PRINCIPLE OF MINIMUM ENTROPY PRODUCTION

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A new principle of minimum entropy production is formulated based on the analysis of previous results.

The principle of minimum entropy production can be formulated (and has until now been formulated) as the Prigogine theorem [1, 2]: a stationary state of a thermodynamic system is a state of the minimum possible entropy production under specified conditions.

The Prigogine theorem has, however, only been proved for states close to equilibrium when the study of production is low and when phenomenological transfer laws with constant coefficients as well as the Onsager reciprocity relations can be applied [1-3]. If, however, it is a question of the principle of minimum entropy production, then it is suggested that the proposition formulated above be used when considering a nonequilibrium stationary state of a thermodynamic system with finite production of entropy. One should also bear in mind that the assumptions made in this problem admit at least two feasible stationary states, one of which one has to be selected, since in actual fact only one stationary state can be observed.

Examples of stationary states in thermodynamic systems which differ essentially from the equilibrium ones though they are characteristic for their minimum possible entropy production are given in the second part of [4] and in [5]. Practical experience of using the principle of the minimum entropy production is also at one's disposal: Its use helps to explain the existence of the critical state in the operation of a gas ejector [6]; conditions can be found for vibratory heat in a tube which is accompanied by longitudinal acoustic vibrations [7] and for turbulent Schmidt numbers determined in a submerged isothermal jet [8].

Since the use of the principle of minimum entropy production may also prove advantageous in our future considerations, it is advisable to discuss the cases known to us from the literature for which this principle is invalid. In the present article two such cases are discussed: 1) the production of entropy in a system of gas-filled vessels joined by a capillary tube and with different temperatures; 2) the entropy production in a layer of heat-conducting matter between two heat reservoirs. It is our aim here to show that the validity or invalidity of the principle of the minimum production of entropy for both these cases depends on how the concept of a feasible stationary state of a thermodynamic system is interpreted, and that the formulation of the minimum production of entropy is needed to improve accuracy.

The first of these cases was analyzed in [4], where the probability of filling the energy levels l_i and m_i by molecules was introduced; under some assumptions it was proved by the methods of statistical mechanics that the entropy production in the vessel system is not minimum in the region of the values l_i and m_i related by

$$\sum_i (l_i + m_i) = 1. \tag{1}$$

In the above-cited article the probabilities of filling l_i and m_i are understood to be the ratios

$$l_i = n_{iA}/N, \quad m_i = n_{iB}/N,$$

where n_{iA} and n_{iB} are the numbers of molecules in the respective vessels (A and B) with energy ε_i, N being the total number of molecules.

Since the methods employed in [4] are those of statistical mechanics, the obtained result indicates that the principle of heat-entropy production is invalid if the feasible stationary states of the system under consideration are understood to be the states characterized by any filling probabilities l_i and m_i related by the
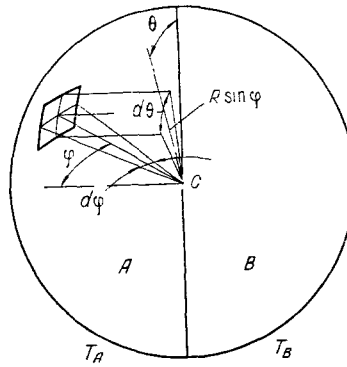

Fig. 1. Hemispherical vessels
with orifice in the common wall.

relation (1). However, the situation changes completely if these states are understood to be only the stationary states satisfying the conditions of the problem and if there is only one and not several such states. Such a situation indeed takes place for the system under consideration: For a stabilized process the exchange of molecules between the vessels and the assumptions for the filling probabilities l_i and m_i adopted in [4] prove to be uniquely determined.

To prove that the set of values l_i and m_i is unique, one considers a system consisting of two hemispherical vessels A and B with a small orifice C at the center of the common wall (Fig. 1). It is assumed that there are N molecules of a single-atom gas in the vessels. Moreover, it is also assumed as in [4], that the temperatures T_A and T_B of the vessel walls are maintained by heat reservoirs A* and B* and that the molecules in the vessels interact only with the vessel walls and are in thermal equilibrium with the reservoirs A* and B*.

The hemispherical vessels are considered in the present article solely to simplify our analysis. It will be seen from our further considerations that the shape of the vessels had no effect on the final conclusions. The replacement of the capillary tube by an orifice was dictated by the fact that the energy of the molecules passing through the capillary tube cannot remain constant. (Since the effusion admittances of a capillary tube and of orifice can be made equal [9], this replacement is of no significance either.) Finally, the analysis of the monatomic gas results from our wish to remain within the framework of the classic (not quantized) description of the molecular energy.

Adopting the hypothesis of molecular chaos (detailed balance), one can write that the total number of molecules in the vessels A and B equal to the given number N can be written as

$$n_A V + N_A + n_B V + N_B = N, \tag{2}$$

where n_A and n_B are the numbers of molecules per unit volume which remain in thermal equilibrium with the reservoirs A* and B*, respectively; V is the volume of each of the vessels A and B; N_A and N_B are the numbers of molecules in the vessels A and B which, having passed through the orifice C, do not reach the walls of the vessels.

A necessary condition for state stationarity in the system under consideration is that the numbers of molecules passing through the orifice C per unit of time from the vessel A to B and from the vessel B to A be equal:

$$\frac{1}{4} n_A \bar{u}_A S_C = \frac{1}{4} n_B \bar{u}_B S_C.$$

In the above condition S_C is the area of the orifice C and $\bar{u}_A$ and $\bar{u}_B$ are the mean velocities of the molecules which are in thermal equilibrium with the reservoirs A* and B*:

$$\bar{u}_A = \sqrt{8kT_A/\pi m}, \ \bar{u}_B = \sqrt{8kT_B/\pi m}, \tag{3}$$

where k is the Boltzmann constant and m is the mass of a molecule for the gas under consideration. In view of the latter, the stationarity condition for the system under consideration implies that
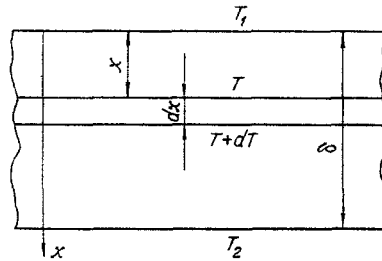
$$n_A \sqrt{T_A} = n_B \sqrt{T_B}. \tag{4}$$

Fig. 2. Heat-conducting layer.

If it is assumed that the radius of the orifice C is very much less than the radius R of the vessels A and B, then it is not difficult to express N_A by n_B and N_B by n_A:

$$N_A = \frac{1}{4} n_B S_C R, \quad N_B = \frac{1}{4} n_A S_C R. \tag{5}$$

To this end one must employ two relations, one of which is sufficiently well known (see, for example, [10]), the other being self-evident:

$$dN = n S_C \left(\frac{m}{2\pi kT} \right)^{3/2} u^3 \exp \left(-\frac{mu^2}{2kT} \right) \sin \varphi \cos \varphi \, d\varphi d\theta du, \tag{6}$$

$$\tau_u = R/u.$$

In these relations, dN is the number of molecules which with temperature T and the velocity ranging from u to u + du pass through the orifice C in the elementary solid angle $\sin \varphi d\varphi d\theta$ (see Fig. 1); τ_u is the time during which which each of the molecules passing through the orifice C reaches the walls of the vessels A and B; n = n_A if T = T_A, but n = n_B if T = T_B.

To avoid any misunderstanding, it is again stated that the expressions (3) and (6) are valid if the velocities of the molecules passing through the orifice C are distributed according to the Maxwell−Boltzmann law,

$$F = n (m/2\pi kT)^{3/2} \exp(-mu^2/2kT).$$

The Maxwell−Boltzmann law is, in turn, valid for an ideal gas if the latter is in thermal equilibrium with a heat reservoir [11]. This equilibrium flow from the vessel A to the vessel B and back with the reservoirs A* and B*, respectively, was adopted in [4] as well as in the present work.

The relations (2), (4), and (5) uniquely determine n_A, n_B, N_A, and N_B in terms of the given quantities N, T_A, T_B, S_C, and R. In particular, the following expression is valid for n_A:

$$n_A = N \Big/ R \left(\sqrt{\frac{T_A}{T_B}} + 1 \right) \left(\frac{2}{3} \pi R^2 + \frac{1}{4} S_C \right). \tag{7}$$

The values of n_A and n_B together with the Maxwell−Boltzmann distribution law uniquely determine the filling probabilities l_i and m_i in terms of the velocities u (or the energies $\varepsilon = mu^2/2$) as well as the entropy production P in the system under consideration:

$$P = P_{A^*} + P_{B^*} = \frac{3\sqrt{2}}{4} \frac{k^{3/2}}{\sqrt{\pi m}} S_C \frac{n_A}{\sqrt{T_A} \, T_B} (T_A - T_B)^2. \tag{8}$$

The quantities P_A^* and P_B^* in this expression denote the entropy productions in the reservoirs A* and B*, the quantity n_A being given by the expression (7).

To derive (8) one has, first of all, to bear in mind that according to the definition [1, 2] the production of entropy in a thermodynamic system is the growth of entropy per unit of time in the thermodynamic system itself. Moreover, one has to determine the energies $U^{(+)}$ and $U^{(-)}$, which together with the molecules are brought to the vessels A and B in unit time and, conversely, are taken away from the vessels. Finally, one has to take into consideration that the differences $U^{(+)} - U^{(-)}$ must be compensated by dissipation or supply of heat in the reservoirs A and B, since the states of gas in the vessels and B are stationary. Then $P_{A^*} = (U_A^{(+)} - U_A^{(-)})/T_A$, etc.

Thus, the results derived in the first part of [4] can be interpreted in a different way than was actually done in [4]. Namely, it can be asserted that in the case under consideration the principle of minimum entropy
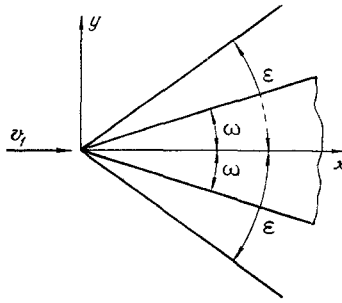
Fig. 3. Supersonic flow past a
wedge.

production is invalid as an expression of some global property of the thermodynamic system, including, in particular, the condition of the system stationarity and the law of mass conservation. However, in the case under consideration this does not imply that the principle of minimum entropy production is invalid, provided all stationary states from which the state of minimum entropy production is selected are feasible: In the case analyzed in [4], such a state is unique.

The analysis of the case of entropy production in a layer of matter through which heat is conducted from one heat reservoir to another lead to a similar conclusion. This is now considered in more detail than is usually the case, since one can also find it described in student handbooks. (For example, in the Bazarov handbook [12], the following can be found: "The principle of the minimum entropy production is only valid if the kinetic coefficients are constant and satisfy the Onsager relations. If the latter are not satisfied, the stationary state is realized without the minimum production of entropy. Thus, temperature distribution in the process of heat propagation in a layer between heat sources with temperatures T_1 and T_2 which corresponds to the minimum entropy production is not stationary if the heat-conduction coefficient for the layer is λ = const/ T^3)".

Thus, a flat layer of solid matter of thickness δ (Fig. 2), on whose one side the temperature (for x = 0) is considered remains equal to T_1 while on whose other side (for x = δ) $-T_2 > T_1$.

The density of the heat flux q (that is, the heat flux per unit time through a unit area of isothermal surface) at the layer section x in this case $-\lambda dT/dx$, is in agreement with the Fourier law, where λ is the coefficient of heat conduction of the substance which is assumed below to depend on temperature only.

One observes that in some cases the relation λ = const/T^3 is adopted only to simplify our discussion. In fact, the relation $\lambda(T)$ in a not too wide range of T is nearly linear for solid matter [13]: $\lambda = \lambda_0[1 + b(T-T_0)]$, where λ_0 is the heat-conduction coefficient of the substance under consideration at the temperature T_0.

In addition, we shall give an expression for $\lambda(T)$ which is essential in future considerations and which follows from the linear thermodynamics of irreversible processes. For isotropic matter this relation is given by (see, for example, [1])

$$\lambda = L_{qq}/T^2,\tag{9}$$

where L_{qq} is the scalar kinetic coefficient in the phenomenological law of heat transfer.

An expression for entropy production in a heat-conducting layer can be obtained by considering an elementary sublayer dx in it (see Fig. 2) and by imagining that on the top of this sublayer there is a heat reservoir with temperature T and on the bottom a heat reservoir with temperature T + dT. For a steady heat transfer, when q(x) = const the entropy of the upper reservoir per unit area will grow by $-q/T$ in unit time. The difference between these quantities gives, of course, the entropy production per unit area of the sublayer $-q/(T + dT)$:

$$dP = -\left(\frac{q}{T} - \frac{q}{T + dT} \right) = -\frac{q}{T^2}\frac{dT}{dx}dx.\tag{10}$$

By replacing q with $-\lambda dT/dx$ in the obtained expression and by integrating with respect to x from 0 to q, the expression is obtained for entropy production P per unit area of the layer:

$$P = \int_0^\delta \frac{\lambda}{T^2}\left(\frac{dT}{dx} \right)^2 dx.$$
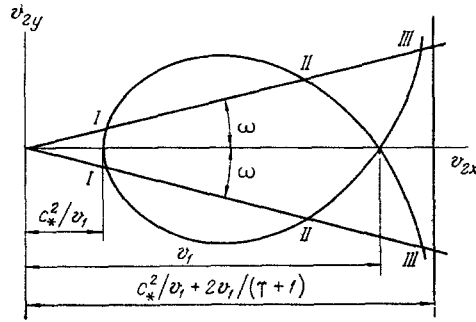
Fig. 4. Shock polar and feasible values
of v_{2x} and v_{2y}.

A necessary extremality condition of the quantity P is that of Euler−Lagrange:

$$\frac{\partial F}{\partial T} - \frac{d}{dx}\left[\frac{\partial F}{\partial(dT/dx)}\right] = 0, \quad F = \frac{\lambda}{T^2}\left(\frac{dT}{dx}\right)^2.$$

Hence, the function T(x) corresponding to the extremal P must satisfy the equation

$$\frac{d^2T}{dx^2} + \left(\frac{1}{2\lambda}\frac{d\lambda}{dT} - \frac{1}{T}\right)\left(\frac{dT}{dx}\right)^2 = 0. \tag{11}$$

On the other hand, the state stationarity of a heat-conducting layer consisting of the quantity q remaining constant for all x can be written as

$$\frac{dq}{dx} = -\lambda\frac{d^2T}{dx^2} - \frac{d\lambda}{dT}\left(\frac{dT}{dx}\right)^2 = 0. \tag{12}$$

If one compares Eqs. (11) and (12), one finds that the above relations are identities in the case when

$$\frac{1}{2\lambda}\frac{d\lambda}{dT} - \frac{1}{T} = \frac{1}{\lambda}\frac{d\lambda}{dT}.$$

In this case, $\lambda = \text{const}/T^2$, which, as implied by (9), is a necessary condition for the Prigogine theorem to be valid for a heat-conducting layer if the kinetic coefficient L_{qq} remains constant. In the general case, however, if $\lambda \neq \text{const}/T^2$, the equations under consideration are different. This is considered as proof that the principle of minimum production of entropy is invalid in a heat-conducting layer.

There is, however, another circumstance which is of no less importance. Already when deriving the expression (10), which implies Eq. (11), the quantity q was regarded as independent of x (see the determination of the entropy change in the rsservoirs with temperatures T and T + dT). In other words, the expression (10) and Eq. (11) are formally valid only if T(x) is given by Eq. (12):

$$\int \exp\left(\int \frac{1}{\lambda}\frac{d\lambda}{dT}\,dT\right)dT = c_1(x + c_2).$$

For a given correspondence between λ and T and given boundary conditions, this dependence is unique. In particular, $\lambda = \text{const}/T^3$ and the previously formulated boundary conditions, one has

$$T = \left(\frac{1}{T_1^2} - \frac{1}{\delta}\frac{T_2^2 - T_1^2}{T_1^2 T_2^2}x\right)^{-0.5}.$$

The uniqueness of T(x) leads to the stationary state of the thermodynamic system also being unique (the same being correspondingly true for the expression of entropy production in this state). In particular, in the case in question one has

$$P = \frac{\text{const}}{2\delta}\frac{(T_2 - T_1)(T_2^2 - T_1^2)}{T_1^3 T_2^3}.$$

Thus, the analysis of the discussed cases shows that the condition for the principle of minimum entropy production to be valid is the condition that there exist at least two stationary states of the thermodynamic system.

In the above-discussed cases the stationary states were determined by the boundary conditions, the transition laws, and the conservation laws. In the general case these states can be additionally determined by the second law of thermodynamics.

In all these cases the feasible stationary states must be stable with respect to small perturbations.

One should mention here that the condition of several feasible stationary states may at first appear to occur rarely. In actual fact, however, this condition is valid in the case of very simple thermodynamic systems, not to mention systems with the so-called internal degrees of freedom.

To illustrate the above, a supersonic flow is considered past a wedge formed by two infinite planes, each making an angle ω with the direction of the oncoming flow of an ideal gas (Fig. 3). It is known that in such a flow, two planar shock waves from the apex of the wedge, which form equal angles ε with the direction of the incoming flow, result. In these waves the entropy of a unit gas mass is changed by a quantity Δs. The production of entropy, however, per unit area for the incoming flow mounts to ΔsM, where M is the mass flux of gas in the incoming flow. In view of the continuity of the flows of mass, energy, and momentum, one finds (see, for example, [14]) that independently of the angle ω the component velocities of the flow downstream the of shock waves v_{2x} and v_{2y} (the coordinate system is shown in Fig. 3) satisfy the following relation referred to as the shock polar:

$$v_{2y}^2 = (v_1 - v_{2x})^2 \left[(v_1 v_{2x} - c_*^2) \middle/ \left(\frac{2}{\gamma + 1} v_1^2 - v_1 v_{2x} + c_*^2 \right) \right].$$

In the above relation, γ is the ratio of gas heat capacities at constant pressure and at constant volume; v_1 is the velocity of the incoming flow, and c_* is the critical velocity of the incoming flow.

The values of v_{2x} and v_{2y} corresponding to the angle ω are the coordinates of the intersection points of the shock-wave curve shown in Fig. 4 with the straight lines $v_{2y} = \pm\tan\omega v_{2x}$. On each side of the axis v_{2x} there are three such points.

Thus, the boundary conditions and conservation laws admit in the case under consideration three feasible stationary states of the system corresponding to the values of v_{2x} and v_{2y} at the points I, II, and III (see Fig. 4). In fact, however, one knows that from these feasible states only the state II is realized, which, similarly to the state I, is stable with respect to infinitely small perturbations [14].

For a further illustration the following is also added. It can be shown that

$$\Delta s_{\mathrm{I}} > \Delta s_{\mathrm{II}} > 0, \ \Delta s_{\mathrm{III}} < 0. \tag{13}$$

Consequently, according to the second law of thermodynamics, one should reject the state III, and according to the principle of minimum entropy production one should select from the states I and II a state II, since in accordance with the definition of P and the first inequality (13) one has $P_{\mathrm{I}} > P_{\mathrm{II}}$.

In view of the shown applicability condition for the principle of minimum entropy production, it is, of course, expedient to modify its formulation so as to avoid all discussion as regards the meaning of a feasible stationary state of a thermodynamic system. This modification can be as follows: From all the stable stationary states of a thermodynamic system satisfying the boundary conditions, the transition laws, and the conservation laws, as well as by the second law of thermodynamics, the state with the minimum entropy production is realized.

The proposed formulation makes the principle of minimum entropy production more interesting: If one feasible stationary state is present, it is obviously not always necessary to know additional special features of this state. By such a formulation the principle of minimum entropy production obviously assumes the meaning of the principle of the maximally possible conservation of the structure of the thermodynamic system in a nonequilibrium state which distinguishes it from other principles, for example, the Gyarmati principle [15] or the evolution criteria [16]. Finally, in the proposed formulation the conditions under which the principle of minimum entropy production can be subjected either to inductive verification or can be based on one or another standard (of course, if this is true at all) are discussed.

NOTATION

l, m   are the filling probabilities;
n   is the number of molecules per unit volume;

N	is the number of molecules;
T	is the temperature;
$\overline{u}$	is the mean velocity;
S	is the area;
R	is the radius;
U	is the energy;
P	is the entropy production;
δ	is the thickness of heat-conducting layer;
q	is the heat flux;
λ	is the thermal-conductivity coefficient;
ω	is the half-angle at wedge vertex;
ε	is the inclination angle of shock wave;
Δs	is the entropy change for unit mass of gas in shock wave;
M	is the mass flow;
v_1	is the incoming flow velocity;
v_{2x} and	
v_{2y}	are the flow velocities of downstream shock wave;
γ	is the ratio of heat capacities.

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