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Extension of Onsager's Theory of Reciprocal Relations. I

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A generalization of Onsager's proof for reciprocal relations between irreversible processes is developed in such a form that it can be used for vectorial and tensorial phenomena. This is achieved by means of an extension of the fluctuation formalism used by Onsager.

The method is applied to heat conduction, diffusion, viscosity, and cross-effects in anisotropic systems, and reciprocal relations are derived for these phenomena.

1. INTRODUCTION

ONSAGER[1] has established reciprocal relations between irreversible phenomena which he derived from the property of microscopic reversibility. These relations have found a wide field of application in the thermodynamics of irreversible processes.[2,3]

However, as Casimir[4] pointed out, Onsager's proof is strictly valid only for scalar phenomena. As a matter of fact Onsager assumes that the irreversible fluxes can be considered time derivates of thermodynamic state variables. This is correct for scalar processes such as chemical reactions and relaxation phenomena, but not for vectorial processes (such as heat conduction, diffusion and electrical conduction) and tensorial processes (such as viscous flow).

Casimir[4] has proposed a method to avoid this difficulty, on which he has elaborated for the case of heat conduction in anisotropic crystals. This method can briefly be described as follows. Equations are established for the regression of an infinite number of local temperature fluctuations. To this set of equations the ordinary Onsager scheme can be applied since the "fluxes" are now indeed time derivatives of state variables (here the local temperatures). In particular, reciprocal relations between corresponding irreversible processes (Onsager relations) are found. However, these relations are only an intermediate result, since the equations used are not identical with the ordinary macroscopic Fourier law of heat conduction. Only by means of a subsequent mathematical treatment was it possible to find the implications of the intermediate Onsager relations on the properties of the heat conduction tensor. In the derivation, constancy of the density of the system (i.e., absence of motion) was assumed.

The present authors[5] have applied a similar method to electrical and heat conduction in the presence of a magnetic field.

In this paper a different method is developed, which avoids the complications inherent in the approach outlined above. The method consists of a generalization of Onsager's original proof and enables one to derive directly reciprocal relations for irreversible processes of vectorial or tensorial nature.

2. FLUCTUATION THEORY

We consider an adiabatically insulated system. The thermodynamic state of the system is described by variables $A_1, A_2, \cdots, A_m$ which are even functions of the particle velocities, and variables $B_{m+1}, B_{m+2}, \cdots, B_n$ which are odd functions of the particle velocities[4] (the B-type variables, or their divergences, may be time derivatives of A-type variables: see also Machlup and Onsager[6] and Secs. 6 and 9). All variables are continuous functions of space and time coordinates. For convenience the system will be divided into a number of cells of volume V^μ, in which the thermodynamic variables may be considered as uniform (here μ numbers the cells). The deviations of the state variables from their equilibrium values are denoted by

$$\alpha_i^\mu = A_i^\mu - (A_i^\mu)_{\text{equ}}, \quad (i=1, 2, \cdots, m) \tag{1}$$

$$\beta_k^\mu = B_k^\mu - (B_k^\mu)_{\text{equ}}, \quad (k=m+1, m+2, \cdots, n). \tag{2}$$

The deviation of the entropy of the system from its equilibrium value is given by the quadratic form

$$\Delta S = -\tfrac{1}{2}\textstyle\sum_{\mu,\nu} V^\mu V^\nu \big(\sum_{i,j} g_{ij}^{\mu\nu}\alpha_i^\mu\beta_j^\nu + \sum_{k,l} h_{kl}^{\mu\nu}\beta_k^\mu\beta_l^\nu\big). \tag{3}$$

Since the entropy is an even function of the particle velocities no cross-terms between α and β variables appear in the expression (3). The probability distribution for the α_i^μ and the β_k^μ is expressed by

$$P \prod_{\mu,i,k} d\alpha_i^\mu d\beta_k^\mu = \exp(\Delta S/k) \prod_{\mu,i,k} d\alpha_i^\mu d\beta_k^\mu \Big/ \int \cdots \int \exp(\Delta S/k) \prod_{\mu,i,k} d\alpha_i^\mu d\beta_k^\mu. \tag{4}$$

The following linear combinations of parameters are introduced:

$$X_i^\mu = (V^\mu)^{-1}\partial\Delta S/\partial\alpha_i^\mu = +\textstyle\sum_\nu V^\nu \sum_j g_{ij}^{\mu\nu}\alpha_i^\nu, \tag{5}$$

$$Y_k^\mu = (V^\mu)^{-1}\partial\Delta S/\partial\beta_k^\mu = -\textstyle\sum_\nu V^\nu \sum_l h_{kl}^{\mu\nu}\beta_l^\nu. \tag{6}$$

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[1] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

[2] I. Prigogine, *Etude thermodynamique des phénomènes irréversibles* (Editions Desoer, Liège, 1947).

[3] S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam and Interscience Publishers, New York, 1951).

[4] H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945).

[5] P. Mazur and S. R. de Groot, Physica **19**, 961, 1953.

[6] S. Machlup and L. Onsager, Phys. Rev. **91**, 1512 (1953).

A number of averages, which will be used later on, can easily be found with the help of (4), (5), and (6):

$$\langle \alpha_i^\mu(t) X_j^\nu(t)\rangle_{\mathrm{Av}} = -k\delta_{ij}\delta_{\mu\nu}/V^\mu, \tag{7}$$

$$\langle \beta_k^\mu(t) Y_l^\nu(t)\rangle_{\mathrm{Av}} = -k\delta_{kl}\delta_{\mu\nu}/V^\mu. \tag{8}$$

Average values of products of α- and β-type variables always vanish.

Passing to the limit of continuous variables, the indices μ and ν of (7) and (8), which indicate the cells, can be replaced by $\mathbf{r}$ and $\mathbf{r}'$, which denote space coordinates, whereas the last two factors of (7) and (8) combine into a Heaviside-Dirac δ function. Consequently (7) and (8) become

$$\langle \alpha_i(\mathbf{r},t) X_j(\mathbf{r}',t)\rangle_{\mathrm{Av}} = -k\delta_{ij}\delta(\mathbf{r}-\mathbf{r}'), \tag{9}$$

$$\langle \beta_k(\mathbf{r},t) Y_l(\mathbf{r}',t)\rangle_{\mathrm{Av}} = -k\delta_{kl}\delta(\mathbf{r}-\mathbf{r}'). \tag{10}$$

From (9) and (10) one can immediately derive the formulas

$$\langle \alpha_i(\mathbf{r},t)\Omega(\mathbf{r}') X_j(\mathbf{r}',t)\rangle_{\mathrm{Av}} = -k\delta_{ij}\Omega(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'), \tag{11}$$

$$\langle \beta_k(\mathbf{r},t)\Omega(\mathbf{r}') Y_l(\mathbf{r}',t)\rangle_{\mathrm{Av}} = -k\delta_{kl}\Omega(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'), \tag{12}$$

where $\Omega(\mathbf{r})$ is a differential operator of the general form

$$\Omega(\mathbf{r}) = \sum_{p,\,q,\,s} a_{p,\,q,\,s}(\mathbf{r})\partial^{p+q+s}/\partial x_1{}^p \partial x_2{}^q \partial x_3{}^s. \tag{13}$$

The coefficients $a_{p,\,q,\,s}$ are independent of the state variables α and β; the cartesian coordinates are denoted by x_1, x_2 and x_3.

The formulas (11) and (12) will serve as an extremely useful basis for the straightforward derivation of the reciprocal relations amongst phenomenological coefficients.

Remark

It may be noted that with (5) and (6) the time derivative of (3) (entropy production per unit time) can be written as

$$d(\Delta S)/dt = \sum_\mu V^\mu \left(\sum_i \dot{\alpha}_i^\mu X_i^\mu + \sum_k \dot{\beta}_k^\mu Y_k^\mu\right), \tag{14}$$

or

$$d(\Delta S)/dt = \int \left\{\sum_i \dot{\alpha}_i(\mathbf{r}) X_i(\mathbf{r}) + \sum_k \dot{\beta}_k(\mathbf{r}) Y_k(\mathbf{r})\right\} d\mathbf{r}, \tag{15}$$

in the limit of infinitely small cells.

3. MICROSCOPIC REVERSIBILITY

As a result of the property of time reversal invariance of the equations of motion for individual particles, the α and β variables[3,4] satisfy the following relations:

$$\langle \alpha_i(\mathbf{r},t)\alpha_j(\mathbf{r}',t+\tau)\rangle_{\mathrm{Av}} = \langle \alpha_j(\mathbf{r}',t)\alpha_i(\mathbf{r},t+\tau)\rangle_{\mathrm{Av}}, \tag{16}$$

$$\langle \alpha_i(\mathbf{r},t)\beta_k(\mathbf{r}',t+\tau)\rangle_{\mathrm{Av}} = -\langle \beta_k(\mathbf{r}',t)\alpha_i(\mathbf{r},t+\tau)\rangle_{\mathrm{Av}}, \tag{17}$$

$$\langle \beta_k(\mathbf{r},t)\beta_l(\mathbf{r}',t+\tau)\rangle_{\mathrm{Av}} = \langle \beta_l(\mathbf{r}',t)\beta_k(\mathbf{r},t+\tau)\rangle_{\mathrm{Av}}. \tag{18}$$

From these three relations it follows that

$$\langle \alpha_i(\mathbf{r},t)(\partial/\partial t)\alpha_j(\mathbf{r}',t)\rangle_{\mathrm{Av}} = \langle \alpha_j(\mathbf{r}',t)(\partial/\partial t)\alpha_i(\mathbf{r},t)\rangle_{\mathrm{Av}}, \tag{19}$$

$$\langle \alpha_i(\mathbf{r},t)(\partial/\partial t)\beta_k(\mathbf{r}',t)\rangle_{\mathrm{Av}} = -\langle \beta_k(\mathbf{r}',t)(\partial/\partial t)\alpha_i(\mathbf{r},t)\rangle_{\mathrm{Av}}, \tag{20}$$

$$\langle \beta_k(\mathbf{r},t)(\partial/\partial t)\beta_l(\mathbf{r}',t)\rangle_{\mathrm{Av}} = \langle \beta_l(\mathbf{r}',t)(\partial/\partial t)\beta_k(\mathbf{r},t)\rangle_{\mathrm{Av}}. \tag{21}$$

Of course the time derivative in the last three relations should be interpreted on a microscope scale as a difference quotient;[4,3] however, for all practical macroscopic purposes this quotient can be considered as a real derivative.

For simplicity's sake we have not taken into consideration the influence of a magnetic field[5] or a rotation of the system on relations (16)–(18).

4. ENTROPY PRODUCTION IN LOCAL FORM

In order to apply the results derived so far to the actual physical processes, the macroscopic thermodynamical theory[2,3] of these phenomena must first be recalled (in this section and the following). Let us consider a system of n components in which the phenomena of heat conduction, diffusion and viscous flow and their cross-effects may occur. The system may also be subject to external conservative forces. The entropy production can be calculated from the fundamental laws of macroscopic physics. In the case under consideration these laws are:

The Mass Laws[7]

$$\rho dc_k/dt = -\mathrm{div}\mathbf{J}_k, \quad (k=1,\,2,\,\cdots,\,n), \tag{22}$$

where ρ is the density, c_k the mass fraction of component k ($\sum_k c_k = 1$), and $\mathbf{J}_k$ the diffusion flow of k with respect to the center of mass motion ($\sum_k \mathbf{J}_k = 0$). Furthermore we have

$$\rho dv/dt = \mathrm{div}\mathbf{v}, \tag{23}$$

with $v = \rho^{-1}$, the specific volume, and $\mathbf{v}$ the barycentric velocity. In both Eqs. (22) and (23) d/dt stands for the substantial time derivative with respect to the center of mass motion

$$d/dt = \partial/\partial t + \mathbf{v}\cdot\mathrm{grad}. \tag{24}$$

With (24) the formulas (22) and (23) can alternatively be written as

$$\partial\rho_k/\partial t = -\mathrm{div}(\rho_k\mathbf{v}) - \mathrm{div}\mathbf{J}_k, \tag{25}$$

$$\partial\rho/\partial t = -\mathrm{div}(\rho\mathbf{v}), \tag{26}$$

where $\rho_k = c_k\rho$ is the density of component k.

The Momentum Law

$$\rho d\mathbf{v}/dt = -\mathrm{Div}\boldsymbol{P} + \sum_k \rho_k \mathbf{F}_k. \tag{27}$$

Here $\mathbf{F}_k$ is the external conservative force per unit

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[7] For vector notation used here, see the Appendix.

mass acting on component k:

$$\mathbf{F}_k = -\mathrm{grad}\, w_k; \quad \text{with} \quad \partial w_k/\partial t = 0, \tag{28}$$

where w_k is the potential energy per unit mass of component k. The pressure tensor $\boldsymbol{P}$ can be split into two parts

$$\boldsymbol{P} = p\boldsymbol{\delta} + \boldsymbol{\Pi}, \tag{29}$$

where $\boldsymbol{\delta}$ is the unit tensor, p the hydrostatic pressure, and $\boldsymbol{\Pi}$ the viscous pressure tensor.

With (24) and (26) one can write (27) alternatively as

$$\partial \mathbf{g}/\partial t = -\mathrm{Div}(\mathbf{v}\mathbf{g} + \boldsymbol{P}) + \textstyle\sum_k \rho_k \mathbf{F}_k, \tag{30}$$

where $\mathbf{g} = \rho\mathbf{v}$ is the momentum density.

The Energy Law

$$\rho de/dt = -\mathrm{div}\mathbf{J}_e, \tag{31}$$

where e is the specific total energy and $\mathbf{J}_e$ the energy flow. These are given by

$$e = u + \tfrac{1}{2}\mathbf{v}^2 + \textstyle\sum_k c_k w_k, \tag{32}$$

$$\mathbf{J}_e = \mathbf{J}_q + \mathbf{v}\cdot\boldsymbol{P} + \textstyle\sum_k w_k \mathbf{J}_k, \tag{33}$$

with u the specific internal energy and $\frac{1}{2}\mathbf{v}^2$ the specific kinetic energy. Relation (33) defines the heat flow $\mathbf{J}_q$.

The first law of thermodynamics is found from (31) with (23) and (27)

$$\rho du/dt = -\mathrm{div}\mathbf{J}_q - \boldsymbol{P} : \mathrm{Grad}\mathbf{v} + \textstyle\sum_k \mathbf{F}_k \cdot \mathbf{J}_k. \tag{34}$$

Introducing the internal energy per unit volume $u_v = \rho u$ and applying (26), Eq. (34) can be written as

$$\partial u_v/\partial t = -\mathrm{div}(u_v\mathbf{v} + \mathbf{J}_q) - \boldsymbol{P} : \mathrm{Grad}\mathbf{v} - \textstyle\sum_k \mathbf{F}_k \cdot \mathbf{J}_k. \tag{35}$$

Gibbs' Law

$$Tds/dt = du/dt + pdv/dt - \textstyle\sum_k \mu_k dc_k/dt, \tag{36}$$

where T is the temperature, s the specific entropy, p the hydrostatic pressure (we consider fluids, where the elastic stress tensor reduces to a hydrostatic pressure only), and μ_k the chemical potential per unit mass.

Entropy Balance

With the help of (22), (23), and (34), Eq. (36) can be brought into the form of a balance equation

$$\rho ds/dt = -\mathrm{div}\mathbf{J}_s + \sigma, \tag{37}$$

where $\mathbf{J}_s$ is the entropy flow,

$$\mathbf{J}_s = (\mathbf{J}_q - \textstyle\sum_k \mu_k \mathbf{J}_k)/T, \tag{38}$$

and where the entropy production σ follows from

$$T\sigma = -\mathbf{J}_q \cdot (\mathrm{grad}T)/T + \textstyle\sum_k \mathbf{J}_k \cdot \{\mathbf{F}_k - T\,\mathrm{grad}(\mu_k/T)\} - \boldsymbol{\Pi} : \mathrm{Grad}\mathbf{v} \geqslant 0. \tag{39}$$

The three terms on the right-hand side are the result of entropy production caused by heat conduction, diffusion, and viscous flow, respectively.

Another useful form of $T\sigma$, which follows from (39) when the definition (38) of the entropy flow is used, is

$$T\sigma = -\mathbf{J}_s \cdot \mathrm{grad}T - \textstyle\sum_k \mathbf{J}_k \cdot \mathrm{grad}\bar{\mu}_k - \boldsymbol{\Pi} : \mathrm{Grad}\mathbf{v} \geqslant 0, \tag{40}$$

where the quantity

$$\bar{\mu}_k \equiv \mu_k + w_k \tag{41}$$

has been introduced.

Just as (35) follows from (34), one can write instead (37),

$$\partial s_v/\partial t = -\mathrm{div}(s_v\mathbf{v} + \mathbf{J}_s) + \sigma, \tag{42}$$

where $s_v = \rho s$ is the entropy per unit volume.

5. THE PHENOMENOLOGICAL EQUATIONS

The entropy production (39) or (40) is a sum of products of "fluxes" and so-called "forces" (or "affinities"). Linear relationships between these quantities can be established: these are called the phenomenological equations. Choosing the quantities occurring in (40) one can write

$$\mathbf{J}_s = -\boldsymbol{L}_{ss} \cdot \mathrm{grad}T - \sum_{k=1}^{n} \boldsymbol{L}_{sk} \cdot \mathrm{grad}\bar{\mu}_k, \tag{43}$$

$$\mathbf{J}_k = -\boldsymbol{L}_{ks} \cdot \mathrm{grad}T - \sum_{k'=1}^{n} \boldsymbol{L}_{kk'} \cdot \mathrm{grad}\bar{\mu}_{k'}, \qquad (k = 1, 2, \cdots, n) \tag{44}$$

$$\Pi_{ij} = -\sum_{m,n=1}^{3} L_{ij,mn}(\mathrm{Grad}\mathbf{v})_{mn}, \quad (i, j = 1, 2, 3) \tag{45}$$

where i, j, m and n indicate cartesian coordinates.

We are not concerned here with cross-effects between vectorial and tensorial quantities, although such effects might exist in anisotropic media. The present formalism could of course be easily extended to such a case. (In isotropic media these cross-effects do not exist according to the so-called Curie principle.)

The quantities $\boldsymbol{L}_{ss}$, $\boldsymbol{L}_{sk}$, $\boldsymbol{L}_{ks}$ and $\boldsymbol{L}_{kk'}$ (k, $k' = 1, 2, \cdots, n$) are tensors (of the second order). Certain relationships between these phenomenological coefficients exist, since not all fluxes and forces are independent. From $\sum_k \mathbf{J}_k = 0$ it follows that[3]

$$\sum_{k=1}^{n} \boldsymbol{L}_{sk} = 0, \quad \sum_{k=1}^{n} \boldsymbol{L}_{k'k} = 0, \quad (k' = 1, 2, \cdots, n); \tag{46}$$

$$\sum_{k=1}^{n} \boldsymbol{L}_{ks} = 0, \quad \sum_{k=1}^{n} \boldsymbol{L}_{kk'} = 0. \quad (k' = 1, 2, \cdots, n). \tag{47}$$

Thus (43) and (44) can be rewritten with independent fluxes and forces:

$$\mathbf{J}_s = -\boldsymbol{L}_{ss}\cdot\mathrm{grad}T - \sum_{k=1}^{n-1} \boldsymbol{L}_{sk}\cdot\mathrm{grad}(\bar{\mu}_k - \bar{\mu}_n), \tag{48}$$

$$\mathbf{J}_k = -\boldsymbol{L}_{ks}\cdot\mathrm{grad}T - \sum_{k'=1}^{n-1} \boldsymbol{L}_{kk'}\cdot\mathrm{grad}(\bar{\mu}_{k'} - \bar{\mu}_n). \qquad (k=1, 2, \cdots, n-1). \tag{49}$$

In (48) and (49) we are left with n^2 phenomenological tensors (that is $9n^2$ phenomenological coefficients).

Let us now discuss the phenomenological equations (45). In the most general case the viscous pressure tensor $\mathbf{\Pi}$ has 9 independent components. We shall be concerned here, however, with the case usually considered of a symmetric tensor $\mathbf{\Pi}$, which has six independent components. Then in (45) only $(\mathrm{Grad}\mathbf{v})^s$, i.e., the symmetric part of $(\mathrm{Grad}\mathbf{v})$ remains. Rewriting (45) for this case, we have

$$\Pi_{(ij)} = -\sum_{m,n=1}^{3} L_{(ij)(mn)}(\mathrm{Grad}\mathbf{v})_{(mn)}, \tag{50}$$

where the notations (ij) and (mn) indicate the symmetrical character in the indices between brackets. Consequently we are left with 36 phenomenological coefficients $L_{(ij)(mn)}$, instead of the 81 coefficients $L_{ij,mn}$ from (45). [When $(\mathrm{Grad}\mathbf{v})$ and $\mathbf{\Pi}$ are brought to principle axes together, only 9 phenomenological coefficients are left.]

6. ENTROPY PRODUCTION IN TERMS OF FLUCTUATIONS

In order to apply the theory outlined in Secs. 2 and 3 to the phenomena described in the foregoing, one must proceed as follows: the change of an insulated system which in formula (3) was expressed in terms of arbitrary parameters α and β, must now be specified as a function of the variables which determine the actual physical state of the system considered in Secs. 4 and 5.

The change of entropy per unit time of the whole system of volume V is

$$dS/dt = \int_v (\partial s_v/\partial t)dV. \tag{51}$$

The local change of entropy $\partial s_v/\partial t$ can be expressed in terms of other state variables by means of the Gibbs' relation (36). This relation is valid along the center of gravity motion.[8] In the case under consideration (isolated system), this motion is a fluctuation. This means that in the Gibbs' relation terms in $\mathbf{v}$ [see formula (24)] are of higher order than the local time derivatives, and may therefore be neglected.[8] Consequently we can write

$$T\partial s/\partial t = \partial u/\partial t + p\partial v/\partial t - \textstyle\sum_k \mu_k \partial c_k/\partial t, \tag{52}$$

or alternatively, since $\sum_k c_k\mu_k = u - Ts + pv$,

$$T\partial s_v/\partial t = \partial u_v/\partial t - \textstyle\sum_k \mu_k\partial\rho_k/\partial t. \tag{53}$$

Introducing (53) into (51) we obtain

$$dS/dt = \int_v T^{-1}(\partial u_v/\partial t - \textstyle\sum_k \mu_k\partial\rho_k/\partial t)dV, \tag{54}$$

which can also be written as

$$dS/dt = \int_v \{-(\Delta T/T_0)T^{-1}(\partial u_v/\partial t - \textstyle\sum_k \mu_k\partial\rho_k/\partial t) + T_0^{-1}(\partial u_v/\partial t - \textstyle\sum_k \mu_k\partial\rho_k/\partial t)\}dV, \tag{55}$$

where $\Delta T = T - T_0$, and where we take for T_0 the equilibrium temperature. The change of total energy E for the whole system follows from (32)

$$dE/dt = \int_V (\partial u_v/\partial t + \textstyle\sum_k w_k\partial\rho_k/\partial t + \partial\frac{1}{2}\rho\mathbf{v}^2/\partial t)dV. \tag{56}$$

Introducing this expression and (53) into (55), one obtains

$$dS/dt = T_0^{-1}dE/dt - \int_V T_0^{-1}(\Delta T\partial s_v/\partial t + \textstyle\sum_k \bar{\mu}_k\partial\rho_k/\partial t + \partial\frac{1}{2}\rho\mathbf{v}^2/\partial t)dV. \tag{57}$$

For an insulated system (constant E) (57) can finally be written as

$$T_0 d\Delta S/dt = -\int_V (\Delta T\partial\Delta s_v/\partial t + \textstyle\sum_k \Delta\bar{\mu}_k\partial\Delta\rho_k/\partial t + \Delta\mathbf{v}\cdot\partial\Delta\mathbf{g}/\partial t)dV. \tag{58}$$

Here the symbol Δ indicates the difference of a quantity and its equilibrium value. Use has been made of the fact that *at equilibrium* all parameters are constant in time, T and μ_k are uniform, and $\mathbf{v}$ vanishes. Furthermore conservation of mass has been applied. In passing from (57) to (58) the difference between ρ and its equilibrium value ρ_0 is immaterial, since third order terms in (58) are neglected. For this reason, $\mathbf{g} \equiv \rho\mathbf{v}$ in (58) can be considered as $\rho_0\mathbf{v}$.

It may be remarked that the result (58) could also have been found from the volume integral of σ (40) under the same conditions and approximations. The derivation of (58) given here is, however, simpler.

It is clear that (58) is of the form (15), which is appropriate for the application of fluctuation theory (Sec. 2) and microscopic reversibility (Sec. 3). The variables $\Delta s_v(\mathbf{r})$, and $\Delta\rho_k(\mathbf{r})$ are of the α type, whereas the components of $\Delta\mathbf{g}(\mathbf{r})$ are β-type variables. (The variables ΔT, $\Delta\bar{\mu}_k$ and the components of $\Delta\mathbf{v}$ are the corresponding X- and Y-type variables.)

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[8] I. Prigogine, Physica 15, 272 (1949).

7. FLUCTUATIONS

To these variables we apply the relations (11) or (12). This gives

$$\begin{aligned}&\langle\Delta s_v(\mathbf{r})\Omega(\mathbf{r}')\Delta T(\mathbf{r}')\rangle_{\text{Av}}=kT_0\Omega(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'),\\&\langle\Delta s_v(\mathbf{r})\Omega(\mathbf{r}')\Delta\bar{\mu}_k(\mathbf{r}')\rangle_{\text{Av}}=0,\\&\langle\Delta s_v(\mathbf{r})\Omega(\mathbf{r}')\Delta v_i(\mathbf{r}')\rangle_{\text{Av}}=0,\end{aligned}\tag{59}$$

$$\begin{aligned}&\langle\Delta\rho_k(\mathbf{r})\Omega(\mathbf{r}')\Delta\bar{\mu}_{k'}(\mathbf{r}')\rangle_{\text{Av}}=kT_0\delta_{kk'}\Omega(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'),\\&\langle\Delta\rho_k(\mathbf{r})\Omega(\mathbf{r}')\Delta T(\mathbf{r}')\rangle_{\text{Av}}=0,\\&\langle\Delta\rho_k(\mathbf{r})\Omega(\mathbf{r}')\Delta v_i(\mathbf{r}')\rangle_{\text{Av}}=0,\end{aligned}\tag{60}$$

$$\begin{aligned}&\langle\Delta g_i(\mathbf{r})\Omega(\mathbf{r}')\Delta v_j(\mathbf{r}')\rangle_{\text{Av}}=kT_0\delta_{ij}\Omega(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'),\\&\langle\Delta g_i(\mathbf{r})\Omega(\mathbf{r}')\Delta T(\mathbf{r}')\rangle_{\text{Av}}=0,\\&\langle\Delta g_i(\mathbf{r})\Omega(\mathbf{r}')\Delta\bar{\mu}_k(\mathbf{r}')\rangle_{\text{Av}}=0,\end{aligned}\tag{61}$$

where $i,j=1,2,3$ indicate Cartesian coordinates. Furthermore, there are no correlations between the β-type variables $\Delta\mathbf{v}$ and $\Delta\mathbf{g}$, and any combination of the α-type variables, because no cross-terms between α's and β's appear in expression (3).

8. RECIPROCAL RELATIONS FOR HEAT CONDUCTION, DIFFUSION, AND CROSS-EFFECTS

In order to derive reciprocal relations for heat conduction diffusion and their cross-effects the following expressions of microscopic reversibility, which are examples of relation (19), are needed

$$\langle\Delta s_v(\mathbf{r})(\partial/\partial t)\Delta s_v(\mathbf{r}')\rangle_{\text{Av}}=\langle\Delta s_v(\mathbf{r}')(\partial/\partial t)\Delta s_v(\mathbf{r})\rangle_{\text{Av}},\tag{62}$$

$$\langle\Delta s_v(\mathbf{r})(\partial/\partial t)\Delta\rho_k(\mathbf{r}')\rangle_{\text{Av}}=\langle\Delta\rho_k(\mathbf{r}')(\partial/\partial t)\Delta s_v(\mathbf{r})\rangle_{\text{Av}},\quad(k=1,2,\cdots,n)\tag{63}$$

$$\langle\Delta\rho_k(\mathbf{r})(\partial/\partial t)\Delta\rho_{k'}(\mathbf{r}')\rangle_{\text{Av}}=\langle\Delta\rho_{k'}(\mathbf{r}')(\partial/\partial t)\Delta\rho_k(\mathbf{r})\rangle_{\text{Av}}.\quad(k,k'=1,2,\cdots,n).\tag{64}$$

Introducing into these relations the entropy balance (42), the mass laws (25), and the phenomenological equations (48) and (49), one obtains

$$\begin{aligned}&\langle\Delta s_v[\operatorname{div}'\{-s_v'\Delta\mathbf{v}'+\boldsymbol{L}_{ss}'\cdot\operatorname{grad}'\Delta T'\\&\quad+\sum_{k=1}^{n-1}\boldsymbol{L}_{sk}'\cdot\operatorname{grad}'(\Delta\bar{\mu}_k'-\Delta\bar{\mu}_n')\}+\sigma']\rangle_{\text{Av}}\\&=\langle\Delta s_v'[\operatorname{div}\{-s_v\Delta\mathbf{v}+\boldsymbol{L}_{ss}\cdot\operatorname{grad}\Delta T\\&\qquad+\sum_{k=1}^{n-1}\boldsymbol{L}_{sk}\cdot\operatorname{grad}(\Delta\bar{\mu}_k-\Delta\bar{\mu}_n)\}+\sigma]\rangle_{\text{Av}},\end{aligned}\tag{65}$$

$$\begin{aligned}&\langle\Delta s_v[\operatorname{div}'\{-\rho_k'\Delta\mathbf{v}'+\boldsymbol{L}_{ks}'\cdot\operatorname{grad}'\Delta T'\\&\quad+\sum_{k'=1}^{n-1}\boldsymbol{L}_{kk'}'\cdot\operatorname{grad}'(\Delta\bar{\mu}_{k'}'-\Delta\bar{\mu}_n')\}]\rangle_{\text{Av}}\\&=\langle\Delta\rho_k'[\operatorname{div}\{-s_v\Delta\mathbf{v}+\boldsymbol{L}_{ss}\cdot\operatorname{grad}\Delta T\\&\qquad+\sum_{k'=1}^{n-1}\boldsymbol{L}_{sk'}\cdot\operatorname{grad}(\Delta\bar{\mu}_{k'}-\Delta\bar{\mu}_n)\}+\sigma]\rangle_{\text{Av}},\end{aligned}\tag{66}$$

$$\begin{aligned}&\langle\Delta\rho_k[\operatorname{div}'\{-\rho_{k'}'\Delta\mathbf{v}'+\boldsymbol{L}_{k's}'\cdot\operatorname{grad}'\Delta T'\\&\quad+\sum_{k''=1}^{n-1}\boldsymbol{L}_{k'k''}'\cdot\operatorname{grad}'(\Delta\bar{\mu}_{k''}'-\Delta\bar{\mu}_n')\}]\rangle_{\text{Av}}\\&=\langle\Delta\rho_{k'}'[\operatorname{div}\{-\rho_k\Delta\mathbf{v}+\boldsymbol{L}_{ks}\cdot\operatorname{grad}\Delta T\\&\qquad+\sum_{k''=1}^{n-1}\boldsymbol{L}_{kk''}\cdot\operatorname{grad}(\Delta\bar{\mu}_{k''}-\Delta\bar{\mu}_n)\}]\rangle_{\text{Av}},\end{aligned}\tag{67}$$

where dashes indicate dependence on $\mathbf{v}'$. In these relations occur the quantities

$$s_v\Delta\mathbf{v}=s_v^0\Delta\mathbf{v}+\Delta s_v\Delta\mathbf{v},\tag{68}$$

$$\rho_k\Delta\mathbf{v}=\rho_k^0\Delta\mathbf{v}+\Delta\rho_k\Delta\mathbf{v},\tag{69}$$

where s_v^0 and ρ_k^0 are equilibrium values.

Applying (59) and (60) to (65), (66) and (67) one gets

$$\operatorname{div}'\{\boldsymbol{L}_{ss}'\cdot\operatorname{grad}'\delta(\mathbf{r}-\mathbf{r}')\}=\operatorname{div}\{\boldsymbol{L}_{ss}\cdot\operatorname{grad}\delta(\mathbf{r}-\mathbf{r}')\},\tag{70}$$

$$\operatorname{div}'\{\boldsymbol{L}_{ks}'\cdot\operatorname{grad}'\delta(\mathbf{r}-\mathbf{r}')\}=\operatorname{div}\{\sum_{k'=1}^{n-1}\boldsymbol{L}_{sk'}\cdot(\delta_{kk'}-\delta_{kn})\operatorname{grad}\delta(\mathbf{r}-\mathbf{r}')\},\tag{71}$$

$$\operatorname{div}'\{\sum_{k''=1}^{n-1}\boldsymbol{L}_{k'k''}\cdot(\delta_{kk''}-\delta_{kn})\operatorname{grad}'\delta(\mathbf{r}-\mathbf{r}')\}=\operatorname{div}\{\sum_{k''=1}^{n-1}\boldsymbol{L}_{kk''}\cdot(\delta_{k'k''}-\delta_{k'n})\operatorname{grad}\delta(\mathbf{r}-\mathbf{r}')\},\tag{72}$$

since averages of third order terms, e.g. $\langle\Delta\rho_k'\Delta s_v\Delta\mathbf{v}\rangle_{\text{Av}}$ or $\langle\Delta s_v\sigma'\rangle_{\text{Av}}$, vanish.

Eliminating the Kronecker δ's and the δ functions[3] from the preceding relations one finds

$$\operatorname{Div}\boldsymbol{L}_{ss}=\operatorname{Div}\boldsymbol{L}_{ss}^{\dagger},\tag{73}$$

$$\boldsymbol{L}_{sk}+\boldsymbol{L}_{sk}^{\dagger}=\boldsymbol{L}_{ks}+\boldsymbol{L}_{ks}^{\dagger},\quad\operatorname{Div}\boldsymbol{L}_{sk}=\operatorname{Div}\boldsymbol{L}_{ks}^{\dagger},\quad(k=1,2,\cdots,n-1)\tag{74}$$

$$\boldsymbol{L}_{k'k}+\boldsymbol{L}_{k'k}^{\dagger}=\boldsymbol{L}_{kk'}+\boldsymbol{L}_{kk'}^{\dagger},\quad\operatorname{Div}\boldsymbol{L}_{k'k}=\operatorname{Div}\boldsymbol{L}_{kk'}^{\dagger},\quad(k,k'=1,2,\cdots,n-1),\tag{75}$$

where the symbol † indicates transposing of the Cartesian coordinates. With the convention of taking all phenomenological coefficients zero in empty space, and the fact that these coefficients do not depend on the shape of the sample it follows

$$\boldsymbol{L}_{ss}=\boldsymbol{L}_{ss}^{\dagger},\tag{76}$$

$$\boldsymbol{L}_{sk}=\boldsymbol{L}_{ks}^{\dagger},\quad(k=1,2,\cdots,n-1)\tag{77}$$

$$\boldsymbol{L}_{kk'}=\boldsymbol{L}_{k'k}^{\dagger}.\quad(k,k'=1,2,\cdots,n-1).\tag{78}$$

Taking into account (46) and (47), relations (77) and (78) are also valid for k, or k', or both, equal to n.

The formulas (76)–(78) are the reciprocal relations, which we wanted to derive for the phenomena of heat conduction, diffusion and cross-effects in anisotropic media.

The preceding theory could alternatively have been developed starting for instance from the form (39) of the entropy production, and corresponding phenomenological equations and sets of variables in Secs. 6 and 7.

Finally, we would like to make the following remark. It may at first sight seem surprising that relations (77) and (78) are found only for values of k and k' up to $n-1$, whereas in the starting point (63) and (64) they could also be equal to n. This can be understood because effectively one of the relations (63), and $2n-1$ of the relations (64) yield no information. From (64) for instance it is seen by summing over k, k' that one obtains

$$\langle\Delta\rho(\mathbf{r})(\partial/\partial t)\Delta\rho(\mathbf{r}')\rangle_{\mathrm{Av}}=\langle\Delta\rho(\mathbf{r}')(\partial/\partial t)\Delta\rho(\mathbf{r})\rangle_{\mathrm{Av}}. \quad (79)$$

Substituting (26) into this last relation this gives

$$\langle\Delta\rho\ \mathrm{div}'\Delta\mathbf{g}'\rangle_{\mathrm{Av}}=\langle\Delta\rho'\ \mathrm{div}\Delta\mathbf{g}\rangle_{\mathrm{Av}}. \quad (80)$$

According to the argument at the end of Sec. 7, both members of (80) vanish. Machlup and Onsager[6] have already discussed that correlations between α variables of the type (79) disappear when β variables, related to the α's in a way as expressed by (26), are necessary to describe the thermodynamic state of the system.

9. RECIPROCAL RELATIONS FOR VISCOSITY

Reciprocal relations for viscosity can be derived from the following expression for microscopic reversibility, which is an example of (21)

$$\langle\Delta g_i(\mathbf{r})(\partial/\partial t)\Delta g_j(\mathbf{r}')\rangle_{\mathrm{Av}}=\langle\Delta g_j(\mathbf{r}')(\partial/\partial t)\Delta g_i(\mathbf{r})\rangle_{\mathrm{Av}}. \qquad (i,\ j=1,2,3). \quad (81)$$

Substituting (30) with (29) and the phenomenological equation (50) into (81) we find

$$\begin{aligned}&\Big\langle\Delta g_i\Big[\sum_{l=1}^{3}\frac{\partial}{\partial x_l'}\Big\{-\Delta v_l'\Delta g_j'+\sum_{m,n=1}^{3}L'_{(lj)(mn)}\\&\quad\times\frac{1}{2}\Big(\frac{\partial\Delta v_n'}{\partial x_m'}+\frac{\partial\Delta v_m'}{\partial x_n'}\Big)\Big\}+\sum_{k=1}^{n}\rho_k'\Big(\frac{\partial\Delta\bar{\mu}_k'}{\partial x_j'}\Big)_T\Big]\Big\rangle_{\mathrm{Av}}\\&=\Big\langle\Delta g_j'\Big[\sum_{l=1}^{3}\frac{\partial}{\partial x_l}\Big\{-\Delta v_l\Delta g_i+\sum_{m,n=1}^{3}L_{(li)(mn)}\\&\quad\times\frac{1}{2}\Big(\frac{\partial\Delta v_n}{\partial x_m}+\frac{\partial\Delta v_m}{\partial x_n}\Big)\Big\}+\sum_{k=1}^{n}\rho_k\Big(\frac{\partial\Delta\bar{\mu}_k}{\partial x_i}\Big)_T\Big]\Big\rangle_{\mathrm{Av}}. \quad (82)\end{aligned}$$

Here use has been made of

$$\begin{aligned}\sum_{k=1}^{n}\rho_k\mathbf{F}_k-\mathrm{grad}p&=-\sum_{k=1}^{n}\rho_k\{\mathrm{grad}(w_k+\mu_k)\}_T\\&=-\sum_{k=1}^{n}\rho_k(\mathrm{grad}\bar{\mu}_k)_T=-\sum_{k=1}^{n}\rho_k(\mathrm{grad}\Delta\bar{\mu}_k)_T, \quad (83)\end{aligned}$$

in which the Gibbs-Duhem relation has been applied, and where the subscript T means constant temperature:

$$\textstyle\sum_k\rho_k(\mathrm{grad}\Delta\bar{\mu}_k)_T=\sum_k\rho_k\,\mathrm{grad}\Delta\bar{\mu}_k-s_v\,\mathrm{grad}\Delta T. \quad (84)$$

Since averages of third order terms vanish and since no correlations exist between α- and β-type variables, we find from (82), with the help of (61)

$$\begin{aligned}&\sum_{l,m,n}\frac{\partial}{\partial x_l'}\Big[L'_{(lj)(mn)}\frac{1}{2}\Big\{\frac{\partial}{\partial x_m'}\delta_{in}\delta(\mathbf{r}-\mathbf{r}')\\&\quad+\frac{\partial}{\partial x_n'}\delta_{im}\delta(\mathbf{r}-\mathbf{r}')\Big\}\Big]\\&=\sum_{l,m,n}\frac{\partial}{\partial x_l}\Big[L_{(li)(mn)}\frac{1}{2}\Big\{\frac{\partial}{\partial x_m}\delta_{jn}\delta(\mathbf{r}-\mathbf{r}')\\&\quad+\frac{\partial}{\partial x_n}\delta_{jm}\delta(\mathbf{r}-\mathbf{r}')\Big\}\Big]. \quad (85)\end{aligned}$$

Eliminating the Kronecker δ's and the δ functions, we find the following results:

$$L_{(lj)(mi)}+L_{(mj)(li)}=L_{(li)(mj)}+L_{(mi)(lj)}, \quad (86)$$

$$\textstyle\sum_m(\partial/\partial x_m)L_{(lj)(mi)}=\sum_m(\partial/\partial x_m)L_{(mi)(lj)}. \quad (87)$$

With the convention that the coefficients vanish in empty space this gives

$$L_{(lj)(mi)}=L_{(mi)(lj)}. \quad (i,\ j,\ l,\ m=1,2,3). \quad (88)$$

These are 15 reciprocal relations amongst the 36 viscosity coefficients. This leaves us with 21 independent coefficients.

It can be noted that in isotropic media one has two independent viscosity coefficients, but no reciprocal relations.

10. CONCLUDING REMARKS

In the preceding sections, reciprocal relations (76)–(78), (88) have been derived for vectorial and tensorial phenomena in continuous systems. In this way general results have been found for heat conduction, diffusion, viscosity and cross-effects in moving media. However, we did not include chemical reactions and other scalar phenomena into the considerations, since Onsager's formalism can be applied to these effects without any extension of the theory. Furthermore, only conservative external forces have been taken into account, which means that electromagnetic phenomena have not been dealt with. This will be done in a subsequent paper.

APPENDIX ON NOTATION

We use essentially the Milne system of tensor notation.[9] The exterior product of an ordered pair of

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[9] L. Rosenfeld, *Theory of Electrons* (North-Holland Publishing Company, Amsterdam, 1951).

vectors **a**, **b** is a tensor

$$\boldsymbol{T}=\mathbf{ab},\ \text{components: } T_{ik}=a_ib_k. \qquad (89)$$

The divergence of a tensor and the gradient of a vector are written as

$$\mathrm{Div}\boldsymbol{T},\ \text{components: } (\mathrm{Div}\boldsymbol{T})_i=\textstyle\sum_k(\partial/\partial x_k)T_{ki}, \qquad (90)$$

$$\mathrm{Grad}\mathbf{a},\ \text{components: } (\mathrm{Grad}\mathbf{a})_{ik}=(\partial/\partial x_i)a_k. \qquad (91)$$

The interior products between a tensor and a vector are denoted by

$$\boldsymbol{T}\cdot\mathbf{a},\ \text{components: } (\boldsymbol{T}\cdot\mathbf{a})_i=\textstyle\sum_k T_{ik}a_k, \qquad (92)$$

$$\mathbf{a}\cdot\boldsymbol{T},\ \text{components: } (\mathbf{a}\cdot\boldsymbol{T})_i=\textstyle\sum_k a_kT_{ki}. \qquad (93)$$

Finally,

$$\boldsymbol{T}:\boldsymbol{U}=\textstyle\sum_{i,k} T_{ik}U_{ki} \qquad (94)$$

is the interior product of two tensors, $\boldsymbol{T}$ and $\boldsymbol{U}$, contracted twice.

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Extension of Onsager's Theory of Reciprocal Relations. II

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The extension of Onsager's theory of reciprocal relations between irreversible processes, developed previously by the authors, is applied to electric conduction in anisotropic crystals, and the symmetry properties of the conduction tensor are derived.

1. INTRODUCTION

In a previous paper[1] the authors have extended Onsager's theory for reciprocal relations between irreversible processes in such a way that it could be directly applied to vectorial and tensorial phenomena (see I, Sec. 1). Results were obtained for heat conduction, diffusion, viscosity, and cross effects. It was assumed that external forces, taken into account, were conservative. Thus electromagnetic irreversible phenomena were not treated. It is the purpose of this paper to apply the general theory outlined in I, Secs. 2 and 3 to electromagnetic processes. We shall consider the case of electric conduction in anisotropic crystals at uniform temperature. In Secs. 2 and 3 the macroscopic phenomenological theory of electric conduction is developed. In Sec. 4 we then derive an expression for the entropy production in an energetically insulated crystal in terms of local fluctuations of state variables, as required for the application in Secs. 5–7 of the formalism from I, Secs. 2 and 3. In such a way the symmetry properties of the conduction tensor are derived.

2. ENTROPY PRODUCTION IN LOCAL FORM

Let us consider a system, consisting of a rigid ion lattice and of electrons, in an electromagnetic field. The entropy production can be calculated as follows:

Charge conservation is expressed by

$$\partial\rho_e/\partial t=-\mathrm{div}\mathbf{i}, \qquad (1)$$

where ρ_e is the electrical charge density, and $\mathbf{i}$ the electric current.

Conservation of energy can be written as

$$\partial e_v/\partial t=-\mathrm{div}\mathbf{J}_e, \qquad (2)$$

where e_v is the density of total energy and $\mathbf{J}_e$ the energy flow. These are given by

$$e_v=u_v+\tfrac{1}{2}(\mathbf{E}^2+\mathbf{B}^2), \qquad (3)$$

$$\mathbf{J}_e=\mathbf{J}_q+c\mathbf{E}\times\mathbf{B}, \qquad (4)$$

with u_v the density of internal energy, $\frac{1}{2}(\mathbf{E}^2+\mathbf{B}^2)$ the density of electromagnetic energy ($\mathbf{E}$ is the electric and $\mathbf{B}$ the magnetic field), and $c\mathbf{E}\times\mathbf{B}$ the Poynting vector. Relation (4) defines the heat flow $\mathbf{J}_q$. Subtracting Poynting's theorem

$$\tfrac{1}{2}\partial(\mathbf{E}^2+\mathbf{B}^2)/\partial t=-\mathrm{div}c\mathbf{E}\times\mathbf{B}+\mathbf{i}\cdot\mathbf{E}, \qquad (5)$$

from (2) one obtains the equation for the internal energy

$$\partial u_v/\partial t=-\mathrm{div}\mathbf{J}_q+\mathbf{i}\cdot\mathbf{E}. \qquad (6)$$

Furthermore, we need the Gibbs' equation

$$Tds_v/dt=du_v/dt-\textstyle\sum_k \mu_k d\rho_k/dt, \qquad (7)$$

where T is the temperature, s_v the density of entropy, μ_k and ρ_k the chemical potential per unit mass and the density of component k (ions or electrons). The time derivatives in this equation are substantial derivatives with respect to the center of mass motion. Taking the velocity of the ion lattice zero we can neglect the center of mass motion, because the ions are heavy as compared

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[1] S. R. de Groot and P. Mazur, preceding paper [Phys. Rev. 94, 218 (1954)], referred to in the following as I.