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2007 J. Phys. A: Math. Theor. 40 371

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On the problem of the minimum entropy production in the nonequilibrium stationary state

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Received 9 October 2006, in final form 24 November 2006

Published 20 December 2006

Online at stacks.iop.org/JPhysA/40/371

Abstract

This study presents a critical review of the Prigogine minimum entropy production principle. The minimum entropy production implies the stationary state of the nonequilibrium system and vice versa: the stationary state of the system implies the minimum entropy production. It was shown that the extension of the principle to the so-called integral case is devoid of this property and, therefore, is less interesting in practical and theoretical terms.

PACS number: 05.70.Ln

1. Introduction

Attempts to find some universal function, whose extremum would determine the development of a system, have been made at all times. A certain success was achieved in optics (Fermat's principle) and mechanics (the principle of least action). Entropy has been doomed to be a quantity describing the progress of nonequilibrium dissipative processes. Great contributions have been made in this respect by two scientists, namely R Clausius, who introduced the notion of entropy and advanced the concept of the thermal collapse of the Universe, and I Prigogine. In 1947 the latter researcher formulated and proved an interesting statement [1, 2], which nowadays is commonly called the minimum entropy production principle (or the Prigogine theorem) and then spent a number of years developing and popularizing the apparatus of nonequilibrium thermodynamics and his principle as applied to description of various nonequilibrium processes.

This principle¹ applies to open linear nonequilibrium systems in the stationary (or approaching the stationary) state and cases where the assumption on the local equilibrium holds. The class of such systems is sufficiently wide and, therefore, this principle attracted (and still attracts) considerable interest. The modern literature cites examples of both the development of ideas underlying the principle and its interesting applications in hydrodynamics

¹ For its rigorous formulation see section 2.

(e.g. [3]), materials science (e.g. [4]), thermal engineering (e.g. [5, 6]), chemistry (e.g. [7]), biology and ecology (e.g. [8–10]), etc. The great interest attached to the principle can be explained by the apparent intuitive simplicity and universality of the proposed statement. This factor just led (and still leads) to numerous misbeliefs on this theorem (see, for example, [11–17, 20]). As a result, two essentially extreme opinions have been formed in the literature. Some scientists glorify the principle and think it is capable of describing the majority of nonequilibrium processes to a certain extent. Other researchers, who observed weak points of the principle and unceasing efforts by Prigogine and his progeny to generalize it [1, 2, 8, 19], are very sceptic about the possibility of formulating universal entropy principles, which would govern so diverse and dissimilar nonequilibrium processes.

We shall review some features of the statement so as to avert its possible misinterpretation or misuse. The focus will be on the so-called integral generalization of the Prigogine theorem.

2. Local formulation

Prigogine originally formulated his principle precisely in the local form² [1, 2]. Let us dwell on it.

Let basic relationships of the linear nonequilibrium thermodynamics be fulfilled a system:

$$J_i = \sum_k L_{ik} X_k, \quad (2.1)$$

$$L_{ik} = L_{ki}, \quad (2.2)$$

where J_i and X_i are thermodynamic flows and forces (the subscript i denotes different flows or vector components depending on particular conditions), L_{ik} is the matrix of kinetic coefficients independent of J_i and X_k .

Let us assume also that irreversible forces X_j ($i = 1, \dots, j; j < n$, n being the number of forces in the system) are maintained constant and the entropy production in the system is a minimum.

Then the system is in the stationary state.

The proof of this theorem is sufficiently simple [1, 2]. It is necessary to substitute (2.1) and (2.2) into the entropy production relation

$$\sigma = \sum_i X_i J_i \quad (2.3)$$

and differentiate it with respect to unfixed forces. Since the entropy production is a minimum under the theorem conditions, the obtained values are zero. However, the obtained expressions are equal, to within constants, to flows numbered $j + 1, \dots, n$. Since all other flows in the system are constant under the problem statement, the system at hand is stationary.

This proof essentially involves only the extreme entropy production. However, because the entropy production is a positive quadratic function of forces, the entropy production extremum corresponds precisely to the minimum.

The inverse formulation is considered frequently [18, 19]: in the case of the stationary nonequilibrium state consistent with external constraints (fixed irreversible forces X_i with $i = 1, \dots, j; j < n$, n being the number of forces in the system), the entropy production in the system is a minimum if (2.1) and (2.2) are fulfilled. The proof of this formulation is virtually analogous to the one adduced above.

² The local form will imply the formulation both for some sufficiently small element of the substance with the local equilibrium and for so-called ‘discontinuous systems’ [2].

Let us briefly discuss the described principle.

- (1) The essence of the theorem is that free (unfixed) thermodynamic forces in the system at hand are mutually adjusted to bring the system to the state with a minimum dissipation. The adduced proof clearly shows that the theorem has sense if several forces are available and some of them are fixed. If only one force is present and it is not zero³, the variation used in the proof vanishes and the speculation about extremalization of the entropy production in the stationary state is empty and incorrect. In this case, the entropy production is fully determined by the preset force and the theorem is null and void. The neglect of this observation and attempts to go beyond the scope of the theorem lead to erroneous results, which allegedly invalidate the local principle [11, 16, 17]. Let us dwell in more detail on one of those most known results (see [11]). We have a section of an electric circuit with parallel connection of conductors (with the resistances R_1 and R_2) kept at different temperatures T_1 and T_2 . The voltage at the ends of this section is maintained constant and equal to U . Obviously, the heat $I_1^2 R_1$ and $I_2^2 R_2$ (I_1 and I_2 being the electric current in the first and second conductors) is released at each resistance and the entropy production in this circuit is $\sigma = I_1^2 R_1 / T_1 + I_2^2 R_2 / T_2$ [11]. Taking into account that the total current is constant ($I_1 + I_2 = I = \text{const}$) at a fixed voltage, it is easy to deduce from the extremum $\partial\sigma/\partial I_1 = 0$ that $I_1 R_1 / T_1 = I_2 R_2 / T_2$. As is known, $I_1 R_1 = I_2 R_2$ holds when conductors are connected in parallel. Therefore, the minimum entropy production principle may be assumed to be erroneous. However, this is exactly the case when one thermodynamic force U is present in the system and one flow I corresponds to this force. The distribution of this flow in the system, which is under this force, has nothing to do with the principle at hand.
- (2) It is seen from the proof that the kinetic coefficients should be independent of thermodynamic forces and flows, but should satisfy the reciprocity relations (2.2). In the general case, these coefficients obviously may be not constants, but may depend, for example, on the concentration and the temperature. Let it be emphasized that the principle is applicable to locally equilibrium systems where a linear dependence is fulfilled between thermodynamic flows and forces. The last fact does not always mean closeness to the equilibrium and large gradients are possible in the system (see, for example, [21]). Probably, the principle also holds for tiny mesoscopic systems where the dynamics is governed by Fokker–Planck-type equations (see, for example, [22]).
- (3) Considering what has been said above, the Prigogine principle in the local formulation is undoubtedly valid⁴. It was discussed and generalized by different researchers [23, 24]⁵ more than once. But a point open to question is if the principle is useful and constructive. A number of researchers are very pessimistic in this respect (see, for example, [11, 26]). The authors [26] hold to the opinion (which is difficult to object) that the information needed for the use of this principle must be so complete that the principle adds nothing new and the direct solution of problems using conservation laws in combination with (2.1) and (2.2) generally proves to be much simpler than the solution involving the minimum principle.

³ If the only force is zero, the system will be in the thermodynamic equilibrium and the further discussion is altogether senseless.

⁴ The validity of local Prigogine's principle is questioned in a recent paper [20]. However, the study [20] is incorrect since the conversion of the formulæ (8) to (9) and (10) (referred to as in [20]) disregarded that the force X_1 should be fixed as X_2 varies.

⁵ It is also noted in [23] that the Prigogine principle may be viewed as a particular case of the Onsager least dissipation principle, which was proposed in 1931 (see also [25]).

- (4) The theorem under discussion allows formulating the so-called evolution criterion meaning that the system will necessarily evolve with time to the stationary nonequilibrium state starting from any nearest state, while the time derivative of the entropy production will be negative [18, 19]. So, the role of σ in the system at hand is similar to the role of thermodynamic potentials in the equilibrium thermodynamics.

3. Integral formulation

In an attempt to extend his principle to a wider class of processes, Prigogine proposed an additional integral formulation of the minimum entropy production principle. This formulation is discussed below.

3.1. Different approaches taken by Prigogine to the proof

Prigogine and his followers proved and illustrated the integral principle taking, most frequently, a simple problem, namely the heat transfer in solids. For this reason, in what follows we shall also refer to this problem. Let us discuss the problem of the heat transfer in a rod having the length l . If the Biot–Fourier linear law holds, the total entropy production P in this system may be written as [2, 18, 19, 27]

$$P = \int_0^l L_{qq} \left(\frac{\partial}{\partial x} \frac{1}{T} \right)^2 dx, \quad (3.1)$$

where T is the rod temperature, x is a coordinate, L_{qq} is the kinetic coefficient related to the thermal conductivity coefficient λ as $L_{qq} = \lambda T^2$.

According to Prigogine (see, for example, [19, 27]), the function $T(x)$, which minimizes (3.1), satisfies the stationary equation for the thermal conductivity

$$\frac{\partial^2 T}{\partial x^2} = 0 \quad \text{or} \quad \frac{\partial T}{\partial t} = 0, \quad (3.2)$$

where t is the time.

The arguments adduced by Prigogine for substantiation of this statement will be given below. At first glance, the case at hand strongly resembles the theorem proved above: the minimum entropy production implies a constant heat flow along the rod or, in other words, a stationary state. It can be seen on the other hand that the proposed formulation considerably differs from the formulation discussed above. Indeed, the spatial temperature distribution is determined from the minimum entropy production in the last case and it is stated that this distribution is stationary. Furthermore, if this formulation is adopted, the system can have only one thermodynamic force (the temperature gradient) and, correspondingly, one flow. Still, the statement seems to be constructive. The last observation points most clearly (see remark 1 in section 2) to differences between the local formulation discussed above and the present integral formulation.

The above considerations and the impracticability of the rigorous mathematical development of the integral principle probably were the reasons why in each of his new papers Prigogine adduced slightly different arguments in support of the integral principle and its relation to the local theorem of the minimum⁶. For example, in [2] he placed the integral principle similar to the principle described above in a separate section under the heading ‘other variational formulations’. In this section he sought for the Lagrangian, the integral

⁶ As a result, some researchers thought the Prigogine integral principle holds for $\lambda \sim T^{-2}$ [14, 15], while others referred it to the case of $\lambda \sim \text{const}$ [12, 13].

of which should have a minimum in the stable stationary state. Taking the case of thermal conductivity, he found this Lagrangian and noted in conclusion that if λT^2 was assumed to be constant, the proved statement transformed to the theorem of the minimum entropy increment. However, since the temperature dependence of the thermal conductivity of the form $\lambda \sim T^{-2}$ was sufficiently specific, the said relation of the principles appeared to be artificial. Therefore, in his next paper [18], Prigogine attempted relating the two principles more intimately and his integral formulation already included the weighted entropy production (the entropy production with some factor). It was emphasized that the phenomenological coefficients (specifically, the thermal conductivity coefficient) should be constants. So, although the point in question was the generalization of the local theorem, an absolutely different quantity was actually introduced, whose minimum determined the temperature distribution. The authors [13] were right to note that this quantity has another dimensionality and it is quite unclear beforehand when a nonequilibrium system has the standard minimum entropy production and when the weighted one. It is also worth noting that in his second attempt aimed at relating the two statements Prigogine had to assume the invariability of the phenomenological coefficients, narrowing the applicability of his local statement (see remark 2 in section 2). Admittedly, Prigogine made the most cogent attempt to relate the two principles in his last paper [19]. Note first that in this paper the author did not mention either a different variational principle or the generalized formulation. He proved the local formulation of his theorem and then gave examples of its applicability to individual systems. Out of the five examples cited, only one example was the integral formulation involving, again, the thermal conductivity problem. We shall look at this example more closely. Rewrite (3.1) taking into account the relation between the kinetic coefficient and the thermal conductivity coefficient:

$$P = \int_0^l \frac{\lambda}{T^2} \left(\frac{\partial T}{\partial x} \right)^2 dx. \quad (3.3)$$

It is assumed that the temperature gradient at the rod ends is sufficiently small and, therefore,

$$T(x) = T_{\text{av}}(1 + \varepsilon(x)), \quad |\varepsilon(x)| \ll 1 \quad (3.4)$$

is fulfilled. Here T_{av} is the average temperature of the rod.

Considering (3.4) and using the traditional assumption on the invariability of the thermal conductivity coefficient, the expression (3.3) can be roughly transformed to

$$P \approx \frac{\lambda}{T_{\text{av}}^2} \int_0^l \left(\frac{\partial T}{\partial x} \right)^2 dx. \quad (3.5)$$

Extremalization of (3.5) using the Euler–Lagrange equation obviously leads to the expression (3.2). So, Prigogine demonstrated that the stationary distribution of the temperature followed from the entropy production extremalization. The basic assumption (3.4) does not look, on the face of it, too strong and unnatural, because the linear nonequilibrium thermodynamics (all the statements were made just in terms of this science) is valid exactly at small thermodynamic forces (specifically, low temperature gradients).

Despite the above proof, some dissatisfaction is felt. Indeed, in most rigorous terms, the linear relationship between the flow and the force can be fulfilled in each element of the volume (for the thermal conductivity this assumption holds almost in all cases), but the difference of temperatures on boundaries of the whole volume can be very large. Therefore, the low temperature gradient (and, also, the invariable λ) at the rod ends essentially is an additional assumption, which is absent in the local theorem. It is not proved for the integral case either that exactly the minimum entropy production, rather than the extremum, provides

the stationary distribution⁷. The inverse proposition is also open to question: if the stationary nonequilibrium state has the minimum entropy production. In this connection, in the following section we shall look once more into the validity of the integral minimum principle.

3.2. Is the integral principle fulfilled or not? Generalized consideration

Considering the recent interest aroused in the applicability of the minimum principle at the power dependence of the thermal conductivity coefficient on the temperature [14, 15], we shall assume

$$\lambda = \lambda_0 T^n, \quad (3.6)$$

where λ_0 is a temperature-independent coefficient and n is an arbitrary number. By setting n equal to 0 or -2 , we can analyse the two approximations used by Prigogine.

We shall consider, as before, the thermal conductivity in the rod. The mathematical statement of the problem is as follows:

$$\frac{\partial T}{\partial t} = a \frac{\partial}{\partial x} \left(T^n \frac{\partial T}{\partial x} \right). \quad (3.7)$$

The boundary conditions

$$T(0, t) = T_0 \quad \text{and} \quad T(l, t) = \gamma T_0. \quad (3.8)$$

The initial condition

$$T(x, 0) = \xi(x). \quad (3.9)$$

It is assumed here that the temperature at the ends of the rod differs γ times. We shall take for certainty that γ is not less than unity. The quantity $\xi(x)$ is the initial distribution of the temperature along the rod. It is assumed in (3.7) for simplicity that the heat capacity, the density and λ_0 are constant and, therefore, these quantities may be removed from the derivative. Hence, the thermal diffusivity a (involving λ_0) is a constant.

If the temperature and the coordinates are scaled as T_0 and l , and the time is scaled as $l^2/T_0^n a$, then (3.7)–(3.9) can be brought to the dimensionless form:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial}{\partial \chi} \left(\theta^n \frac{\partial \theta}{\partial \chi} \right), \quad (3.10)$$

$$\theta(0, \tau) = 1, \quad \theta(1, \tau) = \gamma, \quad (3.11)$$

$$\theta(\chi, 0) = \psi(\chi), \quad (3.12)$$

where θ , χ and τ denote the dimensionless temperature, coordinate and time, respectively, while $\psi(\chi, 0)$ is the dimensionless initial distribution of the temperature correlating with (3.11).

For the problem at hand, the dimensionless entropy production Σ is written in the form

$$\Sigma = \int_0^1 \theta^{n-2} \left(\frac{\partial \theta}{\partial \chi} \right)^2 d\chi. \quad (3.13)$$

The Euler–Lagrange equation, which extremalizes the entropy production (3.13), has the form

$$(n-2) \left(\frac{\partial \theta}{\partial \chi} \right)^2 + 2\theta \frac{\partial^2 \theta}{\partial \chi^2} = 0. \quad (3.14)$$

⁷ The relationship $\partial P/\partial t \leq 0$ (i.e. a perturbed system tends to a state with the minimum entropy production and this state is stable) was proved, for example, in [27], but the approximation (3.4) was decisive for the proof there.

If (3.14) is solved considering (3.11), we have

$$\theta_{\text{var}} = [(\gamma^{n/2} - 1)\chi + 1]^{2/n}, \quad n \neq 0; \quad (3.15)$$

$$\theta_{\text{var}} = \gamma^\chi, \quad n = 0. \quad (3.16)$$

Since the second derivative of the integration element in (3.13) with respect to $\partial\theta/\partial\chi$ is always positive, then, in accordance with the Legendre condition, the obtained extremum is just the minimum.

Let us compare the result of (3.15)–(3.16) with the stationary solution of (3.10)–(3.11), which has the form

$$\theta_{\text{st}} = [(\gamma^{n+1} - 1)\chi + 1]^{1/(n+1)} \quad \text{if } n \neq -1; \quad (3.17)$$

$$\theta_{\text{st}} = \gamma^\chi \quad \text{if } n = -1. \quad (3.18)$$

It is seen from these formulae that the field of temperatures obtained by extremalization of the entropy production (3.13) and the field deduced from the solution of the stationary equation for the thermal conductivity are different in the general case. They coincide in two cases only:

- (1) at any temperature gradient at the rod ends if $n = -2$,
 - (2) if the temperature gradient at the rod ends is very low (γ approaches unity) and $n = 0$.
- Indeed, if (3.16) is expanded into a series to a linear term, we have

$$\theta_{\text{var}} \approx 1 + (\gamma - 1)\chi, \quad (3.19)$$

which coincides with (3.17) in the adopted approximation.

The obtained results generally support the conclusions under p 3.1 (see also [12–15]).

A question arises as to the existence of the inverse statement⁸, that is, if the stationary field of temperatures provides, at least roughly, the minimum entropy production. To verify this supposition, we shall assume that the stationary distribution of the temperature was disturbed by some small perturbation $\Delta(\chi, \tau)$ (the temperature at the rod ends remains unchanged: $\Delta(0, \tau) = \Delta(1, \tau) = 0$ and $\Delta(\chi, 0) = \delta(\chi)$ ($\delta(\chi)$ being some function, $\delta(0) = \delta(1) = 0$). Obviously, the temperature will re-approach with time the stationary value in accordance with the equations (3.10)–(3.12). We shall take a sufficiently long time ($\tau \rightarrow \infty$). In this case, the nonstationary field of temperatures can be presented as the sum of the stationary solution and a small exponentially decreasing addition⁹:

$$\theta(\chi, \tau) = \theta_{\text{st}}(\chi) + \Delta(\chi, \tau) = \theta_{\text{st}}(\chi) + \delta(\chi) e^{-\mu\tau}, \quad (3.20)$$

where $\Delta(\chi, \tau) \ll \theta_{\text{st}}(\chi)$ and μ is some positive constant.

Will the entropy production Σ_p in the state at hand be larger or smaller than the entropy production Σ_{st} in the stationary nonequilibrium state? If it proves to be always larger, the stationary state is characterized exactly by the minimum entropy production. Let us make some calculations¹⁰:

$$\Sigma_p - \Sigma_{\text{st}} = \int_0^1 \left[(\theta_{\text{st}} + \Delta)^{n-2} \left(\frac{\partial\theta_{\text{st}}}{\partial\chi} + \frac{\partial\Delta}{\partial\chi} \right)^2 - \theta_{\text{st}}^{n-2} \left(\frac{\partial\theta_{\text{st}}}{\partial\chi} \right)^2 \right] d\chi. \quad (3.21)$$

⁸ Let us recall that both the direct and inverse statements are valid in the local case.

⁹ It is easy to show that this type of the addition satisfies equations (3.10)–(3.12) at any n with the assumptions adopted (if $n \neq 0$, it is required that $\partial\Delta/\partial\chi \ll \partial\theta_{\text{st}}/\partial\chi$ and $\partial^2\Delta/\partial\chi^2 \ll \partial^2\theta_{\text{st}}/\partial\chi^2$. This is fulfilled near the stationary state).

¹⁰ In a general case, the extremum (3.13) is sought over a wide class of functions. In what follows we shall only compare values of the functionals at temperatures equal to θ_{st} and (3.20). Of course, these problems are nonequivalent. If it proves however that even with this particular choice of functions the functional of the nonstationary distribution is smaller than the functional of the stationary distribution of the temperature, then this example will suffice to disprove the statement that the stationary state has the minimum entropy production.

Considering the smallness of Δ at a long time and limiting ourselves to the terms proportional to $e^{-\mu\tau}$, the last expression can be transformed to

$$\Sigma_p - \Sigma_{st} = \int_0^1 \left[2\theta_{st}^{n-2} \frac{\partial\theta_{st}}{\partial\chi} \frac{\partial\Delta}{\partial\chi} + \theta_{st}^{n-3} (n-2) \Delta \left(\frac{\partial\theta_{st}}{\partial\chi} \right)^2 \right] d\chi. \quad (3.22)$$

Integrating the first term by parts and considering that the temperature at the rod ends is invariable, we have

$$\Sigma_p - \Sigma_{st} = \int_0^1 \left[(2-n)\theta_{st}^{n-3} \left(\frac{\partial\theta_{st}}{\partial\chi} \right)^2 - 2\theta_{st}^{n-2} \frac{\partial^2\theta_{st}}{\partial\chi^2} \right] \Delta(\chi, \tau) d\chi. \quad (3.23)$$

Using (3.17) and (3.18), the last expression can be brought to the form

$$\Sigma_p - \Sigma_{st} = \frac{(2+n)(\gamma^{n+1} - 1)^2}{(n+1)^2} \int_0^1 \left[((\gamma^{n+1} - 1)\chi + 1)^{-\frac{n+3}{n+1}} \right] \Delta(\chi, \tau) d\chi \quad (3.24)$$

if $n \neq -1$, and

$$\Sigma_p - \Sigma_{st} = (\ln \gamma)^2 \int_0^1 \gamma^{-2\chi} \Delta(\chi, \tau) d\chi \quad (3.25)$$

if $n = -1$.

It may be inferred from (3.24) and (3.25) that at $n \neq -2$ the difference of the entropy production between the stationary case and an adjacent perturbed case is negative or positive depending on the sign of the spatial temperature perturbation ($\pm|\delta(\chi)|$). Thus, depending on the initial perturbation of the temperature, the entropy production may be either maximum or minimum in the stationary state in comparison to nearest states formed after the perturbation relaxation¹¹.

If $n = -2$, the consideration of linear terms $e^{-\mu\tau}$ only, when (3.21) is transformed to (3.22), leads to the zero value of $\Sigma_p - \Sigma_{st}$. Using (3.21), write the quadratic contribution

$$\Sigma_p - \Sigma_{st} = \int_0^1 \theta_{st}^{-4} \left[\left(\frac{\partial\Delta}{\partial\chi} \right)^2 - \frac{8\Delta}{\theta_{st}} \frac{\partial\theta_{st}}{\partial\chi} \frac{\partial\Delta}{\partial\chi} + \frac{10\Delta^2}{\theta_{st}^2} \left(\frac{\partial\theta_{st}}{\partial\chi} \right)^2 \right] d\chi.$$

Substituting the explicit form of the stationary temperature distribution (3.17) at $n = -2$ into the last expression, we have

$$\Sigma_p - \Sigma_{st} = \int_0^1 [(\gamma^{-1} - 1)\chi + 1]^4 \left[\left(\frac{\partial\Delta}{\partial\chi} + 4\Delta \frac{(\gamma^{-1} - 1)}{[(\gamma^{-1} - 1)\chi + 1]} \right)^2 - \frac{6\Delta^2(\gamma^{-1} - 1)^2}{[(\gamma^{-1} - 1)\chi + 1]^2} \right] d\chi.$$

It can be shown that the minimum value of the last functional for the class of smooth functions Δ , which satisfy the boundary conditions $\Delta(0, \tau) = \Delta(1, \tau) = 0$, is zero¹². One can conclude therefore that at $n = -2$ the entropy production in the stationary state is minimum for the functions of the form (3.20). Remarkably, the case of $n = -2$ was mentioned by Prigogine in one of his proofs of the integral principle (see above)¹³. The following point must be emphasized here. If one considers the adopted constraints, calculations do not provide complete evidence that the stationary temperature distribution corresponds to the minimum

¹¹ Specifically, numerical calculations [14] gave the maximum entropy production at the initial temperature distribution of 1 (dimensionless units) along the full length of the sample.

¹² This follows from the solution of the Euler-Lagrange equation.

¹³ At $n = -2$ the minimum in the stationary state was obtained from numerical calculations of the entropy production in [14] and analytically in [15].

entropy production. It was shown only that the entropy production is smaller in the one-dimensional stationary state than in the case of the temperature distribution tending with time exponentially to the stationary distribution.

So, on the strength of the calculations made, it may be stated that the stationary temperature field can be obtained from the minimum entropy production only with two temperature dependences of the thermal conductivity coefficient ($n = -2$ and 0 , see (3.6)). In the second case, which is most significant for practical applications, this can be done only roughly on the assumption of a low temperature gradient at the rod ends. The inverse statement is incorrect¹⁴: in the stationary state the entropy production may be either minimum or maximum as compared to the entropy production calculated for other physically possible distributions of the temperature over the rod.

4. Conclusion

The analysis showed that the local minimum principle formulated by Prigogine is correct. The following points, which are often misleading, must be emphasized.

- (1) The principle may be used if two or more thermodynamic forces, some of which are invariable, are available.
- (2) The kinetic coefficients should not depend on flows and forces, but they may depend on thermodynamic parameters (e.g., the temperature).
- (3) The minimum entropy production implies the stationary state of the system and vice versa: the stationary state of the system implies the minimum entropy production.

Attempts to extend the local principle to the so-called integral event are unreasonable and, as a matter of fact, erroneous. Even if additional constraints are introduced as compared to the local formulation (on the relationship between the thermal conductivity coefficient and the temperature, the smallness of the temperature gradient on boundaries of the system under study), the principle proves to be invalid in both directions, probably except the case when the thermal conductivity coefficient is inversely proportional to the squared temperature.

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¹⁴ The only exception may be the case when $n = -2$. It needs further study.

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