$, and the characteristic time of change in thermodynamic forces is $\tau \propto L^2/(\lambda v) = \tau_0 L^2/\lambda^2$. In the case under consideration, $L/\lambda \gg 1$, and hence $\tau \gg \tau_0$. Thus, indeed, there are two essentially different characteristic times in the system, such that the fluxes occurring in Ziegler's scenario (relations (2.5) and (2.6)) start decreasing the thermodynamic forces, which decrease flows, and so on, resulting in entropy production reaching a minimum. A hierarchy of processes is then observed: at short times, the system maximizes entropy production under fixed forces, which results in linear relations between fluxes and forces, and, on long time scales, the system 'varies' its free thermodynamic forces so as to decrease entropy production.

4.3 Jaynes's information approach. Falsifiability of the maximum entropy production principle

A unique approach (the so-called MaxEnt) to the derivation of basic relations of statistical physics based on information entropy was proposed by Jaynes [69, 70] in 1957. Presently, this approach is quite widely used in statistical physics, including in discussions of the MEPP [71, 72, 87, 88]. In describing nonequilibrium processes with the MaxEnt, the trajectory entropy is made extremal with the aim to find the distribution function of trajectories in phase space. The formula for calculating the trajectory entropy is then considered identical to Shannon's formula for information entropy. According to Jaynes, this algorithm is the most objective (unbiased) way to find the distribution function. This maximization is done with the existing (or assumed) constraints taken into account. The obtained distribution function is then used to calculate the relevant nonequilibrium properties of the process. An important feature of this approach is that the disagreement between the predicted properties and the results of experiment is attributed to the wrong constraints having been adopted. The constraints are then refined and the procedure is repeated. Hence, the information approach is in fact a method for establishing a self-consistent set of constraints and experimental data.

We comment on this approach as follows [4, 6].

(1) This approach is apparently the simplest method to construct statistical thermodynamics (classical and quantum), based in fact on a single hypothesis and free of a number of complications (the ergodic hypothesis, etc.).

(2) Although information theory was initially created with the help of some notions borrowed from statistical physics,

presently, following Jaynes, the information approach can be considered the basis for constructing statistical physics. The formalism of statistical mechanics then amounts to a sequence of actions that allow obtaining the best estimate, given essential limitations in the knowledge about the micro world (this is a statistical method for preventing possible errors).

As noted in Section 3, several attempts, mostly unsuccessful, have been made to use the MaxEnt to justify the MEPP, with a number of nonobvious assumptions and constraints adopted [71, 72]. Let us note the principal methodological problem inherent in such attempts [71, 72, 87, 88]. Jaynes's method is a parsimonious algorithm for obtaining a known (generally accepted) solution. But if the solution is not known (or several solutions are possible), then any desired result (equation, law, or principle) can be derived with this method by selecting the corresponding constraints; or, if this is too complicated, other forms of information entropy can always be used, which have recently proliferated in number (for example, Rényi entropy, Tsallis entropy). In this sense, Jaynes's method is highly subjective. This mathematical procedure can generate a set of all possible procedures, but the value of such mathematical exercises is doubtful in physics. Ideas about a close relation between the MaxEnt and MEPP, which are inspired by these exercises, sometimes go as far as the claim that the MEPP, just like the MaxEnt, is not an important principle in physics (in the classic sense) but only some algorithm (method) for making decisions in predicting the behavior of nonequilibrium processes [87, 88]. This is obviously erroneous. Indeed, if one embraces that information standpoint, then both the second law of thermodynamics and other known assertions in physics can be considered not laws or principles but merely useful algorithms that we apply (because one can always choose constraints and the functional form of the information measure so as to obtain any desired law using the MaxEnt, and then directly relate them).

Historically, the MEPP emerged based on the analysis of theoretical and experimental data as a result of extensive and long-term work by various researchers. This makes it akin to other laws and principles accepted in physics. Thus, the MEPP is a physical principle that is fundamentally different from the MaxEnt. The MEPP itself is a key objective constraint on the existing world and on us, the cognizing subjects in this world, similarly to the first and second laws of thermodynamics or the charge conservation law and Heisenberg's uncertainty principle.

That the MEPP is a principle of nature, rather than a mathematical procedure for obtaining the best prediction for the behavior of a system in the conditions of insufficient knowledge about the system, is supported by considering the MEPP from the standpoint of Popper's falsifiability. The opportunities to falsify the MEPP in the sense of Popper are numerous. The simplest experiment[4] on falsifying the MEPP is provided by the measurement of entropy production at the instant of bifurcation of a complex system in the course of its spontaneous evolution.[5] The system must satisfy the basic constraints indicated in Section 3. If the most probable realizable state of the system, among several possible states, turns out to not be the maximum entropy production state, then, according to Popper, the MEPP would be disproved. Hence, from the standpoint of Popper's ideas and those of his followers, the MEPP is falsifiable and is therefore a scientific principle. On the contrary, the MaxEnt can never be disproved by any result of an experiment, and therefore it is only a mathematical procedure.

We believe, however, that the question of disproving any principle (not only the MEPP) is more complicated than can appear at first glance. Considering this question only from the standpoint of Popper's work is an oversimplification, especially after the appearance of the critical work by I Lakatos (1970–1978) on the methods of research programs in science. In accordance with philosophical meditations by Lakatos, the basic criterion of whether an approach (in our case, theories relying on the MEPP) is scientific is an increase in factual knowledge due to the predictive power of the method. The recent growth of the number of publications related to the MEPP and the obtained interesting results in different areas of science, from physics to biology, are the best proof that the MEPP is scientific and is important. Some examples are given in Sections 5 and 6.

4.4 Fluctuation relations

In the last two decades, the theory of nonequilibrium processes, including those far from equilibrium, has been enriched by proofs of a series of theorems, similar in content, generally called fluctuation theorems (see [89–93]). The main claim is that the probability $P(+\Omega)$ of a deviation of the dissipative functional Ω toward equilibrium and the probability $P(-\Omega)$ of a deviation of the dissipative functional in the opposite direction are related as

$$\ln \frac{P(+\Omega)}{P(-\Omega)} = \Omega\,. \tag{4.1}$$

The proof of (4.1), which is based on quite general and fundamental ideas of statistical physics, has been obtained for different nonequilibrium systems (statistical ensembles). The most important quantity involved in the fluctuation theorem (FT), the dissipative functional, is defined as a logarithm of the relative probability of direct and reverse trajectories in the process under consideration. The generalized nature of this functional allows formulating (4.1) for a very broad class of systems, including (which is especially important) those with a very small number of particles, where it is necessary to take fluctuations into account. In the interpretations of (4.1) that aspire to even greater importance, it is claimed (see, e.g., [93]) that the FT essentially generalizes and augments both classical ideas due to Boltzmann and Gibbs on the behavior of thermodynamic entropy (and the second law of thermodynamics associated with it) and Onsager's approach developed to describe weakly nonequilibrium systems [77]. It is then assumed that in 'particular' cases (a large number of particles, the existence of local equilibrium, the smallness of deviations from equilibrium, etc.), Ω reduces to a variation in thermodynamic entropy, which is the basic notion in the classical studies referred to above. This interpretation, if it were valid, would allow using the FT to justify other assertions of nonequilibrium thermodynamics, those already associated with thermodynamic entropy, and the MEPP in particular.

The relation between the MEPP and the FT was discussed, in particular, in [71, 72, 87, 88]. But it was shown in a number of examples that Ω does not always reduce to a

[4] It is precisely experiment that has to be considered here, because any theoretical model is only a reflection, fairly rough and often one-sided, of some part of the phenomenon, whereas the MEPP is a principle that embodies dissipative properties observed in nature, not in a model.

[5] Such experiments are discussed in Section 5.1.

variation in thermodynamic entropy. In [94], in particular, this was demonstrated for the classical nonlinear Schlögl reaction in the case of local equilibrium and a large number of particles. In [95], several examples described by the nonlinear Langevin equation were also used to show that identifying the dissipative functional with entropy production leads to the wrong results. This shows that the importance of the FT for *practical* investigations of nonequilibrium systems is overestimated. The existence of some dissipative functional (*generalized* entropy production, and not *thermodynamic* entropy production), which is necessary for the theorem to hold, is not sufficient, because the form of this dissipative functional and the procedure for its experimental determination are very individual for each of the nonequilibrium systems and require essential information about the structure of the system (the connections and processes existing in it). This information might be available either in working with mathematical models of nonequilibrium processes or in considering the simplest experiments in and of themselves. As a result, the value of the information provided by the FT drastically decreases: the FT does not give new information on an insufficiently studied complex (black box) but establishes the equivalence between two different ways of writing some relation (dissipative functional) whose form is not known for the (unexplored) system under study. This is a major drawback of the FT compared with the MEPP. [6]

5. Nonequilibrium (kinetic) phase transitions and the maximum entropy production principle

Equilibrium phase transitions have been thoroughly studied for a long time. These are transitions from one equilibrium thermodynamic phase to another under variations in thermodynamic parameters. Typical examples are given by transitions from a crystal to a liquid (melting) and then to vapor (boiling) with an increase in temperature. Traditionally, these transitions are divided into first and second order, depending on the jump-wise or continuous change in some thermodynamic parameters under the phase transition (in particular, specific volume and entropy change jump-wise under first-order transitions and are continuous under second-order ones). Kinetic or nonequilibrium transitions conventionally comprise transitions from one nonequilibrium process (mode or phase) to another under a change in a control parameter [102, 103]. The most natural choice of such a parameter in the thermodynamic description is given by a thermodynamic force.

Examples of nonequilibrium transitions are abundant. In particular, these include the transition from bubble boiling to film boiling and the transition from heat transfer due to thermal conductivity to convective transport as the temperature gradient increases; nonequilibrium crystallization attended by a change in the kinetics and the growth pattern of crystals with changes in supersaturation or subcooling; transitions from one type of discharge in plasma to another with a change in voltage; and the transition from the laminar to turbulent flow with a change in the pressure gradient.

The study of general regularities of nonequilibrium transitions has not yet reached the degree of maturity characteristic of equilibrium transitions, and is to a large extent being constructed by analogy with its elder cousin. In particular, the same division into first- and second-order transitions is often used based on the jump-wise or continuous variation in certain transfer parameters, phase (nonequilibrium, morphological) diagrams are being constructed, and a number of notions are invoked such as a binodal (the boundary of the absolute phase stability domain), a metastable domain, a spinodal (boundary of the absolute phase instability domain), and a critical point (see, e.g., [59, 60, 66, 67, 102–107]).

The most important question raised by the strategy to construct a thermodynamic theory of nonequilibrium transitions 'by analogy' is as follows: what is the analogue of the thermodynamic potential under a nonequilibrium transition? Until this question is resolved, the development of a thermodynamic theory of nonequilibrium transitions remains mainly of a terminological, superficial nature, and no mathematical approach similar, e.g., to Landau's theory of equilibrium phase transitions [108, 109] can be constructed. We recall that the notion of thermodynamic potentials was fully legitimized in the physics of equilibrium phase transitions after the introduction of the notion of entropy and the formulation of the second law of thermodynamics — the assertion about the entropy maximum in an isolated system. For nonequilibrium processes, the most important characteristics are the rates or times of transformations. The entropy and time can be used to construct the quantity well known in nonequilibrium thermodynamics, entropy production. Therefore, the idea was expressed in a number of papers to use entropy production as the nonequilibrium potential [56–67, 106]. Based on the MEPP, the following corollary can be formulated [66, 106]: *under a nonequilibrium phase transition in a local* [7] *element of the system, its stable state is the one* (*mode or process*) *corresponding to maximum entropy production*. If two nonequilibrium phases have the same entropy production, they can coexist (i.e., can be observed together for a sufficiently long time). In other words, the equality of entropy production of two nonequilibrium phases allows determining the transition binodal.

In the case of nonequilibrium phase transitions, as for the equilibrium ones, stability is understood as the invariance of the system state under perturbations (either controlled or not). Evidently, such actions lead to attenuation and change the effect that various constraints exert on the system. Consequently, a cause-and-effect relation is established in accordance with the MEPP in this new situation. The position and size of the domain in which such a transition occurs must be directly related to both the features of the nonequilibrium system under consideration and the perturbations (their type, amplitude, energy characteristics, etc.). In turn, the absence or insufficient level of perturbations in the domain where a nonequilibrium transition is possible can lead to establishing a cause-and-effect relation inconsistent with the entropy production maximum. Such a relation can naturally be called metastable. An increase in the perturbation then takes the system into a stable state with the entropy production maximum.

Below, we discuss a number of experimental examples illustrating this corollary (Section 5.1), present the simplest version of the construction of a theory of nonequilibrium transitions like the Landau theory (Section 5.2), and give the

[6] This conclusion does not apply to the area of work close to the FT, associated with the Bochkov–Kuzovlev and Yarzhinskii equalities [96–101], wherein the main emphasis is on the experimentally measurable quantities.

[7] In the spatial, temporal, energy, etc. sense.

results of numerical computations that confirm the hypothesis formulated above (Section 5.3).

5.1 Examples

(1) Shibkov and his collaborators [110, 111] investigated nonequilibrium growth of ice in a film of supercooled double-distilled water. About a thousand measurements were made, with the error in the rate being less than 5%. Several results are shown in Fig. 2. The experiments were performed at atmospheric pressure, and the range of investigated supercoolings was up to 30 °C. Several different nonequilibrium growth patterns and hence several nonequilibrium (in this case, morphological) phase transitions were observed in that range. Only one phase transition was a nonequilibrium first-order type: from a stable needle to a platelet, occurring at supercooling to 7.5 °C.

Following [107], we now discuss this transition from the MEPP standpoint. According to the above experimental data, the dependence of the rate V on the supercooling ΔT near the transition point is described well by a linear function $V = L(\Delta T - \theta)$, where L and θ are some empirically determined dimensional coefficients. The values of L and θ can easily be determined from Fig. 2: they are 0.31 cm $(^\circ\mathrm{C\ s})^{-1}$ and 3.5 °C for a stable needle and 0.78 cm $(^\circ\mathrm{C\ s})^{-1}$ and 5.0 °C for the platelet. From the standpoint of local nonequilibrium thermodynamics, the above expression can be regarded as a kind of relation between the thermodynamic flux (evidently, proportional to the rate of transition from the melt to a crystal) and the thermodynamic force (proportional to supercooling). Because the experimental data in [110, 111] are given for the *local* growth rate (for example, of the top of the needle), the thermodynamic flow also has a local meaning. But the melt is supercooled by ΔT in [110, 111] for the entire sample, and the supercooling is then different from the local supercooling near the boundary, whose growth rate is being measured. Therefore, the coefficient θ can be regarded as a correction to the thermodynamic force occurring in the transition to local supercooling near the boundary and depending on the curvature and surface tension of the morphological phase under consideration.

Entropy production σ, equal to the thermodynamic force times the flux (see (2.2)), can then be represented as $\sigma = kV(\Delta T - \theta)$ or as $\sigma = kL(\Delta T - \theta)^2$, where k is some dimensional constant. The dependence of entropy production on supercooling for the needle and the platelet is shown in Fig. 3. As can be seen from the figure, in the domain of existence of the crystal structures under consideration, $(\Delta T > 5-7\,^\circ\mathrm{C})$, the entropy production for the platelet becomes greater than that for the needle starting with just $\Delta T \approx 7.5\,^\circ\mathrm{C}$, i.e., starting with the value at which a morphological transition from the needle to the platelet is indeed observed in the experiment. We note that the crystal growth rate under the transition at this point changes jump-wise by approximately 30%. We can therefore conclude that the use of the approach based on the MEPP has allowed quantitatively determining the nonequilibrium transition point to within the experimental error.

(2) In the work by Kondepudi's group [112–114], a simple system of conducting balls 4 mm in diameter immersed in oil was studied. The system was taken out of equilibrium by a strong electric field. For this, a voltage in the range of 15–30 kV was applied between the central electrode located at a distance of about 5 cm above the surface of the oil and the grounded ring-shaped electrode placed in the oil (Fig. 4). The

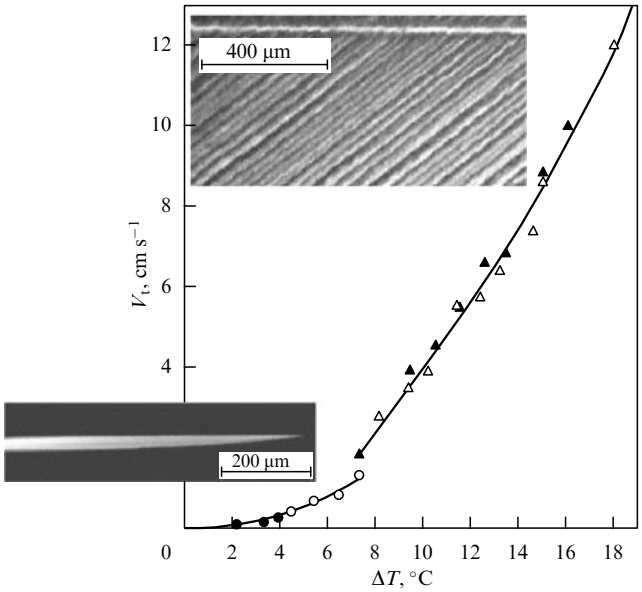

Figure 2. Dependence of the maximal velocity of the tip of the crystal on the original supercooling of distilled water. Dark dots correspond to dendrites, light dots correspond to stable needle-like crystals, and dark and light triangles correspond to respective compact needle-like branches and platelets. (Based on data in [110, 111].)

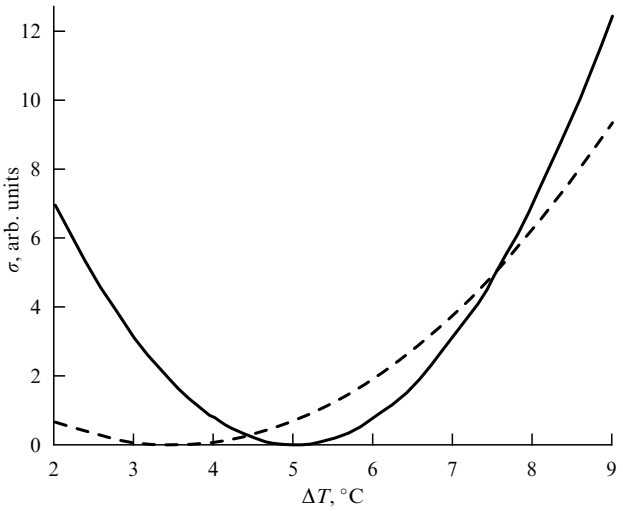

Figure 3. Dependence of entropy production σ at nonequilibrium crystallization of ice on supercooling ΔT. The dashed curve relates to the needle and the solid curve, to the platelet. The left-hand parts of the parabolas have no physical meaning. (From [107].)

strong electric field caused strong convection flows in the oil and motion of the balls. Entropy production Σ in this system at a fixed voltage is directly related to the magnitude of the current, and it was calculated by the well-known formula for Joule heat depending on current measurements (temperature variations in the system were no more than 0.2 °C and did not affect the calculation) [112–114]. The magnitude of the current depends in a complicated way on the coordinate of the ball and on the velocity of motion of the liquid.

Under the action of the field, the balls self-organize into a dendritic structure rooted on the ring-shaped electrode. After its formation, this tree can move along the electrode in a complicated fashion, with slight changes in its shape. Interestingly, if the resistance of the ring-shaped electrode was changed by using a different coating, the root of the tree

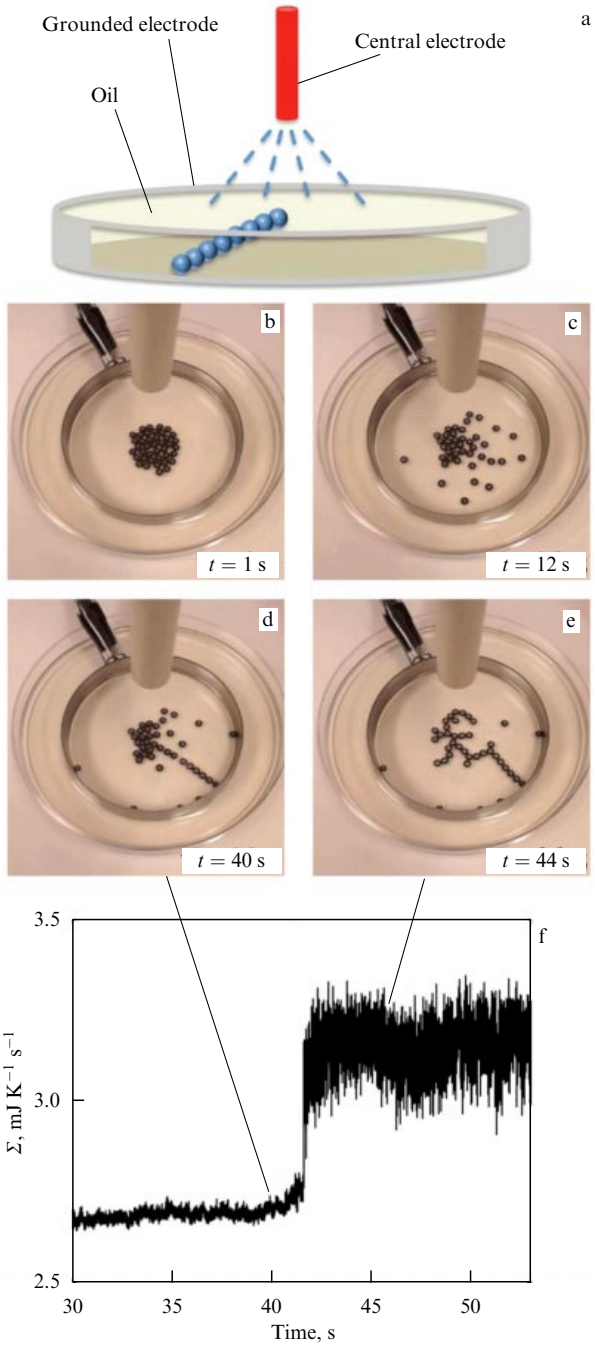

Figure 4. (Color online.) Self-organization of a dendrite-like structure with application of voltage [112]. (a) Setup in which $U = 26$ kV voltage between two electrodes is applied to conducting balls placed into 60 ml of oil. (b–e) Four configurations following one another in time. (e) The tree overall, undergoing slight changes, can move while preserving contact with the annulus. (f) Entropy production rate Σ in the course of formation of a dendrite-like structure. When the tree comes into contact with the grounded electrode, Σ sharply increases.

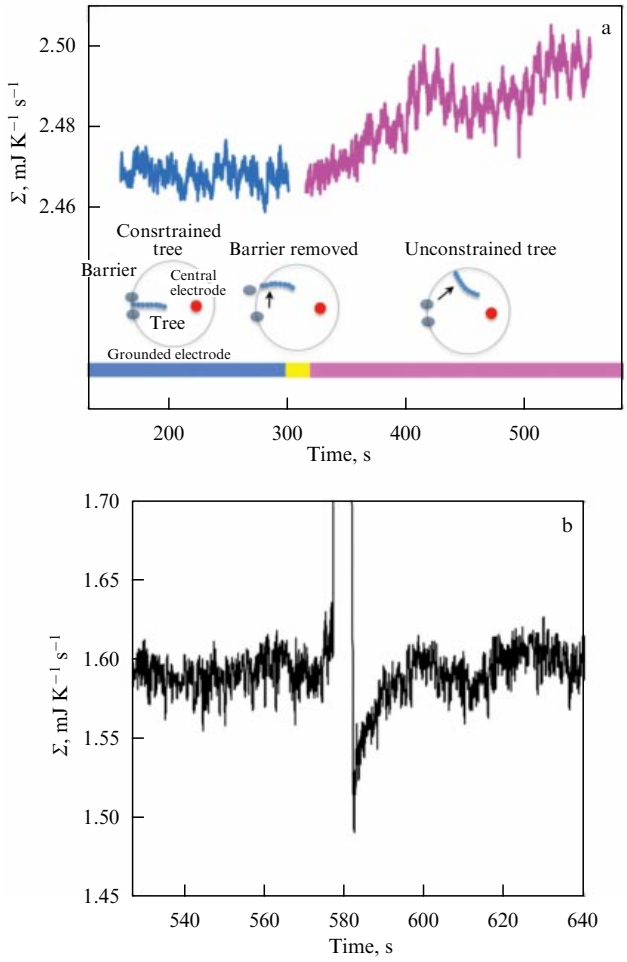

Figure 5. (Color online.) (a) Center of the electrode is displaced and motion of the root of the tree is constrained, which leads to lower entropy production Σ; when the constraints are removed, the tree rapidly moves so as to increase Σ. (b) The system is tilted by 5° for 577–582 s; as a result, the tree moves and acquires a lower value of Σ; when the horizontal position is restored, the tree returns to a higher-Σ state. (From [112].)

avoided locations with higher resistance. It was found (see, e.g., Fig. 4) that this complicated self-organization in each case results in the system arriving at the state with the greatest entropy production (while the structures themselves can have different forms). The value of that maximum depends on the number of balls, on the voltage, and so on. Having arrived at a state with maximum Σ and staying there, the tree can somewhat modify its shape. Such systems differ only little in entropy production. Thus, an apparent coexistence of different structures occurs, with approximately equal entropy production values.

The maximum entropy production state is stable. This can be seen from Fig. 5, which shows that the system returns to the maximum Σ state after a temporary restriction of the possibility of movement along the electrode of the base of the tree or after a temporary tilt of the system.

Another case demonstrating the high stability of the maximum-Σ state is shown in Fig. 6 [114]. If, for example, vibration results in disrupting the stem of the tree, it is restored as time progresses. Under small perturbations, the original dendritic structure and entropy production are rapidly fully restored. Under large perturbations, the tree is restored up to the initial value of Σ (but in a shape somewhat different from the original) in a longer time, which varies from trial to trial.

(3) A much more complicated system was studied experimentally by Bezryadin's group [115, 116]. Carbon nanotubes 2 to 24 nm in diameter and 0.5 to 15 mm in length were spread (suspended) in toluene. The concentration of nanotubes was varied from 0.05 to 0.2 g l^{-1}, which is much below the percolation threshold. This suspended mixture was placed between two electrodes with a voltage applied to them (Fig. 7). It was found in the experiment that, under the action

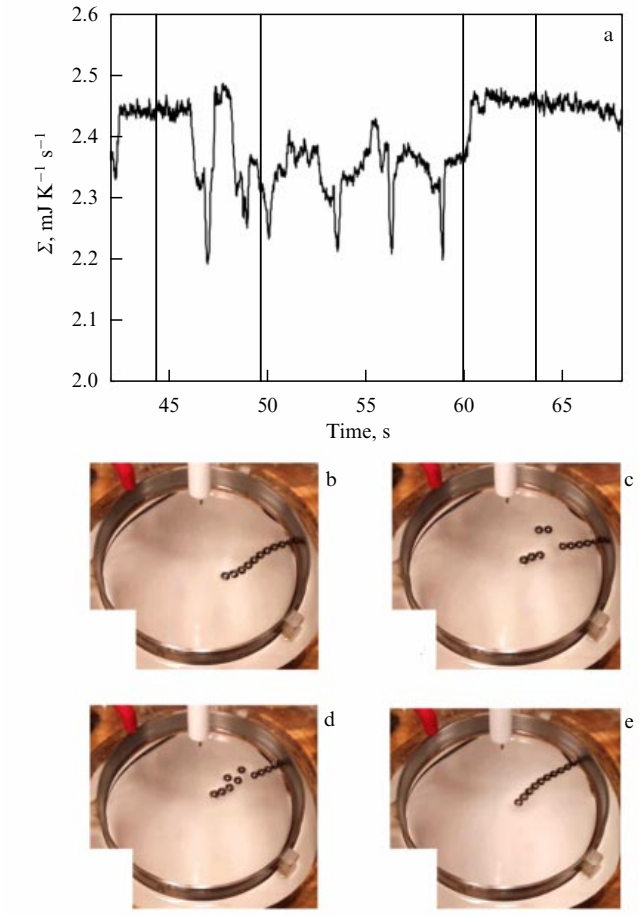

Figure 6. Self-reconstruction of a damaged tree [114]. (a) Entropy production Σ as a function of time. (b–e) States of the tree corresponding to the times indicated by vertical lines in Fig. a.

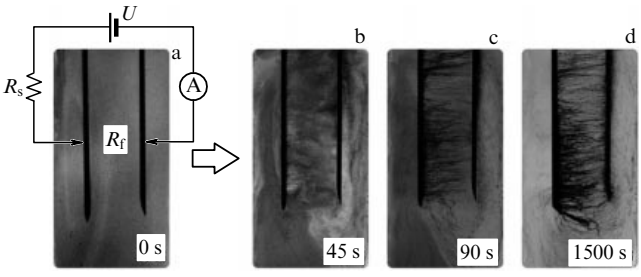

Figure 7. Formation of nanotube chains [115]. The distance between the electrodes is 1 cm, the applied voltage is 400 V, the series resistance R_s is 100 MΩ, and R_f is the resistance of the suspended mixture (liquid with suspended nanotubes). (a) Diagram of the experimental installation and a photograph taken before applying the voltage. Photographs taken in (b) 45 s, (c) 90 s, and (d) 1500 s after applying the voltage.

of the electric field, the suspended mixture passes into an electrically conducting state in a wide range of parameters. This self-organization was attended by a release of heat, which turned out to be proportional to the entropy production (changes in temperature were negligibly small).

It was revealed that the stable state is the one with the maximal entropy production; having reached it in time t_0, the system then remains in that state [8] (Fig. 8). The transition to this maximal state can be either continuous (S1) or jump-like

[8] This time, as is shown in [116], depends on the applied voltage.

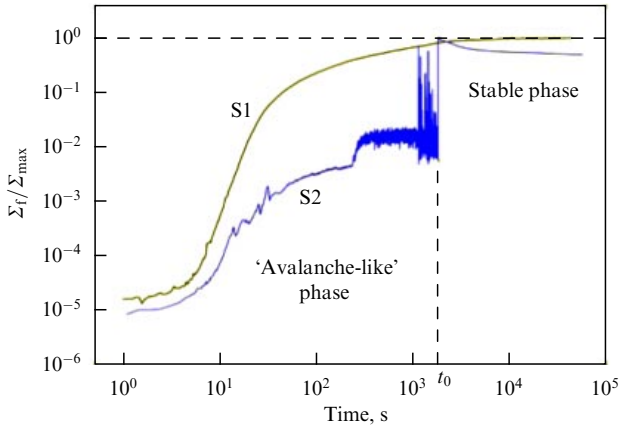

Figure 8. Entropy production normalized to the maximum as a function of time. The concentration of nanotubes is 0.075 g l^{-1}, $R_s = 10$ MΩ. The S1 curve corresponds to $U = 75$ V, S2 to $U = 325$ V. At t_0, the dissipated power reaches a maximum. (From [115].)

(S2) (see Fig. 8). The second path is therefore metastable until t_0. The choice of the path in this complex system depends on a number of factors, including the applied voltage. An important conclusion of the study in [116] is that entropy production is maximized only in the suspended mixture, whereas the global production of entropy of the entire electric circuit (see Fig. 7) is not maximal. This observation confirms the locality of the MEPP.

(4) In [107], the transition from laminar to turbulent motion in a smooth round pipe under the action of a pressure gradient was considered from the MEPP standpoint; the problem addressed by the authors was to predict the lowest critical Reynolds number under arbitrary perturbations of the fluid flow.[9] In the case of local perturbations of the flow near the entry to the pipe or in another part [117–122], the experiment shows that the lowest Re_c is approximately 1760 [118, 119]. Due to the mechanism of their production, these perturbations have relatively short wavelengths. The case of long wave perturbations has been studied less. It is much more complicated to generate such perturbations and analyze the structure of the flow in the vicinity of the transition. Such perturbations can be achieved, for example, by rotating the pipe about a vertical axis. In that case, a volume element of the moving fluid is subjected to the action of the Coriolis force, which results in perturbations of the fluid flow relative to the pipe axis being observed, with a very long wavelength. This amplitude of such a perturbation depends on the Coriolis force, and hence on the angular velocity of the pipe. Such a system was studied experimentally in [123].

An important experimental result obtained in [123] is presented in Fig. 9. As can be seen, as the perturbation amplitude increases in the case of longwave perturbations, Re_c decreases and asymptotically approaches 1200. Numerical calculations of the flow in a round pipe [118, 124, 125] also show the first manifestations of the transition to turbulence: three-dimensional structures, so-called traveling waves, with

[9] In another limit case (infinitesimal perturbations, in progressively more and more accurate experiments), the transition to turbulent motion can be substantially delayed by shifting Re_c to 10^5 or more [117, 118]. However, it can be shown analytically that the considered flow is linearly stable for any Re, and therefore the problem under consideration apparently has no *upper* bound for the transition from the laminar to turbulent mode (no transition spinodal) [118].

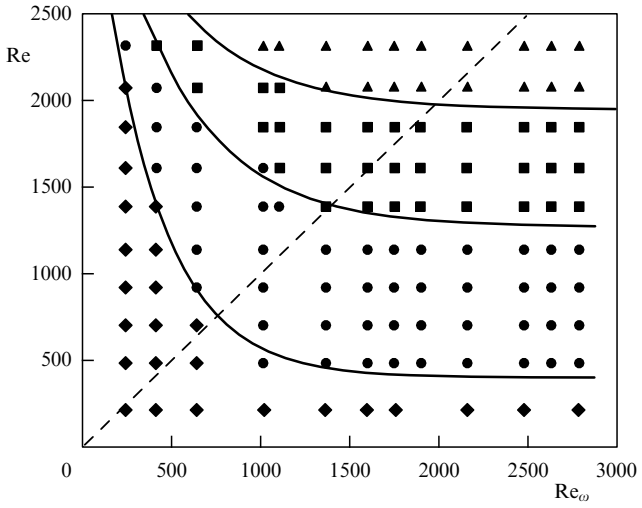

Figure 9. Boundaries of different flows in a pipe. The axes show the standard Re and the so-called oscillation Reynolds number Re_ω (proportional to the angular velocity, which is directly related to the perturbation amplitude). Diamonds correspond to strictly laminar flow, dots, to a nearly laminar flow in the absence of turbulent mixing, squares, to a nonlaminar flow that is transitional to turbulence, and triangles, to strictly turbulent flow. (From [123].)

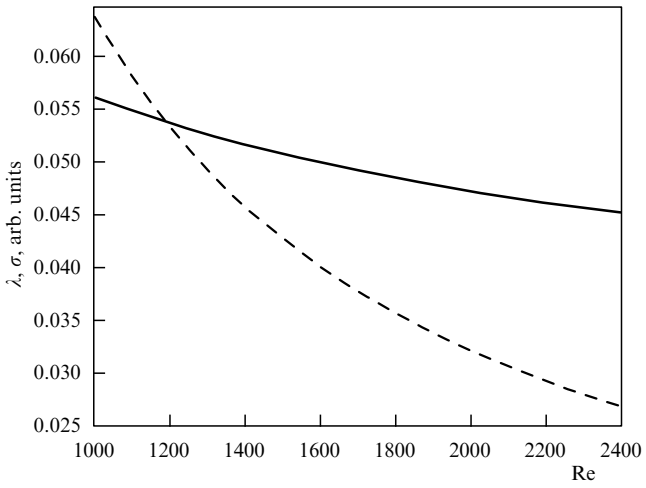

Figure 10. Dependence of the friction factor λ (or entropy production σ) on the Reynolds number Re. The dashed curve relates to a laminar flow (Hagen–Poiseuille curve), and the solid curve, to a turbulent flow (Blasius curve). (From [107].)

a different azimuthal symmetry appear at $\mathrm{Re_c} = 1250$, which corresponds to structures with small azimuthal symmetry (i.e., with a long wavelength).

Entropy production in the motion of liquid in a pipe is directly related to the dissipation of mechanical energy due to forces of pressure (pressure drop Δp between the pipe ends). At constant temperature and density of the liquid, we can assume that the entropy production in the flow under consideration is directly related to the so-called friction (resistance) factor $\lambda(\mathrm{Re})$: $\Delta p \sim \lambda(\mathrm{Re})\mathrm{Re}^2$, $\sigma \sim \Delta p \mathrm{Re} \sim \lambda(\mathrm{Re})\mathrm{Re}^3$ [126–128].

Therefore, the analysis of the behavior of entropy production at a given Re can be replaced with an analysis of λ. For a laminar flow, the resistance (Hagen–Poiseuille) law has the form $\lambda = 64/\mathrm{Re}$, and for turbulent flow (Blasius law),[10] $\lambda = 0.316/\mathrm{Re}^{0.25}$ [126, 127]. In passing from laminar to turbulent flow, the drag factor (and therefore entropy production) experiences a jump from lower values (relating to the Hagen–Poiseuille curve) to large values (relating to the Blasius curve). Following the MEPP, we use the equality of entropy production to find the binodal of the nonequilibrium transition (i.e., just the lowest value of $\mathrm{Re_c}$ that still allows the transition from laminar to turbulent flow) [107] (Fig. 10). This $\mathrm{Re_c}$ is approximately 1200. Thus, with one of the best-studied nonequilibrium transitions, it has been shown that the transition from laminar to turbulent flow in a round pipe occurs in accordance with the MEPP.

5.2 Description of nonequilibrium transitions based on the maximum entropy production principle

At the beginning of Section 5.1, we discussed the example of an analytic calculation of the point of transition from one nonequilibrium pattern of crystal growth to another under changes in supercooling. A feature of that calculation was that, based on experimental data for each nonequilibrium phase, the thermodynamic flux J was represented as a linear function of the thermodynamic force X, $J = a_i(X - b_i)$, with a_i and b_i being some empirical coefficients characterizing the ith nonequilibrium phase. As we have noted, the parameter b_i is necessary for transformation from the average thermodynamic force typically known in experiment to a *local* force. A local value for the flux follows directly from experiment. The use of local values is a consequence of the locality of the MEPP. Next, with the found dependences, expressions of the form $a_i(X - b_i)^2$ were written for the entropy production of each phase, and their equality was used to determine the thermodynamic force at which the nonequilibrium transition occurs. We note that the flux (growth rate in the example under consideration) experienced only a positive jump under the nonequilibrium transition, which was indicative of a first-order transition. But how universal is this result? What would happen if the values of a_i and b_i were arbitrary or the dependences of J on X differed for the two nonequilibrium phases in the vicinity of the transition? We now follow [67] to discuss the result of a theoretical analysis of these questions.

Let the dependence of the thermodynamic flux on the force be linear for one phase and cubic for the other:

$$J_1 = a_1(X - b_1)\,, \tag{5.1}$$

$$J_2 = a_2(X - b_2)^3\,. \tag{5.2}$$

Then, the dependence of entropy production on the thermodynamic force for the two phases takes the form

$$\Sigma_1 = a_1(X - b_1)^2\,, \tag{5.3}$$

$$\Sigma_2 = a_2(X - b_2)^4\,. \tag{5.4}$$

The condition that entropy production be positive and equal to zero at zero force implies that

$$X \geqslant b_1\,, \quad X \geqslant b_2\,, \quad a_1 > 0\,, \quad a_2 > 0\,. \tag{5.5}$$

For convenience in what follows, we move to new variables

$$x = X - b_2\,, \tag{5.6}$$

$$y_i = \frac{J_i}{a_1}\,. \tag{5.7}$$

[10] In the turbulent domain, in contrast to the laminar one, numerous other dependences $\lambda(\mathrm{Re})$ have been found empirically [127, 129]. But the Blasius formula, despite having been among the first to appear, is the best approximation at relatively low Reynolds numbers (which is just the case of interest to us here) [129].

Table 1. Results of analysis for the model in (5.10), (5.11) [67].

Nonequilibrium phase transition type	Constraints on the coefficients	Transition point coordinate	Jump of the thermodynamic flux at the transition point
First-order	$b > 0$, $k > 0$	$x_\sigma = \frac{1}{2\sqrt{k}}\left(1 + \sqrt{1 + 4b\sqrt{k}}\right)$	$\Delta y_\sigma = \frac{b}{2}\left(1 + \sqrt{1 + 4b\sqrt{k}}\right)$
Second-order	$b = 0$, $k > 0$	$x_\sigma = \frac{1}{\sqrt{k}}$	$\Delta y_\sigma = 0$
Reentrant	$-\frac{1}{4\sqrt{k}} < b < 0$, $k > 0$	$x_\sigma = \frac{1}{2\sqrt{k}}\left(1 \pm \sqrt{1 + 4b\sqrt{k}}\right)$	$\Delta y_{\sigma 1} = -\frac{b}{2}\left(1 + \sqrt{1 + 4b\sqrt{k}}\right)$, $\Delta y_{\sigma 2} = \frac{b}{2}\left(1 - \sqrt{1 + 4b\sqrt{k}}\right)$

In terms of the new variables, the dependence of the flux on the force becomes [67]

$$y_1 = x + b\,, \tag{5.8}$$

$$y_2 = kx^3\,, \tag{5.9}$$

and entropy production in the two phases, Eqns (5.3) and (5.4), can be expressed as

$$\sigma_1(x) = (x + b)^2\,, \tag{5.10}$$

$$\sigma_2(x) = kx^4\,, \tag{5.11}$$

where $b = b_2 - b_1$, $k = a_2/a_1 > 0$, and $\sigma_i = \Sigma_i/a_1$.

An analysis of the problem [67] shows that not only a first-order transition, jump-like in the flux, but also a continuous second-order transition (with only the first derivative of the flux experiencing a jump) become possible in this model. The final results for this nonsymmetric model are shown in Table 1.

The transitions listed in Table 1 are illustrated in Figs 11–13. Apparently, the most interesting one is the recurrent transition (see Fig. 13), consisting of a transition from the second phase to the first and then back to the second. We note that, under the second transition, the thermodynamic flux experiences a negative jump. Hence, a negative jump in the flux does not contradict the MEPP: a thermodynamic flux can decrease jump-wise, but the entropy production directly proportional to it passes from a lower value to a higher one. This example shows the falsity of conclusions made in a number of experimental studies (see, e.g., [105]) that the jump-like decrease in thermodynamic flow observed there under a nonequilibrium transition disproves the MEPP.

The obtained constraints on the model coefficients and the revealed relations between the transition type and the form of the dependence of the thermodynamic flux on a force are important for constructing a phenomenological theory of nonequilibrium phase transitions and for describing and classifying transitions of dissipative structures. The approach considered in [67], which had emerged largely under the influence of Landau's theory, well-proven in the physics of equilibrium phase transitions [108, 109], is in need of further analysis, generalizations, and development.

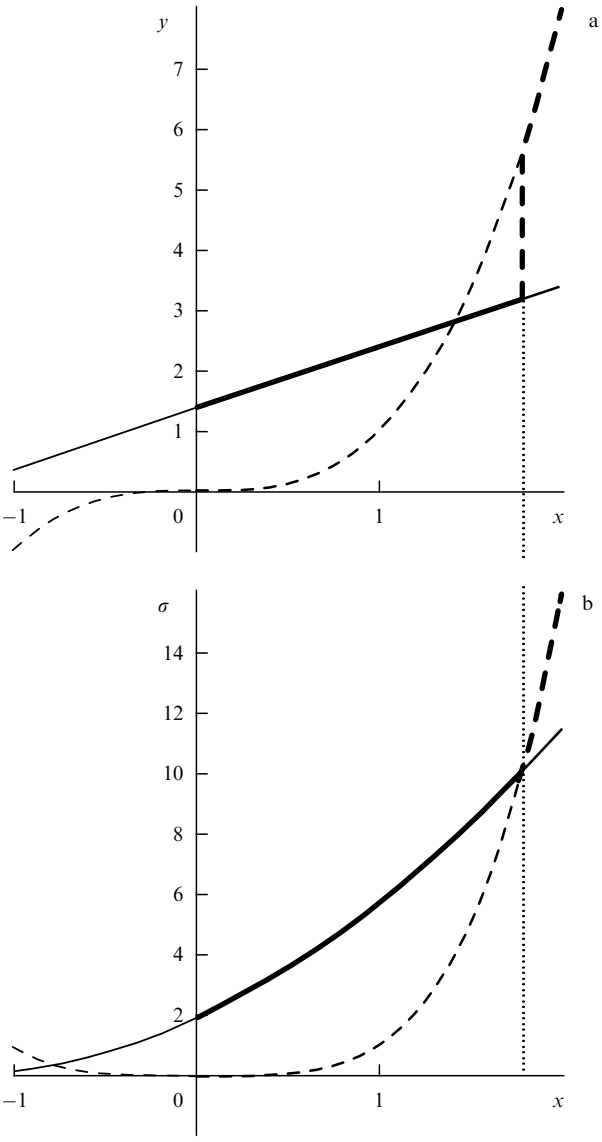

Figure 11. Nonequilibrium first-order phase transition [67]. Dependence of (a) thermodynamic flux and (b) entropy production on the thermodynamic force (in terms of dimensionless quantities). The solid curve corresponds to the first nonequilibrium phase, and the dashed curve, to the second one. The bold line shows the stable phase in accordance with the MEPP, and the thin line, the unstable phase. $b = 2\sqrt{3}/9 + 1$, $k = 1$.

5.3 Full phase diagrams. Metastability

In Section 5.1, we gave examples of the application of the MEPP to the available experimental data. Here, we discuss the case where the use of the principle allowed making a prediction that was subsequently confirmed in a numerical experiment. In the same numerical experiment, the MEPP applicability domain was revealed. We consider this example.

In [106, 130–133], a nonequilibrium phase transition in the course of diffusive growth of particles was studied theoretically in the case where, for certain parameters, morphological

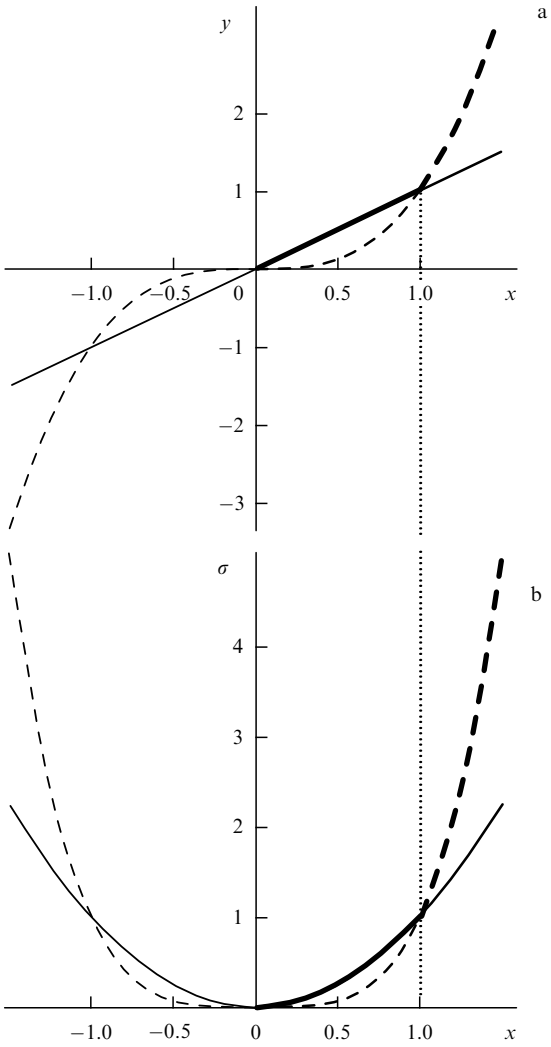

Figure 12. Nonequilibrium second-order phase transition [67]. The solid curve corresponds to the first nonequilibrium phase and the dashed curve, to the second. Bold line shows the stable phase in accordance with the MEPP, and the thin line, the unstable phase. $b = 0$, $k = 1$.

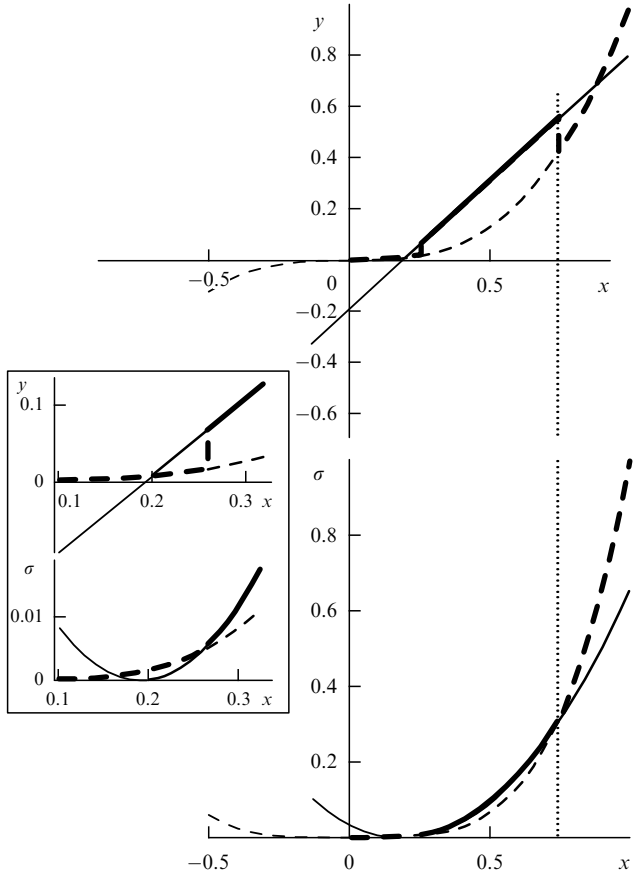

Figure 13. Reentrant nonequilibrium phase transition [67]. The solid curve corresponds to the first nonequilibrium phase, and the dashed curve, to the second. The bold line shows the stable phase in accordance with the MEPP, and the thin line, the unstable phase. The inset shows the range $x \in [0.1, 0.3]$ enlarged. $k = 1$, $b = -\sqrt{3}/9$.

stability was lost, starting with some particle size, and a transition occurred from a regular growth pattern (spherical, cylindrical) to a much more complicated pattern. Morphological stability was studied in the setting traditional for this type of problem: quasistationarity of the process (valid for a relatively small supersaturation) and the isotropy of the kinetic coefficient of crystallization and of the surface tension. The mathematical setting of the problem is as follows:

$$\Delta C = 0\,, \tag{5.12}$$

$$D\,\frac{\partial C}{\partial \mathbf{e}}\bigg|_r = \beta(C_{\rm int} - C_{\rm int}^{\rm eq})\Big|_r\,, \tag{5.13}$$

$$C(r_\infty) = C_\infty\,, \tag{5.14}$$

$$V = \frac{D}{C_{\rm sol} - C_{\rm int}}\,\frac{\partial C}{\partial \mathbf{e}}\bigg|_r\,. \tag{5.15}$$

Here, β is the kinetic coefficient of crystallization, C is the concentration in solution, C_∞ and $C_{\rm int}$ are concentrations of the dissolved substance far from the crystal and near its surface, $C_{\rm int}^{\rm eq}$ is the equilibrium concentration of the dissolved substance near the surface, $C_{\rm sol}$ is the density of the crystal, r is the radial coordinate of the crystal surface, $\mathbf{e}$ is the normal to the crystal surface, D is the diffusion coefficient, r_∞ is the radial coordinate far from the crystal, and V is the local growth rate of the crystal.

Traditionally, the stability analysis is done using a perturbation of the original growth pattern (a disc, a cylinder, or a ball) by individual harmonics of a mode k with an amplitude δ. From the solution of (5.12)–(5.15), a minimal critical size of the crystal is then found at which the growth rate of the perturbation amplitude changes sign from negative to positive. Thus, the critical size is the basic characteristic of a morphological transition. We next discuss the results in [132, 133] only for a round crystal; other growth patterns show only quantitative differences, and the corresponding details can safely be omitted here.

If we assume that the perturbation amplitude is infinitesimal and restrict ourselves to the linear perturbation theory, then the critical stability size $R^{\rm s}$ for the growth of a round crystal can be expressed as [132, 133]

$$R^{\rm s} = \frac{1 + A_i k(k+1) + \sqrt{\big(1 + A_i k(k+1)\big)^2 + 4\alpha k(k+1)}}{2}\,, \tag{5.16}$$

where $\alpha = D/(\beta R^*)$ is a dimensionless combination characterizing the growth mode (at small α, growth is limited by

diffusion, and at large α, by surface phenomena), A_λ is a dimensionless combination related to r_∞, R^* is the critical nucleation radius, and R^s in (5.16) is normalized to R^*.

Formula (5.16) fully determines the stability of the growing round particle under infinitesimal perturbations. Evidently, using the terminology from the physics of equilibrium phase transitions, this size can be considered a spinodal of the morphological transition. Classical linear analysis states nothing when the perturbation amplitude is not infinitesimal. But finding the stability conditions for arbitrary-amplitude perturbations of shape is a very important problem for both theory and practice. To solve that problem, the MEPP was invoked in [132, 133] and the hypothesis was put forward that this allows finding the binodal of the transition under consideration.[11]

The local entropy production Σ in a volume element of a solution in the vicinity of a crystal surface was written as [132, 133]

$$\Sigma \sim V^2 \, d\Omega \,, \tag{5.17}$$

where $d\Omega$ is the volume element of the solution near the crystal surface.

With the adopted hypothesis, solving the equation $\Delta\Sigma = 0$ for the crystal size R, we can find the transition binodal (here, $\Delta\Sigma$ is the difference between local entropy production near the surface of two morphological phases[12]). Solving the equation $\Delta\Sigma = 0$ in the framework of mathematical model (5.12)–(5.15) for a round crystal in the first order in the perturbation amplitude yields the binodal [132, 133]

$$R^b = \frac{1}{2}\left\{1 - \frac{\alpha k}{2k-1} + \frac{2A_\lambda k(k^2-1)}{2k-1} + \sqrt{\left[1 - \frac{\alpha k}{2k-1} + \frac{2A_\lambda k(k^2-1)}{2k-1}\right]^2 + 4a\,\frac{k(2k^2-1)}{2k-1}}\right\}, \tag{5.18}$$

which, as in (5.16), is normalized to the critical nucleation radius. It turns out that, for any parameters $R^b < R^s$, and also for $R > R^b$, entropy production in the new (perturbed) phase is greater than in the original one (particle of a round shape).

The domain between R^b and R^s was assumed to be metastable in [132, 133]. In this domain, depending on the perturbation amplitude, a morphological transition occurs, starting with $R = R^b$ (at arbitrary amplitudes) and up to $R = R^s$ (at an infinitesimal amplitude). Closer to the spinodal size, smaller-amplitude perturbations are capable of causing a nonequilibrium transition. With the use of (5.16) and (5.18), full morphological phase diagrams of the domains of stable, metastable, and unstable crystal growth were constructed analytically in [132, 133]. For a wide domain of parameters, an overlap of metastable domains belonging to different perturbing harmonics was observed, which is indicative of the possible coexistence of a large number of morphological phases. It was also found that the crystal mass increases jump-like under morphological transitions. The magnitude of the jump decreases as the kinetic coefficient of crystallization decreases, as the relative supersaturation decreases, as the surface tension coefficient increases, or as the number of perturbing harmonics increases.

Approximately seven years after the analytic predictions were made in [132, 133], problem (5.12)–(5.15) was numerically investigated in [134, 135] for stability under arbitrary-amplitude harmonic perturbations of the crystal boundary.

Numerical calculations have shown that, for any mode of growth (in the range from diffusion-limited to kinetic) and any mode of initial harmonic perturbations, the dependences of the critical size R_c on δ are similar and have two characteristic special points: R^s as $\delta \to 0$ and a minimum point $\tilde{R}^b$ (Fig. 14). The first size R^s is the spinodal, which were well studied for stability by analytic methods of classical linear analysis, but the existence of $\tilde{R}^b$ appears to be a rather nontrivial result. By its meaning, $\tilde{R}^b$ coincides with the binodal predicted previously. Indeed, let there be a growing round-shape particle and assume that its growth occurs in a medium where perturbations are possible, for example, with some definite mode k and an *arbitrary* amplitude. According to the results of the calculation (see Fig. 14), the transition from stable to unstable growth then occurs at some critical size corresponding to a minimum in the dependence of R_c on δ. If the experiment is performed more 'carefully,' i.e., the level (amplitude) of the perturbation in the medium is below some critical value, then, according to the calculation, the size of the stability domain increases (and the critical radius becomes equal to R^s in the limit of zero amplitude). Thus, depending on the level of perturbation, the transition to unstable growth can be observed in the range from $\tilde{R}^b$ to R^s, which is called the metastable domain.

In Fig. 15, we show the behavior of the metastable domain depending on the growth mode for different harmonics. This diagram was obtained by numerical calculations [134]. In the domain $\alpha < 1$, which corresponds to diffusion-limited growth, the metastable domains corresponding to different harmonics do not overlap. In the transition domain $1 < \alpha < 10$, the binodal of the $(k+1)$th harmonic and the spinodal of the kth harmonic come closer to each other, and at $\alpha > 10$ they intersect, with the result that metastable domains of critical radii overlap for neighboring harmonics. For values $\alpha > 100$ (corresponding to strictly kinetic growth), intersections of three or more metastable domains are possible. Consequently, in the intermediate and kinetic growth modes, in the case of growth in a medium where perturbations of different amplitudes and modes are present, a large number of particles of different shapes — different morphological phases — can coexist and develop from a round seed.

We illustrate the foregoing with a specific example. Let numerous round particles grow in a medium where perturbing actions with $k \geqslant 4$ and an arbitrary amplitude are possible, leading to boundary distortions. We assume that the larger-amplitude perturbations appear less frequently (in both time and space), and, conversely, there are infinitely many perturbations with an infinitesimal amplitude. Let physical and chemical parameters of the medium and the particles located in it correspond to the value $\alpha = 100$. Then, the particles grow along the straight line CE (see Fig. 15). Before point C, all particles have a round shape. In the interval CD, particles of two types can be observed simultaneously: round ones (which are more likely to occur under the

[11] In accordance with the terminology of the theory of phase transitions, a binodal is understood as the boundary separating the domain of an absolutely stable phase from the domain of a metastable or unstable phase.

[12] In this case, one morphological phase is understood as the original round growth pattern, and the other, as the shape perturbed by a certain harmonic.

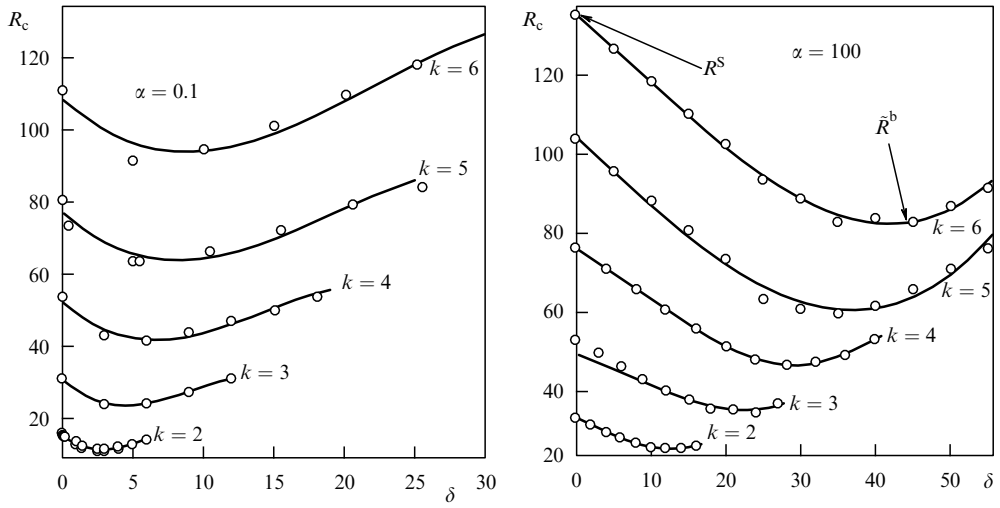

Figure 14. Numerically obtained dependence of the critical size R_c of morphological stability on the perturbation amplitude δ for different growth modes α and perturbing modes k. (From [134].)

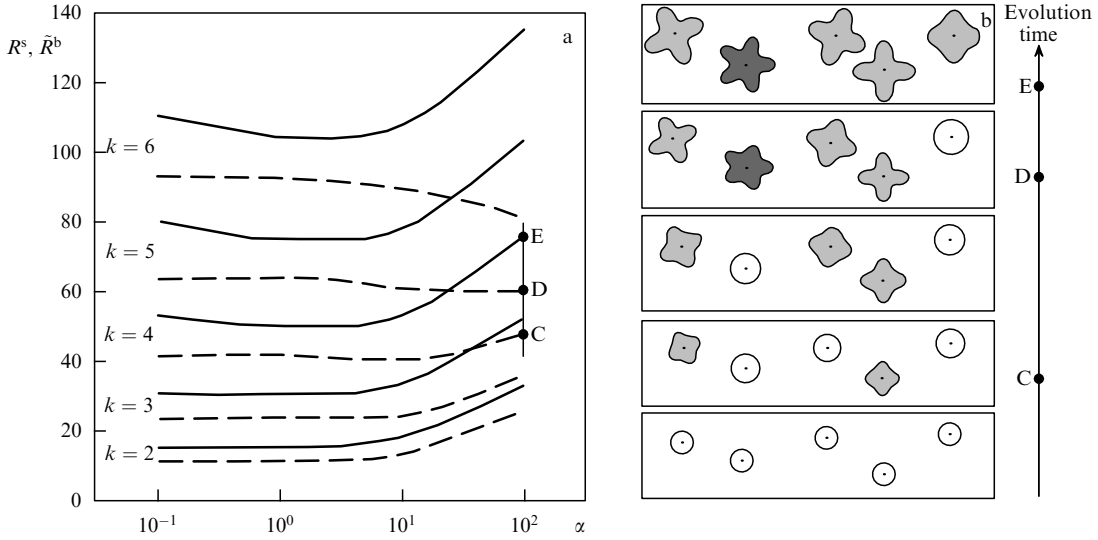

Figure 15. (a) Dependence of the spinodal R^s (solid curve) and the binodal $\tilde{R}^b$ (dashed curve) on the growth mode α for different perturbing modes k. (b) Possible time evolution of particles growing in a medium (corresponding to the CDE trajectory). (From [134].)

above assumptions regarding the statistics of perturbations) and those that have lost stability with respect to perturbations with $k = 4$. After point D (which is the binodal for perturbations with $k = 5$), the appearance of particles of the third type is possible in the medium, due to the loss of stability by round particles under perturbations with $k = 5$. Hence, the coexistence of three morphological phases is observed in the interval DE. After point E (which is the spinodal for perturbations with $k = 4$), all the remaining round particles lose stability with respect to perturbations with $k = 4$.

It thus follows (see Figs 14 and 15) that metastable crystal growth behavior in the mathematical setting under consideration does exist, as was indeed predicted in [132, 133] based on the MEPP. But the most important question is how well the binodal radius calculated with the help of entropy production coincides with the numerically predicted one. A quantitative comparison of the results for a round crystal is given in Table 2.

As can be seen from Table 2, the accuracy of the prediction of binodals based on (5.18) for diffusion and intermediate particle growth regimes is quite good irrespective of the perturbation mode, the discrepancy being in the range of only 2 to 10%. But in the transition to the kinetic mode for perturbations with small values of k, the discrepancy becomes much greater (for $k = 2$, it reaches 35%). A possible explanation is that the MEPP is a principle of nonequilibrium physics and is poorly applicable to systems very close to equilibrium. Indeed, the more we recede from the diffusion growth mode (by increasing α), the more homogeneous the diffusion field becomes at the particle surface. In addition, the more longwave the boundary perturbation is, the closer the curvature (and hence the equilibrium concentration of such perturbed particles) is to its nonperturbed value. As a result, both the absolute value of entropy production and the difference between entropy productions for the perturbed and unperturbed crystal growth patterns are very small.

The conclusion from analytic and numerical work in [130–135] can be that the MEPP indeed allows finding the most stable state in nonequilibrium growth. The transition point defined with the help of the principle is then in quantitative

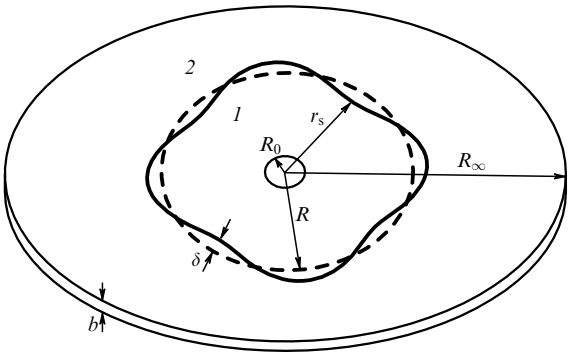

Figure 16. Schematic of a radial Hele-Shaw cell. *1* — displacing fluid, *2* — displaced fluid.

Table 2. Binodal radii for a round crystal obtained numerically [129] and analytically (5.18) [132].

α	k	$\tilde{R}^{\mathrm{b}}$	R^{b}
0.1	2	11.3	10.8
	3	23.6	24.6
	4	41.7	43.2
	5	63.8	66.6
	6	93.7	94.9
1	2	11.8	10.6
	3	23.9	24.4
	4	42.0	43.0
	5	63.8	66.5
	6	92.5	94.5
10	2	14.2	9.2
	3	25.1	23.0
	4	40.9	41.7
	5	60.8	65.2
	6	89.3	93.6

agreement with the results of independent numerical analysis for morphological stability. Such a verification has been done not only for the round crystal considered here but also for spherical crystals.

Besides crystallization, the MEPP has also been used to calculate the binodal and stability in another classical problem, that of morphological stability of an interface of two fluids in the case of displacement in a Hele-Shaw cell [136–138]. In this problem, as is known, if the viscosity of the displacing fluid is less than the viscosity of the fluid being displaced, then, starting with some size, the originally round displacement front is broken and so-called 'fingers' occur. The standard mathematical formulation of the problem is as follows. In a radial Hele-Shaw cell, stationary displacement of two immiscible and incompressible liquids takes place (with the displacing fluid viscosity μ_1 less than the viscosity μ_2 of the fluid being displaced; Fig. 16). The cell has a thickness b and size R_∞. From the center of the cell through an aperture of radius R_0 comes the displacing fluid with a constant surface flow rate Q. The mathematical problem setting has the form [136–138]

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial p_i}{\partial r}\right)+\frac{1}{r^2}\,\frac{\partial^2 p_i}{\partial \varphi^2}=0\,, \tag{5.19}$$

$$-\,M_1\,\frac{\partial p_1}{\partial \mathbf{n}}\bigg|_{R_0}=\frac{Q}{2\pi R_0}, \tag{5.20}$$

$$M_1\,\frac{\partial p_1}{\partial \mathbf{n}}\bigg|_{r_{\mathrm{s}}}=M_2\,\frac{\partial p_2}{\partial \mathbf{n}}\bigg|_{r_{\mathrm{s}}}\,, \tag{5.21}$$

$$p_1-p_2\Big|_{r_{\mathrm{s}}}=\frac{2\varepsilon}{b}+\frac{\pi K\varepsilon}{4}\,, \tag{5.22}$$

$$p_2\Big|_{R_\infty}=0\,, \tag{5.23}$$

where p_i is the pressure in the fluid ($i=1, 2$ for the respective displacing and displaced fluid), ε is the surface tension at the interface between the fluids, $\mathbf{n}$ is the normal to the surface, $M_i=b^2/(12\mu_i)$, and K is the curvature of the distorted interface surface. The initial boundary between the liquids is perturbed harmonically, $r_{\mathrm{s}}=R+\cos(k\varphi)$, where R is the radius of the boundary, δ is the perturbation amplitude, k is the perturbation mode, and φ is the polar angle.

With the help of linear analysis for morphological stability and the MEPP, the transition spinodal and binodal were determined, and domains of the coexistence of different morphological phases under radial displacement were predicted in the mathematical setup in Eqns (5.19)–(5.23) [136–138]. In [139–141], an experiment was performed that qualitatively confirmed predictions of the theory. Quantitative differences are related to the fact that the entirety of approximations used in the classical theory cannot be taken into account in experiment. In the numerical experiment in [142], classical system (5.19)–(5.23) was investigated under conditions fully coincident with theoretical ones. In this experiment, the perturbation of the interface was assumed to be harmonic with an arbitrary amplitude. The theoretically predicted values of the binodals were confirmed in the numerical experiment. Quantitative differences did not exceed 10%. As in the case of diffusive crystal growth, theoretical predictions based on the MEPP and numerical calculations give better results, the more nonequilibrium the displacement process is (i.e., the greater the displacement rate and the difference in viscosity, and also the more the boundary shape differs from the round one).

6. Current directions for the development of the maximum entropy production principle

6.1 Classical directions of development

1. *Theory of nonequilibrium processes*. Not much has been done here recently. We note three areas of work.

The first [37, 143] is related to Beretta's idea about the fastest increase in entropy (steepest entropy ascent), mentioned in Section 2.1. Starting in 2014, Beretta has been advertising and developing his method as a uniform constructive realization of the MEPP for solving nonequilibrium problems at different levels of description. The key role is played here by a geometric metric with respect to which the trajectory length is measured in the state space. With an appropriate metric field defined for an arbitrary nonequilibrium state, it is possible, as Beretta believes, to construct most of the existing nonequilibrium theories such that the nonequilibrium state spontaneously develops in the state space along the path of the fastest increase in entropy among the paths compatible with the existing constraints. In the framework of this method, Beretta discusses statistical models of relaxation, kinetic models like the Boltzmann equation, rational extended thermodynamics, macroscopic

nonequilibrium thermodynamics, chemical kinetics, etc. In fact, the approach presented in [37, 143] is a generalization and significant extension of Ziegler's orthogonality relations (see Section 2.1).

In the second area [144], a generalized nonequilibrium thermodynamics is proposed, where the local equilibrium hypothesis and the assumption of a known local connection of fluxes and forces are replaced with the postulate of the scale invariance of such a relation, i.e.,

$$D^m = \sum_{r,l,\ldots,p=1} L_{\alpha_r,\ldots,\gamma_p} J_r^{\alpha_r} J_l^{\beta_l} \ldots J_p^{\gamma_p}\,, \qquad \alpha_r + \beta_l + \ldots + \gamma_p = k\,, \tag{6.1}$$

where D is a positive dissipative homogeneous function of degree k/m, defined as the product of generalized forces (causes) and generalized fluxes J (responses) in the system; and $k, m, r, l, \ldots, p$, $\alpha_r, \beta_l, \ldots, \gamma_p$ are nonnegative integer numbers. In the case of local equilibrium, D coincides with entropy production.

It has been shown in [144] that the proposed formulation (mainly based on (6.1)) not only allows deducing the fundamental results of classical linear nonequilibrium thermodynamics but also yields a number of known assertions in the nonlinear case (the MEPP, the condition of macroscopic reversibility, and generalized reciprocity relations); the applicability of these assertions is the subject of a discussion in the literature. Dropping the hypothesis of local equilibrium essentially extends the applicability domain of the obtained results, first and foremost due to the greater freedom to choose fluxes and forces compared with the local-equilibrium case. An interesting corollary of the approach proposed in [144] is a possibility (for $k < m$) of the inversely proportional dependence between fluxes and forces. In that case, as a thermodynamic force decreases, the thermodynamic flux increases, and, in the limit of zero force, the flow is infinitely large (we note that D vanishes in this case). Such an exotic relation between a flux and a force can be very important in a number of systems[13] for which classical thermodynamics is inapplicable, for example, because of the absence of thermodynamic equilibrium.

In the third area of work, the relation between the MEPP and the Kolmogorov–Sinai entropy maximization procedure [145, 146] is discussed. The analysis is limited to the simplest Markov chain, the so-called ASEP (asymmetric simple exclusion process), which describes the transport of particles between two reservoirs via direct and reverse probabilities along some one-dimensional chain. This model is one of the most important ones for describing nonequilibrium systems, similarly to the Ising model in the theory of critical phenomena. In working with the ASEP, it is usually assumed that the relation between transition probabilities is known, and the task is to solve the problem exactly for the steady flow. Here, by contrast, this relation is assumed to not be known exactly, and by varying the parameter of the relation, different stationary states are then obtained, and thermodynamic entropy production and the Kolmogorov–Sinai entropy are calculated as functions of this parameter. The authors of [145, 146] show that the dynamical rules that maximize entropy production and the rules that maximize the rate of change of the Kolmogorov–Sinai dynamical entropy agree with each other with high accuracy. The accuracy actually depends on the system size, the degree of nonequilibrity, etc. The revealed relation between two entropies is very important for the further development of the theory of nonequilibrium systems. The authors also note the relation of the above principles to the principle of minimizing the time that the system takes to reach a stationary state (the mixing time) [146, 147].

2. *Work on hydrodynamics*. We note three groups of recent work in this field.

In the work by Glimm's group [148] (see also [149]), the current crisis in numerical modeling of turbulence is noted. This crisis is related to the well-known problem of choosing the computation grid scale and methods of data coarsening in strongly developed turbulence. As the authors mention, this problem only becomes more acute as the computation power increases. They discuss several popular algorithms for a numerical solution to the problem based on different physical approaches. The analysis of old and new results shows that the best solution strategy agrees with the MEPP. We note that the authors of [148, 149] radically insist that a condition necessary for the quality and applicability of numerical algorithms is given by their consistency with the MEPP (which, similarly to a conservation law, must serve as one of the criteria for certification of a numerical method). In recent paper [150], Glimm and collaborators mathematically confirm in a sufficiently general form that maximal entropy production is a necessary condition for selecting a physical solution of the Euler equations for an incompressible fluid. Their results on modeling turbulence actually extend the ideas of Robert and Sommeria, first proposed in 1992 in [151] (a review of this and other papers can be found in [4]).

Overall, to generalize the assertion expressed in [148, 149], any mathematical (or numerical) model for studying nonequilibrium processes must satisfy the MEPP. Consequently, if a model does not satisfy the MEPP, then this is a deficiency of the model, but not a manifestation of the falsity of the principle.[14] However, the 'falsity' of the MEPP or the options for 'improving' it are still being sought along that path. For example, the authors of recent paper [152], using one of the generally accessible software packages for numerically solving problems in fluid mechanics, consider transitions between different structures under thermal convection and conclude that the MEPP must be refined and improved in a number of cases.

The second direction of work that we note is related to the further development of Paltridge's ideas (see Section 2.2). In [153], after a brief critical review of the modern state of climate modeling (including the MEPP-related one), a relatively simple MEPP-reliant model of climate is constructed in order to find vertical energy fluxes and the temperature distribution in the atmosphere. The model differs from the previous ones by a detailed description of energy transformations. Various contributions, including that of the chemical composition of the atmosphere, were taken into account in the modeling. The result of computations in [153] are closer to observations than the results of previous models. In [153], the effect that variations in carbon dioxide concentration exert on climate was also investigated. The authors express the hope that the MEPP models of climate similar to the one that they considered can be very promising in the class of

[13] Such systems are encountered in branches of science such as nano- and astrophysics and neuropsychology.

[14] See also footnote 4.

models that have a small number of fitting parameters, but at the same time are in good agreement with long-duration observations.

In the third area of work [154], the morphological stability of a bubble surface was investigated in the inertial regime of bubble growth described by the Rayleigh equation. In this approximation, the motion of the boundary is entirely determined by the difference between pressures inside and outside the bubble, while thermal processes due to evaporative cooling of the liquid are disregarded (this approximation is valid for growth of small bubbles in a strongly overheated liquid or at decreased pressure). The conclusion consists of the morphological stability of the bubble surface under infinitesimal perturbations in the inertial growth regime. For the first time, a thermodynamic calculation of morphological stability of a bubble was done with the use of entropy production and the MEPP. In accordance with the results of the thermodynamic calculation, bubble inertial growth is always morphologically unstable (unstable to perturbations of an arbitrary, not necessarily infinitesimal, amplitude). This theoretical result for the first time allowed explaining the instability (roughness) of the bubble surface observed in experiment. Previously, explanations of this experimental result required a much more involved mathematical model of bubble growth.

3. *Work in materials science*. Modern investigations, like the preceding ones, are concentrated here on nonequilibrium crystallization and work on deformations, ongoing since Ziegler's time. These investigations are mostly aimed at solving specific problems of practical importance for technology and are hardly of interest to a broad group of researchers; we therefore very briefly mention only some of the recent work.[15]

Paper [156] is a review, augmented with some original results, on rapid solidification of microstructures and the additive manufacturing with beam surface heating (laser, electron flux, etc.). The parameters of the structure (including the scale of the smallest microstructure), temperature, and fluid flow velocity are calculated as functions of the beam parameters. A theory based on the MEPP is used in calculations. In [157] (a paper by Sekhar's research group), experimental results for dilute alloys during solidification are compared with those obtained using a model based on the MEPP. In particular, experimentally determined solute diffusion constant in dilute binary Pb–Sn alloys is compared with predictions of various models; the MEPP model is noted as the preferable one.

Modeling the microstructure evolution under structural phase transformations is currently a complicated subject, mainly because of the competition between potential products of the transformation and the multiscale nature of the relevant processes. In a paper devoted to this subject, Ref. [158], a probabilistic MEPP-type model is developed in which a Fokker–Planck-type equation is derived for the evolution of many microstructure parameters of the resultant phases. The final model, which is free of fitting parameters, is used to study sedimentation in Al–Cu alloys and yields results on the sedimentation sequence and its kinetics, which agree with experimental data.

In [159, 160], a simple phenomenological model based on the MEPP was proposed, which predicts an explicit dependence of the velocity v and size ρ of a dendrite tip on supercooling Δ under dendritic crystallization. By applying the principle to the simplest local heat balance equation on the crystal surface, it follows that $v = c\Delta^2 + d\Delta^3$ and $\rho = a/\Delta + b$ (where a, b, c, and d are some phenomenological coefficients). These dependences were checked against the existing experimental data on stationary growth of dendrites of succinonitrile (SCN) in terrestrial conditions and in microgravity, and their improved quantitative correspondence compared with earlier approximations was observed [159]. Subsequently, the growth of ammonium chloride dendrites from aqueous solution was studied experimentally [160]. The growth rate and the curvature radius of the primary and secondary branches in nonstationary and stationary growth were found as functions of relative supersaturation. It was shown that the results of experiment can be quantitatively described by a phenomenological MEPP model [159]. A hypothesis is also put forward that the values of the a and b coefficients for the primary and secondary branches of the dendrite coincide.

In [161, 162], in experimental studies of nonstationary growth of dendritic and seaweed structures in nonequilibrium crystallization of ammonium chloride in a thin planar capillary, it was revealed that the specific increase in mass (in area for the quasi-two-dimensional system under consideration) is the same for the coexisting *different* parts of the structure (including the primary and secondary dendrite branches). In [75, 163], this was explained using the MEPP. Indeed, as noted above, a corollary of the principle consists in the equality of specific entropy productions in simultaneously growing parts of the crystal. In this case, we can approximately write [75, 163] $j_1\Delta\mu_1/R_1 = j_2\Delta\mu_2/R_2$ for the first and second parts of the crystal, where j_1 and j_2 are the fluxes of the crystallizing component toward the boundaries of the first and second parts of the crystal, and $\Delta\mu_1/R_1$ and $\Delta\mu_2/R_2$ are chemical potential gradients at characteristic distances R_1 and R_2 for the first and second parts. The differences between chemical potentials near the coexisting parts of the crystal under consideration are approximately equal ($\Delta\mu_1 \approx \Delta\mu_2$). In accordance with the mass conservation law at the boundary, we have $j = \dot{m}/R^2$ up to constants (where $\dot{m}$ is the change in time of the crystal mass m). Substituting the expression for the flux in the above equality, we obtain $\dot{m}_1/R_1^3 \approx \dot{m}_2/R_2^3$ or, dividing by the density of the crystal, $\dot{m}_1/m_1 \approx \dot{m}_2/m_2$. Thus, the use of the MEPP allows explaining the experimentally observed equality of specific mass increments for different coexisting parts of a crystal undergoing nonequilibrium growth.

In [164], an analytic three-dimensional model is worked out based on the MEPP for describing a stable state in the case of strong plastic deformation resulting from continuous welding by friction. No a priori hypotheses or measured parameters of the response to the action are assumed. The exactness and universality of the model have been confirmed by experiments with eight types of alloys. The results of the experiments have shown that the model can be used to make precise predictions of the temperature, axial shortening rate, and the welding power based only on the initial condition, sizes, and heat-transfer properties of the materials. The friction factor, traditionally regarded as an empirical parameter, is also amenable to prediction.

6.2 Maximum entropy production principle in biology

The MEPP found wide use in biology about 20 years ago. We briefly summarize some work areas.

[15] A review of work done prior to 2015 can be found in [4, 75, 155].

Based on the MEPP, Juretić and collaborators investigated a number of relevant problems of bacterial photosynthesis and chemotaxis [165–167] and the evolutionary laws of the efficiency of enzymes (see, e.g., [168–170]). Applying nonequilibrium thermodynamics and the MEPP, Kleidon [171–173] studied the role of biota in energy fluxes on Earth (atmospheric circulation, hydrology cycle, biogeochemical cycles).[16] Vallino and collaborators [174–176] modeled natural microbial systems using the MEPP.[17] Making comparisons with the results of field observations, they conclude that the model is extremely viable, although it requires fewer parameters than previous models do. Dewar showed in [177] how the MEPP invites a unified view of different optimization theories proposed previously to describe the life-sustaining activity and evolution of plants.

In what follows, we focus on one research avenue that is of special interest and importance.

Work devoted to biological evolution. A huge number of researchers have touched upon the subject of evolution from the standpoint of approaches related to the MEPP in one way or another. The origin of this subject can be traced back to the classics of the 19th century. Boltzmann's phrase (1886) is well known: "The general struggle for existence of animate beings is therefore not a struggle for raw materials — these, for organisms, are air, water and soil, all abundantly available — nor for energy which exists in plenty in any body in the form of heat (albeit unfortunately not transformable), but a struggle for entropy, which becomes available through the transition of energy from the hot Sun to the cold Earth" [178]. Attempts to relate the driving force of Darwin's evolution — natural selection — to some specific thermodynamic characteristic are numerous. Starting in 1922, these investigations were greatly influenced by the work of Lotka [179–181], who stood for the principle that evolution occurs in the direction that makes the general flow of energy through the system maximal among energy flows for all systems compatible with the existing constraints. In other words, species compete for the acquisition of accessible (free) energy, and those that are more successful in obtaining and using it become the winners. In [182, 183], a modern analysis of Lotka's principle is given, and its relation to the MEPP is discussed. In principle, this relation is obvious: an increase in energy flow inevitably leads to an increase in heat dissipation, because real possibilities of increasing the efficiency factor are very limited.

An important step on the path to the modern formulation of the MEPP was made by Kirkaldy in [184]. His studies were already mentioned in Section 2.2. In 1965, heuristically, he practically guessed the modern view of evolution from the standpoint of thermodynamics, noting that evolution occurs by alternating maximization and minimization of entropy production. He related the maximization of the entropy production of an evolving system to fluctuations resulting in the appearance of new internal relations, and minimization of entropy production to the relaxation of these fluctuations. In 1968, Dolnik used experimental data to show that, as living creatures increase their complexity from protozoa to mammals and birds, specific heat release noticeably increases [185]. The next important work was the study by Ulanowicz and Hannon [186] (1987), where they proposed a number of arguments supporting the hypothesis that living systems produce more entropy compared with the amount that would be produced in the absence of life. We must also mention the studies by Aoki [187, 188], who, starting in 1989, performed calculations of entropy production for different organisms and lake ecosystems and argued for the assertion that, at the initial stage of development of an organism (ecosystem), entropy production increases, and at the final stage, decreases. These arguments give good support to Kirkaldy's ideas and the MEPP.

After 2000, the number of papers discussing evolution (not only the biological one but also cosmic, technological, etc.) from the standpoint of the MEPP or closely related principles drastically increased. We refer the interested reader to reviews [2, 6, 183, 189–199].

We outline the views on evolution from the MEPP standpoint that have taken shape to this day. In accordance with the generalized formulation of the principle, on any occasion at any hierarchical level, a nonequilibrium system in the course of self-organization selects the state that maximizes the entropy production density; or, even more concisely, nature in its development prefers systems that produce more specific entropy.[18] An obvious corollary of this is the emergence of life on Earth, the increase in complexity of living creatures in the course of evolution, the emergence of human beings, and the entire course of the development of our civilization (from humans that started using fire to humans widely using oil fuel and atomic energy).[19] As a result, the MEPP turns out to be the most important principle explaining the direction (progression) of biological and technological evolution. According to this principle, the increase in complexity in the process of evolution is determined by the fact that, at the fixed constraints of the surrounding world (in general, strongly nonequilibrium), systems with maximum entropy production emerge (cells, organs, organisms, communities, etc.). The tendency toward an increase in entropy production is fundamental for both the emergence of biological material and in many cases for natural selection. The MEPP allows a rather original combination of Lamarck's idea of the tendency toward perfection and Darwin's idea, which was its antithesis at a time, of natural selection. Following the MEPP and 'selecting' in accordance with it, organisms naturally become more complex because higher levels of organization and complexity require consuming more free energy, which, being transformed, produces more entropy.

Such increases in complexity in the course of evolution (usually called progressive) is a rather rare evolutionary event. The frequency of such transitions is much lower than the frequency of transformations occurring at a constant, already established, level of complexity. Transitions to the next evolutionary level (establishing new relations between driving forces and the emerging functions) occur in accordance with the MEPP, but, at a given (already attained) stage of system development, its long-term optimization is possible (involving competition and selection), which can notably decrease entropy production (for systems not too far from

[16] These questions pertain to the widely known Gaia paradigm, according to which life is responsible for maintaining homeostatic conditions on Earth. Influence is exerted by tuning Earth's albedo, the carbon dioxide content, etc. Studies by Kleidon [171–173] contain important and extensive information on energy and entropy flows in different geospheres.

[17] A metabolic network is used in the model to represent microbial oxidation–reduction reactions, with the biomass distribution and the reaction rate determined by solving an optimization problem.

[18] In many cases, we can speak not of entropy but of usual heat released.

[19] Indeed, this occurs with a progressively greater specific release of entropy (heat); numerous substantiations can be found in [185–189, 191, 192, 196].

equilibrium). We give the following example. Humanity, in its development, moved to mass use of electric power, which led to a jump-like increase in released heat. However, this was attended by work on more effective (economical) production and consumption of electrical energy. Clearly, this will not bring humanity back to the preceding level of heat release, but is merely a slow-down of civilization before the next dash in the use of energy.

The MEPP offers a nonconventional view of the problems associated with the progress and future of humanity. Currently, because of climate warming, measures are being planned or are already underway on some limitations of heat release and greenhouse gas emissions. In making these plans, the MEPP is currently not taken into consideration. But without due account of this principle, the measures taken to combat climate change can be inadequate or even dangerous for the future of humanity. Indeed, nature follows the underlying principles, including the MEPP. The intentions of human who cares about preserving their habitat are clearly different. If we limit ourselves in transforming available energy, then we might engage in a conflict with our originator, nature. In this case, will Nature choose systems that are more evolutionarily progressive from its point of view, displacing us from the top to which it has previously placed us? These new systems would produce more heat using all the available energy. We are used to looking at the world, placing ourselves and our needs in its center, but if we look from the point of view of Nature, the Universe.... As a result, taking care of our habitat, preserving it for future generations, do we not fall into a trap leading to the death of humanity?

Using the MEPP, we can answer the primal question of biology: what is life? As is known, this question has been discussed many times, but no universally accepted answer has been given. There are more than a hundred definitions [200]. According to the definition proposed in 1994 by NASA when addressing the problem of searching for life in the Universe [201], "life is a self-sustaining chemical system capable of Darwinian evolution." But this definition was then heavily criticized. One of the shortest definitions of life is 'self-reproduction with variations' [200]. All the existing definitions of life involve notions that are often difficult to define rigorously, let alone to measure[20] [200–202]. This entails enormous complications in the search for extraterrestrial life.

Another common important drawback of existing definitions is that a researcher, defining life, ignores the point of view of nature and its laws, chooses the point of view of organisms that are close and understandable to him. This is the origin of notions such as DNA, protein, carbon, water, metabolism, mutation, and reproduction appearing in definitions of life. We should not search for our own kind, from our biased standpoint, and confer the rank of 'living' onto them. But in our search for life we must seek systems that are at the same level of development as we are from the standpoint of the Universe and the laws governing its evolution. Such a definition of life would allow us to be unbiased and get rid of our habitual ego- and anthropocentrism. Just that possibility is offered by the MEPP. From that standpoint, based on the results in [2, 6, 189–193], we can propose the following definition of life (which might still need refinements in the future): life is a space–time domain with the specific entropy production in the range of $10^3 - 10^5$ of the specific entropy production of a star in the vicinity of which this domain is located.

This definition of life and the MEPP implies many corollaries (the state of nonequilibrium characteristic of living organisms, stability, emergence, the ability to evolve, etc.), but this could be the subject of another paper. We make only three important remarks.

(1) The specific production of entropy is calculated per volume. Based on the data in [203] (see also [189, 191, 192]), living organisms release heat in a range from approximately 0.1 to 10 W kg^{-1}, which for standard conditions and quasi-stationary processes corresponds to specific entropy production in the range of 0.1–10 W $(m^3\ K)^{-1}$ (by order of magnitude). Specific entropy production on the Sun is of the order of 10^{-4} W $(m^3\ K)^{-1}$ [204–206]. This yields the ratio given in the definition. Importantly, specific (per volume) entropy production for a main-sequence (MS) star is equal to the solar one with good accuracy [204–206]. Therefore, normalization to this quantity is sufficiently universal for the vast majority of stars (we note that specific, per mass, entropy production changes strongly even for MS stars). Specific production is calculated per volume rather than mass, because volume is a quantitative characteristic (measure) of space, whereas mass is a characteristic of matter–energy in space. Another important reason for that choice is the simplicity of measuring volume rather than mass in astronomical observations.

(2) The domain mentioned in the definition can be inhomogeneous (mosaic-like) in space as regards the level of specific entropy production. In accordance with the MEPP, maximal values of specific entropy production in the domain increase with time.

(3) The proposed definition is not applicable to the next level of organization of living matter (societal, technological, etc.), characterized by the use of energy sources outside the body (for example, fire, electric power facilities). Such systems can easily be given a definition by analogy with the above definition of the living, using estimates based on data on heat release, e.g., in [191, 192].

6.3 New promising applications of the maximum entropy production principle in recent years

Several studies using the MEPP have recently appeared in different areas of science where this principle had not been widely used previously. We briefly mention two promising areas.

6.3.1 Astrophysics of stars. The entropy production of several thousand stars was calculated in [204, 205] based on BV-photometry. It was found, in particular, that specific (per volume) entropy production Σ_V for MS stars is in a narrow range near the solar value of $(6 \pm 2) \times 10^{-5}$ W K^{-1} m^{-3}. Because stars remain in the MS for the most part of their lives, this state can be considered stable (an attractor). In this state, stars coexist with each other for a relatively long time. The equality of Σ_V for coexisting nonequilibrium subsystems in approximately similar external conditions, as we have already mentioned several times, is a corollary of the MEPP. That equality was used in [206] to obtain a relation between the luminosity L and the effective temperature T for MS stars. A characteristic feature of this derivation compared with the results of the classical approaches used previously and relying on the analysis of equations for the stellar structure is its

[20] For example, notions such as 'complexity,' 'self-reproduction with variations,' and 'self-sustained.'

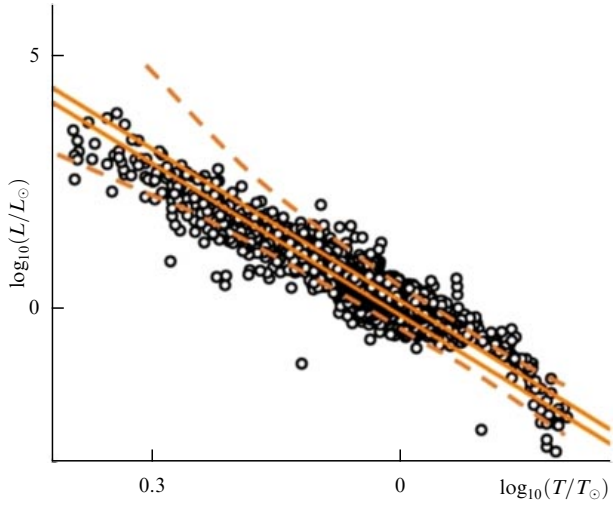

Figure 17. Dependence $L(T)$ of luminosity on temperature obtained by processing photometric data is shown with circles; lines show the theoretical dependence with various errors taken into account. $T_\odot$ and $L_\odot$ are the effective temperature and luminosity of the Sun. (From [206].)

simplicity and total absence of semiempirical constants. The obtained law has the form $\log(L/L_\odot) = 10\log(T/T_\odot)$, where $T_\odot$ and $L_\odot$ are the effective temperature and luminosity of the Sun. The available photometric data for more than 7.5 thousand stars show that the obtained luminosity–temperature dependence is better than dependences used previously [206]. In Fig. 17, we present experimental data and the theoretically obtained $L(T)$ law. The fruitfulness of nonequilibrium thermodynamics and the MEPP, demonstrated in [206] in solving the important problem in astrophysics of MS stars, is apparently not accidental. In the future, it would be interesting to apply this approach to calculate the parameters of other-type stars, and also to analyze the evolution of stars from their formation to death.

6.3.2 Brain and mind. The first discussion of processes occurring in the brain from the standpoint of extremizing entropy production can be traced to 1965, to a study by Kirkaldy [207], who has been mentioned several times in the foregoing and who considered the brain an irreversible system that receives energy flows and information from the environment. Processes in the brain are attended, in Kirkaldy's view, by both a minimization in entropy production (e.g., in learning and deduction) and maximization (e.g., in creative work and induction). Interesting and promising was Kirkaldy's idea that the subjective feeling of time is related in the human brain just to the level of entropy production. However, paper [207] was practically unnoticed, and only very recently have researchers started expressing interest in processes in the brain from the standpoint of the MEPP.

About 25 and 50 years later, in [208] and [209], Kirkaldy's ideas were largely reproduced from the standpoint of the MEPP, then under development. Intellectual activity is considered from the standpoint of nonequilibrium thermodynamics to be a complex dissipative process that produces entropy in interaction with the environment. Maximum entropy production is a necessary condition for this process. An evolving dissipative process (cogitation) can have several states, with transitions occurring between them in interaction with the environment in accordance with the MEPP,[21] which guarantees the stability of each new state. This is the physical foundation for psychological concepts: perception and action. Functions of the brain are considered in this approach in the framework of so-called ecological psychology, i.e., as an extremely complex emergent process of the interaction of a dissipative system with the environment. It is then obvious that this approach to the description of the mind is opposite to the one where the brain is represented as a program containing a list of algorithms for actions in response to all possible stimuli. Work [208, 209] had an effect on the recent investigation [210], where motivational mechanisms of cognitive activity are considered, this being understood as a variation of 'dissipative adaptation.' According to [210], the MEPP determines the goal of this adaptation, and better explains the origin of cognition as a motivational activity. Such MEPP approach provides an opportunity to explain the infinite variety of task-oriented behavior through different manifestations of a single base motive.

The above conclusions about the relation of brain activity to entropy production are quite speculative, being expressed by amateurs in neuropsychology. Recently, however, studies have appeared by Perez Velazquez and collaborators, who directly deal with experimental data on the electric activity of the brain obtained with electro- and magnetoencephalography, as well as other methods [211–213]. Introducing entropy as the measure of complexity of organized and consistent behavior of different cell ensembles of the brain, these authors show, based on the observed signals, that a decrease in that entropy is a signature of pathological states of the brain. On the contrary, high entropy values correspond to normal cognitive activity, a very important role in which is played by the formation and dissipation of energy gradients in ensembles of brain cells (the greater the dissipation, the higher that activity) [213]. Investigations by Perez Velazquez's group [211–213] are important, because they represent the first attempts to relate traditional methods for analyzing signals of the electric activity of the brain (calculation of coherency, phase synchronicity, mutual information, etc.) to thermodynamic characteristics such as energy dissipation and entropy production.[22]

7. Conclusions

The maximum entropy production principle invites us to view the world around us from a common standpoint, without having to divide it into the living and nonliving. At the deepest levels of this world, some 'primitive' physico-chemical processes occur, which obey the MEPP. The construction of higher levels, relating to biology and psychology, is underway before our eyes, and also occurs in compliance with this principle. As a result, the simple and primitive constantly give rise to the progressively more complex and highly organized.

The goal of this review was to show that the MEPP is a universal and very fruitful approach in many branches of science. It has deep roots, a diversified present, and, pinning our hopes on the readers of this review, a very promising

[21] This largely repeats what was already said in Section 5, which also includes a discussion of very instructive results of experiments by Kondepudi, who is the author of the thermodynamic concept of the mind outlined here.

[22] A promising direction for the development of these ideas may apparently be the use of Mihelich's results [145, 146] (see also Section 6.1) on the relation between the MEPP and Kolmogorov–Sinai entropy.

future. Among the promising fundamental directions in physics where manifestations of this principle are to be found, in our opinion, are modern cosmology, the 'eternal' problem associated with the introduction of the notion of time in physics. The origins of the first direction can be found in [214], where it is proposed the anthropic principle be replaced with another principle that resembles the MEPP at its foundation, and then the cosmological constant of our Universe is calculated with outstanding precision. The origins of the second direction are described in [215–217], where the notion of time is introduced based on entropy production and a strategy is outlined to derive the dynamical laws of mechanics, including an analogue of the law of gravity. We believe that the further development of these two directions will open up new horizons for the maximum entropy production principle in constructing a unified scientific worldview.

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