Hooyman, G. J
Groot, S. R. de
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PHENOMENOLOGICAL EQUATIONS AND ONSAGER RELATIONS

THE CASE OF DEPENDENT FLUXES OR FORCES

by G. J. HOOYMAN and S. R. DE GROOT

Instituut voor theoretische natuurkunde, Universiteit, Utrecht, Nederland
Instituut-Lorentz, Universiteit, Leiden, Nederland

Synopsis

The influence of linear dependencies between the fluxes or between the forces occurring in the expression for the entropy production on the phenomenological coefficients and the Onsager reciprocal relations is investigated.

If both sets of variables are dependent the phenomenological coefficients are not uniquely defined. It is shown that they always can be chosen such as to satisfy the Onsager relations.

§ 1. *Introduction.* In the thermodynamics of irreversible processes [1] [2] the entropy production can generally be written as a sum of products of fluxes and corresponding forces. The phenomenological equations describing the irreversible phenomena are introduced as linear equations between these two sets of quantities. For the scheme of phenomenological coefficients the Onsager reciprocal relations then hold.

Since in the proof of the Onsager relations the fluxes as well as the forces are assumed to be independent this formalism should be applied with care if linear dependencies exist amongst the fluxes or amongst the forces. This is, *e.g.*, the case with the flows of matter in a mixture of several components if these flows are taken with respect to some mean velocity [1] [3]. Another example is the condition of vanishing volume flow in a closed vessel which reduces the number of independent absolute flows of matter [2] [4]. Likewise, the number of independent forces may be diminished by a linear dependency such as can result, *e.g.*, from the condition of mechanical equilibrium [1] [2]. An analogous situation arises for the chemical affinities in the case of a triangular reaction [1].

A linear dependency for only one of the two classes of variables gives rise to additional relations amongst the phenomenological coefficients which leave the symmetry of the coefficient scheme unimpaired [1] [5]. However, when both classes of variables, fluxes and forces, are dependent the phenomenological coefficients are not uniquely defined and the validity of the Onsager relations can no longer be guaranteed. Such a situation has been met with by Holtan in his treatment of thermocells [6]) (*v*. p. 44).

It is the purpose of this paper to show that in the latter case the coefficients can always be chosen in such a way that the Onsager relations hold. We shall restrict ourselves to the case of one single linear relation for each class of variables and only write down the formalism for vectorial irreversible phenomena in isotropic media.

§ 2. *The case of dependent fluxes.* With only vectorial irreversible phenomena the entropy production σ can be written in the form

$$\sigma = \Sigma_{k=1}^{n} \mathbf{J}_k \cdot \mathbf{X}_k. \tag{1}$$

If the fluxes $\mathbf{J}_k$ as well as the forces $\mathbf{X}_k$ each constitute a set of independent quantities the phenomenological equations for isotropic media read

$$\mathbf{J}_k = \Sigma_{l=1}^{n} L_{kl} \mathbf{X}_l, \quad (k = 1, \ldots, n), \tag{2}$$

and in the absence of a magnetic field the Onsager reciprocal relations [7]) state that

$$L_{kl} = L_{lk}, \quad (l, k = 1, \ldots, n). \tag{3}$$

The system (2) can be solved for the $\mathbf{X}_l$, the new scheme of phenomenological coefficients again being symmetric.

Let us now suppose that one of the sets of quantities is independent whereas the other quantities are interrelated in a linear way, *e.g.*,

$$\Sigma_{k=1}^{n} a_k \mathbf{J}_k = 0. \tag{4}$$

With $a_n \neq 0$ we then can eliminate $\mathbf{J}_n$ from (1)

$$\sigma = \Sigma_{i=1}^{n-1} \mathbf{J}_i \cdot \{\mathbf{X}_i - a_i \mathbf{X}_n/a_n\}, \tag{5}$$

so that we are left with $n - 1$ independent fluxes and forces. Taking this expression for σ as a starting point it follows by straightforward calculation that the phenomenological equations (2) as well as the reciprocal relations (3) still hold although now a number of relations exist between the coefficients L_{kl}. In fact, starting from (5) we can write for the phenomenological equations

$$\mathbf{J}_i = \Sigma_{j=1}^{n-1} l_{ij} (\mathbf{X}_j - a_j \mathbf{X}_n/a_n), \quad (i = 1, \ldots, n-1), \tag{6}$$

and on comparison with (2) making also use of (4) we find for $i, j = 1, \ldots, n - 1$

$$\left.\begin{aligned} L_{ij} &= l_{ij}, & L_{in} &= -\Sigma_{j=1}^{n-1} a_j l_{ij}/a_n, \\ L_{ni} &= -\Sigma_{j=1}^{n-1} a_j l_{ji}/a_n, & L_{nn} &= \Sigma_{i,j=1}^{n-1} a_i a_j l_{ij}/a_n^2. \end{aligned}\right\} \tag{7}$$

From (7) it is clear that the coefficients L_{kl} now are interrelated by

$$\left.\begin{aligned} \Sigma_{l=1}^{n} a_l L_{kl} &= 0, \\ \Sigma_{k=1}^{n} a_k L_{kl} &= 0, \end{aligned}\right\} \quad (k, l = 1, \ldots, n), \tag{8}$$

a set of $2n - 1$ independent relations which could also be derived directly from (1), (2) and (4) (*cf.* [1]) p. 102).

Since the Onsager relations are valid for the coefficients l_{ij} it follows from (7) that equation (3) still holds.

Of course, equations (2) or (6) can no longer be solved for the n quantities $\mathbf{X}_l$ but only for the $n - 1$ quantities $\mathbf{X}_j - a_j\mathbf{X}_n/a_n$.

§ 3. *Dependent fluxes and forces.* In addition to (4) we will next assume a linear relation

$$\Sigma_{k=1}^{n} b_k \mathbf{X}_k = 0 \tag{9}$$

with $b_n \neq 0$. By eliminating both $\mathbf{J}_n$ and $\mathbf{X}_n$ from (1) we find

$$\sigma = \Sigma_{i=1}^{n-1} \mathbf{J}_i \cdot \{\mathbf{X}_i + (a_i/a_n)\, \Sigma_{p=1}^{n-1} b_p \mathbf{X}_p/b_n\}. \tag{10}$$

The phenomenological equations are now

$$\begin{aligned}\mathbf{J}_i &= \Sigma_{j=1}^{n-1} l_{ij}\, \{\mathbf{X}_j + (a_j/a_n)\, \Sigma_{p=1}^{n-1} b_p \mathbf{X}_p/b_n\} = \\ &= \Sigma_{j=1}^{n-1} \mathbf{X}_j\, \{l_{ij} + (b_j/b_n)\, \Sigma_{p=1}^{n-1} a_p l_{ip}/a_n\}, \quad (i = 1, \ldots, n-1),\end{aligned} \tag{11}$$

and thus in view of (4)

$$\mathbf{J}_n = -\, \Sigma_{j=1}^{n-1} \mathbf{X}_j\, \Sigma_{i=1}^{n-1} \{l_{ij} + (b_j/b_n)\, \Sigma_{p=1}^{n-1} a_p l_{ip}/a_n\}\, a_i/a_n\,. \tag{12}$$

These equations can again be written in the form (2). However, since the forces $\mathbf{X}_k$ are no longer independent (*v.* (9)) there is a certain arbitrariness with respect to the coefficients L_{kl}: in each row of the L_{kl} scheme (*i.e.*, for each value of k) one of the n coefficients can be chosen arbitrarily. On the other hand, because of (4) there exist $n - 1$ linear relations between the L_{kl}. To find these we first eliminate $\mathbf{X}_n$ from (2) by means of (9). The flows are then expressed in terms of independent forces

$$\mathbf{J}_k = \Sigma_{j=1}^{n-1} \mathbf{X}_j (L_{kj} - b_j L_{kn}/b_n), \quad (k = 1, \ldots, n). \tag{13}$$

Now it follows from (4) that

$$\Sigma_{k=1}^{n} a_k (L_{kj} - b_j L_{kn}/b_n) = 0, \quad (j = 1, \ldots, n-1). \tag{14}$$

These $n - 1$ relations combine with the n-fold arbitrariness to leave a sensible set of $(n - 1)^2$ coefficients L_{kl}.

From the foregoing it is clear that the L_{kl} scheme need not be symmetric as the phenomenological coefficients are not uniquely defined. However, it can easily be shown that they can be chosen such as to satisfy the Onsager relations (3). As a matter of fact, by comparing (11) and (12) with (13) we get for $i, j = 1, \ldots, n-1$

$$L_{ij} - b_j L_{in}/b_n = l_{ij} + (b_j/b_n)\, \Sigma_{p=1}^{n-1} a_p l_{ip}/a_n, \tag{15}$$

$$L_{ni} - b_i L_{nn}/b_n = -\, \Sigma_{q=1}^{n-1} (a_q/a_n)\, \{l_{qi} + (b_i/b_n)\, \Sigma_{p=1}^{n-1} a_p l_{qp}/a_n\}, \tag{16}$$

a system of $n(n-1)$ equations for the n^2 coefficients L_{kl}. A possible solution is again given by (7). Since the coefficients l_{ij} are subject to the Onsager relations this solution satisfies (3).

The most general symmetric solution is reached from (15) and (16) by superimposing the conditions

$$L_{in} = L_{ni}, \quad (i = 1, \ldots, n-1). \tag{17}$$

If we then solve the equations for L_{ij} making use of the symmetry in the l_{ij} scheme we find

$$L_{ij} = l_{ij} + b_i b_j \{L_{nn} - \Sigma_{p,q=1}^{n-1} a_p a_q l_{pq}/a_n^2\}/b_n^2, \quad (i, j = 1, \ldots, n-1), \tag{18}$$

an expression which is symmetric in i and j.

The $n(n-1)$ equations (15) and (16) leave an n-fold arbitrariness in the n^2 coefficients L_{kl}. By the conditions (17) one is left with only one single arbitrary choice. If we choose the coefficient L_{nn} in an arbitrary way, the complete scheme is determined.

§ 4. *External magnetic field.* The foregoing treatment is only slightly modified if the system is placed in an external magnetic field H or if it rotates with an angular velocity H. The Onsager relations (3) then read

$$L_{kl}(\mathrm{H}) = L_{lk}(-\mathrm{H}), \quad (k, l = 1, \ldots, n), \tag{19}$$

The coefficients l_{ij} now satisfy the Onsager relations

$$l_{ij}(\mathrm{H}) = l_{ji}(-\mathrm{H}), \quad (i, j = 1, \ldots, n-1), \tag{20}$$

and it can easily be verified that the conclusions of § 2 and § 3 are unimpaired if the coefficients a_k are all either even or odd functions of H. In the case of § 3 the most general solution satisfying (19) is reached by superimposing the conditions

$$L_{in}(\mathrm{H}) = L_{ni}(-\mathrm{H}), \quad (i = 1, \ldots, n-1), \tag{21}$$

while L_{nn} should of course be an even function of H.

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