

Review

On the Existence and Applicability of Extremal Principles in the Theory of Irreversible Processes: A Critical Review

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Abstract: A brief review of the development of ideas on extremal principles in the theory of heat and mass transfer processes (including those in reacting media) is given. The extremal principles of non-equilibrium thermodynamics are critically examined. Examples are shown in which the mechanical use of entropy production-based principles turns out to be inefficient and even contradictory. The main problem of extremal principles in the theory of irreversible processes is the impossibility of their generalization, often even within the framework of a class of problems. Alternative extremal formulations are considered: variational principles for heat and mass transfer equations and other dissipative systems. Several extremal principles are singled out, which make it possible to simplify the numerical solution of the initial equations. Criteria are proposed that allow one to classify extremal principles according to their areas of applicability. Possible directions for further research in the search for extremal principles in the theory of irreversible processes are given.

Keywords: thermodynamics; optimization; variational principles; heat and mass transfer; chemical kinetics



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1. Introduction

A thermodynamic analysis is one of the main methods for studying processes occurring in power and chemical engineering plants. The laws of thermodynamics make it possible to obtain a priori estimates and efficiency limits even in the absence of kinetic information about the systems under study. These abilities of thermodynamics are connected, first of all, with the reducing problems to an equilibrium statement. Together with the postulate about the existence of a unique equilibrium, we obtain information about the method of finding it. Most of the information about the trajectory that led to this state is lost after achieving the equilibrium state. That is, the thermodynamic analysis makes it possible to find equilibrium given an incomplete description of the system (for example, to find the state of phase or chemical equilibrium without knowledge of the mechanism of mass transfer and chemical reactions). The possibility of working under a lack of information about a system under interest is the main reason for the wide applicability of thermodynamic laws.

Let's assume that the subject of research is some physical-chemical system, the description of which includes some basic conservation equations (usually, conservation of mass, energy, and charge). The system characteristics to be determined are naturally related to other variables through conservation equations and other constraints. In the case when the resulting system of equations and inequalities turns out to be incomplete or underdetermined, that is, if the number of variables is greater than the number of non-degenerate relations between them, then we need additional relations that may be quite arbitrary. Based on some principles that can be substantiated by physical intuition or probabilistic considerations, it is possible to redefine and supplement the description of the system. The most natural choice is to define some extremal state corresponding to the extrema of criteria or their combinations, chosen for some reason.

In this paper, we will call an extremal principle a rule for selecting solutions from a set compatible with given constraints. If the number of constraints is already equal

to the number of variables, then the problem of finding an extremum degenerates. A feasible solution becomes extremal (simultaneously both maximum and minimum) due to its uniqueness. In practice, we more often deal with problems in which the set of constraints is less than the number of variables. In this case, the solution can be found based on the extremal principle. In this sense, the extremal principle refines information about the system by filling in or approximating unknown connections between variables (for example, inaccessible during measurements or unidentified, random-like ones). In this regard, the extremal principle is basically a regularization method for ill-posed problems [1]. In some cases, the opposite direction is possible, when some constraints may be presented in the form of extremum conditions.

Extremal principles in classical mechanics have, if not understandable, then at least a familiar form. In statics, this is the search for a minimum of potential energy; in dynamics, it is the principle of least action or its analogues. In the first case, the extremal principle gives the problem of mathematical programming: the search for a minimum under given restrictions on the configuration space. In the second case, the problem is formulated in a variational form: one needs to find the extremal value of the integral, which depends on the trajectories of motion. The variational form can be preserved in the presence of dissipative forces by disregarding the temporal symmetry of the Lagrange function. When the kinetic energy is completely dissipated, the system goes into static equilibrium. The equations of mechanics, however, have several equivalent formulations, and the extremal formulation is just one of the options, which in some cases turn out to be more convenient than others. In other disciplines, extremal principles sometimes turn out to be a non-alternative way of formulating problems: first of all, this, of course, applies to thermodynamics, although the same can be said, for example, about some areas of economics and information science.

In thermodynamics, the extremal principles appear as an inevitable consequence of the rejection of a detailed microscopic description of the systems under study. The lack of information must be compensated, and to this end, extremal principles are used, built on the properties of special functions directly related to entropy.

The extremal form of laws in theory of irreversible processes is often an attempt to extend the traditional equilibrium analysis given by Gibbs. There are a lot of extremal principles in this area, ranging from so formal that they cannot be explained by anything but formulas, and ending with so heuristic that it is impossible to formalize them. The situation is similar to the generation of new definitions and interpretations of entropy. It can be considered as some sort of blurring of the semantic ensembles during their evolution.

The concept of the extremal principle in thermodynamics is not always clearly defined. As a rule, this is not a mechanical principle that leads to a variational problem, but some sort of mathematical programming problem. The stability of thermodynamic equilibrium is related to the stability and uniqueness of the extremum of the corresponding thermodynamic function. The extremum conditions usually do not correspond to the solution of a variational problem, even if the principle is related to the entropy production. Instead, the problem is reduced to the mathematical programming problem, or to estimating the entropy production or quantities related to it. In some cases, the concept of “variational principle” is used because entropy is a statistical function of distribution functions, then the conditions for its extremum have a formal variational statement. The same logic can be, albeit limitedly, extended to entropy production. Variational formulations are usually not considered as a way to obtain the necessary equations in the theory of irreversible processes. More often, the entropy production is a selection criterion for solutions that meet the necessary conditions (conservation laws and boundary conditions), i.e., the solutions follow from the conservation equations, and the extremal principle serves to assess the stability of these solutions. In this sense, the extremal principles in the thermodynamics of irreversible processes are not a full-fledged alternative statement of the problem. Extremal principles can be used to supplement the conservation equations in cases where there is uncertainty related to the multiple solutions or ill-posed conditions.

Naturally, the question arises of the application validity of extremal principles in the thermodynamics of irreversible processes. Most of these principles do not have a strict theoretical justification (at least for fairly complex problems). They are mainly inductive. The statement of principles acquires the features of empirical research when the researcher checks a set of hypotheses for compliance with the phenomena observed in a laboratory. At the same time, however, falsified principles are not always rejected: instead, the limits of their applicability are searched, which, however, do not always fit into ordered schemes in the sense that it is not always possible to predict the working conditions of a particular principle.

The existence of universal extremal principles in the theory of irreversible processes is quite a metaphysical hypothesis explicitly formulated in [2] but implied earlier in other forms. Until now, this hypothesis has not been confirmed. However, researchers continue to believe in the possibility of a positive solution to this problem. The grounds for such a belief are supported, in turn, by partial successes in this area, including the results of non-equilibrium thermodynamics (mainly for small deviations from equilibrium). Further progress, in my opinion, was much more modest: although some extremal principles were stated in several individual examples, they do not possess universality and general applicability comparable to the principles of equilibrium thermodynamics.

Since the scope of extremal principles is boundless, we will consider, first of all, the processes associated with dissipation. The presented review is an attempt to give an overview of the studies on extremal principles in the problems of heat and mass transfer of reacting media, as well as to critically analyze the issues of choosing the form of the extremal principle. Special attention is drawn to the problem of substantiation and generalization of extremal principles. Extremal principles for conservative systems are only mentioned for comparison.

The review is organized as follows. Section 2 gives a recap of the extremal principles of equilibrium thermodynamics and their extensions related to kinetic restrictions on the attainability of equilibrium. Section 3 deals with the extremal principles related to entropy production. Section 4 is devoted to the extremal principles in the theory of heat and mass transfer processes that are not based on entropy or entropy production. Section 5 gives some generalizations of the material discussed above.

2. Equilibrium Thermodynamics

Equilibrium thermodynamics is usually considered as a natural extension of the laws of statics. Thermodynamic potential functions are modified (extended) mechanical potential energy, the extremum of which corresponds to the equilibrium state. The equilibrium condition is the condition of the extremum of the thermodynamic function, which connects the thermal, mechanical, chemical, electromagnetic, and other interactions of the elements of the system under consideration. All of these interactions complete the description of the system with conservation equations. As a rule, the number of state variables in the physicochemical system is greater than the number of constraints imposed by conservation equations and boundary conditions. The extremal principle (entropy maximum or free energy minimum) has a constructive function, supplementing the system of equations with extremum conditions. It is possible to imagine a system in which the extremal principle will not be constructive: for example, in a one-component single-phase system with fixed thermobaric parameters (pure inert gas in a closed volume under ambient conditions), the extremal principle will not provide additional information about the equilibrium state, since the set of feasible solutions to the constraint system degenerates into a single state. In mechanical systems without dissipation, the extreme principles of equilibrium thermodynamics will also be redundant. With the conservation of mechanical energy and without heat transfer, the entropy does not change because the equations of motion admit a unique solution at each moment (we will not touch on the discussion about the foundations of statistical mechanics yet).

The extremal principles of equilibrium thermodynamics have not only a remarkable area of application, but also fairly clear-cut boundaries in this area. The subject of classic thermodynamics is equilibrium, so attempts to apply its apparatus to describe irreversible processes are not always correct. Although in some cases, the relations of equilibrium thermodynamics are valid in a wider class of phenomena than only in states of final equilibrium. For example, in distributed (inhomogeneous in space) and non-stationary (inhomogeneous in time) systems, equilibrium thermodynamic relations hold locally (although the choice of scales often requires additional research and justification).

One of the key properties of entropy is its concavity, so a fairly well-developed convex analysis is suitable for studying its extrema. For ideal physicochemical systems, the convex properties of thermodynamic functions significantly improve the efficiency of using numerical methods to find equilibria. In non-ideal systems, the thermodynamic functions can be non-convex, so the search for local equilibria may be quite a difficult task even in relatively low dimensions. Another important property of entropy is its connection with the Lyapunov functions for the equations of dynamics of physical and chemical systems [3]. In closed systems, the Clausius inequality itself can impose strong restrictions on their dynamics.

Examples of the equilibrium thermodynamics applicability beyond the limits of the traditional range of problems are reviewed in [4]. This extension is based on modified thermodynamic functions for non-equilibrium states introduced in [5]. These functions contain terms proportional to the free energy needed to create additional conditions (external fields, thermostats, chemical membranes) in which this state will become equilibrium. The reversible process is constructed to reduce the problem so that the developed methods of equilibrium thermodynamics can be applied. Such a procedure makes it possible to present entropy as a function of composition and internal energy for systems consisting of locally equilibrium but globally nonequilibrium parts (subsystems). This interpolation (as a rule, implicitly) is widely used in non-equilibrium thermodynamics. The local equilibrium approximation will be discussed separately below.

The formulation of additional relations is the addition of new information about the system [6]. If the number of restrictions, including these additional relations, becomes equal to the number of variables, the extremal principle again loses its constructive function. For example, in the complete system of equations of chemical kinetics, the change in entropy is associated only with the reaction rates. Since the reaction rates are determined, there is no selection of states by the magnitude of the entropy. Then, the thermodynamic criteria serve only as a check for the correctness of the chemical kinetics equations (first of all, the balance of the mechanism and the values of the kinetic coefficients [7,8]).

The papers [9–12] propose methods for simplifying the physical and chemical systems based on the contribution of individual processes to the total increase in entropy. The RCCE approach [13,14] and some others (for example, the entropy operator method [15,16]) are based on the approximation of differential equations for a fast subsystem of dynamic variables by equilibrium relations. In this case, the complexity of the complete system of equations (mainly associated with its numerical solution) is reduced by replacing it with an incomplete system of equations with a partial extremal principle, which in a simpler form gives information about the dynamic behavior. The extremal principle is an approximation, rather than an alternative formulation of the equations: it is valid only asymptotically, but in some cases, this is sufficient for calculations. Naturally, the criteria by which the complete system is divided require additional analysis (for example, based on the spectrum of the Jacobi matrix [17,18]). The physical meaning of the approximation is, as in statistical physics, to suppress the high-frequency modes, whose behavior may become chaotic even for deterministic (not necessarily complex) systems. The extremal principle chooses the most stable configuration of fast variables, smoothing out this uncertainty.

3. Thermodynamics of Irreversible Processes

In the previous section, we considered extremal principles based on entropy (or entropy-related quantities) as a system state function. In the thermodynamics of irreversible processes, along with entropy, its production, i.e., the rate of its change, plays an important role. This quantity does not have the entirety of the properties of the state function. As it was mentioned above, it is rather a qualitative criterion for choosing the direction of the processes. Although in some simple cases, the extrema of entropy production determine the stationary states of systems. An interesting way of representing entropy production as a characteristic of a complex dynamical system is given in [19,20]. However, this approach requires consideration of microscopic dynamics, which is out of scope of this review.

It is necessary to mention the limits of the existence of entropy production. Entropy, as a measure of the probability of states, exists only for equilibrium systems (moreover, deviations from the mean are taken into account, with a certain weight, when calculating entropy). Therefore, in order to calculate changes in entropy, the procedure for constructing equivalent equilibrium systems mentioned in the previous section is required. Usually, the appropriate scales are chosen: if the characteristic spatial and temporal scales are significantly larger than the molecular ones (that is, fluctuations do not significantly affect the values of the averages), then the entropy is considered as a function defined at each point and each moment. In the general case, however, the entropy production can only be considered in a finite-difference sense, and the differential representation is only an approximation [21]. The transition to continuous functions is another example of filling in missing information by choosing a convenient representation of variables. The derivative for the thermodynamic parameters exists only in an averaged sense, and its value is chosen with use of the implicit extremal principle. Namely, we choose the difference grid in order to minimize a weighted error which is a sum of the linearization error due to macroscopic nonlinearity, and the uncertainty of the derivative due to microheterogeneity. The chosen grid step can serve as a characteristic scale in the theory of irreversible processes. The finite-difference representation of the transport equations, usually considered a numerical approximation, is the result of applying the local equilibrium hypothesis.

If the local equilibrium approximation becomes inapplicable, then statistical approaches can be applied that use variable decomposition based on relaxation times (for example, the Fokker–Planck equation approach [22]).

The entropy production is extreme for stationary processes with a linear dependence of the variables' change rate on the deviations of these variables from the equilibrium values. Then, the entropy production is a quadratic form in the variables, and its minimum corresponds to the equilibrium state when the variables take their equilibrium values. Prigogine's theorem states that in the linear region, all variables, except for those specified through the boundary conditions, take equilibrium values, i.e., the production of entropy is extremal, namely, minimal under the existing restrictions. The extremal principle is equivalent, in this case, to the statement that the entropy production has the properties of a potential function, and the symmetry of the kinetic coefficients follows from the properties of the Hessian matrix of this function in the vicinity of a stationary point [23]. This area also includes classical hydrodynamic problems, in which the dissipation function in slow viscous flow reaches a minimum in steady low-velocity flows [24]. Note that the main result of Prigogine's theorem depends on the sequence of applying the operations of fixing the boundary conditions and searching for an extremum [25,26]: in the simplest case, the minimum entropy production is zero.

The extremal principles of the thermodynamics of irreversible processes are usually not variational principles. Formally, the entropy production is a functional of the fields of concentrations, temperatures, pressures, and other variables. However, contradictory results arise when applying the basics of the variational calculus to the extremum problem for such a functional: the Euler–Lagrange equations give conservation equations only under certain restrictions (either a modification of the objective function or fixing some variables) [27–30]. The Glansdorff–Prigogine principle [31], having a variational form is

a generalization of the stability conditions to nonlinear problems giving the necessary stability criterion [32]. The local potential method can be justified rather as a procedure for constructing numerical approximations than a way to obtain equations (it requires a subtle, if not teleological, variation technique). Biot and Gyarmati principles [33–35], in which the desired conservation equations appear explicitly as constraints on solutions, can be attributed to the same category (as well as similar principles proposed in [36,37]).

If irreversible processes occur under conditions when it is impossible to neglect nonlinear dependencies, the second law of thermodynamics, in the form of inequality, again becomes the only justified extremal principle. Although the second law of thermodynamics, as mentioned above, significantly limits the range of feasible solutions, the arbitrariness in the choice remains large. The existence of extremal principles consistent with the conservation equations and boundary conditions turns out in nonlinear dissipative systems to be a fortunate choice of variables rather than a consequence of their general properties. In this regard, variable transformations supporting an extremal form of a problem, are of interest.

The minimum entropy production, even if it does not correspond to the phenomena observed in practice, often turns out to be desirable, for example, in thermal and chemical engineering. A decrease in entropy production may lead to an increase in the efficiency of devices (heat exchangers, engines, chemical reactors). Therefore, the search for conditions under which the entropy production turns out to be minimal is an important problem: finite time thermodynamics is devoted to its study [38–40].

It is necessary to discuss the principle of maximum entropy production. It is used, as a rule, not to obtain solutions, but to select them from a set of possible solutions compatible with boundary conditions and conservation equations. Historically, one of the first principles of this kind is the Ziegler principle, which states that non-stationary processes proceed in such a way as to maximize the entropy production [41,42]. It is necessary to point out that the maximization of the entropy production does not follow the principle of maximum entropy, since the maximum value of entropy can be reached in many different ways. For example, the conversion of an oxygen-hydrogen mixture into water can go through slow oxidation or an explosion: the choice of a specific implementation depends on numerous factors, while the maximum entropy production is achieved during the explosion only. Attempts to substantiate the principle of maximum production begin with the works of Jaynes, where a similar concept is introduced, namely the principle of maximum caliber [5,43]. In the process of evolution, the statistical ensemble retains its phase volume, but the volume inside its hull grows. The linearized Boltzmann equation can demonstrate similar behavior near equilibrium [44,45]. The principle of maximum caliber proposes to select from all possible variants of evolution the one that allows obtaining the maximum volume of the ensemble hull. This option contains the least amount of information about the laws of dynamics (apparently, the linearized Boltzmann equation is an example of such over-reduced dynamics). On the one hand, this approach can give some upper bound for the entropy production consistent with the conservation equations. On the other hand, the actual system behavior may differ from this extremely dissipative one. As pointed out in [46], the maximum entropy production principle needs additional parameters that are difficult to determine unambiguously (for example, integration limits). If dynamic equations are entirely unknown, then nothing prevents the system from moving to a state of final equilibrium (thermal, chemical, and mechanical) during several molecular vibrations. If such a transition does not occur, then the principle should be clarified and supplemented with restrictions on the dynamics. Because such constraints are often non-linear, the extremal properties of the objective function may change. In [47], the existence of special metrics that define the trajectories as geodesics in the state space is assumed (for minimal entropy production principle, see [48]). However, the question of the specific form of such metrics for practically interesting cases remains open.

Some authors assign the principle of maximum entropy production the role of a “hypothesis selection algorithm”, i.e., it implies an iterative cycle of reformulating the

problem until the principle is fulfilled [49–51]. Others consider it more fundamental [52,53], although they do not give clear restrictions on its applicability. For example, in [51], a condition is put forward for the applicability of the principle of maximum entropy production: the system must be complex and far from equilibrium; if the system does not obey the principle, then it is not complex enough and not far from equilibrium. Thus, this principle can be interpreted rather as an attempt to apply thermodynamic criteria to the selection of solutions under the lack of information about the system. For example, some papers on the principle of maximum entropy production are aimed at studying the thermal regimes of planetary atmospheres [52–56]. Other attempts to justify the principle of maximum entropy production, sometimes involving methods from the humanities, can be found in [57]. Note that most of the published works on the principle of maximum entropy production are devoted precisely to attempts to substantiate this principle, and not to its practical application. However, the situation with the principle of minimum entropy production is not better.

Criticism of the principle of maximum entropy production is described in detail in [46,58]. First of all, the generalization of the second law of thermodynamics into dynamics is unjustified. Further, the choice of the process trajectory is ambiguous under conditions when the entropy production turns out to be essentially non-monotonic.

In some papers, the principle of maximum entropy production is partially supported by some results of studies related to specific physicochemical systems (for example, models of autocatalytic and enzymatic reactions [59,60], free convective flow [61], planetary atmospheres from the above works, stellar statistics [62]). However, statements about the universality of the principle, in my opinion, are too exaggerated even for the classes of processes under consideration. It is possible to choose examples of autocatalytic reactions and free-convective flows, in which neither the maximum nor the minimum of entropy production in the same formulation is fulfilled [63–65]. As pointed out in [66], it is difficult to find a phenomenon or process, the description of which with the help of the principle of maximum entropy production is uncontested and, at the same time, adequate. Naturally, for nonlinear systems, the search for a universal extremal principle is a practically hopeless task and attempts to find ordered behavior can be started with the simplest (using the least amount of information about the system) hypotheses. Jaynes's formalism and the hypothesis of molecular chaos are also, in a sense, extreme principles, which are rather difficult to justify, but their application in different problems gives correct physical results. The predictive ability of the maximum entropy production principle remains uncertain.

New varieties of entropy and entropy production are proposed, which may play the role of a state function in the theory of irreversible processes [43,67]. The diversity of approaches suggests that there are still no universal extreme principles in this area. It can be said that the pessimism of the works [2,68,69] has not yet been dispelled: their obituary tone was, apparently, quite appropriate.

The extremal principles of thermodynamics of irreversible processes include the “construction law” on the optimization of system energy transfer [70], which, due to its non-strict formulation, depending on the situation, can be interpreted both in favor of maximum and minimum entropy production [71]. This principle, as the name implies, is focused more on finding the optimal design (similar to the methods of thermodynamics in finite time), and is not a universal law of the organization of matter.

Extremal principles based on the entropy production do not yet have clear limits of applicability, therefore, despite the obvious inconsistency, different authors analyze the same systems from the standpoint of maximum and minimum entropy production with different assumptions and close results [72]. Note that in deterministic systems, each state and each trajectory are unique, therefore, the entropy production in each state and each region has a unique value, that is, both minimum and maximum under the existing restrictions. In this case, the extremal principle is redundant. We may abandon the deterministic description and replace part of the equations and restrictions with the extremum conditions of some new function. Then, for sufficiently complex systems, such

a replacement can be carried out in several ways. Accordingly, the form of the objective function and the type of extremum may change depending on the replacement method.

At the end of the section, it is necessary to mention the seemingly insurmountable problem of extremal principles in chemical kinetics. The previous section briefly mentioned some approaches based on the thermodynamic estimates in the numerical simulation of chemical systems, but these approaches are patchy and woefully not universal. Direct analogies between dynamics and chemical kinetics (which may be expected from the “statics—equilibrium thermodynamics” analogy) do not work at all [73,74]. Attempts to apply extremal principles from the theory of irreversible processes to chemical reactions are still very limited. The relationship between the rate of a chemical reaction and its chemical affinity can be essentially non-linear even for small deviations from equilibrium, and the interaction of numerous chemical reactions leads to the inapplicability of any simplifications. On the other hand, naive attempts to apply the principle of maximum entropy production to chemical transformations also do not lead to any reasonable results [75]. However, in [76,77], the principle of maximum entropy production allowed to construct the trajectories of chemical systems with well-turned approximations for the entropy production in chemical reactions: the numerical results showed that the qualitative results are quite close to the direct kinetic calculations. Authors of [78–80] obtained interesting results on the thermodynamics of complex chemical systems by analyzing the dynamics of different functions from detailed kinetic calculations. Among these functions, the authors singled out a quadratic form for the second derivatives in a certain special norm (related to the thermodynamic properties of the reacting mixture), the integral of which, along the trajectory can be considered as the objective function of the extremal principle. At the same time, however, the extremal principle itself requires knowledge of the kinetic equations, i.e., the same amount of information is needed to write the functional as to write the kinetic equations. Similar functionals were considered in [81,82].

For stationary states in open systems, extremal principles were also proposed, for example, [83] (using kinetic equations) and [84,85] (based on a special “thermodynamic” form of the chemical kinetics equations). Consideration of the chemical reaction as a diffusion process in a space of reaction coordinates was proposed in [86,87], so gradient law formalism can be applied to chemical kinetics problems. In [88,89], the Lyapunov functions for a chemical system were proposed, which are represented in terms of pair correlations for fluctuations of reaction rates and concentrations: to write it, naturally, information about the reaction mechanism and kinetic coefficients is needed.

Three examples of the application of extremal principles to reactive media problems are considered in the Appendix A.

4. Extremal Principles for Dissipative Systems Not Directly Related to Thermodynamic Quantities

As mentioned above, the earlier extremal principles in irreversible processes theory were related to works on viscous fluid dynamics, where stationary laminar flows sometimes obey the minimal dissipation principle [24,90,91]. The dissipation function, however, is directly related to the entropy production [23,92], so they will not be considered below. There are often attempts to associate extremal principles with entropy or entropy production, but this may be inappropriate, for example, if this connection requires unjustified redefining entropy.

The convenience of the extremal formulation led to the development of a theory for solving the inverse variational calculus problem [93]. A sufficient condition for the existence of a variational principle is the potentiality. For example, linear problems can easily be reduced to a potential form. However, this does not mean that the extremal principle does not exist for non-potential problems [94–97]. A variety of “recipes” for constructing extremal principles are proposed in [98–100]. Among them are the transformation of variables and the modification of the functional space. Moreover, some problems admit the existence of several different extremal principles. Variational principles for mechanical

systems with linear friction are proposed in [101–104]. The variational principles for the flow of a viscous fluid (with different limitations of applicability) are proposed in [105–110], including for turbulent flows [111–114]. Some variants of the variational principles for diffusion and heat conduction are given in [115–118]. The variational estimates for the limit intensity of turbulent transport are obtained in [119,120].

The simplest way to formulate the extremal principle for an arbitrary equation is the method of least squares. Such formulations are used, for example, for the numerical solution of differential equations, in mechanics and chemical kinetics [121–123], and convective and random transport [124–126]. For this, however, it is necessary to know in advance the form of the equations: the extremal statement gives a simple computational algorithm.

The extremal principles are sometimes for estimating transport coefficients (for example, for turbulence transport [127–130] and transport in complex media [131,132]). Another area of the application of extremal principles is the numerical solution of heat and mass transfer problems: variational estimates allow one to choose grid parameters [133–137] or construct solutions in series [138,139].

There are a lot of papers on variational approaches in reaction-diffusion equations. Elliptic equations can often be presented in the variational form [140]. First of all, these are the classical equations of chemical engineering (diffusion in catalytic reactors, thermal explosion theory, see), for which the variational statement allows us to obtain fairly good numerical estimates, even at low orders of approximation [141–147]. The propagation velocity of stationary chemical reaction waves also turns out to be related to variational estimates [148–152] (in some cases, they relate to entropy production [153,154]). In chemical kinetics, the variational principles based on the Pontryagin principle have been proposed, which allow one to find the critical values of kinetic parameters and their sensitivity coefficients [155].

An important feature of the examples listed here is that the objective functions and functionals are by no means always directly related to entropy (or entropy production). Moreover, attempts to relate these functions to entropy may be completely unconvincing. For example, the variational principle for reaction-diffusion equations exists even in the approximation of an irreversible reaction (i.e., when chemical equilibrium does not exist in some sense). Friction intensity in mechanical systems determines the entropy production, but it is not determined by its extrema. When using explicit expressions for the friction forces, the entropy production is a deterministic value. Therefore, at each moment and on each interval, it has neither minima nor maxima.

Of course, one can modify the definition of entropy or the definition of entropy in such a way that its extremum coincides with the desired solution. In this case, as already mentioned, the generality of the approach is usually lost. Arbitrariness cannot be introduced at such a fundamental level.

We also note that the heat and mass transfer problems often admit the multiplicity of solutions compatible with the given conditions. The selection of solutions, in this case, occurs as a result of some evolution. For example, the stationary state is reached as the limit of the motion of a dynamical system from a given initial condition at large times. In the deterministic dissipative systems, the initial conditions determine an achievable stationary state. In stochastic dynamics, transition mechanisms lead to a distribution of characteristic residence times corresponding to different admissible states [156]. System entropy (defined in traditional way) and its derivatives do not necessarily determine the observed states. However, one can consider a probabilistic scheme with an ensemble of stationary states between which reversible transitions occur. These transitions may be represented as a process of transfer or transformation, allowing the application of equilibrium thermodynamics formalism. In this case, however, the thermodynamic functions must include information about the frequencies and energy characteristics of these transitions (trajectories). Again, modifications of the objective function are required [43,67,157,158].

5. Optimality and Illusion of Optimality

The previous sections give a brief overview of the extremal principles that arise when describing equilibrium states and irreversible processes. As one can see, for almost every phenomenon it is possible to formulate, if not an exact extremal principle, then at least an asymptotically exact one approximating the behavior of variables in a limited range of conditions. Sometimes the extremal principle appears, in a sense, from a general law of nature (or lack of information about the system under study). In other cases, on the contrary, the extremal principle is rather an artificial construction that allows one to simplify calculations or give a new interpretation of known regularities. However, it is not always possible to unambiguously classify extreme principles. A metaphysical question arises: in what cases can an extremal principle be considered fundamental, and in what cases—artificial?

It seems natural to make genealogical connections between extremal principles and establish which of them lead to valid regularities or formulas, and which are introduced heuristically or using untested hypotheses. However, sooner or later we will find ourselves in the field of axiomatics of physical theories. Since extremal principles are usually postulated, nothing prevents us from introducing new extremal principles, substantiating their necessity by the results obtained. Similarly, we cannot draw the line between those extremal principles which are the only formulation of the problem and those which have an alternative non-extremal statement.

A more reasonable approach, in my opinion, is to estimate the amount of information that the extremal principle allows to obtain. An extremal principle that claims to be fundamental must be constructive. Many solutions must be possible that satisfy the existing restrictions. The principle application should highlight a narrow set of feasible solutions. Another informational advantage of the extremal principle should be the ability to generalize the problem for which it was initially formulated. The principle should give equations for describing processes and phenomena that would be difficult or even impossible to obtain in another way (this remarkable property highlights the least action principle as a more efficient way of formulating the mechanics' equations). Finally, the solutions identified by the principle must correspond to the observed reality, at least within the limits of its applicability. Moreover, the limits of applicability are an integral part of the extremal principle (which is observed for equilibrium thermodynamics and linear non-equilibrium thermodynamics). An alternative set of requirements is proposed in [159] (including possible relativistic extensions).

If the application of the extremal principle requires a preliminary reduction (i.e., an artificial rejection of some information about the system) then the extremal principle loses its epistemological significance (however, it can still be useful, for example, for numerical calculations).

A wide range of tools that allow reducing differential and algebraic equations to an extremal form suggests that not all extremal principles are fundamental. The extremality of the phenomena observed in nature (understood in some sense) is not a property of these phenomena. It is a result of their interpretation (in some cases even “over-interpretation”). As mentioned above, the extremal principle, as a rule, serves to fill the information gap about the system. It can be assumed, slightly changing Jaynes's arguments, that the very existence of the extremal principle means that we do not have a sufficiently definite description of the system (in the sense of the parameters and restrictions necessary for the uniqueness of the solution). We are therefore forced, focusing on the features of the problem, to introduce the regularization of the problem based on some criteria. The choice of these criteria is not always unambiguous, and attempts to relate them to thermodynamic functions (or their derivatives) are not always justified.

It is well-known that the stationary distribution of variables, the transfer of which occurs according to gradient laws (temperature, concentration, momentum in a continuous medium), in the simplest cases, obeys the condition of the minimum gradients squares sum. This fact has several interpretations, ranging from the “intolerance” of nature to

discontinuities and ending with the “tendency” for the minimum production of entropy. On the other hand, a slight change in the system (adding source terms that lead the system to discontinuous or close to such solutions, which are observed, for example, during combustion) will modify the extremal principle, complicating its interpretation. The minimum entropy production hypothesis is not confirmed even in the simplest case (it suffices to consider a non-isothermal system). The extremal principle, which requires minimizing the gradients squares sum, turns out to be just an equivalent form of solving the stationary problem of diffusion transport under certain restrictions on the type of the equations. It has no predictive ability for more complex cases. Both formulations (differential and extremal) lead to the same solution in different ways: this argument is most often used to justify extreme principles, even if they cannot be generalized in any way.

A significant shortcoming of the extremal principles proposed in the thermodynamics of irreversible processes is their “structural instability”. Small changes in the formulation of the problem, the addition of new variables or transfer mechanisms, make the extremal principles unusable and force us to look for new formulations. This inconsistency may result from an overestimation of the extremal principles’ significance for the theory of irreversible processes. Again, the solution of the complete heat and mass transfer equations gives a set of solutions for the desired variables without the application of extremal principles. Extremal principles appear in those cases when the formulation of the problem is incomplete: for example, the initial conditions are uncertain, or the connections between subsystems are unknown. If all of the initial data, boundary conditions and equations are known, there is no need for extremal principles. As in statistical physics, the extremal principle is not something intrinsic to the system under study: it emerges from the limitations of our knowledge of that system [160,161]. In other words, an extreme principle is a scientific way of expressing our ignorance of the description of physical systems. However, many different extremal principles proposed for similar systems express our ignorance in the way of description, and, ultimately, in the physical nature of phenomena. The problem of constructing consistent algorithms for choosing extremal principles in the theory of irreversible processes remains unsolved.

Our selection of a system description always contains some arbitrariness, justified by the results usually obtained from the application of the chosen formalism. Accordingly, the problem of ambiguity in the choice of system boundaries and the extremal principle are closely connected. It can be assumed that the system boundaries determine the extremal principle (as, for example, in equilibrium thermodynamics, the form of the objective function depends on the conditions of the system’s interaction with the environment). In this case, the extremal principle should determine the system state through the boundary conditions in which it exists, in cases where the internal connections (limitations) in the system are not fully known.

Of course, validation of the extremal principle should cover as many examples as possible. Then, the discrepancy between the observed phenomena and the consequences of the principle should serve as a stimulus for reformulating the problem. Ambiguity arises when new information about the system (e.g., empirical information) can be taken into account both in the form of an additional constraint (as, for example, in semi-empirical equilibrium models of chemical engineering processes [162,163]) and by modifying the objective function. In some cases, both methods give equivalent formulations, but in the general case (first of all, when considering irreversible processes), there is no certainty in such equivalence. If the extremal principle is a hypothesis selection rule, then a one-to-one correspondence between the system under study and the extremal principle is implicitly assumed. This statement is not obvious.

The discussion is not intended to refute the existing extremal principles in the thermodynamics of irreversible processes. However, not every law of nature has to take the form of an extreme principle. Leonhard Euler believed that the world provided to us is “the best possible” since everything that happens in it follows the principles of minimum or maximum. However, with the same confidence, it can be argued that our mathematical

tools have developed enough to find the principles of minimum or maximum in everything that happens. Sometimes extremality may be just a pattern that we deliberately look for in the systems under study. In this case, the discovered extreme principle does not necessarily give a broader view of the phenomenon; on the contrary, the search for extrema can lead to misconceptions, which, while retaining the usual form of the extremal principle, are basically local approximations.

In the end, it is necessary to highlight prospects in the area of extremal principles in the theory of irreversible processes. On the one hand, breakthroughs are unlikely in this area, and one of the reasons is development of computational methods and techniques allowing to solve heat and mass transfer problems in a reasonable time (at least, approximately). Proposed principles have a narrow applicability (sometimes, constraints are so stiff that the principle becomes ad hoc procedure). On the other hand, progress in methods in inverse optimization and variational problem solving is remarkable, so we can believe that universal extremal principles for irreversible processes will be found in some form, not necessarily typical for non-equilibrium thermodynamics. Local approximations are not always useless: they may serve as a transition link towards more general theories.

6. Conclusions

In this paper, extremal principles in the theory of irreversible processes (primarily, heat and mass transfer processes) are reviewed. The principles based on the extreme properties of entropy and entropy production are considered in detail. The role of extremal principles is discussed in connection with the choice of solutions from a set of formally admissible ones under conditions of uncertainty that arise due to the incomplete or incorrect formulation of the problem. Since uncertainty and incompleteness are associated with the available information about the system under study, then the unique solution is obtained by a priori statistical estimates (such as entropy and its modifications). In general, the substantiation of the entropy production-based principles is unsatisfactory. The deterministic macroscopic heat and mass transfer equations do not require additional principles for selecting solutions; at the same time, the proposed extremal principles of non-equilibrium thermodynamics, as a rule, do not result in kinetic equations (although in some cases the principles make it possible to estimate the coefficients in approximations). Moreover, there are exact extremal (variational) principles for transfer equations that are not directly related to thermodynamic functions. The results of the review show that the use of the objective function in the form of entropy production limits the possibilities of applying extreme principles to heat and mass transfer processes. It is necessary to expand the toolkit of objective functions: one may look for generalizations among the exact extremal principles for transfer equations, instead of trying to associate a predefined objective function with them.

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Appendix A

Example A1

Let us consider an isothermal diffusion-reaction equation in a porous medium of width L :

$$Dc'' - w = 0 \quad (\text{A1})$$

Here D is diffusivity, c is reagent concentration, and w is reaction rate. Local entropy production is:

$$\sigma = \frac{DR}{2} \frac{(c')^2}{c} + \frac{A}{T} w \quad (\text{A2})$$

Here, R is gas constant, A is reaction affinity. Equation (A2) is valid for an ideal mixture when the chemical potential of the reagent is:

$$\mu = \mu^0 + RT \ln c$$

Reversible reaction occurs with a rate:

$$w = kc - \frac{k}{K^{eq}}(c_0 - c)$$

Here, k is the reaction rate constant, K^{eq} in the equilibrium constant. Then the affinity is:

$$\frac{A}{RT} = \ln K^{eq} + RT \ln \frac{c}{c_0 - c}$$

Extremal entropy production gives Euler–Lagrange equation:

$$Dc'' = w \frac{c_0}{c_0 - c} + \frac{A}{RT} \left(k + \frac{k}{K^{eq}} \right) c + \frac{D}{2c} (c')^2 \quad (\text{A3})$$

This equation is not equivalent to Equation (A1) because it contains some cumbersome terms. It can be shown, however, that Equation (A3) is valid near equilibrium, when $A \approx 0$ and concentration distribution is close to uniform (so $c' \approx 0$). Comparison of numerical solutions is presented in Figure A1 (boundary conditions are $c'(0) = 0$ and $c(L) = c_0$). It can be seen that the extremal entropy production principles overestimate the reaction rate (due to additional terms in the right part of Equations (A3) and (A4)).

It is interesting that using the modified entropy production $\sigma_1 = \sigma c$ we obtain the following equation:

$$Dc'' = w \frac{c_0}{c_0 - c} + \frac{A}{RT} \left[w + \left(k + \frac{k}{K^{eq}} \right) c \right] \quad (\text{A4})$$

Equation (A4) is closer to Equation (A1) due to the absence of a term proportional to gradient squared, but its applicability is still limited to the near-equilibrium area.

Equation (A1) has the exact variational principle [140,164]. Solution of Equation (A1) minimizes a following integral:

$$I = \int \left[\frac{D}{2} (c')^2 + \left(k + \frac{k}{K^{eq}} \right) \frac{c^2}{2} - \frac{k}{K^{eq}} c_0 c \right] dx \quad (\text{A5})$$

Integrand in Equation (A5) do not have direct connection to entropy production. Moreover, this principle cannot be used in non-isothermal conditions or

Example A2

Let us consider the exothermic reaction in a flat layer. The energy equation can be written as follows:

$$\lambda T'' + Qw = 0 \quad (\text{A6})$$

Here, λ is thermal conductivity, T is temperature, Q is reaction heat, w is reaction rate.

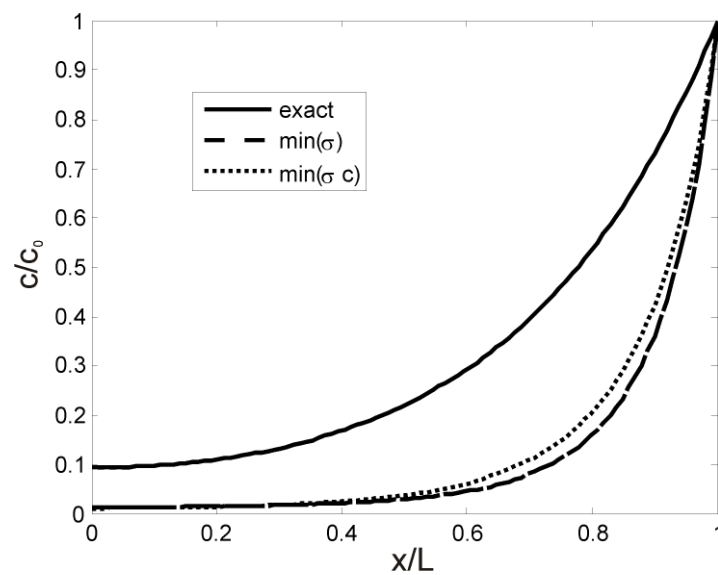


Figure A1. Comparison of numerical solutions of Equations (1), (3), and (4). Values of the parameters: $k = 0.01$; $K^{eq} = 100$; $D = 10^{-5}$; $L = 0.1$; $c_0 = 1$.

Using the combustion theory approximation, we can assume that the below ignition conditions reaction rate is quite low, so we can neglect the reagent depletion. Then Equation (A6) gives the stationary temperature distribution under $w = w(T)$.

Local entropy production in the one-dimensional layer can be written as follows:

$$\sigma = \frac{1}{2} \frac{\lambda}{T^2} (T')^2 + \frac{A}{T} w \quad (\text{A7})$$

Let us introduce the generalized entropy production in a form $\sigma_n = \sigma T^n$, for given number n [165]. Extremal entropy production conditions (Euler–Lagrange equations) give the following Equation for $n = 0$:

$$\lambda T'' - \frac{\lambda}{T} (T')^2 + w \left(Q - A \frac{E}{RT} \right) = 0 \quad (\text{A8})$$

Here, E is the activation energy. Equation (A3) is deduced using approximate relations:

$$\frac{\partial w}{\partial T} \approx w \frac{E}{RT^2} A = -\Delta G^r = -\Delta H^r + T \Delta S^r = Q + T \Delta S^r$$

Equation (A3) implies that the entropy production is extremal for the low reaction affinity and low sensitivity of the reaction rate with respect to temperature:

$$\frac{RT}{E} \gg 1 + \frac{T \Delta S^r}{Q} \quad (\text{A9})$$

Moreover, there is an unwanted term proportional to gradient squared, which terms to zero only at the uniform temperature distribution.

If $n = 1$ then we obtain equation:

$$\lambda T'' + \frac{\lambda}{2T} (T')^2 - w \left[\frac{QE}{RT} + \Delta S^r \left(T + \frac{E}{R} \right) \right] = 0 \quad (\text{A10})$$

Equation (A10) contains a wrong sign of the reaction heat rate term. Again, the gradient squared term is present.

If $n = 2$ then we have an equation closer to Equation (A6):

$$\lambda T'' + \left(Q - A \frac{E}{RT} \right) w = 0 \quad (\text{A11})$$

This equation turns to Equation (A6) under condition Equation (A10). That is, the entropy production is minimal close to equilibrium as it was stated in [166]

Equation (A6) is a classical equation in combustion theory. It is convenient to transit to non-dimensional variables [167]:

$$\xi = \frac{x}{L}; \theta = \frac{E}{RT_0^2}(T - T_0); Ar = \frac{RT_0}{E}; Fk = \frac{QE}{RT_0^2} \frac{L^2}{\lambda} w(T_0)$$

Then, Equation (A6) can be written as follows:

$$\theta'' + Fk \exp\left(\frac{\theta}{1 + Ar\theta}\right) = 0 \quad (\text{A12})$$

If Ar is small (i.e., if E is large) then we can state the variational principle in a form of minimization of the following integral [147,168]:

$$I = \int_0^1 \left[\frac{1}{2} (\theta')^2 - Fk \exp \theta \right] d\xi \quad (\text{A13})$$

This principle is exact for $Ar = 0$, but the approximate principles can be proposed for other values [169]. Interestingly, the stability condition for the solution of Equation (A12) is the local minimum condition of Equation (A13), and the critical condition is the inflection point existence [145,168]. This critical condition for Equation (A13) formally corresponds to the Glansdorff–Prigogine criterion, but only for the case of the generalized entropy production with $n = 2$. Moreover, condition Equation (A9) does not allow using the approximation $Ar \approx 0$.

Example A3

Let us consider catalytic heterogeneous reaction in the thin surface layer. Concentration and temperature at the distance δ is equal to the constant values c_0 and T_0 . Then, we can calculate the stationary diffusion and heat flows near the surface:

$$j = \frac{D}{\delta} (c_0 - c)q = \frac{\lambda}{\delta} (T_0 - T)$$

Here, D is diffusivity, T is surface temperature, and c is surface concentration of reagent. Reversible reaction occurs at the surface with a following reaction rate:

$$w = k_1 c - k_2 (c_0 - c)$$

Then, we can equate the diffusion flow and reaction rate, $j = w$, which gives an equation for the surface reagent concentration:

$$c = \frac{c_0 \left(1 + \frac{Da}{K^{eq}} \right)}{1 + Da \left(1 + \frac{1}{K^{eq}} \right)}$$

Here, Da is the diffusion Damkohler number, K^{eq} is the equilibrium constant. In a limit of large K^{eq} we obtain the usual diffusional kinetics formula [169]. Note, that the kinetic constants are functions of temperature, $k_1 = k_1(T)$ and $k_2 = k_2(T)$, and they relate to each other by mass action law:

$$\frac{k_1}{k_2} = \exp\left(-\frac{\Delta G_0^r}{RT}\right) = K^{eq}$$

Then, the stationary surface temperature can be found:

$$T - T_0 = \frac{D}{\lambda} Q c_0 Da \left(1 + \frac{1}{K^{eq}} \right) \left[\frac{1 + \frac{Da}{K^{eq}}}{1 + Da \left(1 + \frac{1}{K^{eq}} \right)} - \frac{1}{1 + K^{eq}} \right]$$

Here, Da and K^{eq} are temperature-dependent. Using non-dimensional variables, we can write:

$$\theta = \frac{\theta_{ad}}{Le} Da \left(1 + \frac{1}{K^{eq}} \right) \left[\frac{1 + \frac{Da}{K^{eq}}}{1 + Da \left(1 + \frac{1}{K^{eq}} \right)} - \frac{1}{1 + K^{eq}} \right]$$

Here, θ_{ad} is the non-dimensional adiabatic temperature. Introducing the Damkohler number for the ground temperature T_0 and assuming $Ar = 0$, we obtain:

$$\theta = \frac{\theta_{ad}}{Le} Da_0 e^\theta \left(1 + e^{-s\theta} \right) \left[\frac{1 + Da_0 e^{\theta(1-s)}}{1 + Da_0 e^\theta (1 + e^{-s\theta})} - \frac{1}{1 + e^{s\theta}} \right] \quad (A14)$$

Here, s is the relation of the chemical reaction affinity and activation energy ($s = -A_0/E$). Typical behavior of the solutions of Equation (A14) is presented in Figure A2.

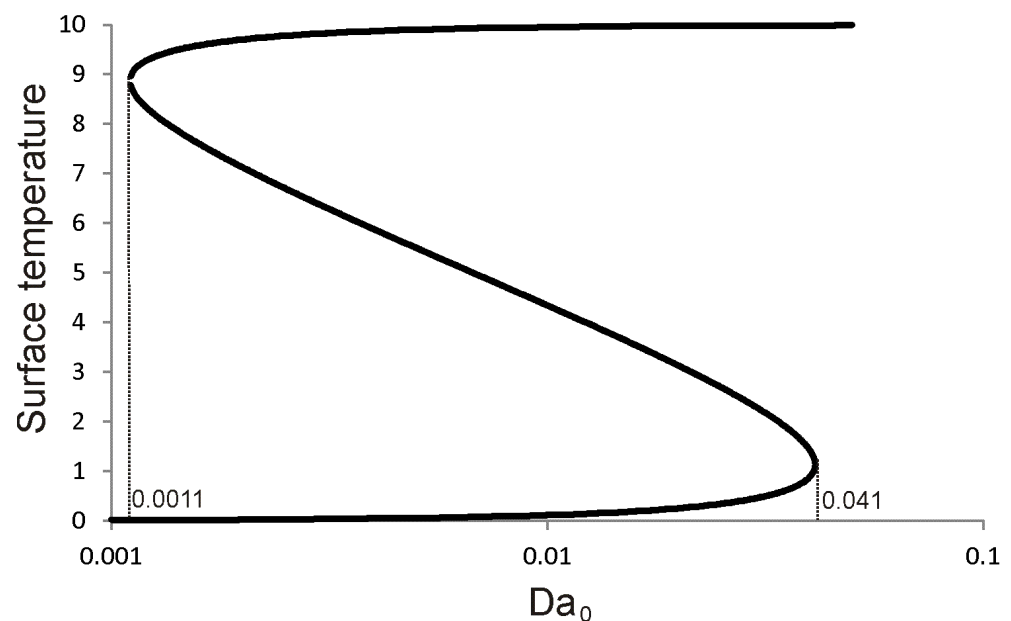


Figure A2. Solutions of Equation (9) at $Le = 1$, $\theta_{ad} = 10$, $s = 10$.

In the range of Da_0 values from 0.0011 to 0.041, the solution becomes ambiguous. That is, at lower values of Da_0 , the surface temperature differs little from the ground temperature, but with an increase in Da_0 (with an increase in the reaction rate or with an increase in diffusion resistance), new solutions appear. The upper (high-temperature) and lower (low-temperature) branches of the solution are stable. The system may end up in one of the stationary states, depending on the initial conditions. In the range of multiple solutions, the entropy production at a fixed Da_0 is minimal on the low-temperature branch and maximum on the high-temperature branch. Entropy production for a given system cannot be non-extremal, since non-extremal stationary states are unstable, but it is impossible to predict a priori in which state of the two extrema the system stays without information about its dynamics. Solutions may have a more complex form, with intermediate stable stationary states: in this case, extreme estimates turn out to be less plausible [170].

In unstable flows (for example, during turbulence), the Damkohler number can fluctuate, so it becomes possible to switch between the branches of the solution. In this case,

knowing the distribution of the Damkohler numbers over observation times and the characteristic fluctuation frequencies, one can estimate the average surface temperature by representing the stationary states as a two-component ensemble.

For each solution shown in Figure A1, the entropy production can be calculated. Moreover, entropy production can be calculated even for those temperatures that cannot be solutions of Equation (A14). An example of such a calculation is shown in Figure A3: it can be seen that Equation (A14) has three stationary solutions at 0.11 (stable), 4.33 (unstable), and 9.96 (stable). In this case, the entropy production has no local extrema and increases monotonically with the temperature (the markers highlight the stationary temperature values).

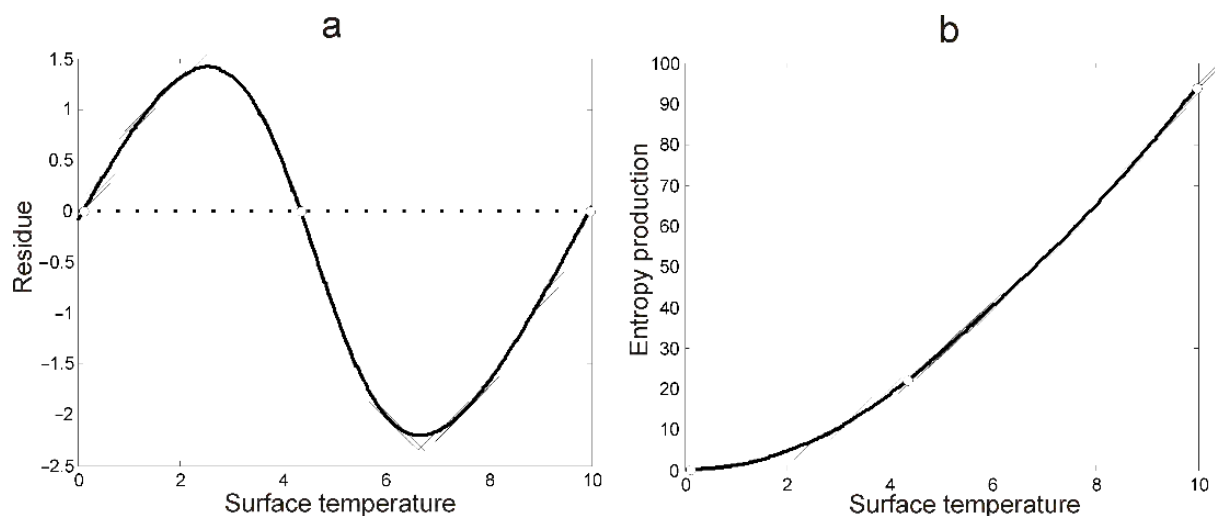


Figure A3. Calculation results for $Da_0 = 0.01$: (a) violation of equality (9); (b) entropy production.

Maximum entropy production principle state that a high-temperature stationary state has a higher probability of observing; minimum entropy production principle state the opposite. These extremal principles are contradictory and unsatisfactory in the presented case.

Critical values of Da_0 (i.e., values that correspond to change in the number of roots) are solutions of the following equation [171]:

$$\frac{\partial Da_0}{\partial \theta} = 0$$

Variations of entropy production do not give the correct stability condition. However, we can estimate one of the critical values (ignition boundary) using an approximation $c_s \approx c_0$, which is applicable in low-temperature conditions. Then temperature can be calculated from the following equation:

$$\theta = \frac{\theta_{ad}}{Le} Da_0 e^\theta \quad (A15)$$

Its solution can be found using the Lambert W-function:

$$\theta = W\left(-\frac{\theta_{ad} Da_0}{Le}\right)$$

The complex in parentheses cannot be less than $-e^{-1}$, and for $\theta_{ad} = 10$ and $Le = 1$ the critical value of Da_0 is 0.037 (which is close enough to 0.041).

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