Investigación *Revista Mexicana de Física* **38**, *No. 1 (1992) 92–102*

Onsager's reciprocity theorem in extended irreversible thermodynamics

L.S. García-Colín* and R.M. Velasco
Departamento de Física
Universidad Autónoma Metropolitana-Iztapalapa, 09340 México, D.F.

Recibido el 16 de julio de 1991; aceptado el 16 de agosto de 1991

Abstract. In this paper we shall discuss the Onsager relations for the transport coefficients in a dilute monatomic gas described by the extended irreversible thermodynamics. Our discussion is based on a 26 variables description of the system and its corresponding comparison with the kinetic calculation. Thermodynamic forces and fluxes are defined and the reciprocity between coefficients is shown.

PACS: 05.70.Ln

1. INTRODUCTION

The study of processes occurring in systems whose states are not in equilibrium is still awaiting the development of a general theory capable of explaining them. From the phenomenological point of view and under the restriction that they belong to the small frequencies (long times) and long wavelengths (small wave numbers) domain, linear irreversible thermodynamics (LIT) has been a successful theory. The cornerstone of this theory, the Onsager reciprocity theorem, was derived in 1931 [1]. The subject matured afterwards due to the efforts of the Groot-Mazur [2], Prigogine [3], Gyarmati [4], Meixner [5], Onsager and Machlup [6] and others [7]. Today we may regard it as the only phenomenological approach dealing both, with non-equilibrium processes and the approach to equilibrium of non-equilibrium states, deeply rooted in the basic laws of microphysics [1,8] and in the kinetic theory of gases [2]. Its application to a wide variety of systems [7,8] as well as the wealth of experimental evidence of the validity of Onsager's symmetry relations [10] fully supports its success.

On the other hand, there is also a handful of physical situations that cannot be described by LIT. A representative number of them have been recently described in several papers [11,14]. To cope with such phenomena efforts have been advanced to modify and/or generalize some of the basic postulates of LIT. One such attempt is based in very old work of Kohlrausch [15] and Maxwell [16] and almost one hundred years later brought back by H. Grad [17] in his work on the properties and solutions to the Boltzmann equation. The basic idea behind this attempt concerns with

---

*Miembro de El Colegio Nacional.

the possibility of having observable states of a given physical system requiring for their description, more than the ordinary locally conserved variables. Grad actually showed how this could be done for a dilute monatomic gas and argued that the best candidates to perform as additional state variables were the heat flux and the stress tensor. Moreover he also proved that these variables obey time evolution equations of the form proposed earlier by Kohlrausch and Maxwell and now known in the literature as the Maxwell-Cattaneo-Vernotte equations [12,13]. Through the work of many other people [18-21] this approach lead to a formalism presently known as a extended irreversible thermodynamics (EIT).

Here we are interested in the discussion of EIT for a particular case in which we have previously performed all the calculations using a kinetic model based on the Boltzmann equation and for which no undetermined coefficients are left [22]. The method is inspired in Grad's own moment method to solve the Boltzmann equation [17]. In fact what we have done in Ref. [22] is to construct the entropy density, the entropy flux and the production of entropy starting from the single particle distribution function expressed in terms of 26 independent moments. Once we obtain those quantities we follow the scheme of EIT, which means that we use the entropy balance equation to write the linearized equations of motion for the relaxation variables. This procedure allows us to identify all the coefficients with some collision integrals and the usual local thermodynamic variables. Using such results, in this paper we complete the scheme of EIT now following Onsager's point of view. This means that we shall use the entropy production as a guiding function to identify the forces and fluxes associated to the nonequilibrium states of the system. Moreover, by appropriate algebraic manipulations one can indeed extract such quantities, identify the corresponding transport coefficients and finally show that Onsager reciprocity type relations are obeyed. This result is interesting enough by itself since it indicates how some characteristics of LIT can be extended to situations for which the locally conserved variables are not sufficient in number to characterize the states of the system. Although here exhibited for the particular case of a dilute monatomic gas it has the enormous advantage of explicitly showing how indeed many well established concepts from LIT may be well extended to more general non-equilibrium states without leaving a single free parameter adjustable through experiment. This is feasible only because for this particular system the support of a microscopic model is in fact available to us.

The structure of the paper is as follows: Sect. 2 will be devoted to a brief summary of EIT for the 26 variables approach. In Sect. 3 we will define the appropriate quantities to show the Onsager reciprocity and lastly in Sect. 4 we discuss our results and emphasize the differences with previous calculations in this subject.

2. SUMMARY OF EIT

To avoid a lengthy and unnecessary introduction to the subject which may be found in several recent papers [12,13,20,21] we will summarize the basic axioms of EIT for the concrete case to be dealt with here namely, that of a system whose states are described by the set of the locally conserved variables, namely, the mass density ρ, hydrodynamic velocity $\vec{v}$, and internal energy e plus the fast or relaxing variables taken to be the heat flux $\vec{q}$, the traceless viscous tensor $\overset{0}{p}$ a symmetric second order tensor $\mathcal{I}_{ij}$ and a third order tensor $\mathbb{P}$ whose seven independent components together with the heat flux is essentially the third moment of the one particle distribution function. Notice should be made of the fact that one such system is a dilute monatomic gas whose time evolution is given by a Grad's moments expansion of the single particle distribution function. This whole set adds up to 26 independent variables which must be known to specify the states of the system. EIT now assumes that a continuous differentiable function η exists such that

$$\eta = \eta(\rho, e, \vec{q}, \overset{0}{p}, \overset{0}{\mathcal{I}}, \mathcal{I}_{rr}, \mathbb{P}), \tag{2.1}$$

where $\overset{0}{\mathcal{I}}$ and $\mathcal{I}_{rr}$ are the traceless part and the trace of tensor $\mathcal{I}_{ij}$.

Equation (2.1) immediately implies that the following generalized Gibbs equation is valid, namely,

$$\begin{aligned}\rho\frac{D\eta}{Dt} = {} & \frac{\rho}{T}\frac{De}{Dt} - \frac{p}{T\rho}\frac{D\rho}{Dt} + \frac{1}{T}\alpha_{01}\mathcal{I}_{rr}\frac{D\mathcal{I}_{rr}}{Dt} + \frac{1}{T}\alpha_{10}\vec{q}\cdot\frac{D\vec{q}}{Dt} \\ & + \frac{1}{T}\left(\alpha_{20}\overset{0}{p} + \alpha_{21}\overset{0}{\mathcal{I}}\right) : \frac{D\overset{0}{p}}{Dt} + \frac{1}{T}\left(\alpha_{30}\overset{0}{p} + \alpha_{31}\overset{0}{\mathcal{I}}\right) : \frac{D\overset{0}{\mathcal{I}}}{Dt} \\ & + \frac{1}{T}\left(\alpha_{40}\mathbb{P} + \alpha_{41}(2\vec{q}\mathbb{I})^0\right)\frac{D\mathbb{P}}{Dt},\end{aligned} \tag{2.2}$$

where p is the local hydrostatic pressure, ρ and T the local values for the density and temperature respectively and the α's are unknown scalar coefficients, functions of the conserved variables. In order to construct Eq. (2.2) the assumption has been made requiring that if a_i is any of the fast relaxing variables, $(\partial\eta/\partial a_i)$ taking all other variables constant, is proportional (linear) to a_j. The proportionality coefficients may in principle depend on all scalar invariants spanning the space in which η is defined. In this paper, as in most work that has been done along these lines [7–9] we shall neglect the dependence in all such invariants except ρ and e, the locally conserved densities.

The time rate of change of the locally conserved variables is governed by the well known conservation equations, namely

$$\frac{D\rho}{Dt} + \rho(\nabla\cdot\vec{v}) = 0, \tag{2.3}$$

$$\rho\frac{D\vec{v}}{Dt} = -\nabla p + \nabla\cdot\overset{0}{p} + \rho\vec{f}, \tag{2.4}$$

$$\rho\frac{De}{Dt} = -\nabla\cdot\vec{q} - p(\nabla\cdot\vec{v}) - \overset{0}{p} : (\nabla\vec{v})^0, \tag{2.5}$$

whereas the time rate of change of the fast variables is unknown. It is the task of the theory to generate their explicit form so the full set of time evolution equations is complete. This task is achieved by introducing the second assumption of EIT, namely that η obeys a balance type equation:

$$\rho\frac{D\eta}{Dt} + \nabla\cdot\vec{J}_\eta = \sigma_\eta, \tag{2.6}$$

where $\vec{J}_\eta$ and σ_η are so far unknown quantities. It is precisely the nature of Eq. (2.6) which has given rise to different opinions and postures as to how one may conceive the content of EIT. Indeed, since η is by no means a priori identifiable with the thermostatic entropy nor with the local entropy of linear irreversible thermodynamics (LIT), $\vec{J}_\eta$ is hardly related to an entropy flux and σ_η to an entropy production. Thus for a group of workers in this field [13,18,23] Eq. (2.6) is simply a closure relation which insures that all the operations performed upon the η function lie in the space $\mathcal{G}$ spanned by the state variables by requiring that $\vec{J}_\eta$ is the most general vector which may be constructed with the vector quantities in $\mathcal{G}$ and similarly, σ_η the most general scalar constructed from the independent variables with coefficients which are space time independent functionals of the scalar conserved variables.

In our case, it is then clear that up to second order in the fast variables,

$$\vec{J}_\eta = (\beta_{10} + \beta_{11}\mathcal{I}_{rr})\vec{q} + \beta_{20}\overset{0}{p}\cdot\vec{q} + \beta_{30}\overset{0}{\mathcal{I}}\cdot\vec{q} + \beta_{40}\mathbb{P} : \overset{0}{p} + \beta_{50}\mathbb{P} : \overset{0}{\mathcal{I}}, \tag{2.7}$$

where the β coefficients are functions of ρ and e. Also,

$$\begin{aligned}\sigma_\eta = {} & (\gamma_{00} + \gamma_{01}\mathcal{I}_{rr})\mathcal{I}_{rr} + \gamma_{10}\vec{q}\cdot\vec{q} + (\gamma_{20}\overset{0}{p} + \gamma_{21}\overset{0}{\mathcal{I}}) : \overset{0}{p} \\ & + (\gamma_{30}\overset{0}{p} + \gamma_{31}\overset{0}{\mathcal{I}}) : \overset{0}{\mathcal{I}} + (\gamma_{40}\mathbb{P} + \gamma_{41}(2q\mathbb{I})^0 \vdots \mathbb{P},\end{aligned} \tag{2.8}$$

where the γ coefficients are also functions of ρ and e. With Eqs. (2.2) and (2.7) one can immediately construct the left hand side of Eq. (2.6) which by consistency should be equal to Eq. (2.8) thus yielding a set of time evolution equations for the fast variables which for our system are:

$$\begin{aligned}\frac{D\vec{q}}{Dt} = \frac{T}{\alpha_{10}} \Big[& \gamma_{10}\vec{q} - \nabla\left(\frac{1}{T}\right) - \beta_{20}\nabla\cdot\overset{0}{p} - \frac{1}{2}\nabla\beta_{20}\cdot\overset{0}{p} - \beta_{30}\nabla\cdot\overset{0}{\mathcal{I}} \\ & - \frac{1}{2}\nabla\beta_{30}\cdot\overset{0}{\mathcal{I}} - \beta_{11}\nabla\mathcal{I}_{rr}\Big],\end{aligned} \tag{2.9}$$

$$\frac{\alpha_{20}}{T}\frac{D\overset{0}{p}}{Dt} + \frac{\alpha_{30}}{T}\frac{D\overset{0}{\mathcal{I}}}{Dt} = \frac{1}{T}(\nabla\vec{u})^0 + \gamma_{20}\overset{0}{p} + \frac{1}{2}(\gamma_{21}+\gamma_{30})\overset{0}{\mathcal{I}} - \beta_{20}(\nabla\vec{q})^0$$

$$- \frac{1}{2}\vec{q}\cdot(\nabla\beta_{20}) - \beta_{40}(\nabla\cdot\mathbb{P}) - \frac{1}{2}\mathbb{P} : \nabla\beta_{40}, \tag{2.10}$$

$$\frac{\alpha_{21}}{T}\frac{D\overset{0}{p}}{Dt} + \frac{\alpha_{31}}{T}\frac{D\overset{0}{\mathcal{I}}}{Dt} = \frac{1}{2}(\gamma_{21}+\gamma_{30})\overset{0}{p} + \gamma_{31}\overset{0}{\mathcal{I}} - \beta_{30}(\nabla\vec{q})^0 - \frac{1}{2}(\vec{q}\nabla\beta_{30})^0$$

$$- \beta_{50}(\nabla\cdot\mathbb{P}) - \frac{1}{2}(\nabla\beta_{50}\cdot\mathbb{P}), \tag{2.11}$$

$$\frac{D\mathbb{P}}{Dt} = \frac{T}{\alpha_{40}}\left[\gamma_{40}\mathbb{P} + \gamma_{41}(2\vec{q}\mathbb{1})^0 - \beta_{40}(\nabla\overset{0}{p}) - \frac{1}{2}\nabla\beta_{40})\overset{0}{p}\right.$$

$$\left. - \beta_{50}(\nabla\overset{0}{\mathcal{I}}) - (\nabla\beta_{50})\overset{0}{\mathcal{I}}\right], \tag{2.12}$$

$$\frac{D\mathcal{I}_{rr}}{Dt} = \frac{T}{\alpha_{00}}\left[\gamma_{00} + \gamma_{01}\mathcal{I}_{rr} - \beta_{11}(\nabla\cdot\vec{q}) - \vec{q}\cdot\nabla\beta_{11}\right]. \tag{2.13}$$

Equations (2.9)–(2.13) together with the conservation equations (2.3)–(2.5) form a closed set of differential equations for the 26 variables describing the states of the gas. Their solution may be in principle obtained for given initial and boundary conditions provided the wealth of coefficients involved, α's, β's and γ's are explicitly known as functions of ρ and e.

It is pertinent to point out that the calculation we have described above is entirely based in the interpretation of Eq. (2.6) given by the Spanish-Belgian school [12,20]. Indeed, for these groups, Eq. (2.6) is interpreted as a balance equation for η, a function which is also identified with an entropy. This is accomplished by imposing the requirement that $\sigma_\eta \geq 0$ thus asserting its consistency with the second law of thermodynamics. This position is rather feeble and although as it has been shown elsewhere [22,25] that there are some realistic basis to assert that σ_η is a non negative function in some well defined cases, no proof exists that η is related to the true entropy of the system in the Clausius sense. Nevertheless some recent evidence [26] indicates that it is more closely related to the information entropy defined by Shannon and extensively used by Jaynes school [27,28] in dealing with non-equilibrium states for macroscopic systems.

It is also interesting to point out that the explicit values for the transport coefficients appearing in Eqs. (2.9)–(2.13) can be computed numerically for a dilute monatomic gas. Indeed as shown in a Table I they are expressed in terms of collision integrals which may be evaluated for some intermolecular potentials [22,24]. This fact not only extricates the theory from previous criticisms but, as we shall see in section 3, allows for some rather interesting conclusions on its general structure.

3. ONSAGER RELATIONS

In the development of any theory dealing with irreversible processes, one of the questions we often ask ourselves is the calculation of the entropy and its production. Here we have performed the steps to construct a pair of quantities somehow extending these concepts beyond the local regime directly from the postulates of the EIT. Moreover the equations describing the time evolution for the fast variables may be directly compared with the kinetic results and therefore lead us to the values of all coefficients which from the point of view of a phenomenological theory are left as unknown quantities. The next question to be answered concerns with the possibility of also extending the definition of the thermodynamic forces, the generalized fluxes and their corresponding Onsager relationships which emerge from LIT. To construct these quantities we will take advantage of the kinetic identification of the above referred coefficients, in such a way that we can show explicitly the existence of the reciprocity symmetry for the physical system we are studying namely, a dilute gas whose states are described by 26 variables.

First of all we recall that the entropy density in the 26 variables approach is given by [22]

$$\eta = S_0 - \frac{K}{m}\left[\frac{2}{3}\frac{\overset{0}{p}}{p} : \frac{\overset{0}{p}}{p} - \frac{m}{3pKT}\overset{0}{\mathcal{I}} : \frac{\overset{0}{p}}{p} + \frac{m}{6KTp^2}\vec{q}\cdot\vec{q} + \frac{m}{6KTp^2}\mathbb{P} \vdots \mathbb{P} \right.$$
$$\left. + \frac{1}{6}\left(\frac{m}{pKT}\right)^2 \overset{0}{\mathcal{I}} : \overset{0}{\mathcal{I}} + \frac{1}{18}\left(\frac{m}{pKT}\right)^2 \mathcal{I}_{rr}^2 \right] + \cdots, \tag{3.1}$$

where all the variables appearing herein have been defined before. S_0 is the local entropy density for the ideal gas.

Equation (3.1) may be also cast in the language of EIT by simply introducing the values of the coefficients α obtained from the kinetic theory. To facilitate the translation of EIT equations (2.2), (2.7) and (2.8) into a kinetic language and viceversa we have collected the value of all coefficients in Table I.

Now we define the thermodynamic forces according to the Onsager's point of view, namely, as the derivatives of the entropy density with respect to the variables chosen to describe the system. These variables are those appearing in Eq. (2.1) and for simplicity they will be here labelled as a_i. Then, we introduce the quantities

$$\mathbb{X}_i = \left(\frac{\partial m\mathcal{S}}{\partial a_i}\right)_{a_j \neq a_i}, \tag{3.2}$$

Coefficients in Eq. (2.2)

$$\alpha_{01} = -\frac{1}{9pT}\left(\frac{m}{KT}\right)^2 \qquad \alpha_{10} = -\frac{4}{9pT}\left(\frac{m}{KT}\right)$$

$$\alpha_{20} = -\frac{4}{3pT} \qquad \alpha_{21} = \alpha_{30} = -\alpha_{40} = \frac{1}{3pT}\left(\frac{m}{KT}\right)$$

$$\alpha_{31} = -\frac{1}{3pT}\left(\frac{m}{KT}\right)^2 \qquad \alpha_{41} = 0$$

Coefficients in Eq. (2.7)

$$\beta_{10} = \frac{1}{T} \qquad \beta_{11} = -\frac{16}{45pT}\left(\frac{m}{KT}\right)$$

$$\beta_{20} = \frac{13}{21pT} \qquad \beta_{30} = -\frac{13}{21pT}\left(\frac{m}{KT}\right)$$

$$\beta_{40} = -\frac{29}{42pT} \qquad \beta_{50} = -\frac{13}{42pT}\left(\frac{m}{KT}\right)$$

Coefficients in Eq. (2.8)

$$\gamma_{00} = 0 \qquad \gamma_{01} = -\frac{1}{18p^2T}\mu_8\left(\frac{m}{KT}\right)^3$$

$$\gamma_{10} = -\frac{2m}{9p^2KT^2}\left(\frac{m}{KT}\right)^{1/2}\mu_1 \qquad \gamma_{20} = -\frac{1}{6Tp^2}\left(4\mu_2 - \frac{m}{KT}\mu_6\right)$$

$$\gamma_{31} = -\frac{1}{6T}\left(\frac{m}{pKT}\right)\left(\frac{m}{KT}\mu_8 - \mu_3\right) \qquad \gamma_{40} = \gamma_{41} = -\frac{m}{6p^2KT^2}\left(\frac{m}{KT}\right)^{1/2}\mu_5$$

$$\gamma_{21} = \gamma_{30} = -\frac{1}{12pT}\left(\frac{m}{pKT}\right)\left[4\mu_3 - \mu_2 + \frac{m}{KT}(\mu_6 - \mu_8)\right]$$

The μ coefficients in the expressions for the γ's are given in terms of some collision integrals, their detailed calculation is given in Ref. [22].

$$\mu_1 = -\frac{16}{15}np\left(\frac{KT}{m}\right)^{1/2}\Omega^{(2,2)} \qquad \mu_2 = -\frac{8}{45}np\left(\frac{19}{2}\Omega^{(2,2)} - \Omega^{(2,3)}\right)$$

$$\mu_3 = -\frac{8}{45}np\left(\Omega^{(2,3)} - \frac{7}{2}\Omega^{(2,2)}\right) \qquad \mu_4 = \mu_5 = -\frac{32}{105}np\left(\frac{KT}{m}\right)^{1/2}\Omega^{(2,2)}$$

$$\mu_6 = -\frac{4}{45}\frac{p^2}{m}\left(11\Omega^{(2,3)} - \frac{325}{12}\Omega^{(2,2)} - \Omega^{(2,4)}\right)$$

$$\mu_7 = \mu_8 = -\frac{4}{45}\frac{p^2}{m}\left(\frac{217}{12}\Omega^{(2,2)} - 5\Omega^{(2,3)} + \Omega^{(2,4)}\right)$$

TABLE I. Identification of TIE coefficients with the kinetic calculation.

Var.	Thermodynamic force	Thermodynamic flux
$\vec{q}$	$\vec{\mathbb{X}}_q = -\frac{m\alpha_{10}}{\rho}\vec{q}$	$\vec{F}_q = \frac{n}{\alpha_{10}}\left(\gamma_{10} + \frac{8}{3}\gamma_{41}\right)\vec{q}$
$\mathbb{P}$	$\mathbb{X}_P = \frac{m\alpha_{40}}{\rho}\mathbb{P}$	$\mathbb{F}_P = \frac{n\gamma_{40}}{\alpha_{40}}\mathbb{P}$
$\mathcal{I}_{rr}$	$\mathbb{X}_j = \frac{m\alpha_{01}}{\rho}\mathcal{I}_{rr}$	$F_j = \frac{n\gamma_{01}}{\alpha_{01}}\mathcal{I}_{rr}$
$\overset{\circ}{p}$	$\overset{\circ}{\mathbb{X}}_p = \frac{m\alpha_{20}}{\rho}\overset{\circ}{p} + \frac{m}{2\rho}(\alpha_{21} + \alpha_{30})\overset{\circ}{\mathcal{I}}$	$\overset{\circ}{\mathbb{F}}_p = \frac{m}{\Delta\rho}[(\gamma_{20}\alpha_{31} + \gamma_{30}\alpha_{21})\overset{\circ}{p} + (\gamma_{21}\alpha_{31} - \gamma_{31}\alpha_{21})\overset{\circ}{\mathcal{I}}]$
$\overset{\circ}{\mathcal{I}}$	$\overset{\circ}{\mathbb{X}}_j = \frac{m}{2\rho}(\alpha_{21} + \alpha_{30})\overset{\circ}{p} + \frac{m\alpha_{31}}{\rho}\overset{\circ}{\mathcal{I}}$	$\overset{\circ}{\mathbb{F}}_j = \frac{m}{\Delta\rho}[(\gamma_{30}\alpha_{20} - \gamma_{20}\alpha_{21})\overset{\circ}{p} + (\gamma_{31}\alpha_{20} - \gamma_{21}\alpha_{21})\overset{\circ}{\mathcal{I}}]$

TABLE II. Values of the thermodynamic forces and their corresponding generalized fluxes.

which we shall identify with the generalized forces for the system. Notice that $\mathbb{X}_i$ will have the same tensorial order as the corresponding independent variable a_i. The forces associated with the conserved variables are the usual ones, but those arising from the derivatives with respect to the relaxation variables are given by some combination of the independent variables themselves.

Once we have defined the forces, whose explicit values are given in Table II, the generalized fluxes conjugated to them are defined as the quantities multiplying the forces in the entropy production, when it is expressed in terms of the $\mathbb{X}$'s. Using the values for the β coefficients appearing in Eq. (2.7) obtained from kinetic theory and collected in Table I, as well as the values for the generalized forces (Table II), Eq. (2.8) can be written as a product of forces and fluxes:

$$\sigma_\eta = \vec{\mathbb{X}}_q \cdot \vec{\mathbb{F}}_q + \overset{\circ}{\mathbb{X}}_p : \overset{\circ}{\mathbb{F}}_p + \overset{\circ}{\mathbb{X}}_j : \overset{\circ}{\mathbb{F}}_j + \mathbb{X}_P : \mathbb{F}_P + \mathbb{X}_j \mathbb{F}_j. \tag{3.3}$$

The result of this calculation is also shown in Table II, where in the last column we give the explicit expression for the flux next to the value of the corresponding force. From the inspection of these terms, it is clear that the generalized fluxes have a rather different structure from the conventional fluxes of EIT and can be written as linear combinations of the thermodynamic forces. Notice should be made that the selection of fluxes is not unique, as one expects if we recall the existence of Meixner transformations. The results of Table II allow us to define the Onsager transport coefficients in the usual way, namely

$$\mathbb{F}_i = \sum_j \mathbb{L}_{ij}\mathbb{X}_j, \tag{3.4}$$

where all the $\mathbb{L}_{ij}$ coefficients are scalars, consistently with the isotropic properties of our system. After arranging the terms in the last column of Table II we may easily see that:

$$\mathbb{L}_{jj} = \frac{n^2 \gamma_{01}}{\alpha_{01}^2}, \tag{3.5}$$

$$\mathbb{L}_{qq} = \frac{n^2}{\alpha_{01}^2}(\gamma_{10} + \tfrac{8}{3}\gamma_{41}), \tag{3.6}$$

$$\mathbb{L}_{PP} = \frac{n^2 \gamma_{40}}{\alpha_{40}^2}, \tag{3.7}$$

$$\mathbb{L}_{pp} = \left(\frac{m}{\Delta\rho}\right)^2 [\alpha_{31}^2 \gamma_{20} + \alpha_{21}^2 \gamma_{31} - \alpha_{21}\alpha_{31}(\gamma_{30} + \gamma_{21})], \tag{3.8}$$

$$\mathbb{L}_{pj} = \left(\frac{m}{\Delta\rho}\right)^2 [\alpha_{21}^2 \gamma_{30} - \alpha_{21}\alpha_{31}\gamma_{20} + \alpha_{20}(\gamma_{21}\alpha_{31} - (\gamma_{31}\alpha_{21})], \tag{3.9}$$

$$\mathbb{L}_{jp} = \left(\frac{m}{\Delta\rho}\right)^2 [\alpha_{21}^2 \gamma_{21} - \alpha_{21}\alpha_{31}\gamma_{20} + \alpha_{20}(\gamma_{30}\alpha_{31} - (\gamma_{31}\alpha_{21})], \tag{3.10}$$

$$\mathbb{L}_{jj} = \left(\frac{m}{\Delta\rho}\right)^2 [\alpha_{21}^2 \gamma_{20} + \alpha_{20}^2 \gamma_{31} - \alpha_{21}\alpha_{20}(\gamma_{30} + \gamma_{21})]. \tag{3.11}$$

It is now clear that the only coefficients that involve "crossed terms" are $\mathbb{L}_{jp}$ and $\mathbb{L}_{pj}$ as shown by Eqs. (3.9) and (3.10). The corresponding Onsager relation will be valid provided $\gamma_{30} = \gamma_{21}$, a condition which in fact occurs when we compare the EIT coefficients with their corresponding values as obtained in the kinetic calculations. These coefficients can also be written in terms of collision integrals, and can be evaluated for some intermolecular potentials as well as from the experimental data for noble gases [19].

Except for some efforts done by Nettleton in this direction [19], in the great majority of the available calculations based on EIT postulates, the expression for the thermodynamic forces, the fluxes and their relationships have been ignored. This is possibly due to the fact that the generalized entropy is not necessarily understood in the same way as in LIT. Here we have shown that it is possible to follow the same steps as in LIT, if we have some way to calculate the phenomenological coefficients either by a kinetic equation or using some other microscopic model. This requirement is necessary in order to see if the Onsager symmetry is valid.

4. CONCLUDING REMARKS

Our main point in this section will be a discussion of some distinctive features of the EIT version we developed in this paper. First of all we emphasize that it follows the steps of the Spanish-Belgian school, in the sense that Eq. (2.6) is taken as an entropy balance equation. Accordingly in Sect. 3 we used the entropy density to define the thermodynamic forces, and the entropy production to construct the generalized fluxes.

Notice should be made however, that the explicit form of this entropy density, as well as the value of the entropy production are not the results of EIT or any other phenomenological method. In fact they come from the comparison with the results of the calculation model based on the Boltzmann equation. Thus a gap may be filled between EIT which allows us to find the structure of the equations and the explicit evaluation of the phenomenological coefficients, a task beyond the scope of phenomenology.

From the point of view of Onsager's approach to irreversible phenomena let us comment that in our set of independent variables only two of them have the same tensorial character, $\overset{0}{p}$ and $\overset{0}{I}$. The Curie principle, which applies to our system being an isotropic gas, tells us that only these variables can be linearly coupled. This implies the existence of one reciprocity relation. The choice of forces and fluxes we have made includes these two tensors, which in fact have the same parity properties under time reversal. This characteristic can be seen directly from their kinetic definition, because they are given as the second and fourth order momenta of the single particle distribution function.

Lastly we recall that in the kinetic calculation we showed that the entropy production is a positive definite quantity [22]. This assertion was proved not only for some model potentials but also for the values taken from experimental data in the case of noble gases.

In what concerns the construction of a theory of irreversible processes, it is clear that all these properties have as a common basis the immediate generalization of LIT to a broader set of independent variables. Here we have taken profit of the results obtained by means of the kinetic calculation, which allows for the calculation of all the phenomenological quantities. This fact has been also rather limitative since for many other systems which in some way have been successfully dealt with by EIT no simple kinetic model is available. The coefficients appearing in these cases may only be known through the experiment.

REFERENCES

1. L. Onsager, *Phys. Rev.* **37** (1931) 2265.
2. S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, Dover Publications Inc Mineola, N.Y. (1984).
3. I. Prigogine, *Introduction to Non-equilibrium Thermodynamics*, Wiley Interscience, New York (1962).
4. I. Gyarmati, *Non-equilibrium Thermodynamics: Field Theory and Variational Principles*, Springer Verlag, Berlin (1970).

5. J. Meixner and H.G. Reik "Thermodynamik der Irreversible Prozesse" in *Handbuch der Physik*, Vol III, Band 2, ed. S. Flügge, Springer Verlag, Berlin (1959).
6. L. Onsager and S. Machlup, *Phys. Rev.* **91** (1953) 1505; *íbid.* **91** (1953) 1512.
7. L.S. García Colín *Termodinámica de Procesos Irreversibles* (in Spanish), Colección CBI, UAM-Iztapalapa, México (1989).
8. R. Haase, *Irreversible Thermodynamics*, Dover Publications Inc. Mineola N.Y. (1987).
9. H. Mori, I. Oppenheim and J. Ross in *Studies in Statistical Mechanics*, Vol. I, p. 217, eds. J. de Boer and G.E. Uhlenbeck, North Holland Publishing Co., Amsterdam (1962).
10. D.G. Miller in *Transport Phenomena in Fluids*, ed. H.M.J. Hanley, M. Dekker, Inc., N.Y. (1969).
11. "Recent Developments in Non-equilibrium Thermodynamics", *Lecture Notes in Physics* **199**, eds. J. Casas-Vázquez, D. Jou and G. Lebon; Springer Verlag, Berlin (1984).
12. D. Jou, J. Casas-Vázquez and G. Lebon, *Rep. Prog. Phys. (London)* **51** (1988) 1105.
13. L.S. García Colín, *Rev. Mex. Fís.* **34** (1988) 344.
14. D.D. Joseph and L. Preziosi, *Rev. Mod. Phys.* **61** (1989) 41; *íbid.* **62** (1990) 375.
15. R. Kohlrausch, *Ann. Phys.* **12** (1847) 393.
16. J.C. Maxwell in *The Collected Papers of J. Clerk Maxwell*, Vol. II, p. 30 ed. W.R. Niven; Dover Publications, N.Y. (1965).
17. H. Grad in *Handbuch der Physik*, Vol. 12, ed. S. Flügge Springer Verlag, Berlin (1958); *Comm. Pure Appl. Math.* **2** (1949) 331.
18. L.S. García Colín, *Acta Phys. Hungarica* **69** (1989) 79.
19. R.E. Nettleton, *Acta Physica Hungarica* **69** (1989) 177 and references therein.
20. See papers by Müller, B.C. Eu and others in Ref. [11].
21. G. Lebon, *Acta Physica Hungarica* **69** (1989) 241.
22. R.M. Velasco, L.S. García Colín, *J. Stat. Phys.* (in press).
23. M. López de Haro and R.F. Rodríguez, *J. Non Equil. Thermodyn.* **14** (1989) 37.
24. R.M. Velasco and L.S. García Colín, *Phys. Rev.* **44 A** (1991), October 15.
25. C. Delale, *J. Stat. Phys.* **37** (1984) 451.
26. A. Vasconcellos, R. Luzzi and L.S. García Colín, *Phys. Rev.* **43 A** (1991) 6622; *íbid.* **43 A** (1991) 6633.
27. B. Robertson, *Phys. Rev.* **144** (1966) 151.
28. E.T. Jaynes in *Maximum Entropy Formalism*, R.D. Levine and M. Tribus, eds. (MIT Press, Cambridge, Mass 1978) p. 278.
29. J. Kestin, K. Knierim, E.A. Mason, B. Najafi, S. T.Ro, and M. Waldman, *J. Phys. Chem. Ref.* data **13** (1984) 229.

RESUMEN. En este trabajo discutimos las relaciones de Onsager válidas para los coeficientes de transporte en un gas monoatómico diluido, cuya descripción se efectúa mediante la termodinámica irreversible extendida. Para ello, se consideran 26 variables independientes y su comparación con el cálculo cinético permite la evaluación de todos los coeficientes. Se definen las fuerzas y flujos termodinámicos que permiten demostrar la existencia de las relaciones de reciprocidad adecuadas.