

TRANSFORMATION PROPERTIES OF THE ONSAGER RELATIONS

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Synopsis

The invariance of the Onsager reciprocal relations under simultaneous linear transformations of the fluxes and forces occurring in the expression for the entropy production is investigated for the cases of scalar phenomena and of vectorial phenomena (heat conduction and diffusion).

The connection between these transformations follows in a natural way from the invariance of the deviation of the entropy from its equilibrium value. The latter condition rather than the invariance of the entropy production guarantees the invariance of the Onsager relations.

§ 1. *Introduction.* In thermodynamics of irreversible processes ^{1) 2)} the entropy production can generally be written as a sum of products of fluxes and corresponding forces, between which linear relationships are assumed. For the scheme of phenomenological coefficients occurring in these equations the Onsager reciprocal relations hold.

M e i x n e r ³⁾ has been the first to investigate the invariance of the Onsager relations under simultaneous linear transformations of the fluxes and forces. With a given linear transformation of the fluxes, the linear transformation of the forces is derived from the invariance of the entropy production and with the help of these transformation formulae the invariance of the Onsager relations is established (*cf.* also ¹⁾ § 78).

However, as D a v i e s ⁴⁾ has pointed out, if the transformations are only subject to the condition of leaving the entropy production invariant, they also include transformations which destroy the Onsager relations. V e r s c h a f f e l t ⁵⁾ previously had given an example.

It is the purpose of this paper to show that the latter type of transformations should be discarded. As a starting point we will take the expression for the deviation of the entropy from its equilibrium value. Then M e i x n e r's result for the connection between the transformation formulae and the invariance of the Onsager relations follow in a natural way.

The same idea is implicit in a paper by P r i g o g i n e ⁶⁾ where he discusses the invariance of the Onsager relations for transformations between 'equivalent systems of chemical reactions'.

§ 2. *Treatment based on the invariance of the entropy production.* In the scheme of thermodynamics of irreversible processes^{1) 2)} the entropy production σ (per unit volume per unit time) can generally be written as a sum of products of a number of independent fluxes J_i (together called j in matrix notation) and corresponding forces X_i (in matrix notation x)

$$\sigma = \tilde{j}x, \quad (1)$$

where the symbol \sim indicates the transposed matrix. Linear relationships are assumed between the fluxes and forces, which we can write as

$$j = Lx. \quad (2)$$

The Onsager reciprocal relations state that the matrix L of phenomenological coefficients be symmetric

$$\tilde{L} = L. \quad (3)$$

We now consider a linear transformation of the fluxes

$$j' = Pj, \text{ with } \det P \neq 0, \quad (4)$$

and a simultaneous transformation of the forces

$$x' = Qx. \quad (5)$$

In the treatment given by M e i x n e r³⁾ and D e G r o o t¹⁾ the matrix Q is generally derived from the condition that the expression (1) for σ remain invariant

$$\sigma = \tilde{j}x = \tilde{j}'x'. \quad (6)$$

From (4), (5) and (6) it is then concluded that

$$Q = \tilde{P}^{-1}. \quad (7)$$

With (7) the phenomenological equations (2) transform into

$$j' = L'x' = PL\tilde{P}x', \quad (8)$$

and the Onsager relation (3) is seen to be invariant since

$$L' = PL\tilde{P} = \tilde{L}'. \quad (9)$$

However, as D a v i e s⁴⁾ has pointed out, the condition that the expression for σ be invariant does not uniquely lead to (7). As a matter of fact, from this condition alone a more general solution for the matrix Q can be found, which includes (7) as a special case. This can be seen by inserting the phenomenological equation (2) in the entropy production (1)

$$\tilde{j}x = \tilde{x}\tilde{L}x \quad (10)$$

and likewise

$$\tilde{j}'x' = \tilde{j}\tilde{P}Qx = \tilde{x}\tilde{L}\tilde{P}Qx. \quad (11)$$

The condition (6) thus leads to

$$\tilde{L} = \tilde{L}\tilde{P}Q + A \text{ or } PL = \tilde{Q}^{-1}(L + A), \quad (12)$$

where A is an arbitrary antisymmetric matrix

$$\tilde{A} = -A, \quad (13)$$

which may differ from zero. The transformed matrix L' follows from (2), (4), (5) and (12)

$$L' = PLQ^{-1} = \tilde{Q}^{-1}(L + A)Q^{-1}. \quad (14)$$

In view of (3) it is thus seen that L' will contain a symmetric part $\tilde{Q}^{-1}LQ^{-1}$ but also an antisymmetric part $\tilde{Q}^{-1}AQ^{-1}$ and so the Onsager relation will break down unless one takes $A = 0$ as was done in (7) and (9).

D a v i e s showed that it is the including of the antisymmetric matrix A which has led V e r s c h a f f e l t⁵⁾ to an example of a linear transformation which leaves the entropy production invariant and yet which destroys the Onsager reciprocal relations. In this example P is taken unity and Q equals $1 - L^{-1}A$. In his note D a v i e s argues that such transformations can be of no physical importance since they depend explicitly on the phenomenological coefficients contained in L and from this argument he concludes the restriction to the case $A = 0$.

However, D a v i e s does not make it clear why the dependence of the transformation matrix on the phenomenological coefficients should be physically meaningless. Actually, there is no reason why such a dependence should be excluded and there exists a number of important cases in which transformations of this type are applied successfully, *e.g.*, in the theories of the thermomolecular pressure difference, the thermomechanical effect, the Soret effect and the Dufour effect, where the transformation matrices contain so-called quantities of transfer depending on the phenomenological coefficients (for examples of these cases, *cf.* 1) ?).

Yet, the connection between the transformations P and Q of fluxes and forces should be as given in (7) and the antisymmetric matrix A should be taken zero. The reason is that the proper condition for these transformations is the invariance of the *deviation of the entropy* from its equilibrium value. If this condition is satisfied, the invariance of the *entropy production* as well as the invariance of the Onsager relations are easily deduced, as will be shown in the following.

§ 3. *Transformation properties derived from the expression for the deviation of the entropy.* We consider an adiabatically insulated system, the thermodynamical state of which is described by a number n of independent variables which are continuous functions of space and time coordinates. The deviations of these variables from their thermostatic equilibrium values are

denoted by $a_i (i = 1, \dots, n)$. Since the entropy S of the system has a maximum in the thermostatic state, the deviation ΔS of the entropy from its equilibrium value can be written as ^{8) 9)}

$$\Delta S = -\frac{1}{2} \iint \sum_{i=1}^n \sum_{k=1}^n a_i(\mathbf{r}) g_{ik}(\mathbf{r}, \mathbf{r}') a_k(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (15)$$

where of course

$$g_{ik}(\mathbf{r}, \mathbf{r}') = g_{ki}(\mathbf{r}', \mathbf{r}), \quad (16)$$

\mathbf{r} and \mathbf{r}' denoting coordinate vectors. Introducing the quantities

$$X_j(\mathbf{r}) \equiv \partial \Delta S / \partial a_j(\mathbf{r}) = -f \sum_k g_{jk}(\mathbf{r}, \mathbf{r}') a_k(\mathbf{r}') d\mathbf{r}', \quad (j = 1, \dots, n), \quad (17)$$

we can write

$$\Delta S = \frac{1}{2} f \sum_i a_i(\mathbf{r}) X_i(\mathbf{r}) d\mathbf{r} \quad (18)$$

and the time derivative $\dot{\Delta S}$ (the entropy production per unit time) is given by

$$\dot{\Delta S} = f \sum_i \dot{a}_i(\mathbf{r}) X_i(\mathbf{r}) d\mathbf{r}. \quad (19)$$

In the same way the system could be described by a new set of state variables $a_i(\mathbf{r})$ which are related to the original variables $a_i(\mathbf{r})$ in the following way

$$a_i(\mathbf{r}) = \sum_{j=1}^n P_{ij} a_j(\mathbf{r}) \text{ or } a_i(\mathbf{r}) = \sum_{j=1}^n P_{ij}^{-1} a_j(\mathbf{r}), \quad (i = 1, \dots, n). \quad (20)$$

This leads to

$$\begin{aligned} \Delta S &= -\frac{1}{2} \iint \sum_{j,l} \sum_{i,k} P_{ij}^{-1} a_j(\mathbf{r}) g_{ik}(\mathbf{r}, \mathbf{r}') P_{kl}^{-1} a_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}' = \\ &= -\frac{1}{2} \iint \sum_{j,l} a_j(\mathbf{r}) h_{jl}(\mathbf{r}, \mathbf{r}') a_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (21)$$

$$\text{with } h_{jl}(\mathbf{r}, \mathbf{r}') = \sum_{i,k} P_{ij}^{-1} g_{ik}(\mathbf{r}, \mathbf{r}') P_{kl}^{-1} = h_{lj}(\mathbf{r}', \mathbf{r}). \quad (22)$$

Instead of the quantities $X_j(\mathbf{r})$ we now have quantities

$$Y_j(\mathbf{r}) \equiv \partial \Delta S / \partial a_j(\mathbf{r}) = -f \sum_l h_{jl}(\mathbf{r}, \mathbf{r}') a_l(\mathbf{r}') d\mathbf{r}' = \sum_i P_{ij}^{-1} X_i(\mathbf{r}), \quad (23)$$

which shows how the $X_j(\mathbf{r})$ are transformed.

Analogous to (18) and (19) we find

$$\Delta S = \frac{1}{2} f \sum_i a_i(\mathbf{r}) Y_i(\mathbf{r}) d\mathbf{r}, \quad (24)$$

$$\dot{\Delta S} = f \sum_i \dot{a}_i(\mathbf{r}) Y_i(\mathbf{r}) d\mathbf{r}. \quad (25)$$

The present theory could be developed for arbitrary combinations of scalar, vectorial and tensorial phenomena in anisotropic media. However, for the sake of clarity we shall only consider two special cases, *viz.*, scalar irreversible processes (chemical reactions, relaxation phenomena) and vectorial ones (heat conduction and diffusion).

A. Transformations between scalar phenomena.

If only scalar processes occur the state variables are uniform throughout the

system and the expression for the entropy production in local form follows from (19) and (25)

$$\sigma = \sum_i \dot{a}_i X_i = \sum_i \dot{a}_i Y_i. \quad (26)$$

The quantities \dot{a}_i and X_i are the irreversible fluxes and the forces occurring in equation (1). From the foregoing it is clear that the transformation of the forces (23) logically follows from the transformation of the fluxes and the expression for ΔS . Comparing (20) with (23) we see that these transformations are connected in the way of equation (7) and that no antisymmetric matrix (as in (12)) can occur. The transformation also leaves the entropy production invariant.

Since the Onsager theory can be applied in terms of the variables a_i as well as in terms of the variables a_i , the invariance of the validity of the Onsager reciprocal relations is guaranteed beforehand. In order to prove it explicitly we consider the phenomenological equations in both descriptions

$$\dot{a}_i = \sum_j L_{ij} X_j, \quad (27)$$

$$\dot{a}_i = \sum_j M_{ij} Y_j. \quad (28)$$

With the help of (20) and (23) we find

$$M_{ij} = \sum_{k,l} P_{ik} L_{kl} P_{jl}. \quad (29)$$

The symmetry of the M_{ij} scheme then immediately follows from the symmetry of the L_{ij} and *vice versa*.

B. Transformations between vectorial phenomena. In the case of vectorial phenomena the irreversible fluxes are no longer time derivatives of thermodynamic state variables nor are the thermodynamic forces given by such linear expressions in these variables as occur in (17). The connection between the thermodynamic fluxes and the state variables is now given by the conservation laws (*e.g.*, of mass and energy) and in the absence of scalar processes (*e.g.*, for diffusion and heat conduction at constant volume) we can write

$$\partial a_i / \partial t = - \operatorname{div} \mathbf{J}_i, \quad (i = 1, \dots, n), \quad (30)$$

where \mathbf{J}_i is the flux connected with the state variable a_i . Thus (19) can be rewritten as

$$\Delta S = - \int \sum_i X_i(\mathbf{r}) \operatorname{div} \mathbf{J}_i(\mathbf{r}) d\mathbf{r} = \int \sum_i \mathbf{J}_i(\mathbf{r}) \cdot \operatorname{grad} X_i(\mathbf{r}) d\mathbf{r}, \quad (31)$$

where we have applied Gauss' theorem and the fact that the flows \mathbf{J}_i vanish at the boundary of the system. The integrand on the right-hand side of (31) is the entropy production σ per unit time and volume¹⁾

$$\sigma(\mathbf{r}) = \sum_i \mathbf{J}_i(\mathbf{r}) \cdot \operatorname{grad} X_i(\mathbf{r}). \quad (32)$$

The thermodynamic force conjugated to the flow $\mathbf{J}_i(\mathbf{r})$ is now $\text{grad } X_i(\mathbf{r})$. With the linear transformation (20) of the state variables the expression (19) for ΔS transforms into (25). The conservation laws (30) transform into

$$\partial a_i / \partial t = -\text{div } \mathbf{I}_i, \quad (i = 1, \dots, n), \quad (33)$$

with

$$\mathbf{I}_i(\mathbf{r}) = \sum_j P_{ij} \mathbf{J}_j(\mathbf{r}). \quad (34)$$

In the same way as (31) followed from (19) with the help of (30), so (25) and (33) lead to

$$\Delta S = \int \sum_i \mathbf{I}_i(\mathbf{r}) \cdot \text{grad } Y_i(\mathbf{r}) d\mathbf{r}, \quad (35)$$

where

$$\text{grad } Y_i(\mathbf{r}) = \sum_j P_{ji}^{-1} \text{grad } X_j(\mathbf{r}), \quad (36)$$

and the local expression for the entropy production is

$$\sigma(\mathbf{r}) = \sum_i \mathbf{I}_i(\mathbf{r}) \cdot \text{grad } Y_i(\mathbf{r}). \quad (37)$$

Again, the transformations (34) and (36) of the fluxes and the forces, resp., are connected in the way of equation (7) and $\sigma(\mathbf{r})$ is invariant.

The Onsager theory (as extended by two of us ⁸⁾) could again be applied in both descriptions and the invariance of the Onsager reciprocal relations is guaranteed beforehand. This is also seen explicitly from the phenomenological equations

$$\mathbf{J}_i = \sum_j \mathbf{L}_{ij} \cdot \text{grad } X_j, \quad (38)$$

$$\mathbf{I}_i = \sum_j \mathbf{M}_{ij} \cdot \text{grad } Y_j, \quad (39)$$

where the \mathbf{L}_{ij} and \mathbf{M}_{ij} are tensors of the second order. The Onsager relations state that in the absence of a magnetic field or an over-all rotation of the system

$$\mathbf{L}_{ij} = \mathbf{L}_{ji}^\dagger, \quad (40)$$

where the symbol \dagger indicates transposing of the Cartesian coordinates. In view of (34), (36), (38) and (39) we have

$$\mathbf{M}_{ij} = \sum_{k,l} P_{ik} \mathbf{L}_{kl} P_{jl}, \quad (41)$$

so that the Onsager relation

$$\mathbf{M}_{ij} = \mathbf{M}_{ji}^\dagger \quad (42)$$

follows from (40) and conversely.

In the foregoing treatment the transformation matrix P_{ij} is supposed to be uniform throughout the system. In practice, P_{ij} might depend explicitly on the phenomenological coefficients contained in \mathbf{L}_{ij} which are functions of the state variables and thus of space coordinates. However, since the Onsager theory is based on expressions for ΔS which are quadratic in the state variables we can restrict ourselves to coefficients P_{ij} which are functions only of the equilibrium values of the state parameters (compare

equation (15) with (21)). In the absence of external fields these equilibrium values are uniform throughout the system and the above treatment is justified. If the system is placed in an external field, the state parameters need not be uniform. If then the P_{ij} are slowly varying functions of space coordinates (as is generally the case) the whole treatment can be applied to small subsystems where P_{ij} can be taken uniform.

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