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# ONSAGER RELATIONS AND EXTENDED IRREVERSIBLE THERMODYNAMICS

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## Abstract

We show that when the thermodynamic fluxes are included as independent thermodynamic state variables of a generalized entropy, the original ONSAGER formulation may be directly used in the space of the fluxes. Therefore, the ONSAGER relations may be derived either in the space of the classical (slow) variables, by using a spatial FOURIER transformation, or in the space of the non-classical (fast) variables such as the physical fluxes, without need of any Fourier transform. Furthermore, we analyse the question of non-linear ONSAGER relations by studying one particular set of evolution equations of the fluxes, and considering the fluctuations of the fluxes around a non-equilibrium steady state. Comparison with kinetic theory is not completely conclusive, because of several open questions which we comment in the concluding remarks.

*Keywords:* ONSAGER relations, extended irreversible thermodynamics, kinetic theory.

## 1. Introduction

In this paper we examine ONSAGER–CASIMIR reciprocity relations (OCRR) in the framework of extended irreversible thermodynamics (EIT) [1]–[4]. The aim of this theory is to systematize in a thermodynamic formalism the phenomenological equations which describe experiments at frequencies comparable to the inverse of the relaxation time of the thermodynamic fluxes (heat flux, viscous pressure tensor, electric current, diffusion flux, and so on) or at wavelengths comparable to the mean free path of the particles of the system.

In our opinion, the study of macroscopic matter should be undertaken simultaneously and in a close collaboration by macroscopic and microscopic methods. Beyond the situations where local equilibrium is a valid macroscopic assumption, classical irreversible thermodynamics (CIT) is no longer satisfactory, but alternatively, more general macroscopic theories have not been sufficiently developed yet. EIT is one of the serious efforts undertaken in this direction. This does not mean that one should be satisfied with only a macroscopic, phenomenological approach: after identifying the macroscopic variables and establishing the equations describing a set of experiments in a satisfactory way, one should try to understand from a molecular approach why such variables and equations turn out to be relevant. We think that limiting ourselves to a microscopic point is unnecessarily restrictive, because it is a well-known fact that a phenomenon relatively well described and understood in macroscopic terms has challenged during many years a valuable microscopic understanding.

Of course, the hope that, on the long run, the macroscopic equations will be supported by a molecular basis, should not prevent us from being aware of the subtleties of the connexions between microscopic and macroscopic descriptions. The latter is independent of any particular molecular model; on the other side, a better molecular understanding may lead to more successful macroscopic descriptions. Therefore, one should try to avoid two possible extremes: either to assume that the scientific description of the world should be restricted to microscopic models or to consider oneself satisfied with the pragmatic success of some phenomenological equations fitting some experimental data, without confronting them with a molecular theory.

In Section 2 we examine the derivation of OCRR in the framework of EIT. In Section 3 thermoelectric phenomena are used as an illustration of how EIT can shed a new light on the reciprocity relations. In Section 4 we analyse the difficulties which arise when one tries to extend the results to the non-linear domain. To be specific, we deal with the second-order constitutive equations of hydrodynamics. It turns out that the reciprocal properties are not satisfied by the equations derived from a second-order analysis of the kinetic theory of gases. However, our results are not completely conclusive, since they are based on a comparison with approximative microscopic models rather than with exact results. Section 5 is devoted to a final discussion on the present state of the art.

## 2. Onsager–Casimir Relations in the Linear Regime

ONSAGER–CASIMIR relations are well understood in the linear regime [5]. Therefore, one could ask whether it is worthwhile to examine again this problem, as, after all, the classical results will be recovered. However, a more thorough understanding of the derivation in the linear case may be helpful in view of a generalization to the non-linear regime.

First of all, we briefly recall the ONSAGER–CASIMIR derivation of the reciprocity relations. Assume that the entropy is a function of several variables $A_1, \dots, A_n$ and denote by $\alpha_\beta$ their deviation from the average equilibrium value $\langle A_\beta \rangle$. The entropy related to the fluctuation state will be

$$S = S_0 - \frac{1}{2}\boldsymbol{\alpha} \cdot \mathbf{G} \cdot \boldsymbol{\alpha} \,, \tag{1}$$

where $S_0$ refers to the entropy of the reference equilibrium state, $S$ is the entropy of the fluctuating state, and $\mathbf{G}$ the matrix of the second derivatives of entropy with respect to variables $\boldsymbol{\alpha}$. Note that in ONSAGER's derivation, the meaning of $\boldsymbol{\alpha}$'s is simply that of 'variables of state', but the physical nature of such variables is never specified [6].

Assume furthermore that the laws describing the relaxation of the fluctuations are linear, in such a way that

$$\frac{d\boldsymbol{\alpha}}{dt} = -\mathbf{M} \cdot \boldsymbol{\alpha} \,. \tag{2}$$

If it is supposed that the microscopic behaviour should satisfy time-reversal symmetry, it follows that the matrix $\mathbf{L} = \mathbf{M} \cdot \mathbf{G}^{-1}$ relating the 'thermodynamic fluxes' $d\boldsymbol{\alpha}/dt$ to the 'thermodynamic forces' $\boldsymbol{X} = \partial S/\partial \boldsymbol{\alpha}$ satisfies the OCRR

$$L_{\gamma\beta} = \varepsilon_\gamma \varepsilon_\beta L_{\beta\gamma} \,, \tag{3}$$

with $\varepsilon_\beta$ giving the time-reversal parity of the variable $\alpha_\beta$ (i.e. $\varepsilon_\beta = +1$ if variable $\alpha_\beta$ is even and $\varepsilon_\beta = -1$ if $\alpha_\beta$ is odd).

However, the usual thermodynamic fluxes like the heat flux or the viscous pressure tensor cannot be expressed as the time derivative of a given variable, neither are generally the thermodynamic forces the derivatives of the entropy. Rather, it is the divergence of the fluxes which is related to the time derivatives of the fluctuations of the basic variables, and it is the spatial gradient of the derivatives of the entropy, which plays the role of thermodynamic forces. Nevertheless, this is not a serious problem: in the Fourier space (and when some non-linear terms appearing in the balance equations are neglected) the Fourier-transforms of the fluxes are indeed proportional to the Fourier-transform of the classical variables. One advantage of EIT is that the ONSAGER relations may be derived in a form which is more akin to the original ONSAGER derivation than the usual presentation found in CIT.

Indeed, the entropy used in EIT takes the form

$$S(\alpha_1, \ldots, \alpha_n, \boldsymbol{J}_1, \ldots, \boldsymbol{J}_n) = S_{eq}(\alpha_1, \ldots, \alpha_n) - \frac{1}{2}\boldsymbol{J} \cdot \mathbf{G}' \cdot \boldsymbol{J} \,. \tag{4}$$

Here, $\alpha_1, \ldots, \alpha_n$ are the classical slow variables whereas $\boldsymbol{J}_1, \ldots, \boldsymbol{J}_n$ are the corresponding fluxes, $S_{eq}(\alpha_1, \ldots, \alpha_n)$ is the classical local-equilibrium entropy corresponding to the values of $\alpha_1, \ldots, \alpha_n$, and $\mathbf{G}'$ is a matrix whose meaning must be specified later on. For instance, in a two-component fluid in the presence of heat flux and diffusion one will take $\alpha_1 = u$ and $\alpha_2 = c_1$, with $u$ the internal energy and $c_1$ the mass fraction of component 1, the corresponding fluxes will be $\boldsymbol{J}_1 = \boldsymbol{q}$, the heat flux, and $\boldsymbol{J}_2 = \boldsymbol{J}$, the diffusion flux of component 1. It may be of interest to recall that in 1953, ONSAGER and MACHLUP [7] considered an entropy depending on both $\alpha_i$ and $d\alpha_i/dt$, i.e. on the variables and their 'fluxes'. However, expression (4) is more general because it does not require that the fluxes should be the time derivatives of the variables $\alpha_i$.

The entropy production of the local-equilibrium entropy takes the classical form

$$\sigma_{eq} = \boldsymbol{J} \cdot \boldsymbol{X} \ , \tag{5}$$

where $\boldsymbol{X}$ are the usual thermodynamic forces, i.e. $\boldsymbol{X}_1 = \nabla T^{-1}$ and $\boldsymbol{X}_2 = -\nabla(\mu T^{-1})$ in the problem where $\alpha_1 = u$ and $\alpha_2 = c_1$. The corresponding entropy production in EIT is [1]

$$\sigma_{EIT} = \boldsymbol{J} \cdot (\boldsymbol{X} - \mathbf{G}' \cdot \dot{\boldsymbol{J}}) \, . \tag{6}$$

Note that the variables conjugated to the fluxes in (6) are not usual thermodynamic forces $\boldsymbol{X}$ but the quantities $\boldsymbol{X} - \mathbf{G}' \cdot \dot{\boldsymbol{J}}$. Whereas the time evolution of the classical variables $\alpha_i$ is given by the usual conservation laws (energy, mass, momentum...) the time derivative of the fluxes, which are independent variables in EIT, are found by requiring that they are compatible with the positiveness of the entropy production. Thus, in the simplest linear version, one will write

$$\boldsymbol{J} = \mathbf{L} \cdot (\boldsymbol{X} - \mathbf{G}' \cdot \dot{\boldsymbol{J}}) \, , \tag{7}$$

with $\mathbf{L}$ a matrix of phenomenological coefficients. In CIT, the reciprocity relations of $\mathbf{L}$ are obtained by applying ONSAGER's formalism in the Fourier-transformed space of $\alpha_i$.

In EIT, the reciprocity relations may be obtained in a more direct way, namely, by studying the fluctuations of the fast variables $\boldsymbol{J}_i$ in an equilibrium state ($\boldsymbol{X}_j = 0$), and without referring to a Fourier-transform. Indeed, when $\boldsymbol{X} = 0$, (7) may be written as

$$\dot{\boldsymbol{J}} = -(\mathbf{G}')^{-1} \cdot \mathbf{L}^{-1} \cdot \boldsymbol{J} \, . \tag{8}$$

This has the form of *Eq.* (2). According to (3), the matrix $\mathbf{L}' = (\mathbf{G}')^{-1} \cdot \mathbf{L}^{-1} \cdot (\mathbf{G}')^{-1}$ should satisfy the reciprocity relations. It follows that the matrix $\mathbf{L}$, which is given by $\mathbf{L} = \mathbf{G}' \cdot (\mathbf{L}')^{-1} \cdot \mathbf{G}'$, satisfies the reciprocity relations, because the matrix $\mathbf{G}'$, which is the second derivative of the EIT entropy, is itself symmetric. Note, however, that the matrix of the relaxation times, defined as $\boldsymbol{\tau} = \mathbf{L} \cdot \mathbf{G}'$, need not be symmetric.

Therefore, the OCRR may be obtained in EIT both in the space of slow variables (where they follow from the time-reversal properties of the correlation function of the slow variables), and in the space of the fluxes (where they follow from the time-reversal properties of the correlation function of the fluxes). However, there is a difference in the relaxation times of both sets of variables. The relaxation time of the conserved variables is very large (it varies with the wavevector $k$ as $k^{-2}$), whereas the relaxation time of the fluxes is of the order of a few collision times. As far as one derives the ONSAGER relations from the formal mathematical properties of the correlation functions, the use of the one or the other set of variables is completely equivalent. However, if one tries to reproduce these properties by molecular simulations, the time reversal of the trajectories may be reproduced only during a few collision times, due to the extreme sensitivity of the trajectory to perturbations. Thus, in such simulations, the analysis in the short-time scale settled by the fluxes would be easier than in the long-time scale corresponding to the classical variables.

This duality in the derivation is easily interpreted from the microscopic point of view. Whereas in CIT the OCRR are obtained by studying the time-reversal of $\langle \alpha_i(0)\alpha_j(t)\rangle$, EIT used another way based on the fluctuation-dissipation theorem. Indeed, the expression of the transport coefficients in terms of the correlation function of the fluxes allows to derive the reciprocity relations from the time-reversal properties of the correlations of the fluxes. It is worth noticing that, whereas the classical theory always refers to the correlation function of the classical variables, EIT exhibits this duality which is also found in a microscopic approach. This is a further manifestation of the fact that EIT is closer to the microscopic theories than CIT.

## 3. An Illustration: Thermoelectric Phenomena

As an illustration, we will deal with thermoelectric phenomena. Consider a rigid and isotropic body, crossed by a heat flux $\boldsymbol{q}$ and an electric current $\boldsymbol{i}$. The generalized Gibbs equation has the form [1]

$$\begin{aligned} ds = T^{-1}du - \mu_\epsilon T^{-1}dz_\epsilon - (\rho T)^{-1}(a_{11}\boldsymbol{q} + a_{12}\boldsymbol{i})\cdot d\boldsymbol{q} \\ -(\rho T)^{-1}(a_{21}\boldsymbol{q} + a_{22}\boldsymbol{i})\cdot d\boldsymbol{i}\ , \end{aligned} \qquad (9)$$

where $z_\epsilon$ is the electric charge per unit mass and $\mu_\epsilon$ the chemical potential of the electrons. Although an explicit identification of the coefficients $a_{ij}$ is not fundamental, it may be of interest to know that $a_{11} = (\tau_1 v/\lambda T^2)$ and $a_{22} = (\tau_\epsilon v/\sigma_\epsilon T)$ with $\tau_1$ and $\tau_\epsilon$ the respective relaxation times of $\boldsymbol{q}$ and $\boldsymbol{i}$, $v$ the specific volume (i.e. $v = \rho^{-1}$) and $\lambda$ and $\sigma_\epsilon$ the thermal and electric conductivity, whereas $a_{12}$ and $a_{21}$ are related to crossed terms in the matrix of relaxation times.

By virtue of the balance equations for $z_\epsilon$ and $u$

$$\rho\dot{z}_\epsilon = -\nabla\cdot\boldsymbol{i}\ , \qquad (10)$$

$$\rho\dot{u} = -\nabla\cdot\boldsymbol{q} + \boldsymbol{i}\cdot\boldsymbol{E}\ , \qquad (11)$$

one obtains for the entropy balance

$$\rho\frac{ds}{dt}+\nabla\cdot\left(\frac{1}{T}\boldsymbol{q}-\frac{\mu_\epsilon}{T}\boldsymbol{i}\right)=\boldsymbol{q}\cdot\left(\nabla T^{-1}-\frac{a_{11}}{T}\frac{d\boldsymbol{q}}{dt}-\frac{a_{21}}{T}\frac{d\boldsymbol{i}}{dt}\right)$$

$$+\boldsymbol{i}\cdot\left(\frac{\boldsymbol{E}}{T}-\nabla\frac{\mu_\epsilon}{T}-\frac{a_{12}}{T}\frac{d\boldsymbol{q}}{dt}-\frac{a_{22}}{T}\frac{d\boldsymbol{i}}{dt}\right), \tag{12}$$

from which follow immediately the expressions of the entropy flux $\boldsymbol{J}^s$ and the entropy production $\sigma^s$. The entropy production, given by the right-hand side of (12), has still the structure of a bilinear form. To obtain the simplest evolution equations for $\boldsymbol{q}$ and $\boldsymbol{i}$ compatible with a positive definite entropy production, one assumes linear relations between the 'thermodynamic forces', i.e. the quantities between parentheses and the fluxes $\boldsymbol{q}$ and $\boldsymbol{i}$. This results

$$\begin{aligned}\nabla T^{-1}-\frac{a_{11}}{T}\frac{d\boldsymbol{q}}{dt}-\frac{a_{21}}{T}\frac{d\boldsymbol{i}}{dt} &= \mu'_{11}\boldsymbol{q}+\mu'_{12}\boldsymbol{i}\,,\\ \frac{\boldsymbol{E}}{T}-\nabla\frac{\mu_\epsilon}{T}-\frac{a_{12}}{T}\frac{d\boldsymbol{q}}{dt}-\frac{a_{22}}{T}\frac{d\boldsymbol{i}}{dt} &= \mu'_{21}\boldsymbol{q}+\mu'_{22}\boldsymbol{i}\,,\end{aligned} \tag{13}$$

with $\mu'_{11}\geq 0$, $\mu'_{22}\geq 0$ and $\mu'_{11}\mu'_{22}\geq(1/4)(\mu'_{12}+\mu'_{21})^2$ as a consequence of $\sigma^s>0$.

To show that the matrix of the coefficients $\boldsymbol{\mu}'$ is symmetric, we start from ONSAGER's original result stating that if the evolution equations are given by $d\boldsymbol{\alpha}/dt=\mathbf{L}\cdot(\partial S/\partial\boldsymbol{\alpha})$, then $\mathbf{L}$ is a symmetric matrix. We may assume that $\nabla T^{-1}$ and $\boldsymbol{E}T^{-1}-\nabla(\mu_\epsilon T^{-1})$ vanish in (13), so that they refer to fluctuations near an equilibrium state. Therefore, *Eqs.* (13) may be cast in the form

$$\begin{pmatrix} d\boldsymbol{q}/dt\\ d\boldsymbol{i}/dt\end{pmatrix}=-T(\mathrm{a}^T)^{-1}\cdot\boldsymbol{\mu}'\cdot\begin{pmatrix}\boldsymbol{q}\\ \boldsymbol{i}\end{pmatrix}. \tag{14a}$$

This expression may be rewritten in terms of the derivatives of the generalized entropy (9) with respect to $\boldsymbol{q}$ and $\boldsymbol{i}$ as

$$\begin{pmatrix} d\boldsymbol{q}/dt\\ d\boldsymbol{i}/dt\end{pmatrix}=\rho T^2[(\mathrm{a}^T)^{-1}\cdot\boldsymbol{\mu}'\cdot\mathrm{a}^{-1}]\cdot\begin{pmatrix}\partial S/\partial\boldsymbol{q}\\ \partial S/\partial\boldsymbol{i}\end{pmatrix}. \tag{14b}$$

According to ONSAGER's results, the matrix $\mathbf{L}=(\mathrm{a}^T)^{-1}\cdot\boldsymbol{\mu}'\cdot\mathrm{a}^{-1}$ is symmetric. Since $\mathbf{a}$ is symmetric, because it is the matrix of the second derivatives of $s$, it follows that $\boldsymbol{\mu}'=\mathrm{a}\cdot\mathbf{L}\cdot\mathrm{a}$ is itself symmetric. The matrix $T^{-1}\boldsymbol{\mu}'^{-1}\cdot\mathrm{a}$ in ?? may be identified with the matrix $\boldsymbol{\tau}$ of the relaxation times. Note that in general $\boldsymbol{\tau}$ is not symmetric because the product of two symmetric matrices is generally not symmetric.

In a non-equilibrium steady state, (13) may be compared with the usual phenomenological equations expressing the coupling between thermal and electrical effects; it is then found that

$$\nabla T^{-1} = \frac{1}{\lambda T^2}\boldsymbol{q} - \frac{\Pi + \mu_e}{\lambda T^2}\boldsymbol{i}\,, \tag{14}$$

$$\boldsymbol{E} - \nabla \mu_e = \frac{\zeta}{\lambda}\boldsymbol{q} - \left(\zeta\frac{\Pi + \mu_e}{\lambda} - r\right)\boldsymbol{i}\,, \tag{15}$$

where $\lambda$ is the thermal conductivity at zero electric current, $\zeta$ the differential thermoelectric power, $\Pi$ the Peltier coefficient, and $r$ the isothermal electric resistivity. By comparison of *Eqs.* (13) and (16), one is led to the identities $\mu'_{11} = (\lambda T^2)^{-1}$, $\mu'_{21} = (\zeta T - \mu_e)(\lambda T^2)^{-1}$, $\mu'_{12} = -(\Pi + \mu_e)(\lambda T^2)^{-1}$, and $\mu'_{22} = rT^{-1} + (\mu_e - T)(\Pi + \mu_e)(\lambda T^2)^{-1}$. From the symmetry of $\boldsymbol{\mu}'$ it follows that $-(\Pi + \mu_e) = \zeta T - \mu_e$, so that $\zeta T = -\Pi$, which is the well-known second Thomson relation.

We wish to emphasize that the argument leading to the symmetry property of the phenomenological matrix $\boldsymbol{\mu}'$ is parallel to that presented by ONSAGER himself, who postulates that thermodynamic fluxes are time derivatives of state variables, whilst the forces are the derivatives of entropy with respect to the state variables. Since in EIT the quantities $\boldsymbol{q}$ and $\boldsymbol{i}$ are basic state variables, it is clear that (14a) and (14b) relate the time derivatives of the basic variables with $\partial S/\partial \boldsymbol{q}$ and $\partial S/\partial \boldsymbol{i}$, just like in ONSAGER's original derivation, where the time derivatives of the basic variables (here, the thermodynamic fluxes) are linearly related to the derivatives of the entropy with respect to these variables (the thermodynamic forces).

## 4. A Non-Linear Situation

In this section we discuss some possible generalization of the OCRR to second-order constitutive equations, either in the linear or in the non-linear regime. Rather than dealing with generalities, we will study in detail one specific problem, concerning some couplings between the heat flux and the viscous pressure in second-order constitutive equations of hydrodynamics.

If one considers the fluxes themselves as variables, the ONSAGER formalism may be directly applied to obtain the usual results, as we have seen in Section 2, with the advantage that one must not identify the fluxes with $d\boldsymbol{\alpha}/dt$, as in CIT.

Here, we study a thermo-hydrodynamic system with heat flux $\boldsymbol{q}$ and viscous pressure $\mathbf{P}^\nu$ as dissipative fluxes, and we assume evolution equations of the form

$$\frac{d\boldsymbol{q}}{dt} = -\frac{1}{\tau_1}[\boldsymbol{q} + \lambda\nabla T] + a\nabla\cdot\mathbf{P}^\nu + b\mathbf{P}^\nu\cdot\boldsymbol{q}\,, \tag{16}$$

$$\frac{d\mathbf{P}^{\nu}}{dt} = -\frac{1}{\tau_2}[\mathbf{P}^{\nu} + 2\eta(\nabla \nu)^{s}] + a'(\nabla \boldsymbol{q})^{s} + b'(\boldsymbol{q}\boldsymbol{q})^{S} , \tag{17}$$

where $\lambda$ is the thermal conductivity, $\eta$ the shear viscosity and $\tau_1$ and $\tau_2$ are the relaxation times of $\boldsymbol{q}$ and $\mathbf{P}^{\nu}$, respectively. In *Eqs.* (16) and (17), there are two different kinds of couplings between $\boldsymbol{q}$ an $\mathbf{P}^{\nu}$: (a) the linear ones, related to the terms with the coefficients $a$ and $a'$; (b) the non-linear ones, given by the terms with the coefficients $b$ and $b'$. We would ask the question whether there is some relation between these various coefficients.

Consider the evolution of the fluctuations of $\boldsymbol{q}$ and $\mathbf{P}^{\nu}$ around a non-equilibrium steady state characterized by a nonvanishing mean heat flux $\boldsymbol{q}_0$ and a nonvanishing mean pressure tensor $\mathbf{P}_0^{\nu}$. According to (16) and (17), the evolution of the fluctuations in the linear approximation is given by

$$\begin{pmatrix} \delta\dot{\boldsymbol{q}} \\ \delta\dot{\mathbf{P}}^{\nu} \end{pmatrix} = -\mathrm{M} \cdot \begin{pmatrix} \delta\boldsymbol{q} \\ \delta\mathbf{P}^{\nu} \end{pmatrix} . \tag{18}$$

with

$$\mathrm{M} = \begin{pmatrix} \tau_1^{-1} & -a\nabla - b\boldsymbol{q}_0 \\ -a'\nabla - 2b'\boldsymbol{q}_0 & \tau_2^{-1} \end{pmatrix} . \tag{19}$$

In order to apply ONSAGER's formalism to this problem, we need the expression for the entropy. In EIT, up to third order in the fluxes, the Gibbs equation for the entropy has the form [8]

$$ds = \theta^{-1}du + \theta^{-1}\pi dv - \left(\frac{\tau_1 v}{\lambda T^2}\boldsymbol{q} - 2\xi\mathbf{P}^{\nu}\cdot\boldsymbol{q}\right)\cdot d\boldsymbol{q} - \left(\frac{\tau_2 v}{2\eta T}\mathbf{P}^{\nu} - \xi\boldsymbol{q}\boldsymbol{q}\right) : d\mathbf{P}^{\nu} \tag{20}$$

in which non-linear contributions $\mathbf{P}^{\nu}\cdot\boldsymbol{q}$ and $\boldsymbol{q}\boldsymbol{q}$ have been introduced, $\theta^{-1}$ and $\pi$ are respectively the absolute temperature and the pressure, and $\xi$ is a phenomenological coefficient depending generally on temperature and pressure. Therefore, the matrix $\mathbf{G}_2'$ related to the second order derivatives of entropy with respct to fluxes is given by

$$\mathbf{G}_2' = -\begin{pmatrix} \tau_1 v/\lambda T^2 & 2\xi\boldsymbol{q}_0 \\ 2\xi\boldsymbol{q}_0 & \tau_2 v/2\eta T \end{pmatrix} . \tag{21}$$

According to ONSAGER, the matrix $\mathbf{L} = \mathrm{M}\cdot(\mathbf{G}')_2^{-1}$ should be symmetric under the following requirements:

(i) the evolution equations are linear,
(ii) the second moments of the fluctuations are given by $(\mathbf{G}')^{-1}$;
(iii) microscopic reversibility is fulfilled.

*Eqs.* (18) and (19) are linear, and therefore, condition (i) is automatically satisfied. The problems are related to conditions (ii) and (iii). With respect to condition (ii), we may assume that the second moments of fluctuations are indeed given by $(\mathbf{G}_2')^{-1}$, as supported by information theory ([1], Chap.5). Concerning condition (iii), and the problem of microscopic reversibility, it must be recalled that here the system is not in equilibrium; therefore, we must invert not only the velocities of the particles, but also the effect of the boundary conditions, i.e. $\nabla$ changes its sign under time-reversal, in analogy with the change of sign of the angular velocity and the external magnetic field in the classical derivation of the OCRR. We are thus led to

$$L_{12}(\nabla) = \varepsilon_1\varepsilon_2 L_{21}(-\nabla). \tag{22}$$

From (19) and (21), we have for the nondiagonal components of the matrix $\mathbf{L}$

$$L_{12} = \frac{2\xi}{\tau_1}\boldsymbol{q}_0 - \frac{\tau_1 v}{\lambda T^2}[a\nabla + b\boldsymbol{q}_0], \tag{23}$$

$$L_{21} = \frac{2\xi}{\tau_2}\boldsymbol{q}_0 - \frac{\tau_2 v}{2\eta T}[a'\nabla + 2b'\boldsymbol{q}_0]. \tag{24}$$

With the conjecture (22) in mind and taking into account that $\varepsilon_{\mathbf{P}^\nu} = +1$ and $\varepsilon_{\mathbf{q}} = -1$, one obtains

$$\frac{\tau_1 v}{\lambda T^2}a = \frac{\tau_2 v}{2\eta T}a', \tag{25}$$

$$\frac{2\xi}{\tau_1} - \frac{\tau_1 v}{\lambda T^2}b = -\frac{2\xi}{\tau_2} + \frac{\tau_2 v}{\eta T}b'. \tag{26}$$

It is of interest to compare these predictions with the results of the kinetic theory of gases. In Grad's expansion, the evolution equations for $\boldsymbol{q}$ and $\mathbf{P}^\nu$ are more general than (16) and (17) and given by [9]

$$\dot{\boldsymbol{q}} = -\frac{k_B T}{m}\nabla\cdot\mathbf{P}^\nu - \frac{5}{2}\frac{pk_B}{m}\nabla T - \frac{2}{3}\rho\gamma\boldsymbol{q} - \frac{7}{5}\boldsymbol{q}\cdot(\nabla\nu)$$
$$-\frac{2}{5}\boldsymbol{q}\cdot(\nabla\nu)^T - \frac{7}{5}\boldsymbol{q}(\nabla\cdot\nu) - \frac{7}{2}\frac{k_B}{m}\mathbf{P}^\nu\cdot\nabla T + \rho\mathbf{P}^\nu\cdot(\nabla\cdot\mathbf{P}^\nu) \tag{27}$$

and

$$\dot{\mathbf{P}}^\nu = -\frac{4}{5}(\nabla\boldsymbol{q})^s - 2p(\nabla\nu)^s - \rho\gamma\mathbf{P}^\nu - \mathbf{P}^\nu\cdot(\nabla\nu) - (\nabla\nu)^T\cdot(\mathbf{P}^\nu)^T$$
$$-\mathbf{P}^\nu(\nabla\cdot\nu) + \frac{2}{3}[\mathbf{P}^\nu : (\nabla\nu)]\mathbf{U}, \tag{28}$$

where the coefficient $\gamma$ is given in terms of the collision integrals ([1] , [9]] and $k_B$ is Boltzmann's constant. When we compare these expressions with the previous ones (16) and (17), we are able to identify

$$a = -k_B T/m; \quad a' = -4/5; \quad \tau_1 = 3/(2\rho\gamma); \quad \tau_2 = 1/(\rho\gamma);$$

$$\lambda = (5pk_B/2m)\tau_1 ; \quad \eta = p\tau_2 . \tag{29}$$

After introducing these expressions into (25), it is verified that

$$\frac{\tau_1 v}{\lambda T^2} a = \frac{\tau_2 v}{2\eta T} a' = -\frac{2v}{5pT} . \tag{30}$$

Note that this result is not surprising since the coefficients $a$ and $a'$ are related with the linear terms of (16) and (17) and we could have derived it directly by using fluctuations around equilibrium ([10]–[12]). Relations (30) can also be found by using projection operator technique in the kinetic theory of gases [13].

In contrast, it is found that relation (26) is not satisfied. Indeed, the coefficient $b$ may be obtained by comparison of (27) and (16). The terms in $\mathbf{P}^\nu \cdot \nabla T$ and $\boldsymbol{q} \cdot (\nabla \nu)$ may be seen as first-order approximations to $\mathbf{P}^\nu \cdot \boldsymbol{q}$. This yields $b = (7/2)(k_B/m\lambda) + (2/5\eta)$ up to first order in the fluxes. On the other side, we see that $b' = 0$ because there is no term of the form $\boldsymbol{qq}$ in (28). Furthermore, the parameter $\xi$ may be obtained from fluctuation theory [8] from the calculation of the third moments of the fluctuations of $\langle \delta q_1 \delta P_{12} \delta q_2 \rangle$, it turns out to be given by $\xi = (9/25)(p^3 T)^{-1}$. When the above values of $b, b'$ and $\xi$ are introduced into (26) it is easily checked that this relation is not fulfilled.

## 5. Concluding Remarks

Here, we propose some arguments why the OCRR may not be satisfied in the non-linear regime. The first is, of course, the conjecture (22): the conditions for time reversal symmetry in a non-equilibrium steady state are not yet clearly established, though they have been tentatively used on some other occasions in the literature in the analysis of fluids in the presence of a velocity shear gradient [14].

A second reason is that the kinetic theory is not an exact one, but rather a model. Therefore, the values of the various coefficients derived from the kinetic theory cannot be considered as absolute and definitive.

Concerning *Eqs* (27) and (28), the absence of a term in $\boldsymbol{qq}$ in relation (28) for $\mathbf{P}^\nu$ may be surprising. In fact, such a term appears neither in GRAD's formalism nor in Chapman–Enskog's approach, where the second-order contributions to the heat flux and the viscous pressure are given by [15]

$$\frac{\rho T}{\eta^2} \boldsymbol{q}^{(2)} = \frac{15}{4} \left( \frac{7}{2} - \frac{T}{\eta} \frac{d\eta}{dT} \right) \nabla^2 \nabla T + \frac{45}{8} \left[ \frac{d_0}{dt} \nabla T - (\nabla \nu) \cdot \nabla T) \right] -$$
$$-3 \nabla p \cdot (\nabla \nu)^s + 3 \nabla \cdot (\nabla \nu)^s + \left( \frac{35}{4} + \frac{T}{\eta} \frac{d\eta}{dt} \right) \nabla T \cdot (\nabla \nu)^s \tag{31}$$

and

$$\frac{p}{\eta^2}\mathbf{P}^{\nu(2)} = \frac{4}{3}\left(\frac{7}{2} - \frac{T}{\eta}\frac{d\eta}{dT}\right)\nabla^2(\nabla\nu)^s + 2\left(\frac{d_0}{dt}(\nabla\nu)^s - 2(\nabla\nu)\cdot\nabla(\nabla\nu)^s\right) +$$

$$+3\frac{p}{\rho T}\nabla\nabla T + \frac{3T}{\eta}\frac{d\eta}{dT}\frac{p}{\rho T^2}\nabla T\nabla T + 8(\nabla\nu)^s\cdot(\nabla\nu)^s\,. \tag{32}$$

In these expressions, $\boldsymbol{q}^{(2)}$ and $\mathbf{P}^{\nu(2)}$ refer to the second-order contribution to $\boldsymbol{q}$ and $\mathbf{P}^{\nu}$, and $d_0/dt$ denotes the first-order approximation to the material derivative, where the time derivative of velocity is given by the Euler equation and where the effects of heat conduction are neglected. Note that relation (25) is also satisfied in this case and that the terms in $\nabla T\nabla T$ do not come from $\boldsymbol{qq}$, but from $\nabla\boldsymbol{q} = \nabla(-\lambda\nabla T)$, and they are due to the temperature dependence of the thermal conductivity $\lambda$. The absence of terms in the form $\boldsymbol{qq}$ may be due to excessive restrictions on the distribution function [9], [15]. Indeed, the restrictions on the value of the mean square of the molecular speed $\nu^2$ are sometimes written in a stricter form than the restrictions on the square of every component of $\nu$. This calls our attention to the form of the caloric and thermal equations of state in a non-equilibrium steady state.

In particular, such equations of state may include second-order contributions in the heat flux. For instance, according to EIT, the viscous pressure tensor in a steady state can be written as [16]

$$\mathbf{P} = \pi\mathbf{U} + \chi(\boldsymbol{qq})^s - 2\eta(\nabla\nu)^s \tag{33}$$

with the condition $3p = 3\pi + \chi\boldsymbol{q}\cdot\boldsymbol{q}$. For an ideal monatomic gas, we find $\chi = 12/(5vp^2)$ with $v$ the specific volume. This shows that more attention should be paid to the second-order equations of state when one is studying non-linear terms.

Finally, third-order terms in the entropy expression may also play a role in the formulation of reciprocal relations. These terms give rise to a non-linear relation between $\boldsymbol{q}$ and $\mathbf{P}^{\nu}$ and $\partial s/\partial\boldsymbol{q}$ and $\partial s/\partial\mathbf{P}^{\nu}$, in such a way that the matrix $\mathbf{G}_1'$ relating the latter to the former in the linear approximation around the non-equilibrium steady state is different from the matrix $\mathbf{G}_2'$ related to the second-order derivatives of the entropy. The OCRR are in principle derived for $\mathbf{M}\cdot\mathbf{G}_2'^{-1}$, and not for $\mathbf{M}\cdot(\mathbf{G}_1')^{-1}$. In the linear situation, $\mathbf{G}_1' = \mathbf{G}_2'$, but in the non-linear case these two matrices are different. This opens another possibility for the breaking of reciprocity relations around a non-equilibrium steady state.

Further analyses about the validity of ONSAGER's relations in higher-order hydrodynamics may be found in a few selected references [17]-[19]. In [17] it is shown that the equations of higher-order hydrodynamics do not agree with ONSAGER's theory, if density, velocity and temperature are used as state parameters. However, it is also pointed out in [18] that the

Chapman-Enskog method can be brought in agreement with the ONSAGER reciprocity relations by using as independent variables not only the former ones, but also their derivatives of any order with respect to the coordinates. In [19], an example of the higher order fluid dynamics possessing the ONSAGER symmetry is constructed and the proposed non-equilibrium extension of entropy depends on gradients of the fluid dynamic state variables. We have indeed seen that in the linear situation the ONSAGER reciprocity relations are satisfied for higher-order linear terms, provided one operates the change $\nabla$ to $-\nabla$ in the coupling terms. Concerning the non-linear regime the possibility of OCRR has also been examined in [20] and [21]. It turns out that on some occasions one may select the expression of the forces in a non-linear regime in such a way that OCRR can be extended far from equilibrium [21]. In the present work we have used a specific example where forces and fluxes are well defined from the start. Finally, let us recall some microscopic studies of the OCRR [2], [22], [23] in view to analyse the validity of nonlinear reciprocity relations. However, these approaches are not directly applicable in their present form to the situation analysed here.

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