Generalized Onsager's theory for a dilute binary mixture*

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ABSTRACT. The Grad's moment approach to solve the Boltzmann equation is applied to a dilute binary mixture of monatomic gases. The quantities involved in the entropy balance equation are constructed and we show how they can be used as a basis to develop the Onsager's theory beyond the usual local equilibrium phenomena. The usual constitutive equations are obtained and the hierarchical relaxation of the system is exhibited.

RESUMEN. El método de Grad para resolver la ecuación de Boltzmann se aplica a una mezcla binaria diluida de gases monoatómicos. Se calculan las cantidades involucradas en la ecuación de balance de la entropía y demostramos que éstas son básicas para desarrollar la teoría de Onsager, más allá del equilibrio local. Las ecuaciones constitutivas usuales se obtienen de manera directa y se muestra la presencia de relajamiento en etapas.

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1. INTRODUCTION

The study of binary mixtures by means of linear irreversible thermodynamics (LIT) is an old subject. The diffusion, thermal conduction and thermal diffusion are the well known direct and cross effects caused by temperature and concentration gradients [1-3]. The corresponding Onsager symmetry is also a well known and experimentally supported relation [4]. However we know that LIT is limited to the local equilibrium hypothesis, besides the use of linear constitutive equations, which a lot of people had tried to overcome in order to consider more general nonequilibrium phenomena than those allowed by the usual treatment [5]. From the phenomenological point of view there exist some approaches that allow the study of some problems beyond local equilibrium. Explicit examples are provided by rational thermodynamics [6], the hidden variables thermodynamic treatment [7], the wave approach [8], etc., where people must introduce some set of hypotheses to take into account how we are considering the particular characteristics of nonequilibrium states. Also extended irreversible thermodynamics (EIT) seems to give us the way to go beyond local equilibrium, by means of the enlargement of the space of variables [9]. The kinetic counterpart of EIT is provided by the Grad's solution method for the Boltzmann equation, at least for dilute gases where it is allowed a full calculation, as shown in the literature [10-12]. Recently we have shown that this kinetic approach can

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be seen as an Onsager theory for states out of local equilibrium [13]. Here we will use those ideas to show how we can also construct thermodynamic forces and fluxes which obey all the postulates established by Onsager sixty years ago [14], for a binary mixture of monatomic gases, which it is assumed to be described by the Boltzmann equation. To simplify the calculation we only consider the 13-moment level of description, allowing for the introduction of three independent vectors and two second order tensors to be coupled according to the isotropy of the system. In Sect. 2 we introduce the kinetic model and calculate the equations of motion. Section 3 is devoted to the calculation of the elements in the entropy balance equation, while in Sect. 4 we demonstrate the Onsager relationship in the context of the general theory. In Sect. 5 we recover the usual Onsager relation between the thermal diffusion coefficients and show how the hierarchical relaxation arises. Lastly in Sect. 6 we emphasize some points in our results.

2. KINETIC MODEL

The binary mixture is assumed to be described correctly by the Boltzmann equation [15], which can be written as

$$\frac{\partial}{\partial t} f_i(\mathbf{c}_i, \mathbf{x}, t) + \mathbf{c}_i \cdot \nabla f_i(\mathbf{c}_i, \mathbf{x}, t) = J(f_i, f_i) + J(f_i, f_j), \quad (i, j = a, b), \tag{2.1}$$

where $f_i(\mathbf{c}_i, \mathbf{x}, t)$ is the single particle distribution function for i–species. The equation for j-species is obtained from Eq. (2.1) by the interchange of f_i by f_j, $\mathbf{c}_i$ is the molecular velocity and $J(f_i, f_i)$, $J(f_i, f_j)$ are the usual collision terms between particles of the same and different species respectively. The local Maxwellian distribution function will be the weight function of the Grad's moment expansion [16] and it contains the conserved variables in the system, namely

$$f_i^{(0)} = n_i \left(\frac{m_i}{2\pi K_B T}\right)^{3/2} \exp\left(-\frac{m_i C_i^2}{2K_B T}\right), \quad (i = a, b), \tag{2.2}$$

where

$$n_i = \int f_i(\mathbf{c}_i, \mathbf{x}, t)\, d\mathbf{c}_i \tag{2.3}$$

is the number density of i–species,

$$\mathbf{C}_i = \mathbf{c}_i - \mathbf{u}_0 \tag{2.4}$$

the peculiar velocity and

$$\mathbf{u}_0 = \frac{1}{\rho}\left(\rho_a \mathbf{u}_a + \rho_b \mathbf{u}_b\right) \tag{2.5}$$

the hydrodynamic velocity, $\rho_i = n_i m_i$ the mass density and

$$\mathbf{u}_i = \frac{1}{n_i} \int \mathbf{c}_i f_i(\mathbf{c}_i, \mathbf{x}, t)\, d\mathbf{c}_i \tag{2.6}$$

the mean velocity of each species. The local temperature T is defined in terms of the total energy in the system

$$\tfrac{3}{2} K_B T (n_a + n_b) = \int \left(\tfrac{1}{2} m_a C_a^2 f_a\, d\mathbf{c}_a + \tfrac{1}{2} m_b C_b^2 f_b\, d\mathbf{c}_b \right). \tag{2.7}$$

According to Grad's method at the level of 13–moment approximation (25 moments for a binary mixture) the distribution function is written as

$$f_i = f_i^{(0)} \left\{ 1 + \frac{m_i}{K_B T} \mathbf{V}_i \cdot \mathbf{C}_i + \frac{m_i}{2 p_i K_B T} \overset{0}{\mathbf{P}}_i : (\mathbf{C}_i \mathbf{C}_i)^\circ \right.$$
$$\left. + \frac{2 m_i}{5 p_i K_B T} \left(\frac{m_i C_i^2}{2 K_B T} - \frac{5}{2} \right) \mathbf{q}_i \cdot \mathbf{C}_i \right\}, \tag{2.8}$$

where

$$\mathbf{V}_i = \mathbf{u}_i - \mathbf{u}_0 \tag{2.9}$$

is the diffusion velocity

$$\overset{0}{\mathbf{P}}_i = \int m_i (\mathbf{C}_i \mathbf{C}_i)^\circ f_i(\mathbf{c}_i, \mathbf{x}, t)\, d\mathbf{c}_i \tag{2.10}$$

is the traceless viscous tensor, $p_i = n_i K_B T$ the partial hydrostatic pressure, and

$$\mathbf{q}_i = \int \left(\frac{m_i C_i^2}{2} - \frac{5}{2 K_B T} \right) \mathbf{C}_i f_i(\mathbf{c}_i, \mathbf{x}, t)\, d\mathbf{c}_i \tag{2.11}$$

the heat flux.

The equations of motion corresponding to the set of independent variables are obtained in a straightforward way by substitution of the distribution function in the Boltzmann equation (2.1). Notice should be made that the higher order momenta appearing in the equations are consistently approximated to the level of a 13–moment description. We only write the linearized equations for the "physical fluxes" $(\mathbf{q}_a, \mathbf{q}_b, \mathbf{V}_a, \overset{0}{\mathbf{P}}_a, \overset{0}{\mathbf{P}}_b)$ since the conservation equations are the usual ones.

The heat fluxes obey the following equations:

$$\frac{D}{Dt} \mathbf{q}_a + \frac{K_B T}{m_a} (\nabla \cdot \overset{0}{\mathbf{P}}_a) + \frac{5}{2} \mathbf{p}_a \nabla \left(\frac{K_B T}{m_a} \right) = -\frac{5 K_B p_a}{2 m_a \lambda_a^\circ} \mathbf{q}_a + A_{22} \mathbf{q}_a + A_{21} \mathbf{V}_a + A_{23} \mathbf{q}_b \tag{2.12}$$

for a–species, and

$$\frac{D}{Dt}\mathbf{q}_b + \frac{K_B T}{m_b}(\nabla \cdot \overset{0}{P}_b) + \frac{5}{2}p_b \nabla\left(\frac{K_B T}{m_b}\right) = -\frac{5K_B p_b}{2m_b \lambda_b^\circ}\mathbf{q}_b + A_{33}\mathbf{q}_b + A_{31}\mathbf{V}_a + A_{32}\mathbf{q}_a \quad (2.13)$$

for b–species. The diffusion velocity also satisfies a relaxation equation, namely

$$\frac{D}{Dt}\mathbf{V}_a + \frac{p}{\rho_a}\mathbf{d}_a + \frac{1}{\rho_a}\nabla \cdot \overset{0}{P}_a - \frac{1}{\rho}\nabla \cdot \overset{0}{P} = \frac{1}{\rho_a}\left(A_{11}\mathbf{V}_a + A_{12}\mathbf{q}_a + A_{13}\mathbf{q}_b\right), \quad (2.14)$$

where

$$\mathbf{d}_a = \nabla\left(\frac{n_a}{n}\right) + \left(\frac{n_a}{n} - \frac{\rho_a}{\rho}\right)\nabla \ln p \quad (2.15)$$

is the usual diffusion force. The equations for the viscous tensors associated with a, b species are given by

$$\frac{D}{Dt}\overset{0}{P}_a + 2p_a(\nabla \mathbf{u}_a)^\circ + \frac{4}{5}(\nabla \mathbf{q}_a)^\circ = -\frac{p_a}{\eta_a^\circ}\overset{0}{P}_a + A_{41}\overset{0}{P}_a + A_{42}\overset{0}{P}_b, \quad (2.16)$$

$$\frac{D}{Dt}\overset{0}{P}_b + 2p_b(\nabla \mathbf{u}_b)^\circ + \frac{4}{5}(\nabla \mathbf{q}_b)^\circ = -\frac{p_b}{\eta_b^\circ}\overset{0}{P}_b + A_{52}\overset{0}{P}_b + A_{51}\overset{0}{P}_a, \quad (2.17)$$

where $(\ )^\circ$ means the corresponding symmetric traceless tensor, λ_a^0, λ_b^0, are the usual thermal conductivities and η_a^0, η_b^0 shear viscosities of the corresponding pure component. The $A_{\alpha\beta}$ coefficients are given in terms of the usual collision brackets and can be written as some combinations of the $\Omega_{ij}^{(r,s)}$ collision integrals as shown in Table I [16]. Those integrals can be evaluated for some interaction potentials between molecules, in such a way that we do not have any undetermined coefficients.

To understand clearly how these equations are constructed, some remarks are convenient. First of all we linearized the equations around the local equilibrium state described by the local Maxwellian distribution function, given in Eq. (2.2). It means that we have a non zero hydrodynamic velocity in the system, that is why we have written the hydrodynamic derivative $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u}_0 \cdot \nabla$ in the equations, the term $\mathbf{u}_0 \cdot \nabla$ is neglected in a usual linear theory. To be consistent with this linearization procedure we neglected terms in which the gradients of a conserved variable appear in a bilinear way, their products with a relaxation variable and of course bilinear terms in the relaxation variables. As a second remark we notice that the gradients of physical fluxes are considered in the scheme, allowing for spatial inhomogeneities other than those allowed by the gradients of conserved variables. Lastly we emphasize that these equations show the relaxation of the physical fluxes, which from now on we call them as state variables.

TABLE I. Kinetic value of coefficients in the equations of motion (2.12)-(2.17).

$$\lambda_i^0 = \frac{75 K_B p_i}{32 \rho_i \Omega_{ii}^{(2,2)}}$$

$$\eta_i^0 = \frac{5 K_B T}{8 \Omega_{ii}^{(2,2)}}$$

$$A_{11} = -\frac{16}{3} n_a \mu_a \rho \Omega_{ab}^{(1,1)}$$

$$A_{12} = \frac{32 \rho_a n_b}{15 p_a} \mu_b^2 \left(\frac{5}{2} \Omega_{ab}^{(1,1)} - \Omega_{ab}^{(1,2)} \right)$$

$$A_{13} = -\frac{32}{15} \frac{\rho_a n_b}{p_b} \left(\frac{m_b}{m_a} \right)^{1/2} \mu_a^{3/2} \mu_b^{1/2} \left(\frac{5}{2} \Omega_{ab}^{(1,1)} - \Omega_{ab}^{(1,2)} \right)$$

$$A_{21} = \frac{16}{3} p_a n_b \mu_b^2 \frac{\rho}{\rho_b} \left(\frac{5}{2} \Omega_{ab}^{(1,1)} - \Omega_{ab}^{(1,2)} \right)$$

$$A_{22} = -\frac{32}{15} n_b \mu_b \left[\frac{5}{4} \left(6\mu_a^2 + 5\mu_b^2 \right) \Omega_{ab}^{(1,1)} - 5\mu_b^2 \Omega_{ab}^{(1,2)} + \mu_b^2 \Omega_{ab}^{(1,3)} + 2\mu_a \mu_b \Omega_{ab}^{(2,2)} \right]$$

$$A_{23} = \frac{n_a m_b}{n_b m_a} A_{32}$$

$$A_{31} = -\frac{16}{3} p_b n_a \mu_a^2 \frac{\rho}{\rho_b} \left(\frac{5}{2} \Omega_{ab}^{(1,1)} - \Omega_{ab}^{(1,2)} \right)$$

$$A_{32} = \frac{32}{15} \frac{p_b n_a}{p_a} \left(\frac{m_a}{m_b} \right)^{1/2} \mu_b^{3/2} \mu_a^{3/2} \left(\frac{55}{4} \Omega_{ab}^{(1,1)} - 5\Omega_{ab}^{(1,2)} + \Omega_{ab}^{(1,3)} - 2\Omega_{ab}^{(2,2)} \right)$$

$$A_{33} = A_{32}$$

$$A_{41} = -\frac{64}{15} n_b \mu_b \left(5\mu_a \Omega_{ab}^{(1,1)} + \frac{3}{2} \mu_b \Omega_{ab}^{(2,2)} \right)$$

$$A_{42} = \frac{64}{15} n_a \mu_a \mu_b \left(5\Omega_{ab}^{(1,1)} - \frac{3}{2} \Omega_{ab}^{(2,2)} \right)$$

$$A_{51} = \frac{64}{15} n_b \mu_a \mu_b \left(5\Omega_{ab}^{(1,1)} - \frac{3}{2} \Omega_{ab}^{(2,2)} \right)$$

$$A_{52} = -\frac{64}{15} n_a \mu_a \left(5\mu_b \Omega_{ab}^{(1,1)} + \frac{3}{2} \mu_a \Omega_{ab}^{(2,2)} \right)$$

$$\mu_i = \frac{m_i}{(m_i + m_j)}$$

3. GENERALIZED ENTROPY CALCULATION

It is well known that the Boltzmann equation can be written in a way resembling an entropy balance equation, when we define the entropy density as the average of $\ln f$, namely

$$\rho_i S_i(\mathbf{x}, t) = -K_B \int\int (\ln f_i - 1) f_i \, d\mathbf{c}_i. \tag{3.1}$$

This expression allows us the calculation of the entropy density associated to the binary mixture, by direct substitution of the distribution function (2.8). The result is expressed in terms of the conserved variables through the local equilibrium contribution $S^{(0)}$, and a bilinear part coming from the relaxation variables, namely

$$\rho S = \rho S^{(0)} - \frac{\rho}{2T\rho_b}\rho_a \mathbf{V}_a \cdot \mathbf{V}_a - \frac{1}{4p_a T}\overset{\circ}{\mathbf{P}}_a : \overset{\circ}{\mathbf{P}}_a - \frac{1}{4p_b T}\overset{\circ}{\mathbf{P}}_b : \overset{\circ}{\mathbf{P}}_b$$
$$- \frac{m_a}{5p_a K_B T^2}\mathbf{q}_a \cdot \mathbf{q}_a - \frac{m_b}{5p_b K_B T^2}\mathbf{q}_b \cdot \mathbf{q}_b + \cdots \tag{3.2}$$

The additional terms not written here come from the expansion of $\ln f$ in Eq. (3.1) but all of them are higher order in the relaxation variables.

In a similar way the entropy flux can be written as

$$\mathbf{J}_{si} = -K_B \int\int (\ln f_i - 1)\mathbf{C}_i f_i \, d\mathbf{c}_i, \tag{3.3}$$

and its value in the 13-moment level of approximation is given by

$$\mathbf{J}_s = \rho_a\left(S_b^{(0)} - S_a^{(0)}\right)\mathbf{V}_a + \frac{1}{T}(\mathbf{q}_a + \mathbf{q}_b) - \frac{1}{2T}\left(\overset{\circ}{\mathbf{P}}_a - \frac{\rho_a}{\rho_b}\overset{\circ}{\mathbf{P}}_b\right)\cdot \mathbf{V}_a$$
$$- \frac{2}{5p_a T}\overset{\circ}{\mathbf{P}}_a \cdot \mathbf{q}_a - \frac{2}{5p_b T}\overset{\circ}{\mathbf{P}}_b \cdot \mathbf{q}_b + \cdots, \tag{3.4}$$

which obviously reduces to the usual value we have in a one component system.

Once we have the entropy density and the flux of entropy, the only thing we need to obtain a complete scheme is the entropy production. The corresponding kinetic definition is given by the addition of four contributions, in such a way that

$$\sigma_s = \sigma_{saa} + \sigma_{sbb} + \sigma_{sab} + \sigma_{sba}, \tag{3.5}$$

where each term is given by an expression of the following form:

$$\sigma_{sij} = -K_B \int\int (\ln f_i - 1) J(f_i, f_j) \, d\mathbf{c}_i, \quad (i, j = a, b). \tag{3.6}$$

To calculate the different terms in Eq. (3.5) we only consider bilinear terms in the relaxation variables, the explicit expression is given by

$$\sigma_s = \frac{1}{2\eta_a^0 T}\overset{0}{\mathbf{P}}_a : \overset{0}{\mathbf{P}}_a + \frac{1}{\lambda_a^0 T^2}\mathbf{q}_a \cdot \mathbf{q}_a + \frac{1}{2\eta_b^0 T}\overset{0}{\mathbf{P}}_b : \overset{0}{\mathbf{P}}_b + \frac{1}{\lambda_b^0 T^2}\mathbf{q}_b \cdot \mathbf{q}_b$$

$$- \frac{\rho}{T\rho_b}\mathbf{V}_a \cdot (A_{11}\mathbf{V}_a + A_{12}\mathbf{q}_a + A_{13}\mathbf{q}_b) - \frac{1}{2p_a T}\overset{0}{\mathbf{P}}_a : (A_{41}\overset{0}{\mathbf{P}}_a + A_{42}\overset{0}{\mathbf{P}}_b)$$

$$- \frac{1}{2p_b T}\overset{0}{\mathbf{P}}_b : (A_{52}\overset{0}{\mathbf{P}}_b + A_{51}\overset{0}{\mathbf{P}}_a) - \frac{2m_a}{5p_a K_B T^2}\mathbf{q}_a \cdot (A_{22}\mathbf{q}_a + A_{21}\mathbf{V}_a + A_{23}\mathbf{q}_b)$$

$$- \frac{2m_b}{5p_b K_B T^2}\mathbf{q}_b \cdot (A_{33}\mathbf{q}_b + A_{31}\mathbf{V}_a + A_{32}\mathbf{q}_a) + \cdots \tag{3.7}$$

Now we are ready to study the properties of the entropy scheme, first of all we notice that $\rho S^{(0)}$, *i.e.*, the local entropy density represents the maximum value of such a function, indeed the bilinear terms in Eq. (3.2) constitute a negative contribution to ρS. On the other hand we can take this expression for the entropy density to define the thermodynamic forces in the Onsager's theory, namely

$$\boldsymbol{X}_{q_a} = \left(\frac{\partial \rho S}{\partial \mathbf{q}_a}\right)_{V_a, q_b, \overset{0}{P}_a, \overset{0}{P}_b} = -\frac{2m_a}{5p_a K_B T^2}\mathbf{q}_a, \tag{3.8}$$

$$\boldsymbol{X}_{q_b} = \left(\frac{\partial \rho S}{\partial \mathbf{q}_b}\right)_{V_a, q_a, \overset{0}{P}_a, \overset{0}{P}_b} = -\frac{2m_b}{5p_b K_B T^2}\mathbf{q}_b, \tag{3.9}$$

$$\boldsymbol{X}_{V_a} = \left(\frac{\partial \rho S}{\partial \mathbf{V}_a}\right)_{q_a, q_b, \overset{0}{P}_a, \overset{0}{P}_b} = -\frac{\rho \rho_a}{T\rho_b}\mathbf{V}_a, \tag{3.10}$$

$$\overset{0}{\boldsymbol{X}}_{\overset{0}{P}_a} = \left(\frac{\partial \rho S}{\partial P_a}\right)_{V_a, q_b, q_a, \overset{0}{P}_b} = -\frac{1}{2p_a T}\overset{0}{\mathbf{P}}_a, \tag{3.11}$$

$$\overset{0}{\boldsymbol{X}}_{\overset{0}{P}_b} = \left(\frac{\partial \rho S}{\partial P_b}\right)_{V_a, q_b, q_a, \overset{0}{P}_b} = -\frac{1}{2p_b T}\overset{0}{\mathbf{P}}_b. \tag{3.12}$$

This means that the relaxation variables $(\mathbf{q}_a, \mathbf{q}_b, \mathbf{V}_a, \overset{0}{\mathbf{P}}_a, \overset{0}{\mathbf{P}}_b)$ play the role of the state variables introduced by Onsager, but now are working around the local equilibrium state. As a first consequence of this definition, we clearly see in Eqs. (3.8)-(3.12) that those forces are proportional to the physical fluxes which are themselves the state variables.

In order to define the thermodynamic fluxes we now turn to the entropy production given in Eq. (3.7) and write it as a linear function of the thermodynamic forces. The quantities which multiply each force are identified as thermodynamic fluxes, namely

$$\boldsymbol{F}_{q_a} = -\frac{5p_a K_B}{2m_a \lambda_a^0}\mathbf{q}_a + A_{21}\mathbf{V}_a + A_{22}\mathbf{q}_a + A_{23}\mathbf{q}_b, \tag{3.13}$$

$$\boldsymbol{F}_{q_b} = -\frac{5p_bK_B}{2m_b\lambda_b^0}\mathbf{q}_b + A_{31}\mathbf{V}_a + A_{32}\mathbf{q}_a + A_{33}\mathbf{q}_b, \tag{3.14}$$

$$\boldsymbol{F}_{V_a} = \frac{1}{\rho_a}(A_{11}\mathbf{V}_a + A_{12}\mathbf{q}_a + A_{13}\mathbf{q}_b), \tag{3.15}$$

$$\overset{0}{\boldsymbol{F}}_{p_a} = -\frac{p_a}{\eta_a^0}\overset{0}{\boldsymbol{P}}_a + A_{41}\overset{0}{\boldsymbol{P}}_a + A_{42}\overset{0}{\boldsymbol{P}}_b, \tag{3.16}$$

$$\overset{0}{\boldsymbol{F}}_{p_b} = -\frac{p_b}{\eta_b^0}\overset{0}{\boldsymbol{P}}_b + A_{51}\overset{0}{\boldsymbol{P}}_a + A_{52}\overset{0}{\boldsymbol{P}}_b. \tag{3.17}$$

Now the entropy production can be written as a product of the thermodynamic forces and their corresponding thermodynamic fluxes, namely

$$\sigma_s = \boldsymbol{X}_{q_a}\cdot\boldsymbol{F}_{q_a} + \boldsymbol{X}_{q_b}\cdot\boldsymbol{F}_{q_b} + \boldsymbol{X}_{V_a}\cdot\boldsymbol{F}_{V_a} + \overset{0}{\boldsymbol{X}}_{p_a} : \overset{0}{\boldsymbol{F}}_{p_a} + \overset{0}{\boldsymbol{X}}_{p_b} : \overset{0}{\boldsymbol{F}}_{p_b}, \tag{3.18}$$

which is the usual form in Onsager's theory. Notice that Eq. (3.18) is a bilinear form in the state variables. It can be shown that it is a positive definite quantity if we take into account the properties of the collision brackets in multicomponent mixtures [15]. To emphasize this point let us recall that those properties are based on the characteristics of inverse collisions. This fact allows us to see that the microscopic reversibility is playing an important role in this description.

4. GENERALIZED ONSAGER'S RECIPROCITY RELATION

The definition of thermodynamic forces and the identification of thermodynamic fluxes done in the last section allow us to write the fluxes as linear combinations of forces. In fact we can define a generalized Onsager matrix of transport coefficients in such a way that

$$\boldsymbol{F}_{(r)} = \sum_{(s)} \boldsymbol{L}_{(r,s)}\boldsymbol{X}_{(s)}, \tag{4.1}$$

where $\boldsymbol{L}_{(r,s)}$ are the Onsager coefficients whose explicit expression in terms of collision integrals is given in Table II, where we have written only the nonzero elements. Notice that coupled forces and fluxes are the ones with the same tensorial character, according to the Curie's principle for an isotropic system, as the one we are working with.

Once we have written the Onsager matrix, it immediately arises the question about its symmetry properties. To analyze them we consider the matrix elements coupling the three vectorial fluxes and compare the off-diagonal elements. We notice that the symmetry property if it exists, depends in a crucial way on the value of the $A_{\alpha\beta}$ coefficients. A careful analysis of them shows that the $\boldsymbol{L}$ matrix elements satisfy the Onsager symmetry, as we

TABLE II. Elements of the Onsager matrix.

$$\boldsymbol{L}(\mathbf{q}_a,\mathbf{q}_a) = -\frac{5p_aK_BT^2}{2m_a}\left(-\frac{5p_aK_B}{2m_a\lambda_a^0}+A_{22}\right)$$

$$\boldsymbol{L}(\mathbf{q}_b,\mathbf{q}_a) = -\frac{5p_aK_BT^2}{2m_a}A_{32}$$

$$\boldsymbol{L}(\mathbf{V}_a,\mathbf{q}_a) = -\frac{5p_aK_BT^2}{2m_a\rho_a}A_{12}$$

$$\boldsymbol{L}(\mathbf{q}_a,\mathbf{q}_b) = -\frac{5p_bK_BT^2}{2m_b}A_{23}$$

$$\boldsymbol{L}(\mathbf{q}_b,\mathbf{q}_b) = -\frac{5p_bK_BT^2}{2m_b}\left(-\frac{5p_bK_B}{2m_b\lambda_b^0}+A_{33}\right)$$

$$\boldsymbol{L}(\mathbf{V}_a,\mathbf{q}_b) = -\frac{5p_bK_BT^2}{2m_b\rho_a}A_{13}$$

$$\boldsymbol{L}(\mathbf{q}_a,\mathbf{V}_a) = -\frac{T\rho_b}{\rho\rho_a}A_{21}$$

$$\boldsymbol{L}(\mathbf{q}_b,\mathbf{V}_a) = -\frac{T\rho_b}{\rho\rho_a}A_{31}$$

$$\boldsymbol{L}(\mathbf{V}_a,\mathbf{V}_a) = -\frac{T\rho_b}{\rho\rho_a^2}A_{11}$$

$$\boldsymbol{L}(\overset{\circ}{\boldsymbol{P}}_a,\overset{\circ}{\boldsymbol{P}}_a) = -2p_aT\left(-\frac{p_a}{\eta_a^0}+A_{41}\right)$$

$$\boldsymbol{L}(\overset{\circ}{\boldsymbol{P}}_b,\overset{\circ}{\boldsymbol{P}}_a) = -2p_aTA_{51}$$

$$\boldsymbol{L}(\overset{\circ}{\boldsymbol{P}}_a,\overset{\circ}{\boldsymbol{P}}_b) = -2p_bTA_{42}$$

$$\boldsymbol{L}(\overset{\circ}{\boldsymbol{P}}_b,\overset{\circ}{\boldsymbol{P}}_b) = -2p_bT\left(-\frac{p_b}{\eta_b^0}+A_{52}\right)$$

would expect. To illustrate this point, let us consider the quotient $\frac{\boldsymbol{L}(\mathbf{q}_a,\mathbf{V}_a)}{\boldsymbol{L}(\mathbf{V}_a,\mathbf{q}_a)}$ and substitute A_{12}, A_{21} taken from Table I, namely

$$\frac{\boldsymbol{L}(\mathbf{q}_a,\mathbf{V}_a)}{\boldsymbol{L}(\mathbf{V}_a,\mathbf{q}_a)} = \frac{2m_a\rho_bA_{21}}{5p_aK_BT\rho A_{12}} = 1. \tag{4.2}$$

In a similar way we can show that all other elements in $\boldsymbol{L}$ matrix are symmetric and this

symmetry depends on the properties of collision brackets [15], as emphasized in Sect. 3. This relationship will be called a "generalized Onsager symmetry property", recalling that we are working in a generalized space of state variables which describes the system beyond local equilibrium.

A very important consequence of this scheme is that up to now these properties are independent of the equations of motion. Now we will establish the connection between those aspects of the same problem. To accomplish such a program let us compare the thermodynamic fluxes given in Eqs. (3.13)-(3.17) with the right hand side of the relaxation equations we constructed directly from the Boltzmann equation. It is clear that Eqs. (2.12)-(2.17) can be rewritten as follows:

$$\frac{D}{Dt}\mathbf{q}_a + \frac{K_B T}{m_a}(\nabla \cdot \overset{0}{\boldsymbol{P}}_a) + \frac{5}{2} p_a \nabla \left(\frac{K_B T}{m_a}\right) = \boldsymbol{F}_{q_a}, \tag{4.3}$$

$$\frac{D}{Dt}\mathbf{q}_b + \frac{K_B T}{m_b}(\nabla \cdot \overset{0}{\boldsymbol{P}}_b) + \frac{5}{2} p_b \nabla \left(\frac{K_B T}{m_b}\right) = \boldsymbol{F}_{q_b}, \tag{4.4}$$

$$\frac{D}{Dt}\mathbf{V}_a + \frac{p}{\rho_a}\mathbf{d}_a + \frac{1}{\rho_a}\nabla \cdot \overset{0}{\boldsymbol{P}}_a - \frac{1}{\rho}\nabla \cdot \overset{0}{\boldsymbol{P}} = \boldsymbol{F}_{V_a}, \tag{4.5}$$

$$\frac{D}{Dt}\overset{0}{\boldsymbol{P}}_a + 2p_a(\nabla \mathbf{u}_a)^0 + \frac{4}{5}(\nabla \mathbf{q}_a)^0 = \overset{0}{\boldsymbol{F}}_{p_a}, \tag{4.6}$$

$$\frac{D}{Dt}\overset{0}{\boldsymbol{P}}_b + 2p_b(\nabla \mathbf{u}_b)^0 + \frac{4}{5}(\nabla \mathbf{q}_b)^0 = \overset{0}{\boldsymbol{F}}_{p_b}. \tag{4.7}$$

To reinterpret the set of Eqs. (4.3)-(4.7) let us recall that the description of our system is given in terms of state variables $(\mathbf{q}_a, \mathbf{q}_b, \mathbf{V}_a, \overset{0}{\boldsymbol{P}}_a, \overset{0}{\boldsymbol{P}}_b)$ which have this label because the entropy density of our system is written as a well behaved function of them. Their time derivative is now proportional to the corresponding thermodynamic flux, a fact that is taken for granted in the Onsager theory. The terms ∇T, $\mathbf{d}_a$, $(\nabla \mathbf{u}_a)^0$, $(\nabla \mathbf{u}_b)^0$ give the contribution of the spatial inhomogeneities in the conserved variables which are present even in local equilibrium. Lastly the quantities $\nabla \cdot \overset{0}{\boldsymbol{P}}_a$, $\nabla \cdot \overset{0}{\boldsymbol{P}}_b$, $\nabla \cdot \overset{0}{\boldsymbol{P}}$, $(\nabla \mathbf{q}_a)^0$ and $(\nabla \mathbf{q}_b)^0$ take into account the spatial inhomogeneities of the state variables, as well as the term $\mathbf{u}_0 \cdot \nabla(\mathbf{q}_a, \mathbf{q}_b, \mathbf{V}_a, \overset{0}{\boldsymbol{P}}_a, \overset{0}{\boldsymbol{P}}_b)$ in the hydrodynamic derivative. In fact Eqs. (4.3)-(4.7) give us the generalization of Onsager's flux definition for an inhomogeneous system, in this particular case for an inhomogeneous binary mixture of dilute gases. The results obtained in this section show how we can generalize to the case of binary mixtures, the formulation we reported recently for a simple gas [13].

5. CONSTITUTIVE EQUATIONS

To complete our development we will obtain the usual constitutive equations for the total heat flux and the diffusion velocity. We start with Eqs. (4.3)-(4.7) and consider

the stationary and homogeneous case for the state variables, in such a way that the gradients of conserved variables are the quantities inducing a nonequilibrium process in our system. In this case the thermodynamic fluxes become proportional to those gradients and according to Eqs. (3.13)-(3.17) they are also some combinations of the physical fluxes. Needless to go into the details to solve the set of equations and find the expressions of the physical fluxes in terms of the gradients of conserved variables. In particular we construct the usual diffusion flux and the total heat flux, namely

$$\begin{aligned}\mathbf{W} &= \mathbf{V}_a - \mathbf{V}_b = \frac{\rho}{\rho_b}\mathbf{V}_a \\ &= \frac{\rho p}{\rho_b \Delta}\left[\left(A_{22} - \frac{5p_a K_B}{2m_a\lambda_a^0}\right)\left(A_{33} - \frac{5p_b K_B}{2m_b\lambda_b^0}\right) - A_{32}A_{23}\right]\mathbf{d}_a \\ &\quad + \frac{\rho}{\rho_b \Delta}\left\{-\frac{5p_a K_B}{2m_a}\left[A_{12}\left(A_{33} - \frac{5p_b K_B}{2m_b\lambda_b^0}\right) - A_{32}A_{33}\right]\right. \\ &\quad \left. - \frac{5p_b K_B}{2m_b}\left[A_{13}\left(A_{22} - \frac{5p_a K_B}{2m_a\lambda_a^0}\right) - A_{12}A_{23}\right]\right\}(\nabla T), \qquad (5.1)\end{aligned}$$

$$\begin{aligned}\mathbf{q}^{\mathrm{tot}} &= \mathbf{q}_a + \mathbf{q}_b \\ &= \frac{p}{\Delta}\left[A_{21}\left(A_{32} - A_{33} + \frac{5p_b K_B}{2m_b\lambda_b^0}\right) + A_{31}\left(A_{23} - A_{22} + \frac{5p_a K_B}{2m_a\lambda_a^0}\right)\right]\mathbf{d}_a \\ &\quad + \frac{1}{\Delta}\left\{\frac{5p_a K_B}{2m_a}\left[A_{11}\left(A_{33} - A_{32} - \frac{5p_b K_B}{2m_b\lambda_b^0}\right) - A_{31}(A_{13} - A_{12})\right]\right. \\ &\quad \left. + \frac{5p_b K_B}{2m_b}\left[A_{11}\left(A_{22} - A_{23} - \frac{5p_a K_B}{2m_a\lambda_a^0}\right) - A_{21}(A_{12} - A_{13})\right]\right\}(\nabla T), \qquad (5.2)\end{aligned}$$

where Δ is the determinant of Eqs. (3.13)-(3.15) in the particular case we are considering now. Equations (5.1)-(5.2) show clearly how the usual thermal diffusion effects appear in this kinetic calculation.

Now the usual Onsager relation will be assured if the coefficient of (∇T) in Eq. (5.1) is equal to the coefficient of $\mathbf{d}_a$ in Eq. (5.2). We notice that the existence of such a reciprocity relation depends on the value of $A_{\alpha\beta}$ collision integrals. The generalized Onsager relation or equivalently the values given in Table I allow us to see that those coefficients have both the same value. The usual solution given in Eqs. (5.1) and (5.2) represents the first order in the expansion in the Knudsen number, so the gradients in the conserved variables account for this kind of spatial inhomogeneities. Then the terms like $\nabla \cdot \overset{0}{\boldsymbol{P}}$ and $(\nabla \mathbf{q})^0$ appearing in the complete set of equations are inhomogeneities in the state variables which contribute to the constitutive equations in a higher order Knudsen expansion.

As a last step in our analysis let us take a nonstationary situation and notice that the equations of motion (2.12)-(2.17) allow the definition of relaxation times for the state

variables. The relaxation times are related with collision brackets and they are associated with each component in the mixture in such a way that they reduce to the corresponding term in a pure gas, namely

$$\begin{aligned} \tau_{p_a} &= \frac{\eta_a^0}{p_a}, & \tau_{p_b} &= \frac{\eta_b^0}{p_b}, \\ \tau_{q_a} &= \frac{2m_a\lambda_a^0}{5K_{\mathrm{B}}p_a}, & \tau_{q_b} &= \frac{2m_b\lambda_b^0}{5K_{\mathrm{B}}p_b}. \end{aligned} \tag{5.3}$$

The relaxation time associated with the diffusion velocity is given by

$$\tau_{V_a} = -\frac{\rho_a}{A_{11}}, \tag{5.4}$$

it is a positive quantity characteristic of the mixture. These definitions show that Eqs. (2.12)-(2.17) have the structure of Maxwell-Cattaneo-Vernotte equations, which have been studied in the literature to support the EIT approach [10-12].

To give an example of the role played by these relaxation times, let us consider a hard sphere interaction potential, where the particles of i–species are characterized by their radius σ_i. The mean free path associated with species i is then defined as

$$\ell_i \cong \frac{1}{n_i\sigma_i^2} \tag{5.5}$$

then the relaxation times given in Eqs. (5.3)-(5.4) satisfy the following relations:

$$\frac{\tau_{p_a}}{\tau_{p_b}} = \frac{\tau_{q_a}}{\tau_{q_b}} = \frac{\ell_a}{\ell_b}\left(\frac{m_a}{m_b}\right)^{1/2}, \tag{5.6}$$

$$\frac{\tau_{p_a}}{\tau_{V_a}} = \frac{5n_b(\sigma_a+\sigma_b)^2}{12n_a\sigma_a^2}\left(1+\frac{\rho_a}{\rho_b}\right)\left[2\left(1+\frac{m_a}{m_b}\right)\right]^{-1/2}. \tag{5.7}$$

All these quantities depend on the size of molecules, but also have a dependence with the corresponding masses. When we have a disparate mass binary mixture ($m_a \ll m_b$), we can define a smallness parameter

$$\delta = \left(\frac{m_a}{m_b}\right)^{1/2} \ll 1 \tag{5.8}$$

in such a way that the relaxation times present a hierarchical ordering, when condition (5.8) holds and the mean free paths are of the same order of magnitude:

$$\tau_{p_a} \cong \tau_{q_a} \cong \tau_{V_a} \ll \tau_{p_b} \cong \tau_{q_b}. \tag{5.9}$$

The consequences of the hierarchical relaxation shown in this model will be studied elsewhere.

6. CONCLUDING REMARKS

Just to emphasize the results shown in this paper let me add some remarks about the kind of processes we are describing. The first thing is that we are working in states which are beyond local equilibrium, where the usual LIT is not valid. To go into this region we have introduced a set of independent state variables and they are the starting point to construct the entropy density and the corresponding entropy production. These elements of the entropy balance allow the application of Onsager's theory to have thermodynamic forces and fluxes satisfying the Onsager symmetry relationship. All these calculations are done on the basis of the validity of the kinetic model we introduced in Sect. 2. We obtained the usual constitutive equations and we have indicated how the usual Onsager relation between Soret and Doufour coefficients appears as a consequence of our development. The last step showed how the relaxation type of equations are contained in our model and the presence of a hierarchical ordering in the relaxation times was exhibited.

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