Consequences of symmetry properties of the phenomenological kinetic coefficients in Onsager-Casimir reciprocity relations for the minimum entropy production law validity are studied. The usually accepted symmetry requirement of the all cross kinetic coefficients for the validity of this law is found to be too strict.

1. Introduction

In his famous work [1, 2] Onsager (1931) derived a symmetry of the coefficients in relations between the thermodynamic forces and conjugated thermodynamic fluxes in linear scope assuming the microscopic reversibility and certain facts of the theory of fluctuation (see, e.g., [3–5]). These relations are referred to as Onsager reciprocity relations (ORR). Under the influence of these and a great deal of consequential papers and experimental results, a common opinion had been established that the so-called cross kinetic coefficients \( L_{ij} \) in these relations are always symmetric \( (L_{ij} = L_{ji}) \). Onsager assumed that the parameters characterizing the system are invariant under time inversion; that is, they do not change sign under inversion \( t \rightarrow -t \) (so-called \( \alpha \) parameters), till Casimir (1945) extended Onsager’s considerations to include parameters that change their sign under time inversion (so-called \( \beta \) parameters) [6]. Consequently, Onsager reciprocity relations \( L_{ij} = L_{ji} \) transform into the form \( L_{ij} = \pm L_{ji} \) referred to as Onsager-Casimir reciprocity relations (OCRR) in the literature.

If the system occurs in an external homogeneous magnetic field \( \vec{B} \) or if it rotates as a whole with an angular velocity \( \vec{\omega} \), this fact must be accounted for in the reciprocity relations because of the influence of the corresponding forces (i.e., Lorentz and Coriolis forces) on the reversibility of motion. Thus, it is necessary to consider in what way the parameters of the system and, consequently, the signs in the relations \( L_{ij} = \pm L_{ji} \) change as a result of the opposite orientation of the vector \( \vec{B} \) and/or \( \vec{\omega} \).

ORR and OCRR were initially considered applicable to purely instantaneous phenomena or, at least, in processes when time lag may be neglected. Later, the reciprocity relations (RR) were extended to other cases as a result of the fluctuation-dissipation theorem by Callen and Green (1952) [7] and a paper by Callen et al. (1952) [8].

The literature devoted to the linear irreversible thermodynamics (LIT) is very extensive and the ORR represent one of its fundamental laws. Nevertheless, little and not quite sufficient attention is paid, both in scientific monographs and textbooks, to the cases in which the antisymmetric kinetic coefficients (especially in the presence of magnetic field) occur and to the consequences of their existence. This is probably caused by the great influence of Onsager’s original works in which only \( \alpha \) parameters were considered when deriving reciprocity relations. The fact that the symmetric reciprocity relations can be used in a majority of particular cases, that is, it is possible to select the system parameters (and consequently the used thermodynamic forces and fluxes) so that the symmetric reciprocity relations are valid, plays a certain role as well. There are, however, cases in which such selection is not possible or is not suitable from physical point...
of view; that is, the ORR are not fulfilled in these cases (e.g., [9–12]).

The paper aims to deal with some problems which are related to the antisymmetric cross kinetic coefficients in reciprocity relations. Namely, it is concerned with the consequences of symmetry properties of $L_{ij}$ for the minimum entropy production law (in)validity.

We prove that, for minimum entropy production law (MEP law), Prigogine’s assumption of the symmetry of the all cross kinetic coefficients is for MEP law validity too strict.

### 2. Symmetric and Antisymmetric Reciprocity Relations

Onsager assumed the linear constitutive relations between so-called thermodynamic fluxes $J_i$ and thermodynamic forces $X_i$ in which the fluxes (in local sense) are identified with time rates:

$$J_i = \frac{d\alpha_i}{dt},$$

where $\alpha_i$ ($i = 1, \ldots, f$) is the mean value deviation of the state parameter from its equilibrium value and forces are (locally) identified with derivatives of the entropy per unit volume; that is,

$$X_i = \frac{\partial s}{\partial \alpha_i}.$$  

Here $f$ is the number of independent scalar forces or components of vector (tensor) forces which characterize the system processes.

Onsager expressed the constitutive relations in the following form:

$$J_i = \sum_j L_{ij} X_j$$  

and, for the phenomenological coefficients, derived the well-known Onsager reciprocity relations:

$$L_{ij} = L_{ji}.$$  

In this case, the matrix of the phenomenological coefficients is symmetric. The phenomenological coefficients $L_{ij} = L_{ji}$ are supposed to be constant, that is, independent of $X_i$. They are entirely determined by the internal structure of the medium and depend on the thermodynamic quantities characterizing the system, for example, the temperature, pressure, and concentration. They are, however, independent of the constraints applied to the system coefficients. Equation (3) expresses the fact (verified by experimental results) that any flux may be caused by several thermodynamic forces that act independently of each other. Onsager’s reciprocity relations (4) represent one of the important laws in LIT and are very useful in studying coupled phenomena (in linear scope) like thermodiffusion, thermelectricity, and thermomechanic effects (see, e.g., [9–12]).

It is possible to reduce the number of independent phenomenological coefficients on the basis of the symmetry arguments. Prigogine [13] proved that in nonequilibrium isotropic thermodynamic systems (in linear range) only irreversible processes of the same tensorial order can be mutually influenced; that is, it can be coupled. This expresses the so-called Curie-Prigogine law. It may simply be shown (see, e.g., [14, 15]) that Curie law is nothing more than an application of the representation theorems to isotropic tensors.

As has already been noted, the ORR were derived for $\alpha$-type state parameters which are even functions of time. Casimir derived a modification of the RR for so-called $\beta$-type parameters, which are odd functions of time and for which

$$L_{ij} = -L_{ji} \quad (i \neq j)$$

holds. The matrix of phenomenological coefficients is skew-symmetric in this case. It may be said that the $\alpha$ parameters have the time inversion parity $+1$ and the $\beta$ parameters parity $-1$. Note that, analogously to parameters of $\alpha$- and $\beta$-type, it is possible to speak of forces of $\alpha$- and $\beta$-type.

Antisymmetry of the cross kinetic coefficients may be also caused by the presence of an external magnetic field ($\vec{B}$) or by rotation of the whole system with angular velocity ($\vec{\omega}$).

The Onsager-Casimir reciprocal relations have then the form (e.g., [3, 5, 6, 16, 17])

$$L_{ij} (\vec{B}, \vec{\omega}) = \varepsilon_i \varepsilon_j L_{ji} (\vec{B}, \vec{\omega}),$$

where $\varepsilon_i = \varepsilon_j = 1$ for the case that coefficients $L_{ij}$ refer to the cross effects that are described only by $\alpha$-type parameters or only by $\beta$-type parameters. In the case of mixed parameters, for example, $\varepsilon_i = 1$ and $\varepsilon_j = -1$.

If the dependence on the angular velocity $\vec{\omega}$ is negligible from the physical point of view, we can write

$$L_{ij} (\vec{B}) = \varepsilon_i \varepsilon_j L_{ji} (\vec{B}).$$  

We note that Sharipov [18, 19] analysed the interesting processes when the cross kinetic coefficients are neither odd nor even with respect to the time reversal and consequently the reciprocal relations should be written in more general form than (6).

### 3. The Minimum Entropy Production Law and the Conditions for Its (In)validity

#### 3.1. Entropy Production

The quantity of entropy production $P$ (or entropy production rate) is defined (e.g., [3–5]) by the following relation:

$$P \equiv \frac{d_m S (\alpha_i)}{dt} = \int_{\partial V} \left( \sum_i X_i \frac{d\alpha_i}{dt} \right) dV = \int_{\partial V} \left( \sum_i X_i J_i \right) dV,$$

where $V$ is the volume of a system. The term $P$ expresses the entropy generated per 1 second inside the system. It is useful to define the entropy production density by

$$\sigma = \frac{d_m S}{dt} dV = \frac{dP}{dV}$$
so that

\[ P = \int (V) \sigma \, dV \]  

(10)
in agreement with (8). In LNT, the relation for the entropy production density

\[ \sigma = \sum_{i} I_{i} X_{i} = \sum_{i, j} L_{ij} X_{i} X_{j} \]  

(11)
is well known. By the second law of thermodynamics, we get the relation

\[ \sigma = \sum_{i, j} L_{ij} X_{i} X_{j} \geq 0 \]  

(12)
implying that the matrix of the coefficients \( L_{ij} \) (coupling matrix) is a positive semidefinite one. Note that \( \sigma \) is not a homogeneous quadratic form in the case of an anisotropic system.

3.2. The Conditions for the Minimum Entropy Production Law Validity. According to the minimum entropy production (MEP) law in the scope of the linear irreversible thermodynamics (see, e.g., [3, 4, 13]), the entropy production density in the system decreases with time and reaches its minimum value in the stationary nonequilibrium (NEQ) state, compatible with the constraints applied to the system. In other words, A NEQ stationary (steady) state has the minimum of entropy production density rate with respect to other possible states with the same boundary conditions. This law, first formulated by Prigogine [13], is derived under the following requirements (assumptions) [15, 16, 20].

(R1) Boundary conditions for the system are time independent.

(R2) Phenomenological laws (3) are linear.

(R3) Kinetic coefficients are considered as constants.

(R4) All the kinetic coefficients considered are symmetric.

To the (R2) and (R3) we remind that near equilibrium when thermodynamic forces remain sufficiently weak, the fluxes may be expanded in power series of forces [3, 11, 15]. Neglecting the second order term and the terms higher of orders we obtain (3) with kinetic coefficients depending only on the equilibrium values of the system parameters (so-called strictly linear region). In the following section, we will consider, from the macroscopic point of view, the consequences for MEP law validity if the requirement (R4) is not fulfilled.

3.3. Conditions for the MEP Law Validity If the Requirement \( L_{ij} = L_{ji}, \ (i, j = 1, \ldots, f) \) Is Not Fulfilled. To date, the conditions for MEP law validity for the case of nonsymmetry of all the cross kinetic coefficients (requirement (R4)) have not been studied yet in detail.

In what follows, we will assume that the first three requirements are fulfilled while no assumptions as to the symmetry properties of cross kinetic coefficients are made.

The MEP theorem makes its physical sense if some forces are free (may change in time) and the remaining ones are fixed.

Consider that the system may be maintained away from equilibrium by constraining some forces to be at fixed nonzero values while leaving the remaining forces free. Let, say, \( m \) forces \( X_{1}, X_{2}, \ldots, X_{m} \) be fixed and the remaining forces \( X_{m+1}, \ldots, X_{f} \) free. At least one force must be fixed. Note that the nonequilibrium stationary state may be (in agreement with de Groot and Mazur [3]) called stationary of degree \( m \). When all the forces were fixed, the system would find in artificially created state with nonzero entropy production density. We do not observe this situation. If all the acting thermodynamic forces were free, the system would attain the equilibrium state in which \( \sigma = 0 \) and all forces and fluxes are zero. Because of the fact that our consideration is not concerned with equilibrium state the matrix (12) is positive definite.

First we will give the condition for a local extremum of the entropy production density (11). The conditions for the bounded extremum with \( X_{1}, \ldots, X_{m} \) being constant (over time) are

\[
\left( \frac{\partial \sigma}{\partial X_{m+1}} \right)_{X_{m+2}, \ldots, X_{f}} = \sum_{i=1}^{f} \frac{\partial f_{i}}{\partial X_{m+1}} X_{i} + J_{m+1} = 0
\]

(13)

\[
\left( \frac{\partial \sigma}{\partial X_{f}} \right)_{X_{m+1}, \ldots, X_{f-1}} = \sum_{i=1}^{f} \frac{\partial f_{i}}{\partial X_{f}} X_{i} + J_{f} = 0.
\]

By (3), consider

\[ f_{i} = L_{ij} X_{j} + \cdots + L_{im+1} X_{m+1} + \cdots + L_{ij} X_{f} \]  

(14)

and, consequently,

\[ \frac{\partial f_{i}}{\partial X_{m+1}} = L_{ij}, \quad \cdots, \quad \frac{\partial f_{i}}{\partial X_{f}} = L_{ij}. \]  

(15)

Substituting (15) into (13), we obtain

\[
\left( \frac{\partial \sigma}{\partial X_{m+1}} \right)_{X_{m+2}, \ldots, X_{f}} = \sum_{i=1}^{f} L_{ij} X_{i} + J_{m+1} = 0
\]

(16)

\[
\left( \frac{\partial \sigma}{\partial X_{f}} \right)_{X_{m+1}, \ldots, X_{f-1}} = \sum_{i=1}^{f} L_{ij} X_{i} + J_{f} = 0.
\]
The type of extremum: for the second derivatives, the following relations hold:

\[
\left( \frac{\partial^2 \sigma}{\partial X_{m+1}^2} \right)_{X_{m+1} = X_1, \ldots, X_f} = L_{m+1,m+1} + L_{m+1,m+2} \\
= 2L_{m+1,m+1} \\
\vdots \\
\left( \frac{\partial^2 \sigma}{\partial X_f^2} \right)_{X_{m+1} = X_1, \ldots, X_f} = 2L_{ff}.
\] (17)

The necessary conditions for the quadratic form

\[\sigma = \sum_{i=1}^{f} J_i X_i = \sum_{i,j} L_{ij} X_i X_j \] (18)
to be positive definite are

\[L_{ii} > 0 \quad (i = 1, \ldots, f). \] (19)

Thus, from relations (16) and (19), it follows that the extremum is a minimum.

Now we express the conditions for the stationary state. In the evolution process, a nonequilibrium system tends towards an equilibrium one in which all fluxes are zero, but fixed forces prevent it from attaining this. During this process, the system reaches the nonequilibrium stationary state in which the fluxes corresponding to the fixed forces remain constant and unfixed/free forces adjust so as to make their corresponding fluxes zero [5, 21]. Thus, for fluxes, the stationarity condition

\[J_{m+1} = J_{m+2} = \cdots = J_f = 0 \] (20)
is fulfilled.

For fluxes conjugated with the free forces, we then have

\[J_{m+1} = L_{m+1,m+1} X_1 + \cdots + L_{m+1,m+2} X_{m+2} + \cdots + L_{m+1,f} X_f = 0 \]
\[\vdots \]
\[J_f = L_{f1} X_1 + \cdots + L_{ff} X_f = 0. \] (21)

The conditions for the minimum of the entropy production density (16) and the conditions for the stationary state (21) will be simultaneously fulfilled if the relations

\[L_{i,m+1} = L_{m+1,i} \]
\[\vdots \quad (i = 1, 2 \cdots f) \] (22)
\[L_{if} = L_{fi} \]
hold. In this case we obtain in particular

\[\sum_{i=1}^{f} L_{i,m+1} X_i = \sum_{i=1}^{f} L_{m+1,i} X_i = J_{m+1} \]
\[\vdots \]
\[\sum_{i=1}^{f} L_{i,f} X_i = \sum_{i=1}^{f} L_{f,i} X_i = J_f \]
and, substituting (23) into (16), we receive

\[\left( \frac{\partial \sigma}{\partial X_{m+1}} \right)_{X_{m+1} = X_1, \ldots, X_f} = 2J_{m+1} = 0 \]
\[\vdots \]
\[\left( \frac{\partial \sigma}{\partial X_f} \right)_{X_{m+1} = X_1, \ldots, X_f} = 2J_f = 0. \] (24)

Equation (22) can be written briefly in the form

\[L_{il} = L_{li} \quad (i = 1, \ldots, f, \ l = m+1, \ldots, f), \] (25)

where \(m\) is the number of fixed forces. If (25) is fulfilled, the stationary nonequilibrium state will be at the same time the state with minimum entropy production density \(\sigma_{\text{stat}} = \sigma_{\text{min}}\). If (25) is not fulfilled, that is, if the cross coefficients \(L_{il} (i = 1, \ldots, f, \ l = m+1, \ldots, f)\) are not symmetric, the stationary state will not be a state with minimum of entropy production density; that is,

\[\sigma_{\text{stat}} \neq \sigma_{\text{min}}. \] (26)

Condition (25) means that, for MEP law validity, the symmetry requirement (R4) does not refer to all the cross kinetic coefficients; in other words, for the MEP law to be valid, the requirement (R4) is too strict. From (25) we can see that the requirement of the symmetry refers only to the cross coefficients with indices corresponding to the forces one of which (at most) is fixed. The symmetry requirement does not refer to cross coefficients corresponding to the forces that are both fixed. The possible antisymmetry of these coefficients does not influence the MEP law validity. We can conclude in agreement with [22] that the symmetry of the all kinetic coefficients is sufficient but not the necessary condition to ensure the MEP law validity. The necessary condition for the MEP law validity is expressed by (25).

In a relatively simple and common system with two independent forces \((f = 2)\), if one force is fixed \((m = 1)\), condition (25) gives the well-known result \(L_{12} = L_{21} \) with \(\sigma_{\text{stat}} = \sigma_{\text{min}}\).

The present authors analysed a system with coupled thermo-electro-magnetic effects (for more see, e.g., [23]) where the symmetric and antisymmetric cross coefficients are present. The studied system is described by four thermodynamic forces and four fluxes. Considering three situations with (a) one force is fixed (the remaining forces are free),
(b) two forces are fixed, and (c) three forces are fixed, we found that (25) is not fulfilled in all these cases, which means that a stationary state is not a state with minimum entropy production density.

Note that the view that stationary states without minimum entropy production exist is mentioned by de Groot and Mazur [3], however, not in the context with symmetry properties of the kinetic (cross) coefficients discussion. Some other authors show examples of systems (mostly for electrical circuits) in which the MEP law is not valid, even in the strictly linear region [20, 24–26]. Browne [27] analyzed examples of simple electrical circuits, for example, LR circuit (inductor-resistor DC circuit) with battery, in their stationary states and proved that these states do not coincide with minimum entropy production density. These results imply that the MEP law in electrical circuits is not of general validity.

4. Conclusions

The choice of the state parameters (and consequently forces and fluxes) that characterize the system is limited due to their possible physical applicability and suitability and so it is not unequivocal. For some choice of the parameters, antisymmetric kinetic coefficients may occur and OCRR must be used.

When minimizing the number of the independent coefficients in the (linear) relations between forces and coupled fluxes their symmetry properties under time inversion play an important role. This stresses the importance of OCRR as compared with ORR because OCRR take into account the parity of both types $\alpha$ and $\beta$ quantities. At the same time, the number of the independent coefficients can also be minimized by considering the spatial symmetry properties of the system. While the behavior of the parameters under time inversion (i.e., the time parity) has a general character, their spatial symmetry properties significantly depend on the specific system structure and thus require special treatment such as considering homogeneity/nonhomogeneity and isotropy/anisotropy of crystal structure.

The problem of the validity (or invalidity) of the minimum entropy production density law in a stationary state of a system may be discussed from different points of view [28]. The aim of the present paper was the analysis of this problem in connection with the symmetry properties of the kinetic coefficients. We derived (using methods of linear nonequilibrium thermodynamics) conditions for the stationary state to be (or not to be) a state with minimum of entropy production density. For the case when some of the forces are fixed and the remaining ones are free, we proved that the symmetry requirement for MEP law validity does not refer to all the cross kinetic coefficients. The symmetry requirement relates to these coefficients for which (25) is fulfilled. Thus, the symmetry requirement for all the cross kinetic coefficients (for which Prigogine was one of the assumptions when deriving the MEP law) is for MEP law validity too strict.

As an example of the application of the obtained results we gave an analysis of the thermo-electro-magnetic phenomenon [23]. Our analysis gives the result that in this case the condition for the MEP law validity, that is, (25), is not fulfilled, thus MEP law is not valid.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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