Investigación *Revista Mexicana de Física* **41**, *No. 3 (1995) 342–357*

The linear standard Enskog theory revisited: the case of a binary mixture

PATRICIA GOLDSTEIN
Departamento de Física, Facultad de Ciencias
Universidad Nacional Autónoma de México
04510 México, D.F., México

Recibido el 29 de agosto de 1994; aceptado el 24 de febrero de 1995

ABSTRACT. Within the framework of a revisit to the linear Standard Enskog Theory, the kinetic theory for a binary mixture of rigid spheres is proved to be consistent with linear irreversible thermodynamics in terms of the thermodynamic forces and fluxes derived from the kinetic definition of the entropy production. A straightforward calculation of the Onsager coefficients is presented.

RESUMEN. Dentro del contexto de una reconsideración de la teoría de Enskog estándar linealizada, se muestra la consistencia de la teoría cinética de una mezcla binaria de esferas duras con la termodinámica irreversible lineal en términos de flujos y fuerzas termodinámicos derivados de la definición cinética de la producción de entropía. Se presenta un cálculo directo de los coeficientes de Onsager correspondientes.

PACS: 05.20.Dd

1. INTRODUCTION

In order to describe the behavior of a simple dense gas of rigid spheres, D. Enskog proposed in 1921 a kinetic equation which essentially modifies the collision term of the Boltzmann equation [1,2], assuming that only binary collisions need to be considered and that the molecular chaos hypothesis still holds. Due to the finite diameter σ of the rigid spheres, collisions do not occur at a given point in space. Thus, the point where the distribution function of the colliding sphere in the collision term is evaluated must be modified, which means that the term

$$f(\mathbf{r},\mathbf{v},t)f(\mathbf{r},\mathbf{v}_1,t)$$

in Boltzmann's equation must be replaced by

$$f(\mathbf{r},\mathbf{v},t)f(\mathbf{r}\pm\sigma\mathbf{k},\mathbf{v}_1,t),$$

where $\mathbf{k}$ is a unit vector along the line which joins the centers of the colliding molecules. On the other hand, taking into consideration the fact that in the case of a dense gas the probability of a collision increases with increasing density, an additional factor, the equilibrium value of the nonequilibrium pair correlation function χ^{E}, is introduced in the collision term; χ^{E} is a function of density, position and time and reduces to unity in the case of the dilute gas. With these modifications, Enskog equation reads

$$\frac{\partial}{\partial t}f + \mathbf{v}\cdot\frac{\partial}{\partial r}f + \mathbf{F}\cdot\frac{\partial}{\partial \mathbf{v}}f = J^{\mathrm{E}}(f,f), \tag{1}$$

where

$$\begin{aligned} J^{\mathrm{E}}(f,f) = \iint \Big\{ &\chi^{\mathrm{E}}(\mathbf{r}+\tfrac{1}{2}\sigma\mathbf{k})f'(\mathbf{r})f_1'(\mathbf{r}+\sigma\mathbf{k}) \\ &- \chi^{\mathrm{E}}(\mathbf{r}-\tfrac{1}{2}\sigma\mathbf{k})f(\mathbf{r})f_1(\mathbf{r}-\sigma\mathbf{k})\Big\}\sigma^2\mathbf{g}\cdot\mathbf{k}\,d\mathbf{k}\,d\mathbf{v}_1. \end{aligned} \tag{2}$$

The evaluation of the factor χ^{E} in the case of a fairly rare uniform simple gas goes back to Boltzmann and Clausius up to second order in the density. In the case of a non-uniform gas, one should expect that this factor may also involve a dependence on the space derivatives of the density.

In an unpublished work [1], H.H. Thorne generalized Enskog's theory to the case of a binary mixture introducing three types of factors, χ_{11} and χ_{22} related respectively to collisions between pairs of molecules of species 1 and between pairs of species 2, and, $\chi_{12} = \chi_{21}$ corresponding to the collisions between pairs of dissimilar species, in terms of the densities of both, their diameter and the distance between their centers. Solving the Enskog like equations using the Chapman-Enskog method, he obtained an expression for the diffusion forces, the heat flux ,the coefficient of diffusion and the thermal conductivity.

Following the same ideas, an extension of Thorne's work to the case of a multicomponent dense fluid mixture was studied by Tham and Gubbins [3]. Some inconsistencies in both works were brought into consideration by García-Colín, Barajas and Piña [4–6] basically due to the way in which the point of evaluation of the functions χ_{ij} is taken. They showed that these functions may be evaluated in any arbitrary point located between the centers of the colliding molecules. The only quantity which is affected by the choice of this point is the diffusion force. This result was taken as an argument to assert that Enskog's theory for mixtures is incompatible with linear irreversible thermodynamics (LIT) [6]. This last description together with the preceeding ones are known in the literature as the standard Enskog theory (SET) [7]. Starting from the fact that SET is a theory which apparently exhibits inconsistencies with LIT, mainly an incompatibility with Onsager reciprocity relations, a new kind of approach was taken which may be embodied in the so called revised Enskog theory (RET) [7–15] which has not been modified in the last ten years [16]. A thorough revision of RET will not be made in this paper. Here, we shall revisit SET and prove that, contrary to what was mentioned above, there is a very simple case of the linear SET which is consistent with LIT, in particular, the Onsager reciprocity relations are satisfied. Although in some works [17] the fact that SET may be compatible with LIT has been mentioned using techniques such a maximization of the entropy, we consider worthwhile to present this version of the linear case of SET and show in a transparent way its compatibility with LIT using a different method that the one used in Ref. [17]. In order to avoid cumbersome notation we shall restrict ourselves to a binary mixture of dissimilar hard spheres. In Sect. 2, we develop the generalized SET linear kinetic equations; in Sect. 3 we find the corresponding thermodynamic fluxes and forces that arise from the kinetic definition of the entropy production. In Sect. 4, we prove that these forces and fluxes follow Onsager symmetry relations. Finally, in Sect. 5, we discuss the important aspects of this work.

2. THE LINEAR KINETIC EQUATIONS IN THE REVISITED STANDARD ENSKOG THEORY

Let us consider a system consisting of a binary mixture of dissimilar rigid spheres with diameters σ_i, number density n_i, and masses m_i $(i = 1, 2)$.

In the absence of external forces, the Enskog type equations for a binary mixture proposed by Barajas, García-Colín and Piña [5] for the single particle distribution function f are given by

$$\begin{aligned}\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{r}} \equiv \mathcal{D}_t f_i = \sum_{j=1}^{2} \iint \big\{ &\chi_{ij}(\mathbf{r}_i + y_{ij}\mathbf{k}) f_j'(\mathbf{r}_i + \sigma_{ij}\mathbf{k}) f_i'(\mathbf{r}_i) \\ &- \chi_{ij}(\mathbf{r}_i - y_{ij}\mathbf{k}) f_j(\mathbf{r}_i - \sigma_{ij}\mathbf{k}) f_i(\mathbf{r}_i) \big\} \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j \\ = J(f_i, f_j),& \end{aligned} \tag{3}$$

where $\mathbf{v}_k$, $\mathbf{v}_k'$ are the molecular velocities before and after the collision, respectively; χ_{ij} is the generalization of Enskog's function evaluated in an arbitrary point y_{ij} located between the centers of the colliding particles, and

$$\sigma_{ij} \equiv \frac{\sigma_i + \sigma_j}{2}, \qquad \mathbf{k} \equiv \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|},$$

$$\mathbf{g}_{ji} \equiv \mathbf{v}_j - \mathbf{v}_i, \qquad y_{ij} + y_{ji} = \sigma_{ij} = \sigma_{ji}.$$

The novel aspect of this present work is that we shall here assume that χ_{ij} is a general and unknown function of the density, that is

$$\chi_{ij} = \chi_{ij}(n_i, n_j).$$

In order to obtain the linearized expression for the kinetic equation (3), we must first expand the distribution function f_i and the Enskog function χ_{ij} in Taylor series up to the first order in gradients. Then, in order to solve this linear equation we shall follow the Chapman-Enskog method considering consistently the solution also up to the first order.

The expansions of f_i and χ_{ij} may be written as

$$\chi_{ij}(\mathbf{r} \pm y_{ij}\mathbf{k}) \simeq \chi_{ij}^0 \pm y_{ij}\mathbf{k} \cdot \nabla \chi_{ij}, \tag{4}$$

with

$$\nabla \chi_{ij} = \sum_{k=1}^{2} \left(\frac{\partial \chi_{ij}}{\partial n_k} \right) \nabla n_k, \tag{5}$$

and χ_{ij}^0 is the equilibrium value of χ_{ij} evaluated in the point of contact, and

$$f_i(\mathbf{r} \pm \sigma_{ij}\mathbf{k}) = f_i(\mathbf{r}) \pm \sigma_{ij}\mathbf{k} \cdot \nabla f_i(\mathbf{r}). \tag{6}$$

Using the Hilbert-Enskog method for the solution of Eq. (3), we may write, keeping only linear terms,

$$f_i = f_i^0 + f_i^1 + \cdots = f_i^0\{1 + \phi_i^1 + \cdots\}, \tag{7}$$

where f_i^0 is the local Maxwellian distribution function,

$$f_i^0 = n_i \left(\frac{m_i}{2\pi k_{\mathrm{B}} T} \right)^{3/2} \exp\left\{ -\frac{m_i c_i^2}{2k_{\mathrm{B}} T} \right\}, \tag{8}$$

and the number density n_i is given by

$$n_i = \int f_i^0 \, d\mathbf{v}_i, \tag{9}$$

$\mathbf{c}_i = \mathbf{v}_i - \mathbf{u}$ is the thermal velocity, and the local hydrodynamic velocity $\mathbf{u}$ is

$$\rho \mathbf{u} = \sum_{i=1}^{2} \int f_i^0 m_i \mathbf{v}_i \, d\mathbf{v}_i, \tag{10}$$

and the local temperature T is given through

$$\tfrac{3}{2} n k_{\mathrm{B}} T = \sum_{i=1}^{2} \int f_i^0 \tfrac{1}{2} m_i c_i^2 \, d\mathbf{v}_i. \tag{11}$$

Using the expansions given by Eqs. (4)-(8), we may rewrite the linearized form of the kinetic equation (3) as

$$\mathcal{D}_t f_i^0 = \sum_{j=1}^{2} \mathcal{L}_{ij}^1(f^0 f^1) + \sum_{j=1}^{2} \sum_{k \neq 1}^{3} \mathcal{L}_{ij}^k(f^0), \tag{12}$$

where

$$\mathcal{L}^1_{ij}(f^0 f^1) = \chi^0_{ij} \iint f_i^0 f_j^0 (\phi_i + \phi_j - \phi_i' - \phi_j') \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j, \tag{13}$$

$$\mathcal{L}^2_{ij} \equiv \chi^0_{ij} \iint \mathbf{k} \cdot (f_i^{0\prime} \nabla f_j^{0\prime} + f_i^0 \nabla f_j^0) \sigma_{ij}^3 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j, \tag{14}$$

$$\mathcal{L}^3_{ij} \equiv \iint \mathbf{k} \cdot \nabla \chi_{ij} (f_i^{0\prime} f_j^{0\prime} + f_i^0 f_j^0) y_{ij} \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j. \tag{15}$$

In order to obtain the corresponding conservation equations in the linear regime we shall multiply Eqs. (12) by the collisional invariants, namely

$$\psi_i = 1, \qquad m_i \mathbf{c}_i, \qquad m_i c_i^2/2.$$

Performing an integration over the velocity space, and carrying out a summation over species 1 and 2, we recover the conservation equations in the Euler regime [5], namely:

i) For $\psi_i = 1$, the equation of continuity,

$$\frac{D}{Dt} n + n \nabla \cdot \mathbf{u} = 0, \tag{16}$$

where $n = \sum_i n_i$.

ii) For $\psi_i = m_i \mathbf{c}_i$, the equation of motion,

$$\frac{D}{Dt} \mathbf{u} + \frac{1}{\rho} \nabla p_0 = 0, \tag{17}$$

where $\rho = \sum_i \rho_i = \sum_i m_i n_i$.

iii) For $\psi_i = \frac{1}{2} m_i c_i^2$, the energy conservation equation,

$$\frac{1}{T} \frac{D}{Dt} T + \frac{2 p_0}{3 n k_{\mathrm{B}} T} \nabla \cdot \mathbf{u} = 0. \tag{18}$$

In Eqs. (16)-(18) we have denoted

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla,$$

and we have recognized in Eqs. (17)-(18) the hydrostatic pressure p_0 of the hard spheres system given by the equation of state

$$p_0 = \sum_{i=1}^{2} n_i k_{\mathrm{B}} T \left(1 + \sum_{j=1}^{2} \beta_{ij} n_j \chi^0_{ij} \right) = \sum_{i=1}^{2} p_{0i}, \tag{19}$$

with

$$\beta_{ij} = \tfrac{2}{3}\pi\sigma_{ij}^3.$$

Using the conservation equations (16)-(18) in Eq. (12) we finally arrive to the linearized kinetic equation

$$\sum_{j=1}^{2} \chi_{ij}^0 \iint f_i^0 f_j^0 (\phi_i + \phi_j - \phi_i' - \phi_j') \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{v}_j =$$

$$-f_i^0 \left\{ \mathbb{K}_i \left(\mathcal{C}_i^2 - \tfrac{5}{2}\right) \mathbf{c}_i \cdot \nabla \ln T + \tfrac{n}{n_i} \mathbf{d}_{ij} \cdot \mathbf{c}_i + 2\mathbb{K}_i' \left[\mathcal{C}_i \mathcal{C}_i\right]_s : \nabla \mathbf{u} + \tfrac{2}{3} \tfrac{n_j}{n} \mathbb{K}_i'' \left(\mathcal{C}_i^2 - \tfrac{3}{2}\right) \nabla \cdot \mathbf{u} \right\}, \qquad (20)$$

where $\mathcal{C}_i \equiv (m_i / 2k_{\mathrm{B}}T)^{1/2} \mathbf{c}_i$, $[\quad]_s$ represents the traceless symmetric part of a tensor, and $\mathbf{d}_{ij}$ defines the diffusion force, namely,

$$\mathbf{d}_{ij} = \frac{\rho_i \rho_j}{\rho n_i k_{\mathrm{B}} T} \left(\frac{1}{\rho_i} \nabla p_{0i} - \frac{1}{\rho_j} \nabla p_{0j} \right)$$

$$+ \frac{n_j}{n_i} \beta_{ji} n_i \chi_{ij}^0 \left\{ \nabla \ln \left(\frac{n_j}{n_i} \right) + (M_{ij} - M_{ji}) \nabla \ln T + \frac{2y_{ij} - \sigma_{ij}}{\sigma_{ij}} \nabla \ln \chi_{ij} \right\}, \qquad (21)$$

where

$$\mathbf{d}_{ij} = -\mathbf{d}_{ji}, \qquad (22)$$

and

$$M_{ij} = \frac{m_i}{m_i + m_j},$$

$$\mathbb{K}_i \equiv 1 + \tfrac{12}{5} \sum_{j=1}^{2} \beta_{ij} n_j \chi_{ij}^0 M_{ij} M_{ji}, \qquad (23)$$

$$\mathbb{K}_i' = 1 + \tfrac{4}{5} \sum_{j=1}^{2} \beta_{ij} n_j \chi_{ij}^0 M_{ji}, \qquad (24)$$

$$\mathbb{K}_i'' = 1 + 2 \sum_{j=1}^{2} \beta_{ij} n_j \chi_{ij}^0 M_{ji} - \frac{p_0}{n k_{\mathrm{B}} T}. \qquad (25)$$

Following the same procedure as the one used to solve Boltzmann's equation in the case of a dilute binary mixture [1], the solution of the linearized kinetic equation, Eq. (20) may be written as

$$\phi_i = -\mathbf{A}_i(\mathbf{c}_i) \cdot \nabla \ln T - n \mathbf{D}_i(\mathbf{c}_i) \cdot \mathbf{d}_{ij} - \mathbb{B}_i(\mathbf{c}_i) : \nabla \mathbf{u} - H_i(\mathbf{c}_i) \nabla \cdot \mathbf{u}, \qquad (26)$$

with $\mathbf{A}_i$, $\mathbf{D}_i$, $\mathbb{B}_i$ and H_i satisfying the following integral equations:

$$\sum_{j=1}^{2} \chi_{ij}^0 \iint f_i^0 f_j^0 [\mathbf{A}_i + \mathbf{A}_j - \mathbf{A}_i' - \mathbf{A}_j'] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = \mathbb{K}_i f_i^0 \big(\mathcal{C}_i^2 - \tfrac{5}{2}\big)\mathbf{c}_i \tag{27}$$

$$\sum_{j=1} \chi_{ij}^0 \iint f_i^0 f_j^0 [\mathbf{D}_i + \mathbf{D}_j - \mathbf{D}_i' - \mathbf{D}_j'] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = \tfrac{1}{n} f_i^0 \mathbf{c}_i \tag{28}$$

$$\sum_{j=1}^{2} \chi_{ij}^0 \iint f_i^0 f_j^0 [\mathbb{B}_i + \mathbb{B}_j - \mathbb{B}_i' - \mathbb{B}_j'] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = 2\mathbb{K}_i' f_i^0 \{\mathcal{C}\mathcal{C}\}_s, \tag{29}$$

$$\sum_{j=1}^{2} \chi_{ij}^0 \iint f_i^0 f_j^0 [H_i + H_j - H_i' - H_j'] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = \mathbb{K}_i'' f_i^0 (\mathcal{C}_i^2 - \tfrac{3}{2})\mathbf{c}_i. \tag{30}$$

By means of the transformations

$$\begin{aligned} n_i \to n_i \mathbb{K}_i\,, \qquad & \sigma_{ij}^2 \to \frac{\chi_{ij}^0 \sigma_{ij}^2}{\mathbb{K}_i \mathbb{K}_j} && \text{in Eqs. (27),} \\ & \sigma_{ij}^2 \to \chi_{ij}^0 \sigma_{ij}^2 && \text{in Eqs. (28),} \\ n_i \to n_i \mathbb{K}_i'\,, \qquad & \sigma_{ij}^2 \to \frac{\chi_{ij}^0 \sigma_{ij}^2}{\mathbb{K}_i' \mathbb{K}_j'} && \text{in Eqs. (29),} \end{aligned} \tag{31}$$

Equations (27)-(29) may be compared with the corresponding integral equations for the Boltzmann equation for the dilute binary mixture [1]:

$$\sum_{j=1}^{2} \iint f_i^0 f_j^0 \big[\mathbf{A}_i^{\mathrm{B}} + \mathbf{A}_j^{\mathrm{B}} - \mathbf{A}_i^{\mathrm{B}\prime} - \mathbf{A}_j^{\mathrm{B}\prime}\big] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = f_i^0 \big(\mathcal{C}_i^2 - \tfrac{5}{2}\big)\mathbf{c}_i \tag{27a}$$

$$\sum_{j=1}^{2} \iint f_i^0 f_j^0 \big[\mathbf{D}_i^{\mathrm{B}} + \mathbf{D}_j^{\mathrm{B}} - \mathbf{D}_i^{\mathrm{B}\prime} - \mathbf{D}_j^{\mathrm{B}\prime}\big] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = \tfrac{1}{n} f_i^0 \mathbf{c}_i \tag{28a}$$

$$\sum_{j=1}^{2} \iint f_i^0 f_j^0 \big[\mathbb{B}_i^{\mathrm{B}} + \mathbb{B}_j^{\mathrm{B}} - \mathbb{B}_i^{\mathrm{B}\prime} - \mathbb{B}_j^{\mathrm{B}\prime}\big] \sigma_{ij}^2 (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k}\, d\mathbf{c}_j = 2 f_i^0 \{\mathcal{C}\mathcal{C}\}_s. \tag{29a}$$

Since the solutions for the functions $\mathbf{A}^{\mathrm{B}}$, $\mathbf{D}^{\mathrm{B}}$, and $\mathbb{B}^{\mathrm{B}}$ are already known, we may use these respectively for our functions $\mathbf{A}$, $\mathbf{D}$, and $\mathbb{B}$, simply by applying the transformations given in Eq. (31). Since we have no need for these functions here, they will not be written explicitly [5].

3. THE ENTROPY PRODUCTION

The definition for the entropy density ρs for the binary mixture in terms of the single particle distribution function is given by [18,19],

$$\rho s = -k_{\mathrm{B}} \sum_{i=1}^{2} \int f_i (\ln f_i - 1)\, d\mathbf{v}_i . \tag{32}$$

Taking the time derivative of Eq. (32), and after performing a partial integration, we obtain the following expression,

$$\begin{aligned} \frac{\partial \rho s}{\partial t} &= \nabla \cdot \left\{ k_{\mathrm{B}} \mathbf{u} \sum_{i=1}^{2} \int f_i (\ln f_i - 1)\, d\mathbf{v}_i \right\} + \nabla \cdot \left\{ k_{\mathrm{B}} \sum_{i=1}^{2} \int \mathbf{c}_i f_i (\ln f_i - 1)\, d\mathbf{v}_i \right\} \\ &\quad - k_{\mathrm{B}} \sum_{i=1}^{2} \sum_{j=1}^{2} \int J^{\mathrm{E}}(f_i f_j) \ln f_i \, d\mathbf{v}_i , \end{aligned} \tag{33}$$

where $J^{\mathrm{E}}(f_i f_j)$ is defined in Eq. (2). Equation (33) has the form of the entropy balance equation, namely,

$$\frac{\partial \rho s}{\partial t} = -\nabla \cdot (\rho s \mathbf{u} + \mathbf{J}_s) + \sigma , \tag{34}$$

where

$$\mathbf{J}_s = -k_{\mathrm{B}} \sum_{i=1}^{2} \int \mathbf{c}_i f_i (\ln f_i - 1)\, d\mathbf{v}_i \tag{35}$$

represents the entropy flux, and the entropy production σ is recognized as [20,21]

$$\sigma = -k_{\mathrm{B}} \sum_{i=1}^{2} \sum_{j=1}^{2} \int J^{\mathrm{E}}(f_i f_j) \ln f_i \, d\mathbf{v}_i , \tag{36}$$

where $J^{\mathrm{E}}(f_i f_j)$ is defined in Eq. (2). We emphasize that in Eq. (36) we are not taking into account contributions to σ that arise from correlations between two or more particles.

We shall now calculate the entropy production σ given by Eq. (36) for the binary mixture. Using the first order term in Chapman-Enskog approximation,

$$f_i = f_i^0 (1 + \phi_i^1),$$

the entropy production up to this order in the gradients may be written as

$$\sigma^1 = -k_{\mathrm{B}} \sum_{i=1}^{2} \sum_{j=1}^{2} \int J^{\mathrm{E}(1)}(f_i f_j) \phi_i^1 \, d\mathbf{v}_i, \tag{37}$$

where

$$J^{\mathrm{E}(1)}(f_i f_j) = \mathcal{D}_t f_i^0,$$

and

$$\begin{aligned} \mathcal{D}_t f_i^0 = f_i^0 \Bigg\{ & \mathbf{c}_i \cdot \frac{1}{n_i} \nabla n_i + \mathbf{c}_i \left(\mathcal{C}_i^2 - \tfrac{3}{2} \right) \cdot \frac{\nabla T}{T} + \frac{m_i}{k_{\mathrm{B}} T} \mathbf{c}_i^0 \mathbf{c}_i : \nabla \mathbf{u} \\ & + \tfrac{2}{3} \left(\mathcal{C}_i^2 - \tfrac{3}{2} \right) \left(1 - \frac{p_0}{n k_{\mathrm{B}} T} \right) \nabla \cdot \mathbf{u} - \frac{m_i \mathbf{c}_i}{k_{\mathrm{B}} T} \cdot \frac{\nabla p_0}{\rho} \Bigg\}. \end{aligned} \tag{38}$$

Making use of the fact that $\chi_{ij} = \chi_{ij}(n_i, n_j)$ given in Eq. (5), as well as the hard sphere equation of state, namely Eq. (8),

$$p_0 = \sum_{i=1}^{2} n_i k_{\mathrm{B}} T \left(1 + \sum_{j=1}^{2} \beta_{ij} n_j \chi_{ij}^0 \right) = \sum_{i=1}^{2} p_{0i},$$

the entropy production to first order in the gradients σ may be rewritten as follows:

$$\sigma^1 = -k_{\mathrm{B}} \left\{ \frac{1}{m_1 n_1} \mathbf{J}_1^1 \cdot \nabla n_1 + \frac{1}{m_2 n_2} \mathbf{J}_2^1 \cdot \nabla n_2 + \frac{1}{k_{\mathrm{B}} T} \mathbf{J}_q^{1\prime} \cdot \frac{\nabla T}{T} + \frac{\mathbb{T}^1}{k_{\mathrm{B}} T} : \nabla \mathbf{u} \right\}, \tag{39}$$

that is, σ is of the form

$$\sigma^1 = \sum_l \mathbf{J}_l \odot \mathbf{X}_l, \tag{40}$$

where $\mathbf{J}_l$ and $\mathbf{X}_l$ are the thermodynamic fluxes and forces, respectively, and the product $\odot$ couples the forces and fluxes of the same tensorial character. In this case

i) $\mathbf{J}_i^1$ represents the mass flux:

$$\mathbf{J}_i^1 = m_i \int f_i^0 \phi_i^1 \mathbf{c}_i \, d\mathbf{v}_i, \tag{41}$$

where $\mathbf{J}_1 + \mathbf{J}_2 = 0$.

ii) $\mathbf{J}_q^1$ is the energy flux:

$$\mathbf{J}_q^1 = \sum_{i=1}^{2} \tfrac{1}{2} m_i \int f_i^0 \phi_i^1 c_i^2 \mathbf{c}_i \, d\mathbf{v}_i, \tag{42}$$

and

$$\mathbf{J}_q^{1\prime} = \sum_{i=1}^{2} \tfrac{1}{2} m_i \int f_i^0 \phi_i^1 (c_i^2 - h_i) d\mathbf{v}_i, \tag{43}$$

where h_i is the specific enthalpy.

iii) $\mathbb{T}^1$ is the stress tensor:

$$\mathbb{T}^1 = \sum_{i=1}^{2} m_i \int f_i^0 \phi_i^1 \mathbf{c}_i^0 \mathbf{c}_i \, d\mathbf{v}_i. \tag{44}$$

The entropy production may be written in alternative ways. Equation (39) may be expressed in terms of the concentrations c_i, which characterizes the representation in which the barycentric mass flux $\mathbf{J}_i^1$ is defined [20]. It may be shown that [20]

$$\frac{\partial n_i}{\partial c_i} = \frac{n_i n_j}{n c_i c_j},$$

so that Eq. (39) is transformed into the following expression:

$$\sigma^1 = -k_{\mathrm{B}} \left\{ \frac{1}{m_1 n_1} \frac{n_1 n_2}{n c_1 c_2} \mathbf{J}_1^1 \cdot \nabla c_1 + \frac{1}{m_2 n_2} \frac{n_1 n_2}{n c_1 c_2} \mathbf{J}_2^1 \cdot \nabla c_2 \right.$$
$$\left. + \frac{1}{k_{\mathrm{B}} T} \mathbf{J}_q^{1\prime} \cdot \nabla \ln T + \frac{\mathbb{T}^1}{k_{\mathrm{B}} T} : \nabla \mathbf{u} \right\}, \tag{45}$$

but, since $\nabla c_1 = -\nabla c_2$, we may rewrite σ in terms of only one concentration, namely,

$$\sigma^1 = -k_{\mathrm{B}} \left\{ \frac{n_1 n_2}{n c_1 c_2} \left(\frac{1}{m_1 n_1} \mathbf{J}_1^1 - \frac{1}{m_2 n_2} \mathbf{J}_2^1 \right) \cdot \nabla c_1 + \frac{1}{k_{\mathrm{B}} T} \mathbf{J}_q^{1\prime} \cdot \nabla \ln T + \frac{\mathbb{T}^1}{k_{\mathrm{B}} T} : \nabla \mathbf{u} \right\}. \tag{46}$$

Finally, we may cast the entropy production σ^1 in terms of the diffusive force $\mathbf{d}_{12}$ given by Eq. (21). This force may be rewritten as

$$\mathbf{d}_{12} = \mathcal{B} \nabla \ln T + (\mathcal{A}_1 - \mathcal{A}_2) \frac{n_1 n_2}{n c_1 c_2} \nabla c_1, \tag{47}$$

with

$$\mathcal{B} = \frac{\rho_2}{\rho n}\left(2n_1 + \beta_{11}n_1^2\chi_{11}^0 + \beta_{12}n_1n_2\chi_{12}^0\right) - \frac{\rho_1}{\rho n}\left(2n_2 + \beta_{22}n_2^2\chi_{22}^0 + \beta_{12}n_1n_2\chi_{12}^0\right),$$
$$+ \frac{n_2}{n_1}\beta_{12}n_1\chi_{12}^0(M_{12} - M_{21}), \tag{48}$$

$$\mathcal{A}_1 = \frac{\rho_2}{\rho n}\left[2 + \beta_{11}\left(2\chi_{11}^0 n_1 + n_1^2\frac{\partial\chi_{11}}{\partial n_1}\right)\right] + \beta_{12}\left(n_2\chi_{12}^0 + n_1n_2\frac{\partial\chi_{12}}{\partial n_1}\right)\left[\frac{\rho_2}{\rho_n} - \frac{\rho_1}{\rho n}\right]$$
$$+ \frac{n_2}{n_1}\beta_{12}n_1\left[\frac{1}{n_1}\chi_{12}^0 + \left(\frac{2y_{12} - \sigma_{12}}{\sigma_{12}}\right)\frac{\partial\chi_{12}}{\partial n_1}\right], \tag{49}$$

$$\mathcal{A}_2 = -\frac{\rho_1}{\rho n}\left[2 + \beta_{22}\left(2\chi_{22}^0 n_2 + n_2^2\frac{\partial\chi_{22}}{\partial n_2}\right)\right] + \beta_{12}\left(n_1\chi_{12}^0 + n_1n_2\frac{\partial\chi_{12}}{\partial n_2}\right)\left[\frac{\rho_2}{\rho_n} - \frac{\rho_1}{\rho n}\right]$$
$$+ \frac{n_2}{n_1}\beta_{12}n_1\left[\frac{1}{n_2}\chi_{12}^0 + \left(\frac{2y_{12} - \sigma_{12}}{\sigma_{12}}\right)\frac{\partial\chi_{12}}{\partial n_2}\right]. \tag{50}$$

Therefore, the entropy production may be expressed as

$$\sigma^1 = -k_{\mathrm{B}}\left\{\frac{\mathbb{T}^1}{k_{\mathrm{B}}T} : \nabla\mathbf{u} + \left[\frac{J_q^{1\prime}}{k_{\mathrm{B}}T} - \frac{\mathcal{B}}{\mathcal{A}_1 - \mathcal{A}_2}\left(\frac{\mathbf{J}_1^1}{m_1n_1} - \frac{\mathbf{J}_2^1}{m_2n_2}\right)\right]\nabla\ln T\right.$$
$$\left. + \frac{1}{m_1n_1}\frac{1}{\mathcal{A}_1 - \mathcal{A}_2}\mathbf{J}_1^1\cdot\mathbf{d}_{12} + \frac{1}{m_2n_2}\frac{1}{\mathcal{A}_1 - \mathcal{A}_2}\mathbf{J}_2^1\cdot\mathbf{d}_{21}\right\}. \tag{51}$$

4. COMPATIBILITY WITH LIT AND THE ONSAGER RECIPROCITY RELATIONS

As we know from the literature [20], the entropy production may be written in alternative forms provided these expressions present the same structure given by Eq. (40) for the new forces $\mathbf{X}_l'$ and fluxes $\mathbf{J}_l'$. Indeed one has that

$$\sigma = \sum_l \mathbf{J}_l \odot \mathbf{X}_l = \sum_l \mathbf{J}_l' \odot \mathbf{X}_l'.$$

It is important to point out that the derivation of Onsager's reciprocity relations within the framework of kinetic theory may not be straightforward in any representation whatsoever. In the case of a binary mixture, it is not entirely clear that the reciprocity relations between the cross effects coefficients, that is, the thermal diffusion and Dufour coefficients, hold in the concentration representation [20].

In the case of mixtures, it has been shown, both from the kinetic point of view starting from the Boltzmann equation [22] as well as from the macroscopic version of the theory [23], that the diffusive force $\mathbf{d}_{ij}$ is the most adequate thermodynamic force conjugate to the corresponding mass flux $\mathbf{J}_i$. In the case of a dense binary mixture in the context of the present paper we will show that indeed $\mathbf{d}_{ij}$ is compatible with Onsager requirements.

Since we are interested in proving the symmetry of the cross effects of a vectorial character, for sake of simplicity, we shall ignore in these calculations the contributions due to the stress tensor $\mathbb{T}$ in ϕ_i^1.

The solutions (26) to Eqs. (20) may be written in this case as

$$\phi_1^1 = -\mathbf{A}_1 \cdot \nabla \ln T - n\mathbf{D}_1 \cdot \mathbf{d}_{12}, \tag{52}$$

$$\phi_2^1 = -\mathbf{A}_2 \cdot \nabla \ln T - n\mathbf{D}_2 \cdot \mathbf{d}_{21}. \tag{53}$$

Using well known arguments on tensorial homogeneity [1],

$$\mathbf{A}_1(\mathbf{c}_1) = a_1(\mathbf{c}_1)\mathbf{c}_1, \tag{54}$$

$$\mathbf{A}_2(\mathbf{c}_2) = a_2(\mathbf{c}_2)\mathbf{c}_2, \tag{55}$$

$$\mathbf{D}_1(\mathbf{c}_1) = d_1(\mathbf{c}_1)\mathbf{c}_1, \tag{56}$$

$$\mathbf{D}_2(\mathbf{c}_2) = d_2(\mathbf{c}_2)\mathbf{c}_2, \tag{57}$$

where $\mathbf{A}_1$, $\mathbf{A}_2$, $\mathbf{D}_1$, $\mathbf{D}_2$, satisfy the integral Eqs. (27)-(28).

In order to find the validity of Onsager's reciprocity relations we must first write down the expressions for the mass and energy fluxes. The mass fluxes may be written as

$$\mathbf{J}_1 = -\tfrac{1}{3}m_1 \int f_1^0 a_1 c_1^2 \, d\mathbf{c}_1 \nabla \ln T - \tfrac{1}{3}nm_1 \int f_1^0 d_1 c_1^2 \, d\mathbf{c}_1 \, \mathbf{d}_{12}, \tag{58}$$

$$\mathbf{J}_2 = -\tfrac{1}{3}m_2 \int f_2^0 a_2 c_2^2 \, d\mathbf{c}_2 \nabla \ln T - \tfrac{1}{3}nm_2 \int f_2^0 d_2 c_2^2 \, d\mathbf{c}_2 \, \mathbf{d}_{21}, \tag{59}$$

and the energy flux

$$\begin{aligned}
\mathbf{J}_q^{1''} &= \mathbf{J}_q^1 - \tfrac{5}{2}\frac{k_{\mathrm{B}}T}{m_1}\mathbf{J}_1^1 - \tfrac{5}{2}\frac{k_{\mathrm{B}}T}{m_2}\mathbf{J}_2^1 \\
&= -\tfrac{1}{3}k_{\mathrm{B}}T \left\{ \int f_1^0 a_1 c_1^2 \left(\tfrac{5}{2} - \mathcal{C}_1^2\right) d\mathbf{c}_1 + \int f_2^0 a_2 c_2^2 \left(\tfrac{5}{2} - \mathcal{C}_2^2\right) d\mathbf{c}_2 \right\} \nabla \ln T \\
&\quad - \tfrac{1}{3}k_{\mathrm{B}}T \left\{ \int f_1^0 n d_1 c_1^2 \left(\tfrac{5}{2} - \mathcal{C}_1^2\right) d\mathbf{c}_1 \right\} \mathbf{d}_{12} \\
&\quad - \tfrac{1}{3}k_{\mathrm{B}}T \left\{ \int f_1^0 n d_1 c_1^2 \left(\tfrac{5}{2} - \mathcal{C}_1^2\right) d\mathbf{c}_1 \right\} \mathbf{d}_{21}.
\end{aligned} \tag{60}$$

Equations (58)-(60) may be rewritten, using the integral equations, Eqs. (27)-(28), and after symmetrizing the integrands read as

$$\mathbf{J}_1^1 = -\tfrac{1}{6} m_1 n \sum_{j=1}^{2} \Big\{ \chi_{1j}^0 \iiint \big[(\mathbf{A}_1 + \mathbf{A}_j - \mathbf{A}_1' - \mathbf{A}_j') \cdot (\mathbf{D}_1 + \mathbf{D}_j - \mathbf{D}_1' - \mathbf{D}_j') f_1^0 f_j^0 \\ (\mathbf{g}_{j1} \cdot \mathbf{k}) \sigma_{1j}^2 \, d\mathbf{k} \, d\mathbf{c}_1 \, d\mathbf{c}_j \big] \Big\} \nabla \ln T - \tfrac{1}{3} n m_1 \int f_1^0 d_1 c_1^2 \, d\mathbf{c}_1 \, \mathbf{d}_{12}, \tag{61}$$

$$\mathbf{J}_2^1 = -\tfrac{1}{6} m_2 n \sum_{j=1}^{2} \Big\{ \chi_{2j}^0 \iiint \big[(\mathbf{A}_2 + \mathbf{A}_j - \mathbf{A}_2' - \mathbf{A}_j') \cdot (\mathbf{D}_2 + \mathbf{D}_j - \mathbf{D}_2' - \mathbf{D}_j') f_2^0 f_j^0 \\ (\mathbf{g}_{j2} \cdot \mathbf{k}) \sigma_{2j}^2 \, d\mathbf{k} \, d\mathbf{c}_2 \, d\mathbf{c}_j \big] \Big\} \nabla \ln T - \tfrac{1}{3} n m_2 \int f_2^0 d_2 c_2^2 \, d\mathbf{c}_2 \, \mathbf{d}_{21}, \tag{62}$$

$$\mathbf{J}_q^{1''} = -\tfrac{1}{3} k_{\mathrm{B}} T \left\{ \int f_1^0 a_1 c_1^2 \big(\tfrac{5}{2} - \mathcal{C}_1^2\big) \, d\mathbf{c}_1 + \int f_2^0 a_2 c_2^2 \big(\tfrac{5}{2} - \mathcal{C}_2^2\big) \, d\mathbf{c}_2 \right\} \nabla \ln T \\ - \tfrac{1}{6} k_{\mathrm{B}} T n \frac{1}{\mathbb{K}_1} \sum_{j=1}^{2} \Big\{ \chi_{1j}^0 \iiint \big[(\mathbf{A}_1 + \mathbf{A}_j - \mathbf{A}_1' - \mathbf{A}_j') \cdot (\mathbf{D}_1 + \mathbf{D}_j - \mathbf{D}_1' - \mathbf{D}_j') \\ f_1^0 f_j^0 (\mathbf{g}_{j1} \cdot \mathbf{k}) \sigma_{1j}^2 \, d\mathbf{k} \, d\mathbf{c}_1 \, d\mathbf{c}_j \big] \Big\} \mathbf{d}_{12} \\ - \tfrac{1}{6} k_{\mathrm{B}} T n \frac{1}{\mathbb{K}_2} \sum_{j=1}^{2} \Big\{ \chi_{2j}^0 \iiint \big[(\mathbf{A}_2 + \mathbf{A}_j - \mathbf{A}_2' - \mathbf{A}_j') \cdot (\mathbf{D}_2 + \mathbf{D}_j - \mathbf{D}_2' - \mathbf{D}_j') \\ f_2^0 f_j^0 (\mathbf{g}_{j2} \cdot \mathbf{k}) \sigma_{2j}^2 \, d\mathbf{k} \, d\mathbf{c}_2 \, d\mathbf{c}_j \big] \Big\} \mathbf{d}_{21}. \tag{63}$$

Equations (61)-(63) may then be expressed as

$$\mathbf{J}_1^1 = m_1 \mathbb{L}_{1q} \nabla \ln T + \mathbb{L}_{11} \mathbf{d}_{12}, \tag{64}$$

$$\mathbf{J}_2^1 = m_2 \mathbb{L}_{2q} \nabla \ln T + \mathbb{L}_{22} \mathbf{d}_{21}, \tag{65}$$

$$\mathbf{J}_q^{1''} = \mathbb{L}_{qq} \nabla \ln T + \frac{k_{\mathrm{B}} T}{\mathbb{K}_1} \mathbb{L}_{q1} \mathbf{d}_{12} + \frac{k_{\mathrm{B}} T}{\mathbb{K}_2} \mathbb{L}_{q2} \mathbf{d}_{21}, \tag{66}$$

where we can clearly see that

$$\mathbb{L}_{1q} = \mathbb{L}_{1q} = -\tfrac{1}{6} n \sum_{j=1}^{2} \Big\{ \chi_{1j}^0 \iiint \big[(\mathbf{A}_1 + \mathbf{A}_j - \mathbf{A}_1' - \mathbf{A}_j') \cdot (\mathbf{D}_1 + \mathbf{D}_j - \mathbf{D}_1' - \mathbf{D}_j') \\ f_1^0 f_j^0 (\mathbf{g}_{j1} \cdot \mathbf{k}) \sigma_{1j}^2 \, d\mathbf{k} \, d\mathbf{c}_1 \, d\mathbf{c}_j \big] \Big\}, \tag{67}$$

$$\mathbb{L}_{2q} = \mathbb{L}_{2q} = -\tfrac{1}{6} n \sum_{j=1}^{2} \Big\{ \chi_{2j}^{0} \iiint \big[(\mathbf{A}_2 + \mathbf{A}_j - \mathbf{A}_2' - \mathbf{A}_j') \cdot (\mathbf{D}_2 + \mathbf{D}_j - \mathbf{D}_2' - \mathbf{D}_j')$$

$$f_2^0 f_j^0 (\mathbf{g}_{j2} \cdot \mathbf{k}) \sigma_{2j}^2 \, d\mathbf{k} \, d\mathbf{c}_2 \, d\mathbf{c}_j \big] \Big\}. \qquad (68)$$

Thus, the Onsager reciprocity relations hold true and this case of the linear SET is compatible with linear irreversible thermodynamics. We must emphasize here that this compatibility is incomplete since the non negative property for the entropy production has not yet been proved. This question has been partially examined in the literature both for SET [24] and RET [25–29]. We shall come back to it in a future publication.

5. CONCLUDING REMARKS

We have proved in a simple and straightforward way that the present version of the linear standard Enskog theory is consistent with linear irreversible thermodynamics. It is important to emphasize that we obtain results that do not depend on the specific dependence of the function χ_{ij} on the density. In this sense, this result superseeds and corrects the statement made by Barajas *et al.* [5] twenty years ago in the sense that Thorne's and Tham and Gubbins' versions of the theory was not compatible with LIT. The statement was based on a comparison between the diffusive force given in irreversible thermodynamics by Hirschfelder [23] and an expansion up to terms of second order in density of the force given by Thorne [1]. It is important to point out that we have chosen the thermodynamic fluxes and forces that are derived directly from the definition of the entropy production in terms of the single particle distribution function only and which coincide with those of linear irreversible thermodynamics. Besides, this representation is compatible with Onsager's theory. Although in the past Karkheck and Stell [28] proved that SET is compatible with LIT, it is important to stress that they used a principle of maximization of entropy which is not equivalent to our present work. It is necessary at this point to discuss some important features. As we are considering a form for the entropy which depends only on the distribution function of a single particle we do not obtain the collisional contributions to the fluxes. In order to obtain these contribution we should consider other kind of presentation where the starting point would be the entropy up to the distribution function of two particles. Also, we are dealing with a system which is defined in the Euler regime. If we consider an expansion for the original kinetic equation [Eq. (1)] up to the second order in the gradients we would now be dealing with the Navier Stokes regime and surely this presentation would be totally modified. At this point we have not yet proven an H-Theorem. We should stress that in our results the function χ_{ij} is at this point left unspecified. The question still remains concerning the explicit determination of such a function and whether it is or not unique. This problem was brought up by Piña [30] but the complete answer to this question has not been given yet. As it will be shown in a future work, one can give an answer to this question provided that other restrictions are imposed on the χ_{ij} function [31]. In this case, the definition of the entropy ρs will require an additional contribution arising from the correlations between two particles represented by a term depending on the two particle distribution function.

As it has been mentioned above, the diffusion force in SET exhibits a dependence on the arbitrary point y_{ij} where χ_{ij} is evaluated. Nevertheless, the Onsager transport coefficients are independent of this choice. This fact leads to the conclusion that the reciprocity relations hold true for an infinite number of diffusion forces.

Furthermore, this work also brings into the fore a deeper question. Revised Enskog theory [8] was devised, among other things, to correct a failure now shown not to exist taking χ_{ij} as the local equilibrium pair distribution function for a non-uniform state of a gas mixture expanded in terms of Mayer graphs. The question that may be raised concerns the existence of a relationship between the two approaches pointing out their common views and disagreements as well as the reasons showing why both, being different, are compatible with LIT. And, furthermore, one could ask if there is a more general way of modifying Enskog's equation on the basis of assuming a specific functional dependence of χ_{ij} with the density as in RET, or if it can be done for a general unspecified functionality. This will be discussed in a future paper.

ACKNOWLEDGEMENTS

The author is grateful to Dr. L.S. García-Colín and Dr. E. Piña for helpful and enlightening comments and discussions

REFERENCES

1. S. Chapman, T.G. Cowling, *The mathematical theory of non uniform gases*, Third Edition, Cambridge University Press, Cambridge (1990).
2. P. Resibois, M. de Leener, *Classical kinetic theory of fluids*, John Wiley and Sons, New York (1977).
3. M.K. Tham, K.E. Gubbins, *J. Chem. Phys.* **55** (1971) 268.
4. L.S. García-Colín, L. Barajas, E. Piña, *Phys. Lett.* **37A** (1971) 395.
5. L. Barajas, L.S. García-Colín, E. Piña, *J. Stat. Phys.* **7** (1973) 161.
6. E. Piña, *J. Stat. Phys.* **11** (1974) 433.
7. J.M. Kincaid, *Phys. Lett.* **64A** (1978) 429.
8. H. Van Beijeren, M.H. Ernst, *Physica* **68** (1973) 437.
9. H. Van Beijeren, M.H. Ernst, *Physica* **70** (1973) 225.
10. H. Van Beijeren, *Phys. Rev. Lett.* **51** (1983) 1503.
11. J. Karkheck, G. Stell, *J. Chem. Phys.* **71** (1979) 3620.
12. M. López de Haro, E.G.D. Cohen, J.M. Kinkaid, *J. Chem. Phys.* **78** (1983) 2746.
13. J.M. Kinkaid, M. López de Haro, E.G.D. Cohen, *J. Chem. Phys.* **79** (1983) 4509.
14. M. López de Haro, E.G.D. Cohen, *J. Chem. Phys.* **80** (1984) 408.
15. J.M. Kinkaid, E.G.D. Cohen, M. López de Haro, *J. Chem. Phys.* **86** (1987) 963.
16. E.G.D. Cohen, *Physica* **194A** (1993) 229.
17. J. Karkheck, G. Stell, *Phys. Rev.* **25A** (1982) 3302.
18. R.E. Nettleton, M.S. Green, *J. Chem. Phys.* **29** (1958) 1365.
19. D.C.J. Wallace, *J. Chem. Phys.* *87* (1987) 2282.
20. S.R. de Groot, P. Mazur, *Nonequilibrium thermodynamics*, Dover, New York (1984).

21. L.S. García-Colín, *Teoría cinética de los gases*, Universidad Autónoma Metropolitana-Iztapalapa, Colección CBI, México, D.F. (1990).
22. R.M. Velasco, *Rev. Mex. Fís.* **39** (1993) 352.
23. J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular theory of gases and liquids*, John Wiley and Sons, New York (1964).
24. M. Gramela, L.S. García-Colín, *Phys. Rev.* **22A** (1980) 1295.
25. P. Resibois, *J. Stat. Phys.* **19** (1978) 593.
26. M. Mareschal, *Phys. Rev.* **27A** (1983) 1727.
27. M. Mareschal, *Phys. Rev.* **29A** (1984) 926.
28. J. Karkheck, G. Stell, *Phys. Rev.* **25A** (1982) 3302.
29. J. Karkheck, E. Martina and G. Stell, *Phys. Rev.* **25A** (1982) 3328.
30. E. Piña, *J. Stat. Phys.* **11** (1974) 433.
31. E. Piña, L.S. García-Colín and P. Goldstein, *Physica* **A** (1995) (in press).