

# ONSAGERS'S RECIPROCAL RELATIONS AND THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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Received: March 10, 1997

## Abstract

A critical assessment is presented of ONSAGER's original derivation of reciprocal relations. These relations hold if the irreversible fluxes (time derivatives of state variables) are linear functions of the driving forces, but the latter may themselves be nonlinear functions of the state variables. This is an example amongst others of nonlinear behaviour that falls within the framework of (quasi) linear thermodynamics of irreversible processes. The discussion includes the variation principle of the least dissipation of energy.

*Keywords:* Onsager's relation, thermodynamics, irreversible processes.

## 1. Introduction

At a meeting of which a main theme is formed by reciprocal relations for irreversible processes within the framework of *nonlinear thermodynamics* it may be desirable to take once again a look at *Onsager's reciprocal relations* in order to ascertain how far *their* validity is limited to a strictly linear theory.

ONSAGER's reciprocal relations were the culmination, at the time of their establishment, of a long history [1], which has its roots in the first half of the nineteenth century when interest arose in heat conduction in crystals. Both DUHAMEL [2] in 1828, and STOKES [3] in 1851, studied this phenomenon from a theoretical point of view and came for different reasons and without absolutely convincing arguments to the conclusion that the heat conductivity tensor should be symmetric. Experimentally this conjecture was confirmed by SORET [4] and more accurately by VOIGT [5]

In the meantime, W. THOMSON [6], Lord KELVIN, had established in 1854 a reciprocal relation for thermoelectric phenomena, characterizing the coupling between heat- and electric conduction in an isotropic system. To derive the reciprocal relation, THOMSON makes the assumption, which he considers extremely plausible, that the thermoelectric process is reversible. By similar quasi-thermodynamic arguments symmetry relations had been derived for a variety of other cases. HELMHOLTZ [7] established a relation for the crosseffects between electric conduction and diffusion, while EASTMAN [8] and WAGNER [9] found one between heat conduction and diffusion.

All these reciprocal relations were confirmed by experiment. However, the fundamental principles of thermodynamics alone were not sufficient to justify their derivations. As pointed out already by BOLTZMANN [10], the second law of thermodynamics only leads to a number of *inequalities* for the coefficients occurring in the phenomenological equations.

ONSAGER published his derivation of reciprocal relations in two papers in 1931 [11]. He had already announced the essential result that these relations could be derived without reference to a particular case from the principle of microscopic reversibility at two meetings [12] in 1929 and 1930. But this major achievement remained largely without response for a surprising number of years. It finally gained wider acceptance as a result also of a paper by CASIMIR [13]. In this paper CASIMIR presents a streamlined and compact version of ONSAGER's derivation, which is the one generally presented and which we therefore shall review here.

## 2. Derivation of ONSAGER's Reciprocal Relations

Consider an adiabatically insulated and aged system, characterized by the fluctuations  $\alpha_i (i = 1, 2, \dots, n)$  of a set of (macroscopic) variables with respect to their equilibrium, or most probable, values. The entropy  $S$  of the system has a maximum  $S_0$  at equilibrium so that  $\Delta S = S - S_0$  can be written as a quadratic expression

$$\Delta S = -\frac{1}{2} \sum_{i,k}^n g_{ik} \alpha_i \alpha_k, \quad g_{ik} = -\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_k}, \quad (1)$$

where  $g_{ik}$  is a positive definite form. With Boltzmann's entropy postulate one has for the probability density of the  $\alpha_i$

$$f(\alpha_1, \dots, \alpha_n) = f(0, \dots, 0) e^{\Delta S/k_B}, \quad (2)$$

where  $k_B$  is BOLTZMANN's constant.

ONSAGER also introduces conjugated variables

$$X_i \equiv k_B \frac{\partial \ln f}{\partial \alpha_i} = \frac{\partial \Delta S}{\partial \alpha_i} = -\sum_k g_{ik} \alpha_k \quad (3)$$

which are linear combinations of the  $\alpha_i$ .

The proof of the reciprocal relations can be given in three steps. First, it follows from the definition (3), that

$$\langle \alpha_i X_j \rangle = -k_B \delta_{ij} \quad (\delta_{ij} = 0 \text{ if } i \neq j; \delta_{ii} = 1), \quad (4)$$

where the brackets  $\langle \dots \rangle$  denote an average over the distribution function (2).

Next one must state the requirement of microscopic reversibility for the time behaviour of fluctuations in an aged system. Here ONSAGER imposes a restriction on the class of variables studied and takes only those into account which are even functions of the velocities of individual particles. To state the property of microscopic reversibility, he focuses attention on their time correlation functions. For these, time reversal invariance of the microscopic equations of motion results in the equality

$$\langle \alpha_i(t)\alpha_j(t + \tau) \rangle = \langle \alpha_j(t)\alpha_i(t + \tau) \rangle. \tag{5}$$

We now come, after the two results (4) and (5) of general statistical mechanics, to the third ingredient of ONSAGER's theory: his mean regression hypothesis. Suppose that in a certain domain, not too far from equilibrium, but not necessarily in the range of equilibrium fluctuations, the variables  $\alpha_i$  obey linear macroscopic equations

$$\frac{d\alpha_i(t)}{dt} = - \sum_j M_{ij} \alpha_j(t) = \sum_k L_{ik} X_k(t), \tag{6}$$

where the so-called ONSAGER coefficients  $L_{ik}$  are defined as

$$L_{ik} = \sum_j M_{ij} g_{jk}^{-1}, \tag{7}$$

and where the  $X_i$  are the variables conjugated to the  $\alpha_i$  according to Eq. (3). ONSAGER's hypothesis is that fluctuations evolve in the mean according to the same macroscopic laws, and that one therefore has, when evaluating a correlation function  $\langle \alpha_i(t)\alpha_j(t + \tau) \rangle$  for short time intervals  $\tau$ , according to (8)

$$\alpha_j(t + \tau) = \alpha_j(t) + \tau \sum_k L_{jk} X_k(t). \tag{8}$$

Using then Eq. (8) for both members of Eq. (5), and observing the result (6), one obtains the reciprocal relations

$$L_{ij} = L_{ji}. \tag{9}$$

In other words, the matrix of coefficients  $L_{ij}$  must be symmetric.

In this version of ONSAGER's derivation of reciprocal relations it would seem that their validity has been established for the case in which the phenomenological equations are ordinary linear differential equations in the  $\alpha$ 's and moreover the thermodynamic forces, the conjugated variables are in turn also linear functions thereof. Indeed, at the first IUPAP International Conference on Statistical Mechanics, held 1948 in Florence, CASIMIR [14] presented a paper 'On some aspects of ONSAGER's theory of reciprocal relations' in which he remarks '... in its present form ONSAGER's theory applies

only to Equations of type [of Eq. (6)]. As soon as the situation arises where the macroscopic equations are not of the type [of Eq. (6)] a new investigation becomes necessary.'

ONSAGER, who attended the conference in question offered the following comment [15]: 'Linear relations between rates of flow and driving forces (gradients of temperature and potential) are assumed in my derivation of reciprocal relations.' He then concludes his comment with a second sentence to which we will presently return.

### 3. Modified Version of ONSAGER's Derivation; Validity of Reciprocal Relations

It is not entirely clear from ONSAGER's comment whether he agrees that his theory only applies to equations of the type (6). With this in mind, we now restate the derivation given in the previous section, in a modified form. We again consider an adiabatically insulated system in the state described by the fluctuations  $\alpha_i$  of a set of macroscopic variables with respect to their equilibrium values. The entropy,  $S$ , has a maximum,  $S_0$ , at equilibrium, but  $\Delta S$  need not be a quadratic form, and can be a more general function of the  $\alpha$ 's:

$$S = S_0 + \Delta S(\alpha_1, \dots, \alpha_n) \quad \left( \frac{\partial \Delta S}{\partial \alpha_i} \right)_{\alpha=0} = 0, \quad (10)$$

The probability density of the  $\alpha_i$  is of the form (2), but with a more general function  $\Delta S(\alpha)$  in the exponent, so that the conjugated variable  $X_i$ , the thermodynamic forces, are no longer necessarily linear combinations of the  $\alpha_k$ :

$$X_i(\alpha) \equiv \frac{\partial \Delta S}{\partial \alpha_i} = k_B \frac{\partial \ln f}{\partial \alpha_i}. \quad (11)$$

It follows again from the definition that:

$$\langle \alpha_i X_j \rangle = -k_B \delta_{ij} \quad (\delta_{ij} = 0 \text{ if } i \neq j; \delta_{ii} = 1), \quad (12)$$

while the property of microscopic reversibility retains the form (cf. Eq. (5)):

$$\langle \alpha_i(t) \alpha_j(t + \tau) \rangle = \langle \alpha_j(t) \alpha_i(t + \tau) \rangle. \quad (13)$$

Suppose now that the macroscopic laws for the time rates of change of the  $\alpha_i$  are linear in the thermodynamic forces

$$\frac{d\alpha_i}{dt} = \sum_k L_{ik} X_k(t). \quad (14)$$

ONSAGER's regression hypothesis then implies that one has, in the mean, when evaluating a correlation function for small time intervals,  $\tau$ :

$$\alpha_j(t + \tau) = \alpha_j(t) + \tau \sum_k L_{jk} X_k(t). \quad (15)$$

Introducing Eq. (15) into both members of Eq. (13) one then finds, with property (12),

$$L_{ij} = L_{ji}. \quad (16)$$

The reciprocal relations are thus obtained here for the case that the macroscopic equations are linear in the thermodynamic forces, without being linear also in the state variables of which they describe the rates of change.

In the first version, the coefficients  $M_{ij}$  are the basic kinetic coefficients, and the ONSAGER coefficients  $L_{ij}$  are defined by multiplying the kinetic coefficients by the thermodynamic quantities  $g_{jk}^{-1}$ , c.f. Eqs. (1) and (7). In the modified version, the ONSAGER coefficients play themselves the role of basic phenomenological coefficients, defined by the regression laws (13).

Even though ONSAGER in the paper containing the derivation gives the quadratic form (1) (which, as he indicates, is sufficient to calculate fluctuations of the  $\alpha_i$  with the distribution function (2)), it may be argued that the derivation that is given by him is essentially identical with the modified version.

The conclusion is therefore that ONSAGER's reciprocal relations are valid for macroscopic laws, *linear in the thermodynamic forces*. It is this linearity of the dissipative laws in the driving forces which characterizes the scheme of linear thermodynamics of irreversible processes. The corresponding differential equations for the state variables are nonlinear if, as in the above derivation, the thermodynamic forces are nonlinear functions.

However, if the thermodynamic forces are linear(ized) in the variables  $\alpha_i$ , the corresponding differential equations considered above form a linear system of equations: this is the fully linearized scheme of thermodynamics of irreversible processes.

We shall return to the characteristics of linear thermodynamics of irreversible processes in our final conclusions. For the present discussion of the validity of ONSAGER's reciprocal relations, a few remarks are of more immediate relevance.

1. It has been assumed in the course of the derivation that the macroscopic laws, which hold in the mean for macroscopic values of the  $\alpha_i$ , also remain valid for initial states in the domain of an average equilibrium fluctuation. CASIMIR [13] makes the following comment: 'Of course the fact that the macroscopic laws are linear partly justifies an extrapolation to very small deviations, but in principle one may imagine a pseudolinearity holding at reasonably large amplitudes.' However, experiments in equilibrium systems have shown that time correlation functions (whose dominant contributions lie in the range of

equilibrium fluctuations) have indeed the form predicted on the basis of macroscopic laws [16].

2. Using Eq. (15) it follows that

$$\lim_{\tau \downarrow 0} \delta \langle \alpha_i(t) \alpha_j(t + \tau) \rangle / \delta \tau = -L_{ij}. \quad (17)$$

On the other hand, microscopic reversibility (cf. condition (13)) demands that  $\langle \alpha_i(t) \dot{\alpha}_j(t) \rangle = 0$ . The apparent contradiction here (which is not really there if one accepts that  $\langle \alpha_i(t) \dot{\alpha}_j(t + \tau) \rangle$  has a discontinuity at  $\tau = 0$ ) is removed if one realizes that the macroscopic laws are valid on a hydrodynamic time scale  $\tau$ , such that  $\tau_c \ll \tau \ll \tau_r$ , where  $\tau_c$  is a characteristic molecular time and  $\tau_r$  a typical macroscopic relaxation time. The linear laws (6) or (13) therefore only hold after a time lag  $\tau_0 \ll \tau_r$ . ONSAGER himself draws attention to this fact in [11] and remarks that 'for practical purposes the time lag can be neglected in all cases that are likely to be studied, and this approximation is always involved in the formulation of laws like [Eq. (13)].'

3. ONSAGER briefly mentions that in the presence of external magnetic fields  $B$  (or of Coriolis forces), when microscopic reversibility demands that particle velocities as well as fields be reversed, the reciprocal relations (15) must be modified and become

$$L_{ij}(B) = L_{ji}(-B). \quad (18)$$

Finally, he also shows that in the absence of external magnetic fields, and for the even variables considered, the reciprocal relations demanded by microscopic reversibility are equivalent to the variation principle of the least dissipation of energy. We shall discuss this principle in the next section.

#### 4. The Principle of the Least Dissipation of Energy

The quantity referred to here by ONSAGER [11] as dissipation of energy is essentially the entropy production  $\sigma$ , which for the adiabatically insulated closed system is given by:

$$\sigma = \frac{dS(\alpha)}{dt} = \sum_i \frac{\partial S}{\partial \alpha_i} \dot{\alpha}_i. \quad (19)$$

Introducing into this expression the definition of the thermodynamic forces (11) as well as the macroscopic laws (14) we obtain for  $\alpha$  the positive quadratic form:

$$\sigma = \sum_i \dot{\alpha}_i X_i(\alpha) = \sum_{i,j} L_{ij} X_i X_j. \quad (20)$$

With this quadratic form in the thermodynamic forces  $X_i$ , ONSAGER shows that a general principle of 'least dissipation of energy holds for the macroscopic phenomenological equations, if the reciprocal relations are obeyed.'

For the purpose of demonstration one defines the function  $P$

$$P = 2 \sum_i \dot{\alpha}_i X_i - \sum_{i,j} L_{ij} X_i X_j . \tag{21}$$

The extremum of this function for given fluxes,  $\dot{\alpha}$ , and with respect to variations of the thermodynamic forces, is determined by the conditions

$$\dot{\alpha}_i - \frac{1}{2} \sum_j (L_{ij} + L_{ji}) X_j = 0 . \tag{22}$$

These conditions are equivalent to the macroscopic laws when the reciprocal relations (16) are satisfied.

As a special case of this principle ONSAGER then observes that reciprocal relations must hold if one demands that the entropy production has an extremum at the stationary state (a statement which is the converse of PRIGOGINE's[17] well-known theorem of minimum entropy production). This then provides an explanation for the fact that quasi thermodynamic theories led to correct reciprocal relations: THOMSON's hypothesis [6] that the thermoelectric effect is reversible, is tantamount to demanding that the entropy production for this phenomenon has a minimum at the stationary state when no electric current flows.

It should however be noted and must be emphasized that the equivalence between the reciprocal relations and the variation principle breaks down in the presence of an external magnetic field, so that the variational requirement cannot replace the more fundamental principle of microscopic reversibility in the derivation of these relations.

### 5. Concluding Remarks

We have seen above that ONSAGER's reciprocal relations are valid for *dissipative laws (fluxes), linear in the thermodynamic forces,* and that this linearity is compatible with a nonlinearity of the forces in the state variables which leads to nonlinear differential equations for the latter.

It was shown later [18] that *for transport processes* reciprocal relations can also be derived within the framework of the kinetic theory of gases, and follow again from microscopic reversibility (of the binary collision process). Although the class of systems for which the derivation holds is more restricted (dilute gases) it is once more valid for dissipative fluxes *linear* in the driving forces, but includes now for the differential equations describing the phenomena's time behaviour a greater variety of sources of nonlinear

behaviour. Such additional sources of nonlinear behaviour are e.g. the presence of convection terms and the dependence of the transport coefficients on the state variables. But all these nonlinearities still occur within a domain for which linear thermodynamics of irreversible processes holds.

ONSAGER's comment at the IUPAP meeting of 1949, quoted above, remains fully applicable to the present considerations and underscores the importance of investigating *concrete* genuinely nonlinear cases[19]. At the time ONSAGER concluded his brief comment with a second sentence: 'The possibilities of *useful* generalizations have not been fully explored; none have been found so far.'

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