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A critical analysis of the minimum entropy production theorem and its application to heat and fluid flow

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Abstract

We discuss the principle of minimum entropy production as proposed by Prigogine, providing two examples (heat conduction in a fluid at rest and the combined shear flow and heat conduction in an incompressible fluid) for which the principle produces field equations that do not agree with the balance equations of continuum mechanics. We have not been able to find any special assumption on the temperature dependence on the phenomenological coefficients (such as thermal conductivity and dynamical viscosity) under which a general agreement between standard balance equations and balance equations determined by the minimum entropy production principle can be stated. A critical analysis of the theorem proof shows that the minimum entropy production of system in a stationary state cannot be different from zero.

1. Introduction

Variational principles occupy a prominent position in the history of science, because they provide a rational and elegant explanation of physical phenomena. Moreover, since the 19th century they have had a tremendous impact on engineering design, because they allow complex, multivariable problems to be solved by simple variational calculus.

Among others, the so-called principle of minimum entropy production rate is certainly the most debated among scientists. The general statement of the minimum entropy production principle reads: "A steady state has the minimum rate of entropy production with respect to other possible states with the same boundary conditions". In other words, the theorem of minimum entropy production asserts that, under certain assumptions, the global entropy production rate of a given system attains a minimum value when the processes in the system become stationary. As a special case, one finds the equilibrium states, where entropy is maximum and its rate of production becomes zero.

The earliest formulation of this principle is to be found in Rayleigh's least dissipation principle [1,2]; later, Onsager [3] gave a proof based on his reciprocity relations (which imply the hypotheses of local equilibrium and microscopic reversibility), in the absence of magnetic fields or Coriolis forces. However, this principle became famous principally thanks to Prigogine [4–6], who derived the property of minimum entropy production for discontinuous systems (i.e., systems composed of several sub-systems, in which state variables show discontinuous jumps passing from one sub-system to another). In particular, Prigogine's aim was to extend the Le Chatelier–Braun principle to account for irreversible processes in open systems [7]. An analogous result applies to continuous systems [8]. The key aspect of this work is that it contains a rigorous mathematical proof, so that one should use the word "theorem" rather than "principle".

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Nomenclature

F	function
J	generalised thermodynamic flux
J_s	entropy flux
k	thermal conductivity
L	length
L_{ij}	Onsager phenomenological coefficient
p	pressure
q	heat flux
s	entropy
t	time
t_{ij}	stress tensor
T	temperature
u	internal energy
v	velocity component
V	volume
X	generalised thermodynamic force

Greek symbols

δ_{ij}	Kronecker symbol
λ	Lagrange multiplier
μ	viscosity
ρ	density
σ	entropy production

The impact of this work was huge, because it provided a theoretical landscape where new concepts were born and grown, such as the finite time thermodynamics [9–12], the theory of dissipative structures [13] and more recently Bejan's *constructal theory* of organization in nature [14], which are often erroneously thought to be straightforward consequences of the minimum entropy production theorem.

However, the acceptance of Prigogine's work in the scientific community has always been controversial, and gave rise to huge debates both in the scientific and in the non-scientific literature, often raising strong criticism [15]. As a matter of fact, despite the principle of minimum entropy production contributed much to attract attention on non-equilibrium thermodynamics, in a recent and comprehensive review article it is simply ignored [16].

A natural weakness of the theory lies in one of the hypotheses on which it is based: the fact that the entropy production of a system is minimum in stationary states only if the phenomenological coefficients are constant implies that the overall gradients of the thermodynamic parameters over the complete system must be sufficiently small, but there are no general guidelines to establish how small they should be. Furthermore, one can find situations of systems in a stationary state whose entropy production is not minimum. Perhaps the most famous example was given by Landauer [17], who after a general discussion about the inadequacy of entropy in characterising stationary states, showed how this principle fails to correctly describe even the behavior of simple thermodynamic systems such as electric resistances. Previously, Ziman [18] had developed a variational principle for transport processes that actually shows that entropy production is maximum in the steady state.

In this paper, we analyze critically the minimum entropy production theorem, describing in detail two examples for which it does not agree with the equations of continuum mechanics. Then, we consider the proof originally proposed by Prigogine [4] for discontinuous systems, showing that if the condition describing a stationary state is taken into account correctly, the entropy production of a linear dissipative system satisfying Onsager's reciprocity relations must be zero.

2. Field equations

To determine the basic fields of thermodynamics of irreversible processes we rely on the field equations based on the mass, momentum, energy conservation principles. The corresponding conservation laws, in the usual tensorial form are

$$\begin{aligned} &\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i) = 0 \\ &\frac{\partial}{\partial t}(\rho v_i) + \frac{\partial}{\partial x_j}(\rho v_i v_j - t_{ij}) = 0 \\ &\frac{\partial}{\partial t}(\rho u) + \frac{\partial}{\partial x_i}(\rho u v_i + q_i) = t_{ij}\frac{\partial v_i}{\partial x_j} \end{aligned} \tag{1}$$

where ρ is density, v_i, t_{ij} and q_i are the components of the velocity vector, of the stress tensor and of the heat flux vector, respectively, and u is the internal energy. The entropy balance is written as $\rho\dot{s} + \frac{\partial}{\partial x_i}(J^i_s) = \sigma$, with $J^i_s = \frac{q_i}{T}$ and $\sigma = -\frac{1}{T^2} q_i \frac{\partial T}{\partial x_i} + \frac{1}{T} t_{\langle ij \rangle} \frac{\partial v_i}{\partial x_j}$; T is the absolute temperature, J^i_s are the components of the entropy flux vector, σ is the (non-negative) density of entropy production, and $t_{\langle ij \rangle}$ denotes the deviatoric stress. The global entropy production is defined as: $\frac{d_i S}{dt} = \int_V \sigma \, dV$, where V is the volume of the system.

Let us restrict the discussion to an incompressible Navier–Stokes–Fourier fluid for which we introduce the following constitutive relations:

$$\begin{aligned} &t_{ij} = -p\delta_{ij} + \mu(T)\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \\ &q_i = -k(T)\frac{\partial T}{\partial x_i} \\ &u = u(T) \end{aligned} \tag{2}$$

where p is the hydrodynamic pressure, μ is the shear viscosity, and k is the thermal conductivity. The combination of the constitutive equations with the conservation equations provides a full set of equations for the basic fields of the thermodynamics of irreversible processes. In steady state, these equations reduce to

$$
\begin{aligned}
&\frac{\partial v_i}{\partial x_i} = 0 \\
&\rho v_j \frac{\partial v_i}{\partial x_j} + \frac{\partial p}{\partial x_i} - \frac{\partial}{\partial x_j}\left[\mu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)\right] = 0 \\
&\rho c v_j \frac{\partial T}{\partial x_j} - \frac{\partial}{\partial x_j}\left(k\frac{\partial T}{\partial x_j}\right) = \frac{1}{2}\mu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)
\end{aligned}
\tag{3}
$$

where $c = \frac{\mathrm{d}u}{\mathrm{d}T}$ is the specific heat. The density of entropy production is given by:

$$
\begin{aligned}
\sigma = {} & \frac{k}{T^2}\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_i} \\
& + \frac{1}{2}\frac{\mu}{T}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right)\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right)
\end{aligned}
\tag{4}
$$

3. One-dimensional heat conduction

Let us analyze the one-dimensional problem of stationary heat conduction in a fluid at rest, where the temperature field depends only on one spatial coordinate. This case is significant because the analysis of transient conduction data may erroneously induce to believe that the minimum entropy production principle is verified [19,20].

The continuity equation is identically satisfied, and the momentum equation says that pressure is constant. Without loss of generality, the last of Eq. (3) can be written under this form:

$$
\left[\frac{\mathrm{d}}{\mathrm{d}T}\ln(k)\right]\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 + \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} = 0 \tag{5}
$$

Eq. (5) is the appropriate equation for the temperature field, which can be solved for prescribed boundary values, once the functional dependence of the thermal conductivity on the temperature field is given.

Let us determine the same field equation as it can be derived from the principle of minimum entropy production. To do so, we formulate the following variational problem: “find such a temperature distribution that fulfills prescribed boundary conditions and minimizes the global entropy production”, or $\frac{\mathrm{d}_i S}{\mathrm{d}t} = \int_V \frac{k}{T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 \mathrm{d}V = \min$. Setting: $F = \frac{k}{T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2$ the Euler–Lagrange equation reads

$$
\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\partial F}{\partial\left(\frac{\partial T}{\partial x_j}\right)}\right) - \frac{\partial F}{\partial T} = 0 \tag{6}
$$

which can be reduced to

$$
\left[\frac{\mathrm{d}}{\mathrm{d}T}\ln\left(\frac{\sqrt{k}}{T}\right)\right]\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 + \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} = 0 \tag{7}
$$

Eqs. (5) and (7) are equivalent if and only if the thermal conductivity can be written as $k = \frac{L}{T^2}$, where L is a constant.

This shows that the principle of minimum entropy production is material-dependent. In particular, if we consider the “linear case” defined by the linear (or linearised) Fourier constitutive equation with constant thermal conductivity, the field equations for temperature obtained in the two approaches are different. From this analysis one must conclude that in the problem there should be an open parameter, totally or at least partially determined by the principle, introduced into the model under the form of a phenomenological coefficient.

As a particular case, we observe that the minimum entropy production principle leads to a contradiction with the energy balance equation for the heat conduction process through a plate assuming that the boundary surfaces are kept at constant temperatures. In fact, the temperature distribution resulting from the minimum entropy production theorem is $T(x) = T_0\left(\frac{T_L}{T_0}\right)^{x/L}$, where L is the plate thickness, while the temperature distribution determined by solving the heat conduction equation, with the assumption that surfaces are kept at constant temperatures, is $T(x) = T_0 + (T_L - T_0)(x/L)$. The absolute error between the two methods reduces to zero as the ratio between the extreme temperatures approaches one, that is, when there is no heat flux through the wall

$$
\lim_{T_L/T_0 \to 1} \frac{\Delta T}{(T_L - T_0)} = \lim_{T_L/T_0 \to 1}\left(\frac{x}{L} + \frac{1 - (T_L/T_0)^{x/L}}{T_L/T_0 - 1}\right) = 0 \tag{8}
$$

This shows that the minimum entropy production principle cannot be considered as a variational principle. More modestly, it must be identified with an approximation method.

4. Shear flow

As a second example, we study the steady state shear flow with heat conduction of incompressible fluids. We assume that the velocity field $v_i = (0, v(x), 0)$ is unidirectional and depends on a single spatial coordinate, as well as the temperature field $T = T(x)$.

The first of Eq. (3) is identically satisfied, while the second one requires that the pressure is a linear function of the spatial coordinate $p = p_0 + p'x$. The momentum balance equation reads

$$
\frac{\mathrm{d}\mu}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}\frac{\mathrm{d}v}{\mathrm{d}x} + \mu\frac{\mathrm{d}^2 v}{\mathrm{d}x^2} = p' \tag{9}
$$

and the energy equation reduces to

$$
\left[\frac{\mathrm{d}}{\mathrm{d}T}\ln(k)\right]\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 + \frac{\mathrm{d}^2 T}{\mathrm{d}x^2} + \frac{\mu}{k}\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)^2 = 0 \tag{10}
$$

The model defined by Eqs. (9) and (10) can be solved for prescribed boundary values of the velocity and temperature fields once the functional dependences of the thermal conductivity and of the shear viscosity on the temperature field are given.

We compare now these field equations with the equations obtained from the minimum entropy production principle according to the variational approach. Setting

$$
\begin{aligned}
F = {} & \frac{k}{T^2}\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_i} \\
& + \frac{1}{2}\frac{\mu}{T}\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}-\frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right)\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}-\frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right) \\
& - 2\lambda(x_i)\frac{\partial v_i}{\partial x_i}
\end{aligned}
\tag{11}
$$

the Euler–Lagrange equations are

$$
\frac{\partial}{\partial x_i}\left(\frac{\partial F}{\partial\left(\frac{\partial T}{\partial x_i}\right)}\right)-\frac{\partial F}{\partial T}=0
\tag{12}
$$

$$
\frac{\partial}{\partial x_i}\left(\frac{\partial F}{\partial\left(\frac{\partial v_j}{\partial x_i}\right)}\right)-\frac{\partial F}{\partial v_j}=0
\tag{13}
$$

We have introduced the Lagrange multiplier $-2\lambda(x_i)$ to take into account the fluid incompressibility. The Euler–Lagrange equations (12) and (13) can be re-written as

$$
\begin{aligned}
& \left[\frac{\mathrm{d}}{\mathrm{d}T}\ln\left(\frac{\sqrt{k}}{T}\right)\right]\frac{\partial T}{\partial x_i}\frac{\partial T}{\partial x_i}+\frac{\partial^2 T}{\partial x_i\partial x_i}-\frac{T^2}{2k} \\
& \quad\times\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mu}{2T}\right)\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}-\frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right)\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}-\frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right) \\
& \quad = 0
\end{aligned}
\tag{14}
$$

$$
\begin{aligned}
& \left[\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mu}{T}\right)\right]\frac{\partial T}{\partial x_i}\left(\frac{\partial v_i}{\partial x_j}+\frac{\partial v_j}{\partial x_i}-\frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right) \\
& \quad+\frac{\mu}{T}\left(\frac{\partial^2 v_i}{\partial x_i\partial x_j}+\frac{\partial^2 v_j}{\partial x_i\partial x_j}-\frac{2}{3}\frac{\partial v_k}{\partial x_k}\delta_{ij}\right) \\
& \quad=\frac{\partial\lambda(x_i)}{\partial x_j}
\end{aligned}
\tag{15}
$$

Under the assumptions made above for the velocity and temperature fields, Eq. (14) reduces to the form

$$
\left[\frac{\mathrm{d}}{\mathrm{d}T}\ln\left(\frac{\sqrt{k}}{T}\right)\right]\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2+\frac{\mathrm{d}^2T}{\mathrm{d}x^2}-\frac{T^2}{2k}\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mu}{T}\right)\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)^2=0
\tag{16}
$$

Eq. (15) says that the Lagrange multiplier must depend linearly on the spatial coordinate: $\lambda=\lambda_0+\lambda' x$, with constant λ_0 and λ', and reduces to

$$
\left[\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mu}{T}\right)\right]\frac{\mathrm{d}T}{\mathrm{d}x}\frac{\mathrm{d}v}{\mathrm{d}x}+\frac{\mu}{T}\frac{\mathrm{d}^2v}{\mathrm{d}x^2}=\lambda'
\tag{17}
$$

The comparison of Eqs. (9) and (10) with Eqs. (16) and (17) shows that the equations obtained from the minimum entropy production principle do not agree with the standard thermodynamic balance equations.

We have not been able to find any special assumptions about the functional dependence of the thermal conductivity and shear viscosity on temperature which make the two methods agree with each other. In particular, even the so-called "linear case" does not make the results of the minimum entropy production principle and the balance equations compatible.

We also note that both Eqs. (9) and (10) and Eqs. (16) and (17) contain an arbitrary constant. However, in Eqs. (9) and (10) the constant represents the streamwise pressure gradient, while in Eqs. (16) and (17) it takes into account the incompressibility condition.

5. Analysis of the theorem proof

To find a reason for the results obtained above, one can analyse the proof of the minimum entropy production theorem originally proposed by Prigogine [4] for discontinuous systems described by N state variables, corresponding to N fluxes J_k $(k=1,2,\ldots,N)$. According to the formalism of irreversible thermodynamics the entropy production is given by

$$
\frac{\mathrm{d}_iS}{\mathrm{d}t}=\sum_{k=1}^{N}J_kX_k>0
\tag{18}
$$

Fluxes are related to generalised thermodynamic forces through the phenomenological coefficients

$$
J_k=\sum_{j=1}^{N}L_{kj}X_j
\tag{19}
$$

where $L_{kj}=L_{jk}$ due to Onsager's reciprocity relations. When the system is at equilibrium with respect to one of its state variables, the corresponding flux vanishes

$$
\sum_{j=1}^{N}L_{kj}X_j=0
\tag{20}
$$

and finally one finds that the entropy production is steady with respect to the thermodynamic force generating the flux

$$
\frac{\partial}{\partial X_k}\left(\frac{\mathrm{d}_iS}{\mathrm{d}t}\right)=\sum_{j=1}^{N}(L_{kj}+L_{jk})X_j=2\sum_{j=1}^{N}L_{kj}X_j=0
\tag{21}
$$

However, using Eq. (18) to calculate the derivative in Eq. (21) is not appropriate: in fact, Eq. (20) provides an additional relation among generalised thermodynamic forces, which changes the functional dependence of entropy production on thermodynamic forces, and therefore it should be taken into account *before* calculating the derivative.

As a simple example, one can consider a process consisting in the simultaneous mass and energy transfer between two phases at different temperatures, described by the equation

$$
\frac{\mathrm{d}_iS}{\mathrm{d}t}=J_1X_1+J_2X_2>0
\tag{22}
$$

and by the phenomenological relations

$$J_1 = L_{11}X_1 + L_{12}X_2 \tag{23}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \tag{24}$$

with $L_{12} = L_{21}$. At a stationary state

$$J_2 = L_{21}X_1 + L_{22}X_2 = 0 \tag{25}$$

and according to Eq. (22)

$$\frac{\mathrm{d}_iS}{\mathrm{d}t} = L_{11}X_1^2 + 2L_{21}X_1X_2 + L_{22}X_2^2 > 0 \tag{26}$$

Following the classical procedure one would find that

$$\frac{\partial}{\partial X_2}\left(\frac{\mathrm{d}_iS}{\mathrm{d}t}\right)_{X_1} = 2(L_{21}X_1 + L_{22}X_2) = 2J_2 = 0 \tag{27}$$

so that the two conditions $J_2 = 0$ and $\frac{\partial}{\partial X_2}\left(\frac{\mathrm{d}_iS}{\mathrm{d}t}\right)_{X_1} = 0$ are completely equivalent.

On the other hand, if one takes into account Eq. (25), the entropy production of the system at steady state with respect to the generalised flux J_2 is different from Eq. (26); moreover, in general the entropy production is non-negative (and not just strictly positive), so that Eq. (26) should be more correctly re-written as

$$\frac{\mathrm{d}_iS}{\mathrm{d}t} = L_{11}X_1^2 + 2L_{21}X_1X_2 + L_{22}X_2^2 = \frac{L_{22}(L_{11}L_{22} - L_{21}^2)}{L_{21}^2}X_2^2 \geqslant 0 \tag{28}$$

Thus, Eq. (27) must be replaced by

$$\frac{\partial}{\partial X_2}\left(\frac{\mathrm{d}_iS}{\mathrm{d}t}\right)_{X_1} = 2\frac{L_{22}(L_{11}L_{22} - L_{21}^2)}{L_{21}^2}X_2 \tag{29}$$

According to Eq. (29) the two conditions $J_2 = 0$ and $\frac{\partial}{\partial X_2}\left(\frac{\mathrm{d}_iS}{\mathrm{d}t}\right)_{X_1} = 0$ are not completely equivalent. In fact, for $L_{22} > 0$ and $L_{21} \neq 0$ one finds

$$L_{11}L_{22} - L_{21}^2 = 0 \tag{30}$$

According to a well-known theorem of linear algebra, to ensure the existence of a non-trivial solution of Eqs. (23) and (24) with the reciprocity relations satisfied, the system must obey the following conditions:

$$J_1 = 0 \quad \text{and} \quad J_2 = 0 \tag{31}$$

As a consequence of Eq. (31), the entropy production in a stationary state of a linear dissipative system is minimum if and only if it equals zero.

Applying a similar procedure to a system with N variables, and taking into account the reciprocity relations, one finds that the minimizing the entropy production with respect to thermodynamic forces lowers the rank of the matrix of phenomenological coefficients ($\det L_{ik} \equiv 0$), so that all generalised fluxes must be zero.

6. Conclusions

The principle of minimum entropy production, which is commonly used to characterise the stationary states of linear dissipative systems obeying Onsager's reciprocity relations, has been reviewed critically. The rigorous analysis of two examples (the heat conduction in a fluid at rest and the combined shear flow and heat conduction in an incompressible fluid) based on the comparison of the theorem's results with those of the field equations of continuum mechanics shows that this theorem cannot be considered as a general variational principle, but at best an approximation method, which converges to the exact solution as the system converges to equilibrium.

The theorem proof, as formulated by Prigogine, leads to an erroneous conclusion because the condition of stationary state is not taken into account correctly in the expression of entropy production. When the additional relationship among generalised thermodynamic forces is introduced into the expression of the entropy production, the theorem shows that for systems in a stationary state the entropy production must be zero.

In conclusion, one can formulate the following proposition: "Provided that the Onsager reciprocal relations are satisfied, the minimum entropy production theorem as formulated by Prigogine is valid only when generalised thermodynamics fluxes are simultaneously equal to zero at non zero values of the generalised thermodynamics forces".

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