

## On the Reciprocal Relations of Onsager

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Given any linear relation between forces and fluxes in irreversible thermodynamics, it is shown that redefinition of forces and fluxes by linear combination yields a relation with symmetric matrix. The rate of production of entropy is unchanged by the redefinition. Thus, unless "forces" and "fluxes" are defined by some property more specific than mere occurrence in the expression for production of entropy, there is no content in the statement that the matrix of phenomenological coefficients is or is not symmetric.

CONSIDER a set of  $n$  "thermodynamical fluxes"  $J_i$  which are linear functions of  $n$  "thermodynamical forces"  $X_i$ :

$$J_i = \sum_{j=1}^n L_{ij} X_j. \quad (1)$$

The "reciprocity theorem of Onsager,"<sup>1</sup> in its most commonly accepted version,<sup>2-4</sup> states the following. If each flux  $J_i$  is the time derivative of a thermodynamic variable  $a_i$ ,

$$J_i = \dot{a}_i, \quad (2)$$

if each  $a_i$  is an even function<sup>5</sup> of the velocities of the atoms constituting the system and enters into an equation of the form

$$S = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n g_{ij} a_i a_j, \quad (3)$$

where  $S$  is the entropy of the system (to within a time-independent constant), and if, further, the forces  $X_j$  have been chosen so that

$$X_j = (\partial S / \partial a_j) = \sum_{i=1}^n g_{ij} a_i, \quad (4)$$

then, the matrix  $\|L_{ij}\|$  of the phenomenological coefficients  $L_{ij}$  in Eq. (1) is symmetric; i.e.,

$$L_{ij} = L_{ji}, \quad (5)$$

for all pairs  $i, j$ .

It is assumed throughout this article that the thermodynamical fluxes are independently variable, i.e., free from constraints such as  $\sum_i J_i = 0$ . Modifications necessary when fluxes and forces are redundant are discussed by Meixner<sup>6</sup> and by Hooyman and de Groot.<sup>7</sup>

Equation (3) yields the following expression for the time derivative of the entropy:

$$\dot{S} = \sum_{i=1}^n \sum_{j=1}^n g_{ij} \dot{a}_i a_j. \quad (6)$$

On comparing this expression with Eqs. (2) and (4), we see that in order for the fluxes  $J_i$  and the forces  $X_i$  in Eq. (1) to obey Eqs. (2)-(4) of the hypothesis of the reciprocity theorem of Onsager, it is *necessary* that

$$\dot{S} = \sum_{i=1}^n X_i J_i. \quad (7)$$

Now, the fact that Eq. (7) follows from Eqs. (2)-(4) does not mean that the reciprocity theorem of Onsager implies the validity of Eq. (5) for all thermodynamical forces and fluxes which obeys Eqs. (1) and (7). For, even if we ignore the requirement that the fluxes be related to variables which are even functions of atomic velocities, Eqs. (1) and (7) are *not sufficient* for the validity of Eqs. (2)-(4). Merely to exhibit the bilinear form (7) for the production of entropy and to assume its entries  $J_i$  and  $X_i$  linearly related does not imply that the  $J_i$  are time derivatives of thermodynamic variables  $a_i$  or that the  $X_i$  are determined by Eq. (4). Although this point seems to have been realized by Casimir<sup>2</sup> in 1945, and although his work is mentioned in recent texts,<sup>8,9</sup> the recent literature<sup>10</sup> still abounds with indiscriminate selections of factors  $J_i$  and  $X_i$  in Eq. (7) on the basis, apparently, of physical intuition, with no reference to the requirements (2)-(4).

It is not the purpose of the present communication either to confirm or to criticize the Onsager reciprocity theorem itself, but rather to remark that the notion that Eqs. (1) and (7) imply Eq. (5) is self-contradictory.

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<sup>1</sup> L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

<sup>2</sup> H. B. Casimir, Revs. Modern Phys. **17**, 343 (1945).

<sup>3</sup> S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951) Chap. I, Sec. 2, pp. 5-9.

<sup>4</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, New York, 1954), Chap. 11, Sec. 2a, pp. 705-708.

<sup>5</sup> The modifications required when some of the  $a_i$  are odd functions of the velocities are given by Casimir (see footnote 2).

<sup>6</sup> J. Meixner, Ann. Physik (5) **43**, 244 (1943).

<sup>7</sup> G. J. Hooyman and S. R. de Groot, Physica **21**, 73 (1955).

<sup>8</sup> See de Groot (footnote 3), Chap. IV, Sec. 18, p. 41.

<sup>9</sup> See Hirschfelder *et al.* (footnote 4), p. 708, for an indirect reference.

<sup>10</sup> See the discussions in de Groot (footnote 3) of *ordinary diffusion* (Chap. VIII, Sec. 48) and the *Soret effect* (Chap. VIII, Sec. 49). The "Onsager reciprocal relations" derived in the discussion of *momentum transport* on page 710 of Hirschfelder *et al.* (footnote 4) have not been shown to be connected in any way with "microscopic reversibility"; of course, the relations derived there are long familiar consequences of the fact that the response of a fluid is the same for all observers.

Suppose that  $J_i$  and  $X_i$  are thermodynamical fluxes and forces which obey Eqs. (1), (7), and (5). We shall show that by linear combination of the  $J_i$  and  $X_i$  we can always construct new fluxes  $J_i'$  and forces  $X_i'$  which obey Eqs. (1) and (7),

$$J_i' = \sum_{j=1}^n L_{ij}' X_j', \quad (1')$$

$$\sum_{i=1}^n X_i' J_i' = \sum_{i=1}^n X_i J_i = \dot{S}, \quad (7')$$

but yet have a *nonsymmetric* matrix  $\|L_{ij}'\|$  of phenomenological coefficients  $L_{ij}'$ . Indeed, we can do this in an infinite number of ways. For, let  $\|W_{ij}\|$  be any nonzero  $n \times n$  skew matrix; i.e., let the components of  $\|W_{ij}\|$  be such that for all pairs  $i, j = 1, 2 \dots n$ ,

$$W_{ij} = -W_{ji} \quad (8)$$

and for at least one such pair with  $j \neq i$  let  $W_{ij} \neq 0$ . Consider the set of fluxes  $J_i'$  and forces  $X_i'$  defined as follows:

$$J_i' = J_i + \sum_{j=1}^n W_{ij} X_j \quad (9)$$

$$X_i' = X_i \quad (10)$$

for all  $i, j = 1 \dots n$ . Then

$$\sum_{i=1}^n J_i' X_i' = \sum_{i=1}^n J_i X_i + \sum_{i=1}^n \sum_{j=1}^n W_{ij} X_j X_i. \quad (11)$$

The second term on the right in Eq. (11) is the trace of the product of a skew matrix  $\|W_{ij}\|$  with a symmetric matrix  $\|X_j X_i\|$ , and hence, by a well-known theorem of algebra, is zero. Thus, the  $J_i'$  and  $X_i'$  obey Eq. (7'). Furthermore, our assumption that the  $X_i$  and  $J_i$  obey Eq. (1) and the definitions (9) and (10) yield

$$J_i' = \sum_{j=1}^n L_{ij} X_j + \sum_{j=1}^n W_{ij} X_j = \sum_{j=1}^n (L_{ij} + W_{ij}) X_j'. \quad (12)$$

On comparing Eq. (12) with Eq. (1') we see that the  $J_i'$  and  $X_i'$  also obey Eq. (1'), with a matrix  $\|L_{ij}'\|$  which is given by

$$\|L_{ij}'\| = \|L_{ij}\| + \|W_{ij}\|. \quad (13)$$

Since  $\|L_{ij}'\|$  is the sum of a symmetric matrix  $\|L_{ij}\|$  and a nonzero skew matrix  $\|W_{ij}\|$ ,  $\|L_{ij}'\|$  is nonsymmetric. Thus, for every choice of forces and fluxes which obey Eqs. (1), (7), and (5), there exist infinitely many choices of forces and fluxes which also obey Eqs. (1) and (7) but which do not obey Eq. (5).

The argument given in the foregoing is reversible in the following sense. Let  $J_i$  and  $X_i$  be thermodynamical fluxes and forces obeying Eqs. (1) and (7) but not Eq. (5). Then, the nonsymmetric matrix  $\|L_{ij}\|$  has a

unique decomposition into the sum of a symmetric matrix  $\|D_{ij}\|$  and a nonzero skew matrix  $\|W_{ij}\|$ :

$$\|L_{ij}\| = \|D_{ij}\| + \|W_{ij}\|. \quad (14)$$

Let us define a new set of fluxes  $J_i^*$  and forces  $X_i^*$  as follows:

$$J_i^* = J_i - \sum_{j=1}^n W_{ij} X_j \quad (15)$$

$$X_i^* = X_i. \quad (16)$$

We have

$$\sum_{i=1}^n J_i^* X_i^* = \sum_{i=1}^n J_i X_i - \sum_{i=1}^n \sum_{j=1}^n W_{ij} X_j X_i = \sum_{i=1}^n J_i X_i;$$

i.e., the  $J_i^*$  and  $X_i^*$  obey Eq. (7). From the assumption that the  $J_i$  and  $X_i$  obey Eq. (1), and from Eqs. (15) and (16), we get

$$J_i^* = \sum_{j=1}^n L_{ij} X_j - \sum_{j=1}^n W_{ij} X_j = \sum_{j=1}^n (D_{ij} + W_{ij}) X_j - \sum_{j=1}^n W_{ij} X_j = \sum_{j=1}^n D_{ij} X_j^*;$$

i.e., the fluxes  $J_i^*$  are related to the forces  $X_i^*$  through Eq. (1), but with a symmetric matrix  $\|D_{ij}\|$  of phenomenological coefficients. Thus, corresponding to any linear phenomenological relation with a nonsymmetric matrix it is possible, by a mere linear combination of forces and fluxes, to find another yielding the same production of entropy and having a symmetric matrix.

Since any linear phenomenological relation may be replaced by an equivalent one with a symmetric matrix, it might be thought that a phenomenological meaning for Onsager's theorem could be found in some special property of the symmetric case. This is not so. Meixner<sup>11</sup> has shown that if Eqs. (7), (1), and (5) hold for one set of fluxes  $J_i$  and forces  $X_i$ , then there exist infinitely many other choices of fluxes  $J_i^*$  and forces  $X_i^*$  also satisfying Eqs. (7), (1), and (5). To find  $J_i^*$  and  $X_i^*$  with this property one may use the equations

$$X_i^* = \sum_{k=1}^n A_{ik} X_k \quad (17)$$

$$J_i^* = \sum_{k=1}^n \tilde{A}_{ik}^{-1} J_k, \quad (18)$$

where  $\|A_{ik}\|$  is an arbitrary invertible (nonsingular)

<sup>11</sup> See Meixner (footnote 6). For a review of this matter, see Sec. 8 of J. Meixner and H. G. Reik, "Thermodynamik der irreversiblen Prozesse," *Handbuch der Physik* (Springer-Verlag, Berlin, 1959), Vol. 3, Part 2.

matrix and  $\|\tilde{A}_{ik}^{-1}\| = \|A_{ki}\|^{-1}$ . Indeed,

$$X_i^* J_i^* = \sum_{k=1}^n \sum_{l=1}^n A_{ik} X_k \tilde{A}_{il}^{-1} J_l = \sum_{k=1}^n \sum_{l=1}^n \delta_{kl} X_k J_l = \sum_{k=1}^n X_k J_k,$$

and if the  $J_i, X_i$  obey Eq. (1), then so do the  $X_i^*, J_i^*$ , with a matrix of phenomenological coefficients  $L_{ij}^*$  which is the solution of

$$\sum_{l=1}^n \sum_{k=1}^n \tilde{A}_{ik} L_{kl}^* A_{lj} = L_{ij};$$

i.e.,

$$\|L_{ij}^*\| = \|\tilde{A}_{ik}\|^{-1} \|L_{kl}\| \|A_{lj}\|^{-1}. \tag{19}$$

This congruence transformation clearly preserves the symmetry of  $\|L_{ik}\|$ .

If the matrix  $\|L_{ij}\|$  in Eq. (1) is invertible, as is usually assumed, then Eqs. (9) and (10), and also (15) and (16), may be regarded as representing *linear transformations* carried out separately on the fluxes and forces, rather than as defining new forces and fluxes by joint linear combinations of the old. For example, Eqs. (9) and (10) may be written

$$J_i' = \sum_{k=1}^n B_{ik} J_k \tag{9'}$$

$$X_i' = \sum_{k=1}^n C_{ik} X_k, \tag{10'}$$

where

$$\|B_{ik}\| = \|\delta_{ik}\| + \|W_{ij}\| \|L_{jk}\|^{-1} \tag{20}$$

and

$$\|C_{ik}\| = \|\delta_{ik}\|. \tag{21}$$

Of course, Eqs. (20) and (21) make the linear transformations given by Eqs. (9') and (10') of a different kind from those given by Eqs. (17) and (18), and this is why Eqs. (9') and (10') are able to destroy the symmetry of  $\|L_{ij}'\|$ . It is easy to show that in order for the linear transformations of the form shown in Eqs. (9') and (10') to be compatible with Eqs. (2)-(4), with  $S$  being kept invariant, it is necessary and sufficient that the matrices  $\|B_{ik}\|$  and  $\|C_{ik}\|$  be related as follows:

$$\|B_{ik}\| = \|C_{ki}\|^{-1}. \tag{22}$$

In other words, if we take Eqs. (1)-(4) as the hypothesis of Onsager's theorem, then the choice of the fluxes and forces is greatly limited, and, in fact, if we change the forces and fluxes by linear transformations, the transformations must be of the type discussed by Meixner and exhibited in Eqs. (17) and (18). Such transformations preserve the symmetry of  $\|L_{ik}\|$ . Hence, a reciprocity theorem based on Eqs. (1)-(4) does not suffer from the logical defects of one based on Eqs. (1) and (7).

In summary, it seems, in phenomenological theories based on Eqs. (7) and (1) alone, there is no content in the statement that  $\|L_{ij}\|$  is or is not symmetric. Of the two alternative phenomenological treatments of Onsager's theorem to be found in the current literature, only in that based upon Eqs. (1)-(4) may any physical interpretation be found. In many applications, such as the theory of diffusion, there is no evidence that Eqs. (2) and (4) are satisfied. It is notorious that phenomenological theories of various kinds easily yield a relation of the type (7), while relations of the type (2)-(4) are more difficult to establish. Of course, it is possible that some other choice of fluxes might also lead to Eq. (5). But until the forces and fluxes in any particular case, are *physically identified* by some property more specific than their mere entry into the bilinear form (7), application of Onsager's theorem is precarious.

We close with some remarks on "minimum dissipation principles." Consider a quadratic form  $\Phi$  characterized by a symmetric matrix  $\frac{1}{2}R_{ij}$ :

$$\Phi(J_k) = \frac{1}{2} \sum_{j=1}^n \sum_{i=1}^n R_{ij} J_i J_j.$$

Of course, *any* quadratic form can be characterized in such a manner by a *symmetric* matrix. We now note that the statement

$$\dot{S} - \Phi(J_k) = \text{extremum}, \tag{23}$$

i.e.,

$$\delta\{\dot{S} - \Phi(J_k)\} = 0, \tag{24}$$

has no meaning until the manner in which  $\dot{S}$  is assumed to depend on the variables  $J_k$  is specified. If, in particular, we agree to take  $\dot{S}$  as given by Eq. (7) and also to hold the forces  $X_i$  constant in computing the variation, then Eq. (24) is equivalent to

$$\sum_{i=1}^n \{(\delta J_i)(X_i - \sum_{j=1}^n R_{ij} J_j)\} = 0. \tag{25}$$

Equation (25) is equivalent in turn to

$$X_i = \sum_{j=1}^n R_{ij} J_j. \tag{26}$$

Now, if we add the usual assumption that  $R_{ij}$  is non-singular, Eq. (26) is equivalent to Eqs. (1) and (5). On the other hand, if we assume that  $\dot{S}$  is given by Eq. (6), with  $\dot{a}_i = J_i$ , and if in Eq. (24) we agree to hold  $\sum_{ij} g_{ij} \dot{a}_i$  constant in computing the variations, then it can easily be shown that Eq. (24) is equivalent to the assertion that Eqs. (1)-(4) imply Eq. (5).

It has just been shown that two different variational principles arising from Eq. (24) lead to a linear phenomenological relation with a symmetric matrix. The

latter principle is precisely equivalent to the formulation in terms of conjugate variables, mentioned at the beginning of the paper. The former, which includes the latter as a special case, is precisely equivalent to the bare assertion of symmetry, shown before to be meaningless unless the variables are identified by some property beyond their mere entry into the bilinear form (7). Thus the principles of minimum dissipation do not in themselves offer any basis for symmetry beyond whatever is present in a direct treatment.

We remark also that the variational principle based on Eqs. (24) and (7) alone is really an infinite family of principles. For each different possible choice of forces and fluxes in Eq. (7), a different set of quantities is held constant in the variations. This fact makes the arbitrariness of the result still more plain and casts further light upon the need for physical identification of forces

and fluxes is a self-consistent statement of "Onsager relations" is to be found.<sup>12</sup>

<sup>12</sup> *Note added in proof.* There is earlier literature on the difficulties noted here. In attempt to demonstrate "an error in the calculation of Meixner," J. E. Verschaffelt, *Bull. Cl. Sci. Acad. R. Belg.* **37**, 853 (1951) gave an example of a linear transformation preserving the production of entropy but destroying the symmetry of linear phenomenological relations. R. O. Davies, *Physica* **18**, 182 (1952), in an attempt to answer Verschaffelt, exhibited a general class of such transformations, including as a special case our Eqs. (20) and (21), but claimed that those destroying the symmetry "can be of no physical importance." Hooyma, de Groot, and Mazur, *Physica* **21**, 360 (1955) deny Davies' physical argument but try to straighten the matter out by formulating in more general terms a rule such as Eq. (4) of the present paper for defining the force conjugate to a given flux. Their method is open to the objection raised above. In concrete situations, such as diffusion, to which "irreversible thermodynamics" is said to apply, the variables actually used have never been shown to obey their Eq. (17). Without that equation, their analysis falls back to Meixner's.

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## Quantum Yield for Energy Transfer by Resonance

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The theoretical prediction of quantum yields for electric dipole-dipole energy transfer by resonance is discussed. The common approximation which neglects transfers from each donor to all but the nearest acceptor is extended so as to include transfers to the second-nearest acceptor and, in the limit of very high acceptor concentration, to the third and fourth as well. The total quantum yield and the fractional yields due to transfers to the individual categories of nearest acceptors are evaluated, and the merits of the various approximations are discussed quantitatively.

**T**HE present theoretical discussion concerns the phenomenon of transfer of electronic excitation energy by the mechanism of electrodynamic resonance. The initially excited energy donors (sensitizers) and the potential acceptors (activators) may be atoms or molecules distributed throughout a given medium.

Mathematical discussions in this field are frequently based on the simplifying assumption that one arrives at essentially correct quantitative predictions of observable effects if one considers energy transfer from each donor to its nearest acceptor only. This "first approximation" is, naturally, a satisfactory one when applied to systems in which the acceptor concentration is very low.<sup>1</sup> In the case of concentration depolarization of fluorescence, a slight modification of the approximation in question seems to justify an extension of its applicability to the so-called critical concentration range.<sup>2</sup> In the theory of resonance transfer of energy in

crystals, moreover, first-order transfer yields have been considered adequate<sup>3-5</sup> on the ground that the rapid decrease of the transfer probability with increasing interparticle separation would render improbable transfers to all but nearest acceptors.<sup>4</sup> The assumed random distribution of energy acceptors makes this argument not entirely convincing, however. The importance of transfers to other acceptors will be demonstrated in the following.

We shall discuss quantitatively the merits of the first approximation and of the next one in which the possibility of transfer to the second-nearest acceptor is taken into account. In the limit of very high acceptor concentration we shall include transfers to up to four nearest acceptors ( $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$ ) as counted from each donor. In each case we shall, in addition, evaluate the individual contributions to the average total

<sup>1</sup> Th. Förster, (a) *Ann. Physik* **2**, 55 (1948); (b) *Fluoreszenz organischer Verbindungen* (Vandenhoeck and Ruprecht, Göttingen, 1951), pp. 172-180.

<sup>2</sup> A. Ore, *J. Chem. Phys.* **31**, 442 (1959).

<sup>3</sup> D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).

<sup>4</sup> D. L. Dexter and J. H. Schulman, *J. Chem. Phys.* **22**, 1063 (1954).

<sup>5</sup> S. C. Ganguly and N. K. Chaudhury, *Revs. Modern Phys.* **31**, 990 (1959).