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New Look at an Old Principle: An Alternative Formulation of The Theorem of Minimum Entropy Production

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Abstract

We formulate a direct generalization of the Prigogine's principle of minimum entropy production, according to a new isoperimetric variation principle by classical non-equilibrium thermodynamics. We focus our attention on the possible mathematical forms of constitutive equations. Our results show that the Onsager's reciprocity relations are consequences of the suggested variation principle.

Furthermore, we show by the example of the thermo-diffusion such reciprocity relations for diffusion tensor, which are missing in Onsager's theory. Our theorem applied to the non-linear constitutive equations indicates the existence of dissipation potential. We study the forms of general reciprocity with the dissipation potential. This consideration results in a weaker condition than Li-Gyarmati-Rysselberhe reciprocity has. Furthermore, in the case of electric conductivity in the magnetic field, our theorem shows the correct dependence of the Onsager's kinetic coefficient by the axial vector of magnetic induction. We show in general that the evolution criterion of the global entropy production is a Lyapunov-function, and so the final stationer state is independent of the initial, time-independent boundary conditions.

Keywords: General Reciprocal Relations, Minimum-Entropy-Production, Bertalanffy's Equifinality

Introduction

The first formulation of the minimum entropy production for the non-continuous system was firstly formulated by Prigogine [1], [2]. This theorem was generalized by introducing the order of stationarity by de Groot [3]. The present theorem valid also for continuous systems and dealing with the dynamics and stability of the stationer systems was formulated by Glansdorff and Prigogine [4], [5]. Their work shows that the entropy production in the frame of linear Onsager's thermodynamic theory both the dynamics and the stability of the system correctly described, ranging the entropy production in the thermodynamics of linear stationer systems like the entropy in thermostatics. However, in the case of non-linear constitutive equations, this significant role of the entropy production vanishes and only the partial derivatives of entropy production by thermodynamical forces have such attributions like the entropy production itself in the linear Onsager's theory. Gyarmati had proved [6] that a realistic generalization of Onsager's principle of last dissipation of energy is equivalent to the above Glansdorff-Prigogine theorem. These considerations feature again the dissipation potentials introduced by Rayleigh and Onsager. The theories mentioned above emphasize a strong correlation between the existence of minimum entropy production and the possible form of constitutive equations of dissipative forces and currents.

Onsager proved the symmetry-relations and the potential dissipation behavior of entropy production by methods of fluctuation-theory. Hence the properties of constitutive equations connected to the extremal behavior of entropy production are not consistent with the field theory formulation of the non-equilibrium thermodynamics. In non-linear cases, unfortunately, such a generalized method does not exist to prove the potential behavior of the entropy production, (like for example to prove the higher-order Onsager's relations). However, by the strong correlation of the stationary behavior of the entropy production and the mathematical form of the constitutive equations, an interesting question arises: when we accept the extremal behavior of the entropy production what the consequences on the form of constitutive equations of non-linear thermodynamics are?

To study this, we investigate the constitutive equations with condition fix the extreme (more general stationer) behavior of the entropy production.

Materials and Methods

Formulation of the extremum principle

Let us study a stationer non-equilibrium thermodynamical system, containing a transport of n various in extensive, having ${}^{i}a$ and ${}^{i}\mathbf{j}$ densities and current-densities. We assume that the system is in cellular equilibrium. In this case, the Gibbs relation is valid, and the entropy density of the system (s) is a state-function of n different ${}^{i}a$ quantities. We define the conjugated intensives to ${}^{i}a$ extensive as:

$$ {}^{i}\Gamma = \frac{\partial s}{\partial\, {}^{i}a} \tag{1}$$

According to the second law of the non-equilibrium processes, the entropy production density of the system is:

$$\sigma = \sum_{i=1}^{n} {}^{i}\mathbf{j} \cdot \nabla {}^{i}\Gamma \geq 0 \tag{2}$$

while ${}^{i}\Gamma {}^{i}\mathbf{j}$ entropy current transported together with the i-th extensive.

The complete entropy production (P) and the complete detailed entropy-flux (Φs) are:

$$\begin{aligned} P &= \int_V \sigma\, dV = \int_V \sum_{i=1}^{n} {}^{i}\mathbf{j} \cdot \nabla {}^{i}\Gamma dV, \\ \Phi_s &= \oint_\Omega \sum_{i=1}^{n} {}^{i}\Gamma\ {}^{i}\mathbf{j} \cdot \mathbf{dA} = \int_V \sum_{i=1}^{n} \nabla \cdot \left({}^{i}\Gamma\ {}^{i}\mathbf{j}\right) dV \end{aligned} \tag{3}$$

where we used the Gauss-theorem in the second equation, and V and Ω are the volume and surface of the system, respectively. Simplifying the notations, we use the Einstein's sum-convention like:

$$\begin{aligned} P &= \int_V \sum_{i=1}^{n} {}^{i}\mathbf{j} \cdot \nabla {}^{i}\Gamma dV := \int_V {}^{i}\mathbf{j} \cdot \nabla {}^{i}\Gamma dV \\ \Phi_s &= \oint_\Omega \sum_{i=1}^{n} {}^{i}\Gamma\ {}^{i}\mathbf{j} \cdot \mathbf{dA} := \oint_\Omega {}^{i}\Gamma\ {}^{i}\mathbf{j} \cdot \mathbf{dA} = \int_V \nabla \cdot \left({}^{i}\Gamma\ {}^{i}\mathbf{j}\right) dV \end{aligned} \tag{4}$$

The extremum theory of entropy production is formulated like a conditional extremum principle:

$$P = \min, \qquad when \quad \Phi_s = const \tag{5}$$

This could be more precisely written in the isoperimetric variation-principle:

$$S=\int_V L dV = stac, \quad L := (\lambda+1)\ {}^i\mathbf{j}\cdot\nabla^i\Gamma + \lambda^i\Gamma\nabla\cdot^i\mathbf{j} \tag{6}$$

where λ is a constant scalar multiplicator. This isoperimetric variation task could be reformulated by dual form when we investigate the conditional stationarity of Φs concerning constant P. In this case, the variation-principle and the Lagrangian are:

$$S=\int_V L dV = stac, \quad L := (\lambda+1)^i\Gamma\nabla\cdot^i\mathbf{j} + \lambda\ {}^i\mathbf{j}\cdot\nabla^i\Gamma \tag{7}$$

The case of linear constitutive laws

The material equations are:

$$\nabla^i\Gamma = \mathbf{R}_{ik}{}^k\mathbf{j} \tag{8}$$

where Rik is the second-order tensor of the Onsager's kinetic coefficients, characteristic for the given material. In consequence of (7) the actual form of the Lagrangian is:

$$L=(\lambda+1)\ {}^i\Gamma\nabla\cdot^i\mathbf{j} + \lambda\mathbf{R}_{ik}{}^k\mathbf{j}\cdot^i\mathbf{j}+ \tag{9}$$

The Euler-Lagrange- equation belonging to the variation of the current densities as sufficient condition for an extremum is:

$$\lambda\left(\mathbf{R}_{ik}+\mathbf{R}_{ki}^T\right)^k\mathbf{j} = (\lambda+1)\mathbf{R}_{ik}{}^k\mathbf{j} \quad \rightarrow \quad \lambda\mathbf{R}_{ki}^{T\ k}\mathbf{j} = \mathbf{R}_{ik}{}^k\mathbf{j} \tag{10}$$

where the upper index T refers to the transpose of the tensor.

The entropy-production from this considering its constant demand, we get:

$$\lambda\mathbf{R}_{ik}^{T\ i}\mathbf{j}\cdot^k\mathbf{j} = \mathbf{R}_{ik}{}^k\mathbf{j}\cdot^i\mathbf{j} \tag{11}$$

It could be valid in all the arbitrary cases of current densities only, when λ=1, so the following Onsager's symmetry-relations are valid:

$$\mathbf{R}_{ki}^T = \mathbf{R}_{ik} \tag{12}$$

The entropy-production will be minimal in this case, and this result remains valid in the case of quasi-linear constitutive cases as well. The symmetry-relations in (12) are more general than the original Onsager's theory. This will be shown in the case of the thermo-diffusion.

Results and Discussion

$$P=\int_V\left[{}^q\mathbf{j}\cdot\nabla\left(\frac{1}{T}\right) - {}^\alpha\mathbf{j}\cdot\nabla\left(\frac{{}^\alpha\mu}{T}\right)\right]dV = \tag{13}$$
$$=\int_V\left[{}^q j^i\frac{\partial}{\partial x^i}\left(\frac{1}{T}\right) - {}^\alpha j^i\frac{\partial}{\partial x^i}\left(\frac{{}^\alpha\mu}{T}\right)\right]dV$$

$$\Phi_s = \int_V \left[\frac{1}{T}\nabla\cdot{}^q\mathbf{j} + {}^q\mathbf{j}\cdot\nabla\left(\frac{1}{T}\right) - \frac{{}^\alpha\mu}{T}\nabla\cdot{}^\alpha\mathbf{j} - {}^\alpha\mathbf{j}\cdot\nabla\left(\frac{{}^\alpha\mu}{T}\right)\right] dV = \tag{14}$$

$$= \int_V \left[\frac{1}{T}\frac{\partial {}^q j^i}{\partial x^i} + {}^q j^i \frac{\partial}{\partial x^i}\left(\frac{1}{T}\right) - \frac{{}^\alpha\mu}{T}\frac{\partial {}^\alpha j^i}{\partial x^i} - {}^\alpha j^i \frac{\partial}{\partial x^i}\left(\frac{{}^\alpha\mu}{T}\right)\right] dV$$

Thermodiffusion in the triclinic system

In the case of thermodiffusion the global entropy-production and the detailed global entropy flux are [6]:

Let us consider the following linear constitutive equations:

$$\frac{\partial}{\partial x^i}\left(\frac{1}{T}\right) = \mathrm{K}_{ik}\,{}^q j^k - {}^\alpha\mathrm{K}_{ik}\,{}^\alpha j^k \tag{15}$$

$$\frac{\partial}{\partial x^i}\left(\frac{{}^\alpha\mu}{T}\right) = -{}^{\alpha\beta}D_{ik}\,{}^\beta j^k - D_{ik}\,{}^q j^k$$

With these equations the Lagrangian of (7) is:

$$L = \frac{\lambda+1}{T}\frac{\partial {}^q j^i}{\partial x^i} + (\lambda+1)\frac{{}^\alpha\mu}{T}\frac{\partial {}^\alpha j^i}{\partial x^i} + \lambda(\mathrm{K}_{ik}\,{}^q j^i\,{}^q j^k - {}^\alpha\mathrm{K}_{ik}\,{}^q j^i\,{}^\alpha j^k \tag{16}$$

$$- D_{ik}\,{}^q j^i\,{}^\alpha j^k - {}^{\alpha\beta}D_{ik}\,{}^\alpha j^i\,{}^\beta j^k)$$

Determination of the kinetic coefficients of (15) is possible from the Euler-Lagrange- equations belonging to the variation of i-th coordinate qji and αji of the heat and α-the chemical component current densities:

$${}^q j^i(\lambda\mathrm{K}_{ik} - \mathrm{K}_{ik}) + {}^\alpha j^i\left(\lambda\,{}^\alpha\mathrm{K}_{ki} - D_{ik}\right) = 0 \tag{17}$$

$${}^q j^i\left(\lambda\,{}^\alpha\mathrm{K}_{ki} - D_{ik}\right) + {}^\alpha j^i\left(\lambda\,{}^{\alpha\beta}D_{ik} - {}^{\beta\alpha}D_{ki}\right) = 0$$

From these (due to the arbitrary current densities) we receive:

$${}^q j^i(\lambda\mathrm{K}_{ik} - \mathrm{K}_{ik}) = 0 \tag{18}$$

$${}^\alpha j^i\left(\lambda\,{}^\alpha\mathrm{K}_{ki} - D_{ik}\right) = 0$$

$${}^\alpha j^i\left(\lambda\,{}^{\alpha\beta}D_{ik} - {}^{\beta\alpha}D_{ki}\right) = 0$$

Using the (14) the λ=1, and hence we get the symmetry relations:

$$\mathrm{K}_{ik} = \mathrm{K}_{ik}, \quad {}^\alpha\mathrm{K}_{ki} = D_{ik}, \quad {}^{\alpha\beta}D_{ik} = {}^{\beta\alpha}D_{ki} \tag{19}$$

Last relations obtained elements of diffusion tensor αβDik are more general than found in the available literature [7].

General evaluation of the extremum principle: Based on the above description we show below an essential consequence of the extremum principle: it is the existence of the dissipation potential for the case of non-linear constructive equations. Very general symmetry relations (like was established by Li-Gyarmati-Rysselberghe [8], [9], [10]) are the consequence of the dissipation potential. Suppose n different constitutive equations describe the system, instead of the linear constitutive equations (8). In this case, the Euler-Lagrange equations as conditions of extremum are:

$$\nabla^i\Gamma={}^i\mathbf{f}\left({}^j\Gamma,{}^j\mathbf{j}\right) \tag{20}$$

$${}^j\mathbf{f}=\lambda\frac{\partial^i\mathbf{f}}{\partial^j\mathbf{j}}\,{}^i\mathbf{j} \tag{21}$$

Using (21), we get the following derivative tensors:

$$\frac{\partial^j\mathbf{f}}{\partial^i\mathbf{j}}=\lambda\left(\frac{\partial^i\mathbf{f}}{\partial^j\mathbf{j}}+\frac{\partial^2\,{}^i\mathbf{f}}{\partial^i\mathbf{j}\partial^j\mathbf{j}}\,{}^i\mathbf{j}\right),\quad \frac{{}^i\mathbf{f}}{\partial^j\mathbf{j}}=\lambda\left(\frac{\partial^j\mathbf{f}}{\partial^i\mathbf{j}}+\frac{\partial^2\,{}^j\mathbf{f}}{\partial^j\mathbf{j}\partial^i\mathbf{j}}\,{}^j\mathbf{j}\right) \tag{22}$$

Assuming the continuity of second-order derivatives, using Young's theorem, we obtain generalized reciprocity relations:

$$\frac{\partial^j\mathbf{f}}{\partial^i\mathbf{j}}=\frac{{}^i\mathbf{f}}{\partial^j\mathbf{j}} \tag{23}$$

These relations are necessary and sufficient for the existence of a $\Phi({}^j\Gamma,{}^j\mathbf{j})$ dissipation potential with the conditions:

$$\nabla^i\Gamma={}^i\mathbf{f}=\frac{\partial\Phi}{\partial^i\mathbf{j}},\quad {}^i\mathbf{j}\cdot\frac{\partial\Phi}{\partial^i\mathbf{j}}\geq 0,\quad \left.\frac{\partial\Phi}{\partial^i\mathbf{j}}\right|_{{}^j\mathbf{j}=0}=0\,, \tag{24}$$

The dissipation potential is tightly connected to the entropy production density.

To show this calculation, the partial derivatives of σ by ${}^i\mathbf{j}$ and using (21), we get from (2):

$$\frac{\partial\sigma}{\partial^i\mathbf{j}}={}^i\mathbf{f}+\frac{\partial^i\mathbf{f}}{\partial^i\mathbf{j}}\,{}^i\mathbf{j}=\frac{\lambda+1}{\lambda}\,{}^i\mathbf{f}=\frac{\lambda+1}{\lambda}\frac{\partial\Phi}{\partial^i\mathbf{j}}\,, \tag{25}$$

In consequence:

$$\sigma=\frac{\lambda+1}{\lambda}\Phi+\Phi_0\left({}^j\Gamma\right), \tag{26}$$

moreover, from (24) follows:

$$ {}^{i}\mathbf{j}\cdot\frac{\partial\sigma}{\partial\,{}^{i}\mathbf{j}}=\frac{\lambda+1}{\lambda}{}^{i}\mathbf{j}\cdot\,{}^{i}\mathbf{f}=\frac{\lambda+1}{\lambda}\sigma \quad , \tag{27} $$

Disregarding the scalar function $\Phi_0({}^{j}\Gamma)$ which depends only on the intensives, in consequence of (26) and (27) the dissipation potential satisfies the following significant relation:

$$ {}^{i}\mathbf{j}\cdot\frac{\partial\Phi}{\partial^{i}\mathbf{j}}=\frac{\lambda+1}{\lambda}\Phi=\Theta\Phi,\quad \Theta=\frac{\lambda+1}{\lambda} \quad , \tag{28} $$

Hence the dissipation potential Φ is Θ-the order homogenous Euler-function of the current transport densities. The entropy production density is zero at zero current densities, so Θ >0. However, due to the non-negativity of entropy production, Θ≥2, and an integer. In the case of Θ=2 the constitutive equations are linear, the reciprocity relations are Onsager-type and the Lagrange multiplicator λ=1.

The Li-Gyarmati-Rysselberghe's non-linear constitutive equations are derived from the Taylor series of the general equation (20):

$$ \nabla^{i}\Gamma={}^{i}\mathbf{f}\left({}^{j}\Gamma,{}^{j}\mathbf{j}\right)\cong{}^{i}\mathbf{R}_{j}\,{}^{j}\mathbf{j}+{}^{i}\mathbf{R}_{jk}\,{}^{j}\mathbf{j}^{k}\mathbf{j} \tag{29} $$

where ${}^{i}\mathbf{R}_{j}$ és ${}^{i}\mathbf{R}_{jk}$ are the second- and third-order tensors of the kinetic coefficients.

As we have seen above, in consequence of the various principles the dissipation potential is a homogeneous Euler function of the current transport densities. On the other hand, the first-order partial derivatives of the Euler functions (in our case the constitutive equations) are also Euler functions having an order less than the original was. Because the constitutive equations (29) are not homogeneous Euler functions, they cannot be derived from the dissipation potential. Consequently the linear equation alternatively, the second-order equation

$$ \nabla^{i}\Gamma={}^{i}\mathbf{f}\left({}^{j}\Gamma,{}^{j}\mathbf{j}\right)\cong{}^{i}\mathbf{R}_{j}\,{}^{j}\mathbf{j} \tag{30} $$

$$ \nabla^{i}\Gamma={}^{i}\mathbf{f}\left({}^{j}\Gamma,{}^{j}\mathbf{j}\right)\cong{}^{i}\mathbf{R}_{jk}\,{}^{j}\mathbf{j}^{k}\mathbf{j} \tag{31} $$

could be derived from the potentials of second- and third-order. These could be constructed, for example, by the method of Vainberg [11] as follows:

$$ {}^{(2)}\Phi\left({}^{j}\Gamma,{}^{j}\mathbf{j}\right)=\int_{0}^{1}{}^{j}\mathbf{j}\cdot{}^{i}\mathbf{R}_{j}\left(\tau\,{}^{j}\mathbf{j}\right)d\tau=\frac{1}{2}{}^{j}\mathbf{j}\cdot{}^{i}\mathbf{R}_{j}\,{}^{j}\mathbf{j} \tag{32} $$

$$ {}^{(3)}\Phi\left({}^{j}\Gamma,{}^{j}\mathbf{j}\right)=\int_{0}^{1}{}^{j}\mathbf{j}\cdot{}^{i}\mathbf{R}_{jk}\left(\tau\,{}^{j}\mathbf{j}\right)\left(\tau\,{}^{k}\mathbf{j}\right)d\tau=\frac{1}{3}{}^{j}\mathbf{j}\cdot{}^{i}\mathbf{R}_{jk}\,{}^{j}\mathbf{j}^{k}\mathbf{j} $$

From the above potentials, we get in the case of the linear equation the while in non-linear case the reciprocal relations.

$$ {}^{i}\mathbf{R}_{j}=\left({}^{j}\mathbf{R}_{i}\right)^{T} \tag{33} $$

$$^{i}\mathbf{R}_{jk} = \left(^{j}\mathbf{R}_{ik} \right)^{TT} \tag{34}$$

These last reciprocal relations are weaker than the Li-Gyarmati-Rysselberghe's because that allows changing the cycle of the indexes of the third-order kinetic tensor, while (34) does not change the cycle of the indexes, only shifts ahead twice the last index, ie.

$$^{i}R_{uvw} = {}^{i}R_{vwu} \tag{35}$$

Also, these relations are a generalization of Li-Gyarmati-Rysselberghe-type reciprocal relation. The original reciprocity was introduced by Onsager for the case of α-type variables having even-functions of the velocities of molecular particles [12], [13]. This was generalized by Casimir for β-type variables, having odd-functions of the given velocities, [14]. The generalized reciprocity relations containing both the conditions are called Casimir-Onsager-reciprocity relation, (CORR). Due to the unreasoning meaning of the velocity in quantum-mechanical conditions, there are certain doubts about the correctness of CORR.

On the other hand in case of the magnetic field and rotating movements for the reversibility of the orbits of particles the mirroring of the axial vectors (like B and ω) is necessary. Accepting, however, the role of the molecular velocities in CORR, the mirroring has to be seen in the constitutive equations too. This is investigated below connected to the electric conductivity in triclinic system.

Electric conductivity in the triclinic system in the presence of external magnetic field

For simplicity, we suppose the investigated process is isotherm. In this case, the entropy density and the specific entropy current density could be written as:

$$\sigma = \frac{1}{T}\mathbf{j}\cdot\mathbf{E} = -\frac{1}{T}\mathbf{j}\cdot\nabla\varphi, \quad \mathbf{j}_s = -\frac{1}{T}\mathbf{j}\varphi \;, \tag{36}$$

where the intensity parameter φ is the electric potential. The linear constitutive equation is:

$$\nabla\varphi = -\mathbf{Rj} - \kappa\,\mathbf{j}\times\mathbf{B} := \mathbf{R(B)j}, \quad \frac{\partial\varphi}{\partial x_i} = -R_{ij}j_j - \kappa\varepsilon_{ijk}j_jB_k \tag{37}$$

where R is the specific resistivity tensor of the given crystal, κ is constant material characteristics, and εijk is a permutation symbol, equal 1 when the series of I,j,k is even or -1 when odd permutation of numbers 1,2,3. The corresponding Lagrangian is:

$$L = -(\lambda+1)\varphi\frac{\partial j_i}{\partial x_i} + \lambda R_{ij}j_ij_j + \lambda\kappa\varepsilon_{ijk}j_ij_jB_k \tag{38}$$

With a variation of the j-th coordinate j_j of electric current density, we get the following Euler-Lagrange-equations:

$$\begin{aligned}&\lambda\left(R_{ij}+R_{ji}\right)j_i + \lambda\kappa\left(\varepsilon_{ijk}j_iB_k + \varepsilon_{jik}j_iB_k\right) = \\ &= (\lambda+1)\left(R_{ij}j_i + \varepsilon_{ijk}j_iB_k\right)\end{aligned} \;, \tag{39}$$

which by algebraic rearrangement leads to the equations:

$$\lambda R_{ji} j_i + \lambda \kappa \varepsilon_{jik} j_i B_k = R_{ij} j_i + \varepsilon_{ijk} j_i B_k \, , \tag{40}$$

Regarding the λ=1 in case of linear constitutive equations as is, we receive the relations:

$$R_{ji} j_i + \kappa \varepsilon_{jik} j_i B_k = R_{ij} j_i + \kappa \varepsilon_{ijk} j_i B_k \, , \tag{41}$$

which is valid for every j_j and Bk. However it could be satisfied only when the elements of the resistivity tensor

$$R_{ij}(B) := R_{ij} + \kappa \varepsilon_{ijk} B_k , \quad (i, j, k = 1,2,3) \, , \tag{42}$$

satisfy the well-known reciprocity relations.

$$R_{ij}(B) := R_{ji}(-B) \tag{43}$$

A nonlinear generalization of the Prigogine-Glansdorff's evolution criterion

Introducing the dissipation potentials depending on the thermodynamic forces by Legendre transformation:

$$\Psi\left(\nabla^j \Gamma\right) = {}^i\mathbf{j} \cdot \nabla^i \Gamma - \Phi\left({}^j\mathbf{j}\right) = \sigma - \Phi\left({}^j\mathbf{j}\right) \tag{44}$$

In this case, using (26) we obtain:

$$\Psi = \frac{1}{1+\lambda} \sigma \tag{45}$$

Hence

$$\frac{d}{dt} \int_V \Psi dV = \frac{1}{1+\lambda} \frac{d}{dt} \int_V \sigma dV = \frac{1}{1+\lambda} \frac{dP}{dt} \tag{46}$$

It was shown by Prigogine and Glansdorff that the Ψ thermodynamic potential depending on the thermodynamic forces at time-independent boundary conditions satisfies the following general condition of evolution:

$$\frac{d}{dt} \int_V \Psi dV \leq 0 \tag{47}$$

In consequence of this and (44) the global entropy production (in the same way as was in the case of linear constitutive equations) satisfies the following general criterion of evolution:

$$\frac{dP}{dt} = \frac{d}{dt} \int_V \sigma dV \leq 0 \tag{48}$$

This means that the global entropy production of a system with time-independent boundary conditions always decreases, till it reaches its stationer value determined by the global entropy-flux as a restriction.

When the global entropy production in case the fluctuations of the thermodynamical forces and the current densities satisfy the condition:

$$\delta P \geq 0 \tag{49}$$

Then the stationary value is minimum, and regarding the (48) evolution criterion of the global entropy production is a Lyapunov-function. It has two significant consequences. First is that the stationer state is stable, and second that the system starting in any neighboring states of the final stationer, one always reaches the same final state by its evolution. Shortly: these systems (in this general formulation also) show the Bertalanffy's equifinal behaviour [15].

Conclusions

We have demonstrated, that a suggested modification of the principle of minimum entropy production has essential applications in the theory of constitutive laws of non-equilibrium thermodynamics, including reciprocal relations. In the rigorous phenomenology, we may regard the reciprocal relations as experimentally proven axioms, or we have to derive them on the direct phenomenological way. We have to accept the opinion of Truesdell [16]: „if the reciprocal relations are true, we have to derive them by pure phenomenology also". We did this job, showing the Onsager's reciprocal relations and their dependence on magnetic induction field is a consequence of a phenomenological variations principle in the frame of linear constitutive equations. The existence of the dissipation potential is a consequence of the various principles, which was valid only in linear cases till now. In non-linear cases, these relations can be derived from a dissipation potential which is the homogeneous function of the current transport densities. The potential is at the same time assures the validity of the more general reciprocal relations than the Onsager's. We had shown furthermore, that compatible theory with dissipation potential does not exist in the case of Li-Gyarmati–Rysselberghe's constitutive equation; which anyway is frequently used in the non-equilibrium thermodynamics, because these are not homogeneous Euler's functions.As a consequence of this and the general reciprocal relations, we have limits for the kinetic tensors of the Taylor approximation. The second-order tensor in the linear approximation shows asymmetry relation which is identical with the well-known Onsager's reciprocal relation. This result suggests that the Onsager's reciprocal relations are general in linear cases. Consequently, this approximation is same accurate as the linear case itself.

In linear theory, the global entropy production decreased by evolution to stationer state (at constant boundary conditions) and became minimal when the system reaches its stationary case. Consequently, the derivative of the global entropy production concerning time is nonpositive. Two parts of the time-derivative of global entropy production (containing the time-derivatives of the thermodynamical forces and the time derivatives of thermodynamical currents) are equal and decreasing with the time-evolution of the system, realizing the minimal entropy production conditions. In non-linear case, the part that contains the time- derivatives of the thermodynamical forces decreases in the same way as in the linear one. However, we have no information about another part that contains the time-derivation of the thermodynamical currents. By Legendre transformation of the dissipation potentials depending on the current densities introduced another dissipation potential, which is a function of thermodynamic forces and we had proven their proportionality to the density of entropy-production. According to Prigogine-Glansdorff's evolution criterion and the properties of Legendre transformation, the time-derivative of this dissipation function is nonpositive.

Consequently, the global entropy production decreases in every case and has a similar role in this non-linear theory as the entropy has in the linear thermodynamics. In consequence of this, the Prigogine-Glansdorff's general evolution criteria are valid for the global entropy production like it is valid in the linear theory. When in stationer state the global entropy production of a system has a local minimum than it is described by a Lyapunov function. According to Bertalanffy, this system is equifinal, having equivalent final state starting in the vicinity of the stationer state. In case of convex dissipative functions when the local and global minima are equal, all the initial states are equifinal.

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