ISSN 1330–0008
CODEN FIZAE4

ON THE EQUIVALENCE BETWEEN ONSAGER'S PRINCIPLE OF THE LEAST DISSIPATION OF ENERGY AND MAXIMUM ENTROPY PRODUCTION PRINCIPLE. CONDUCTION OF HEAT IN AN ANISOTROPIC CRYSTAL.

PAŠKO ŽUPANOVIĆ [a], DAVOR JURETIĆ [a] and SREĆKO BOTRIĆ [b]

[a]*Faculty of Natural Sciences, Mathematics and Education, University of Split, Teslina 12, 21000 Split, Croatia*

[b]*Faculty of Electrical Engineering, Mechanical Engineering and Naval Architecture, University of Split, R. Boškovića b.b., 21000 Split, Croatia*

E-mail addresses: pasko@pmfst.hr, juretic@pmfst.hr, srecko.botric@fesb.hr

Dedicated to the memory of Professor Vladimir Šips

Received 13 September 2004; Accepted 21 December 2004
Online 31 October 2005

An application of the Onsager's principle of the least dissipation of energy to the problem of the heat conduction in an anisotropic crystal is revisited. In the case of a steady spatial distribution of the temperature it is shown that this principle is equivalent to the principle of maximum entropy production. This means that components of the actual heat flux are distributed in such a way as to achieve the state of the maximum entropy production.

PACS numbers: 05.70.Ln,65.40.Gr UDC 536.75
Keywords: entropy production, principle of the least dissipation of energy

1. *Introduction*

It was Ehrenfest (Enzykl. Math. Wissensch, IV, 2(II) fasc.6, p82, note23, 1912) who first asked the question does there exist some function which, like the entropy in the equilibrium state of an isolated system, achieves its extreme value in the stationary non-equilibrium state.

L. Onsager [1, 2] showed that phenomenological laws of non-equilibrium thermodynamics, like the Fourier's law of heat conduction, diffusion or chemical processes close to the equilibrium state, can be derived from the principle of the least dissipation of energy.

Besides this phenomenological approach, there is a less known microscopical one introduced by Kohler [3]. Kohler's approach starts from the Boltzman's transport equation. Assuming small departure of the distribution of molecules in the phase space from the equilibrium (Maxwell-Boltzmann) distribution, he found that the stationary state is the state of the maximum entropy production. Ziman applied his method to the system of free electrons and also found that the stationary state is the one with the maximum entropy production [4].

Finally, there is the third approach to the problem of the non-equilibrium processes, based on the Shannon's definition of the information measure [5], launched by Jaynes [6, 7]. The result of this approach is the maximum entropy production principle, which claims that stationary processes are characterized by the maximum entropy production. It was Dewar who put this principle on the firm ground [8].

It seems from the aforementioned that the Onsager's principle of the least dissipation offers a different answer to the question posed by Ehrenfest. We revisit the problem of the stationary heat conduction in an anisotropic crystal and show that the principle of the least dissipation of energy [1] and the maximum entropy production principle are equivalent in this case.

The paper is organized in the following way. The first section starts with the phenomenological equations of the heat conduction in an anisotropic crystal. The entropy production is introduced using the first law of the thermodynamics and continuity equation. The second section deals with the principle of the least dissipation of energy. Non-equilibrium states are defined in terms of the heat flux in the third section. It is shown that the entropy production is a bilinear function of fluxes if the non-equilibrium state is close to the equilibrium state. The equivalence between the principle of the least dissipation of energy and the maximum entropy production is the subject of the fifth section. Finally, in the last section we stress that maximum entropy production principle governs the non-stationary processes, at least in the linear regime.

2. *Heat conduction in anisotropic crystal and entropy production*

Heat conduction in an anisotropic crystal is described by the following system of linear equations [1]

$$
\begin{aligned}
X_1 &= R_{11}j_1 + R_{12}j_2 + R_{13}j_3 \,, \\
X_2 &= R_{21}j_1 + R_{22}j_2 + R_{23}j_3 \,, \\
X_3 &= R_{31}j_1 + R_{32}j_2 + R_{33}j_3 \,,
\end{aligned}
\tag{1}
$$

where

$$X_k = -(1/T)\partial T/\partial x_k \tag{2}$$

is the thermodynamic force in the k^{th} direction and j_k is the conjugated heat flux. In the case of an isotropic crystal, heat flux is equal to the heat transferred through a unit surface perpendicular to the temperature gradient per unit of time. Finally, R_{kl} are the elements of the tensor of thermal resistivity.

In the process considered in this paper, heat is the only mechanism of the exchange of energy between elementary volume $\mathrm{d}V$ and its surroundings. Therefore, due to the first law of thermodynamics and local equilibrium assumption, we get

$$\frac{\mathrm{d}Q}{\mathrm{d}V} = q = Ts, \tag{3}$$

where q and s are the heat and entropy densities, respectively. Assuming no source of heat within the elementary volume, the equation of continuity for heat gives

$$\frac{1}{T}\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{1}{T}\,\mathrm{div}\,\mathbf{j}. \tag{4}$$

Standard methods of the vector calculus give

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\oint \frac{1}{T}\,\mathbf{j}\cdot\mathbf{dS} + \int\limits_V \mathbf{j}\cdot\nabla\left(\frac{1}{T}\right)\mathrm{d}V. \tag{5}$$

The rate of the change of the entropy of the whole crystal is [1]

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\int\limits_V \frac{1}{T}\,\mathrm{div}\,\mathbf{j}\;\mathrm{d}V. \tag{6}$$

The rate of the exchange of entropy of the crystal with its surroundings is

$$\frac{\mathrm{d}_e S}{\mathrm{d}t} = -\oint_S \frac{1}{T}\,\mathbf{j}\cdot\mathbf{dS}. \tag{7}$$

The difference between the total change of entropy and the rate of exchange of the entropy between system and surroundings gives the entropy production,

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \frac{\mathrm{d}S}{\mathrm{d}t} - \frac{\mathrm{d}_e S}{\mathrm{d}t} = \int \mathbf{j}\cdot\nabla\left(\frac{1}{T}\right)\,\mathrm{d}V \tag{8}$$

In terms of the thermodynamic forces (2), we get

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \int\limits_V \frac{1}{T}\sum_{k=1}^{3} j_k X_k\;\mathrm{d}V \tag{9}$$

By means of Eqs. (6), (7) and (9), the rate of the change of the entropy of the whole crystal becomes

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\oint_S \frac{1}{T}\mathbf{j}\cdot \mathrm{d}\mathbf{S} + \int\limits_V \frac{1}{T}\sum_{k=1}^{3} j_k X_k \; \mathrm{d}V. \tag{10}$$

This equation shows that entropy can be considered as some sort of the fluid the source of which is the heat flux.

3. Principle of the least dissipation of energy

Formulation of the principle of the least dissipation of energy is related to the dissipation function originally introduced by Lord Rayleigh [11]

$$2\phi(j,j)T = \sum_{k,l=1}^{3} R_{kl} j_k j_l, \tag{11}$$

where

$$R_{kl} = R_{lk}. \tag{12}$$

One can easily verify that

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} - \int\limits_V \Phi(j,j)\,\mathrm{d}V = \mathrm{maximum} \tag{13}$$

generates the system of equations (1). The above condition is known as the principle of the least dissipation of energy.

4. Non-equilibrium state of the system close to the equilibrium state

In the previous section, the entropy production is defined by means of the thermodynamic forces and conjugated fluxes (see Eq. (9)). The non-equilibrium state of the elementary volume is a function of temperature, its gradient and flux. Assuming that the non-equilibrium state is close to the equilibrium state, the expansion of the density of the entropy production $\mathrm{d}_i s/\mathrm{d}t$ in terms of the fluxes gives

$$\frac{\mathrm{d}_i s}{\mathrm{d}t} = \left.\frac{d_i s}{dt}\right|_{\mathrm{eq}} + \sum_{k=1}^{3} a_k j_k + \sum_{k,l=1}^{3} \frac{1}{T} R_{kl} j_k j_l + \sum_{k,l,m=1}^{3} R_{klm} j_k j_l j_m + \mathcal{O}(j^4). \tag{14}$$

A free term vanishes since it corresponds to the entropy production in the equilibrium state. Furthermore, due to the symmetry of the crystal on the operation of inversion, it holds that

$$\frac{\mathrm{d}_i s}{\mathrm{d}t}\left(-\mathbf{j}\right) = \frac{\mathrm{d}_i s}{\mathrm{d}t}\left(\mathbf{j}\right). \tag{15}$$

Due to this symmetry property, all odd powers vanish and for the state not far from equilibrium state, we get the entropy production as the bilinear function in fluxes

$$\frac{\mathrm{d}_i s}{\mathrm{d}t} = \sum_{k,l=1}^{3} \frac{1}{T} R_{kl} j_k j_l. \tag{16}$$

5. *Principle of the maximum entropy production*

The definition of the entropy production (9) and expression (16) give

$$\int\limits_V \frac{1}{T} \sum_k X_k j_k \,\mathrm{d}V = \int\limits_V \sum_{k,l=1}^{3} \frac{1}{T} R_{kl} j_k j_l \,\mathrm{d}V. \tag{17}$$

The system of equations (1) can be deduced from the principle of maximum entropy production

$$\frac{\mathrm{d}_i S}{\mathrm{d}t} = \int\limits_V \frac{1}{T} \sum_{k,l=1}^{3} \frac{1}{T} R_{kl} j_k j_l \,\mathrm{d}V = \text{maximum}, \tag{18}$$

assuming a steady spatial distribution of temperatures.

Indeed, defining the Ψ_h function

$$\Psi_h = \int\limits_V \frac{1}{T} \sum_{k=1}^{3} j_k X_k \,\mathrm{d}V - \int\limits_V \frac{1}{T} \sum_{k,l=1}^{3} R_{kl} j_k j_l \,\mathrm{d}V = 0, \tag{19}$$

the standard procedure of the variational calculus of the conditional extremum [12]

$$\delta\left[\frac{d_i S}{dt} + \lambda \Psi_h\right] = 0, \tag{20}$$

gives

$$\lambda X_k + 2\left(1-\lambda\right) \sum_{l=1}^{3} R_{kl} j_l = 0. \tag{21}$$

Multiplying the above equation with j_k, summing over index k and integrating over the crystal, we get

$$\lambda \int_V \sum_{k=1}^{3} j_k X_k \, \mathrm{d}V + 2\,(1-\lambda) \int_V \sum_{k,l=1}^{3} R_{kl} j_k j_l \, \mathrm{d}V = 0. \tag{22}$$

Due to the condition (17), we find $\lambda = 2$. Evidently, in this case the system of equations (21) becomes the system of phenomenological equations (1).

This shows that the thermal fluxes (j_k) are distributed in such a way as to achieve the state of the maximum entropy production.

6. Discussion

The non-equilibrium state of the anisotropic crystal is a function of temperature, its gradient and flux. If the non-equilibrium state is not far from the equilibrium state, the entropy production is a bilinear function of the fluxes. Combining the bilinear dependence of the entropy production with its standard definition (9), we find that the system of the phenomenological equations of the heat conduction in the anisotropic crystal can be derived from the principle of the maximum entropy production. In this way, we show the equivalence between the principle of the least dissipation of energy and the principle of the maximum entropy production.

We note that the principle of maximum entropy production based on the Jaynes formulation of the statistical mechanics holds only for stationary processes [8, 9]. The result of our analysis is that this principle holds also for non-stationary processes, at least in the linear regime. This discrepancy will be a subject of our further work.

We have shown that stationary currents in a linear electric network distribute themselves so as to achieve the state of the maximum entropy production [10].

Two of the present authors have shown recently [13] that chemical cycle kinetics close to the equilibrium state can be described by an analogue electric circuit, i.e., these processes are governed by the principle of the maximum entropy production, too.

It is our belief that the principle of maximum entropy production is valid in the linear non-equilibrium thermodynamics, i.e., we are convinced that it is just the principle Ehrenfest was looking for.

Acknowledgements

The present work was supported by the Croatian Ministry of Science and Technology, project no. 0177163.

References

[1] L. Onsager, Phys. Rev. **37** (1931) 405.

[2] L. Onsager, Phys. Rev. **38** (1931) 2265.

[3] M. Kohler, Z. Physik **124** (1948) 172.

[4] J. M. Ziman, Can. J. Phys. **124** (1948) 172.

[5] C. E. Shannon, *The Mathematical Theory of Communications*, University of Illinois, Chicago (1998).

[6] E. T. Jaynes, Phys. Rev. I Chem. **31** (1980) 579.

[7] E. T. Jaynes, Phys. Rev. II Chem. **31** (1980) 579.

[8] R. Dewar, J. Phys. A. Math. Gen. **36** (2002) 631.

[9] R. Dewar, *The Path Information Formalism of NESM in the Linear Regime*, private communication (2004).

[10] P. Županović, D. Juretić and S. Botrić, Phys. Rev. E **70** (2004) 056108.

[11] J. W .S. Rayleigh, *Theory of Sound*, Dover Publications, New York (1945).

[12] M. I. Krasnov, G. I. Makarenko and A. I. Kiselev, *Problems and Exercises in the Calculus of Variation*, Mir Publishers, Moscow (1975).

[13] P. Županović and D. Juretić, Croatica Chemica Acta **77** (2004) 561.

JEDNAKOVALJANOST ONSAGEROVOG PRINCIPA NAJMANJEG RASIPANJA SLOBODNE ENERGIJE I PRINCIPA NAJVEĆE BRZINE RASTA ENTROPIJE. VOĐENJE TOPLINE U ANIZOTROPNOM KRISTALU

Obnavljamo pitanje primjene Onsagerovog principa najmanjeg rasipanja slobodne energije na problem vođenja topline u anizotropnom kristalu. U slučaju stalne prostorne raspodjele temperature, pokazuje se da je taj princip jednakovaljan principu najveće brzine rasta entropije. Stoga se komponente toplinskog toka raspodijele tako da se postigne stanje najveće brzine rasta entropije.