Transport of mass and energy in a mixture far from equilibrium

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ABSTRACT

An overview of recent works on mass and heat transport in a dilute binary mixture under steady shear flow is presented. The physical situation is such that an *arbitrary* shear rate coexists with a *weak* concentration gradient. Under these conditions mass and heat transport are induced in the system and the relevant transport coefficients are explicitly obtained. The analysis is made following a perturbation solution in powers of the concentration gradient but taking the steady shear flow as the reference state. In the first order of the expansion the results show that the mass and heat fluxes are proportional to the concentration gradient but, due to the anisotropy of the problem, mutual diffusion and Dufour tensors are identified, respectively. Both tensors are explicitly determined in terms of the shear rate and the parameters of the mixture (particles masses, concentrations, and force constants).

1   INTRODUCTION

The description of systems in which different transport processes occur, is well established for states near equilibrium. For such states, the Curie principle forbids the coupling between fluxes and forces of different tensorial rank [1]. For instance, when a fluid mixture is simultaneously subjected to both weak velocity and concentration gradients, the presence of the velocity gradient (second-rank tensorial quantity) cannot modify vectorial quantities such as mass and heat fluxes, which are generated by the concentration gradients. Nevertheless, beyond the linear regime, Curie's principle is not necessarily satisfied and the mass and heat fluxes can be modified by the shear flow even if the concentration gradient is small.

A prototype system for the study of such a nonlinear problem is a binary mixture in the low density regime. From a kinetic point of view, the state of the system

is characterized by the one-particle velocity distribution functions $f_s(\mathbf{r}, \mathbf{v}; t)$ ($s \equiv 1, 2$) of each species. In terms of the first moments of f_s, the number density n_s, the mean velocity $\mathbf{u}_s$, and the "temperature" T_s of species s, are defined, respectively, as

$$\{n_s, n_s\mathbf{u}_s, n_s k_B T_s\} = \int d\mathbf{v}\{1, \mathbf{v}, (\mathbf{v} - \mathbf{u}_s)^2\}f_s, \quad (1)$$

where k_B is the Boltzmann constant and m_s is the mass of a particle of species s. From the above partial quantities, one can define the hydrodynamic fields of the mixture, namely, the total number density $n = n_1 + n_2$, the flow velocity $\mathbf{u} = \sum_s \rho_s \mathbf{u}_s / \rho$, $\rho_s = m_s n_s$ being the mass density of species s, $\rho \equiv \rho_1 + \rho_2$, and the temperature of the mixture T as

$$nk_B T = \sum_{s=1}^{2} \left(n_s k_B T_s + \frac{1}{3}\rho_s(\mathbf{u}_s - \mathbf{u})^2 \right). \quad (2)$$

The corresponding balance equations associated with the conserved quantities (mass of each species, total momentum, and total energy) define the dissipative fluxes of mass

$$\mathbf{j}_s = \int d\mathbf{v} m_s(\mathbf{v} - \mathbf{u})f_s = \rho_s(\mathbf{u}_s - \mathbf{u}), \quad (3)$$

momentum (pressure tensor)

$$\mathsf{P} = \sum_{s=1}^{2} \int d\mathbf{v} m_s(\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u})f_s = \sum_{s=1}^{2} \mathsf{P}_s, \quad (4)$$

and energy (heat flux)

$$\mathbf{q} = \sum_{s=1}^{2} \int d\mathbf{v} \frac{m_s}{2}(\mathbf{v} - \mathbf{u})^2(\mathbf{v} - \mathbf{u})f_s = \sum_{s=1}^{2} \mathbf{q}_s. \quad (5)$$

These fluxes define the relevant transport coefficients of the mixture. In particular, in a mixture the presence of a concentration gradient not only induces a mass current

but also a heat flux. According to linear irreversible thermodynamics, the macroscopic linear relations governing such fluxes can be written as [1]

$$\mathbf{j}_s = -\frac{m_1 m_2 n}{\rho} D_0 \nabla n_s \;,\tag{6}$$

$$\begin{aligned} \mathbf{j}_q &\equiv \mathbf{q} - \frac{5}{2} k_B T \sum_{s=1}^{2} \frac{\mathbf{j}_s}{m_s} \\ &= -\frac{k_B \rho}{\rho_1 \rho_2} L_0 \nabla n_1 \;. \end{aligned}\tag{7}$$

In writing these equations, for simplicity, we have assumed that n and T are constants and have chosen $-\nabla[\mu_1 - \mu_2]/T \equiv -(k_B \rho/\rho_1 \rho_2)\nabla n_1$ as the force conjugate to $\mathbf{j}_s$ and $\mathbf{j}_q$, μ_s being the chemical potential of species s. In Eqs. (6) and (7), we have introduced the mutual diffusion coefficient D_0 and the Dufour coefficient L_0.

In the low-density regime, the evolution of the binary mixture is described by the set of two coupled nonlinear Boltzmann equations [2]. However, it is a very hard task to find explicit solutions of the Boltzmann equations, especially in states far from equilibrium. One of the rare exceptions corresponds to the so-called uniform shear flow (USF). In this state the only non-zero gradient is $\partial u_x / \partial y = a = \text{const}$, where $\mathbf{u}$ is the flow velocity of the mixture. The relevant transport coefficients of USF are the nonlinear shear viscosity η and viscometric functions $\Psi_{1,2}$ which are related to the total pressure tensor P. In the case of a single monocomponent gas of Maxwell molecules (repulsive r^{-4} potential), Ikenberry and Truesdell [3] obtained explicit expressions of the rheological properties η and $\Psi_{1,2}$ for arbitrary values of the shear rate a. Recently, this solution has been extended to the case of multicomponent systems with arbitrary values of masses, concentrations, and force constants [4].

The aim of this review is to analyze the transport of mass and energy created by a concentration gradient in a binary mixture under USF. The physical situation is such that an *arbitrary* shear rate is coupled with a *weak* concentration gradient. Firstly, under these conditions, one expects that the mass and heat fluxes are proportional to the concentration gradient [c.f. Eqs. (6) and (7)] but, due to the anisotropy induced by the shear flow, mutual diffusion and Dufour tensors rather than scalars can be identified. In the case of the diffusion tensor, we have derived an explicit expression of this tensor from the Boltzmann equation in the case of Maxwell molecules. Such an expression generalizes previous results derived in the case of tagged particles (self-diffusion) [5, 6, 7] and tracer particles [8, 9]. In the case of the Dufour tensor, we have not been able to get an explicit expression of this tensor from the exact Boltzmann equation. The main reason is

that we need the fourth-degree moments of USF whose explicit expressions are not known in the context of the Boltzmann equation. In order to overcome such difficulty, we use a convenient kinetic model that preserves the essential features of the Boltzmann equation but admits more practical analysis. Specifically, we consider the well-known Gross-Krook (GK) model [10] for a binary mixture of Maxwell molecules, for which an exact solution of the USF state has also been recently obtained [11].

The organization of the paper is as follows. In Section 2 we describe the uniform shear flow state and introduce the GK model. Section 3 contains the main results of the review. By performing a perturbation expansion around the shear flow solution, we compute the mass and heat fluxes to linear order in the concentration gradient. The associated transport coefficients are identified and given as nonlinear functions of the shear rate and the parameters of the mixture (mass ratio, concentration ratio, and force constant ratios). The shear-rate dependence of these coefficients is illustrated for several values of the parameters of the mixture, and, in the case of the diffusion tensor, a comparison between the results derived from the Boltzmann and GK equations is carried out. Finally, we close the paper in Section 4 with some concluding remarks.

2   UNIFORM SHEAR FLOW

Let us consider a dilute binary mixture under uniform shear flow. This state is macroscopically characterized by constant partial densities n_s, uniform temperatures T_s, and a linear profile of the x component of the flow velocities along the y direction:

$$n_s = \text{cte.}\;,\tag{8}$$

$$\nabla T_s = 0\;,\tag{9}$$

$$u_{s,i} = u_i = a_{ij} r_j\;, \;\; a_{ij} = a \delta_{ix} \delta_{jy}\;,\tag{10}$$

a being the constant shear rate. Equation (8) implies that there is no mutual diffusion in the USF problem. Consequently, the shear rate is the only nonequilibrium parameter of the system and the momentum transport is the relevant phenomenon. This transport is measured through the pressure tensor, which defines the main transport coefficients of the problem, i.e., the *nonlinear* shear viscosity

$$\eta(a) = -\frac{P_{xy}}{a}\;,\tag{11}$$

and the viscometric functions

$$\Psi_1(a) = -\frac{P_{yy} - P_{xx}}{a^2}\;,\tag{12}$$

$$\Psi_2(a) = -\frac{P_{zz} - P_{yy}}{a^2} . \qquad (13)$$

In the USF problem, the temperature increases in time due to viscous heating, so that the state is not stationary. Nevertheless, in the long time limit, it is possible to get a stationary description using convenient scaled quantities. In this context, Eqs. (11)–(13) must be understood in the long-time limit, where the influence of the initial conditions have disappeared.

At a microscopic level, the USF corresponds to a state that is uniform when one refers the velocities of the particles to the Lagrangian frame moving with the flow velocity $\mathbf{u}$. In this local frame, the velocity distribution function adopts the homogeneous form $f_s(\mathbf{r}, \mathbf{v}; t) = f_s(\mathbf{V}, t)$, where $V_i = v_i - a_{ij} r_j$. Therefore, the corresponding set of Boltzmann equations can be written as

$$\frac{\partial}{\partial t} f_1 - \frac{\partial}{\partial V_i} a_{ij} V_j f_1 = J_{11}[f_1, f_1] + J_{12}[f_1, f_2], \qquad (14)$$

and a similar equation for f_2. Here, $J_{sr}[f_s, f_r]$ is the Boltzmann collision term, which in standard notation reads [2]

$$\begin{aligned} J_{sr}[f_s, f_r] &= \int d\mathbf{v}_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \sigma_{rs}(\mathbf{v} - \mathbf{v}_1, \theta) \\ &\times [f_s(\mathbf{v}') f_r(\mathbf{v}'_1) - f_s(\mathbf{v}) f_r(\mathbf{v}_1)] . \end{aligned} \qquad (15)$$

In the particular case of Maxwell molecules, Eq. (14) can be recursively solved by the moment method. The key point is that the collision rate $g\sigma(g, \theta)$ is independent of the relative velocity g, so that the collisional moments of order k only involve moments of degree smaller than or equal to k [3].

Exact expressions for the nonzero elements of the pressure tensor of a binary mixture of Maxwell molecules under uniform shear flow have been recently obtained [4]. As we will see later, the knowledge of the pressure tensor (second-degree moments) allows us to analyze the influence of the shear field on the mass flux generated by a concentration gradient [13].

Nevertheless, in order to study the effect of the shear flow on the heat flux, we need the fourth-degree moments of USF whose explicit expressions are not known in the context of Boltzmann equation. For this reason, we use the GK model [10], where the exact collision integral of the Boltzmann equation is replaced by a relaxation term of the form

$$J_{sr}^{GK}[f_s, f_r] = -\nu_{sr}(f_s - f_{sr}) , \qquad (16)$$

where the reference distribution function f_{sr} is given by

$$f_{sr} = n_s \left(\frac{m_s}{2\pi k_B T_{sr}}\right)^{3/2} \exp\left[-\frac{m_s}{2k_B T_{sr}}(\mathbf{v} - \mathbf{u}_{sr})^2\right] , \qquad (17)$$

and

$$\mathbf{u}_{sr} = \frac{m_s \mathbf{u}_s + m_r \mathbf{u}_r}{m_s + m_r} , \qquad (18)$$

$$T_{sr} = T_s + 2\frac{m_s m_r}{(m_s + m_r)^2}\left[(T_r - T_s) + \frac{m_r}{6k_B}(\mathbf{u}_s - \mathbf{u}_r)^2\right] . \qquad (19)$$

It is worth remarking that the above terms are explicitly obtained when one requires that the collisional transfer of momentum and energy given by Eq. (16) are the same as those of the Boltzmann equation for Maxwell molecules [10]. This leads to identify the effective collision frequency ν_{sr} as

$$\nu_{sr} = A n_r \left(\kappa_{sr} \frac{m_s + m_r}{m_s m_r}\right)^{1/2} , \qquad (20)$$

where A is a pure number and κ_{sr} is a proportionality constant in the force law. This constant A will be fixed by requiring that the model reproduces some transport coefficient of the Boltzmann equation. The GK model has been recently solved in the USF state [11]. In particular, the GK predictions for the pressure tensor are in good agreement with those obtained from the exact Boltzmann equation. This shows again the reliability of the GK model in computing nonlinear transport properties.

Before analyzing the incidence of the velocity gradient in the mass and heat fluxes, it is instructive to show that Eq. (14) (and its corresponding GK version) admits a nice scaling property in the case of Maxwell molecules. Let us introduce the scaled quantities

$$\overline{\mathbf{V}} = e^{-\alpha t}\mathbf{V} , \qquad (21)$$

$$\overline{f}_s(\overline{\mathbf{V}}, t) = e^{3\alpha t} f_s(\mathbf{V}, t) , \qquad (22)$$

where α is an arbitrary constant. In terms of these scaled variables, Eq. (14) reduces to

$$\frac{\partial}{\partial t}\overline{f}_1 - \frac{\partial}{\partial \overline{V}_i}(a_{ij}\overline{V}_j + \alpha\overline{V}_i)\overline{f}_1 = J_{11}[\overline{f}_1, \overline{f}_1] + J_{12}[\overline{f}_1, \overline{f}_2] . \qquad (23)$$

In deriving Eq. (23), use has been made of the property $\overline{J}_{sr}[\overline{f}_s, \overline{f}_r] = J_{sr}[\overline{f}_s, \overline{f}_r]$ which only applies for Maxwell molecules [14]. Equation (23) can be seen as the Boltzmann equation in the USF under the action of a nonconservative drag force

$$\mathbf{F}_s = -m_s \alpha \mathbf{V} . \qquad (24)$$

This shows the equivalence between the description with and without the external forces $\mathbf{F}_s$ in the case of Maxwell molecules. Most computer simulations of USF use forces of this kind to enforce constant temperature [15]. In this context, α is chosen as a function of the shear rate by

the condition that the temperature achieves a constant value in the long-time limit. We will adopt this point of view and will incorporate isothermal constraints. For non-Maxwell molecules, the presence of the thermostat does not play a neutral role in the results and a certain influence in the evaluation of the rheological properties exists [14].

3 MASS AND HEAT TRANSPORT UNDER SHEAR FLOW

As said before, in a binary mixture the presence of a concentration gradient simultaneously produces mass and heat fluxes. Both fluxes define two relevant transport coefficients: the mutual diffusion coefficient D_0, defined by Eq. (6), and the Dufour coefficient L_0, defined by Eq. (7). In the absence of shear field, both transport coefficients can be obtained by using the Chapman-Enskog expansion [2]. In the case of the Boltzmann equation for Maxwell molecules, $L_0 = 0$ and $D_0 = k_B T/n\lambda_{12}$, where

$$\lambda_{12} = 1.69\pi \left(\kappa_{12}\frac{m_1 m_2}{m_1 + m_2}\right)^{1/2}. \qquad (25)$$

The fact that $L_0 = 0$ is a consequence of the particular potential considered (Maxwell molecules), since for other potentials the Boltzmann equation leads to additional contributions to the Dufour coefficient. The GK model also predicts $L_0 = 0$ while its mutual diffusion coefficient is the same as the Boltzmann one when one chooses the constant $A = 1.69\pi$. Henceforth, we will take this value for A.

The main goal of this paper is to analyze the effect of the shear flow on the mass and heat fluxes generated by a small concentration gradient. In this situation, symmetry arguments suggest that the above-mentioned fluxes are still proportional to the concentration gradient, Eqs. (6) and (7), although the coefficients D_0 and L_0 must be replaced by their corresponding shear-rate dependent mutual diffusion D and Dufour L tensors, respectively. The presence of new transport coefficients (which do not exist for hydrodynamics near equilibrium) is a consequence of the anisotropy induced in the mixture by the presence of the shear flow. The evaluation of these tensors as a function of the shear rate and the parameters characterizing the mixture (mass ratio $\mu \equiv m_1/m_2$, concentration ratio $\delta \equiv n_1/n_2$, and force constant ratios $w_{ii} \equiv \kappa_{ii}/\kappa_{12}$) is the main result of this review. The analysis will be made for a mixture of Maxwell gases from the exact Boltzmann equation (in the case of the diffusion tensor) and from the GK model (in the case of both the diffusion and Dufour tensors).

Let us assume that we perturb the USF state by intro-

ducing a weak concentration gradient ∇n_s. On physical grounds, we also assume that the total density n and temperature T are constant. As a consequence, the concentration gradients are not independent but satisfy the relation $\nabla n_1 = -\nabla n_2$. These are the typical experimental conditions for measuring the mutual diffusion coefficient in a binary mixture close to equilibrium. At a kinetic level, we will look for solutions in which all the space dependence occurs through a functional dependence on the densities n_s, since the space dependence on the flow velocity is completely absorbed by the peculiar velocity $\mathbf{V}$. In other words, we look for *normal* solutions of the form $f_s(\mathbf{r}, \mathbf{v}) = f_s(n_1(\mathbf{r}), n_2(\mathbf{r}); \mathbf{V})$. Therefore, in the steady state, the Boltzmann equations for the mixture are given by

$$-\frac{\partial}{\partial V_i}(a_{ij}V_j + \alpha V_i)f_1 + (V_i + a_{ij}r_j)\frac{\partial}{\partial r_i}f_1 = $$
$$J_{11}[f_1, f_1] + J_{12}[f_1, f_2] \qquad (26)$$

and similarly for f_2. Here, we have introduced the thermostat force (24) to keep the temperature constant. In the following, we will focus on the properties of species 1. The corresponding properties for species 2 can be easily obtained by changing the indices.

In the same spirit as the usual Chapman-Enskog expansion [2], we solve Eq. (26) by means of an expansion in powers of ∇n_1 but taking the pure shear flow state as the zeroth order approximation. This is the main feature of our method. Thus, we write

$$f_1 = f_1^{(0)} + f_1^{(1)} + \cdots, \qquad (27)$$

where $f_1^{(q)}$ is of order q in ∇n_1 but retains all the hydrodynamic orders in the shear rate. The distribution function $f_1^{(0)}$ corresponds to the USF distribution but taking into account now the local dependence on densities n_s. In this review, we will only consider the first order of the expansion, and will solve the kinetic equations for $f_1^{(1)}$ and $f_2^{(1)}$ by using the Boltzmann and GK equations.

3.1 Description based on the Boltzmann equation

In the first order approximation, the steady Boltzmann equation for $f_1^{(1)}$ is

$$-\frac{\partial}{\partial V_i}(a_{ij}V_j + \alpha V_i)f_1^{(1)} + (V_i + a_{ij}r_j)\frac{\partial}{\partial r_i}f_1^{(0)} = J_{11}^{(1)} + J_{12}^{(1)},$$
$$(28)$$

where $J_{sr}^{(1)} = J_{sr}[f_s^{(0)}, f_r^{(1)}] + J_{sr}[f_s^{(1)}, f_r^{(0)}]$. Some remarks follow from the structure of the balance equations associated with Eq. (28) and its counterpart for $f_2^{(1)}$. First,

the mass and total momentum balance equations imply that

$$a_{ij} r_j \frac{\partial}{\partial r_i} n_1 = 0 , \qquad (29)$$

$$a_{ik} u_k^{(1)} + \alpha u_i^{(1)} = -\frac{1}{\rho} \frac{\partial}{\partial r_k} P_{ik}^{(0)} , \qquad (30)$$

where $u^{(1)}$ is the first order perturbation to the velocity of the mixture, i.e.,

$$\mathbf{u}^{(1)} = \frac{1}{\rho} \sum_{s=1}^{2} \int d\mathbf{v} \, m_s \mathbf{V} f_s^{(1)} \qquad (31)$$

and $P^{(0)}$ is the total pressure tensor in the uniform shear flow state. Equation (29) implies that, in order to keep the mixture in a steady state, the concentration gradient must be orthogonal to the direction of the shear flow, i.e., $\partial n_1/\partial x = 0$. On the other hand, according to Eq. (30), only in the case that the total pressure tensor is uniform the velocity field is not perturbed by the presence of the concentration gradient. If $a = 0$, $P_{ij}^{(0)} = n k_B T \delta_{ij} = $ cte., so $u^{(1)} = 0$. For nonzero shear rates, there are only two limit cases for which $P^{(0)}$ is constant: the case of mechanically equivalent particles [7] ($\mu = 1, \kappa_{11} = \kappa_{22} = \kappa_{12}$) and the tracer limit ($n_1 \ll n_2$) [9]. In both cases $P_{ij}^{(0)} = n k_B T F(a)$, $F(a)$ being a nonlinear function of the *constant* shear rate. Beyond these limit cases the pressure tensor depends on space through its dependence on the partial densities, so that the concentration gradient not only induces a mass flux but it also disturbs the linear shear flow. The solution to Eq. (30) is

$$u_i^{(1)} = -\frac{1}{\rho \alpha} \left(\delta_{ik} - \frac{a_{ik}}{\alpha} \right) \frac{\partial}{\partial r_j} P_{kj}^{(0)} . \qquad (32)$$

The mass flux $\mathbf{j}_1^{(1)}$ is given by

$$\mathbf{j}_1^{(1)} = \tilde{\mathbf{j}}_1^{(1)} - \rho_1 \mathbf{u}^{(1)} \qquad (33)$$

where $\tilde{\mathbf{j}}_1^{(1)}$ is the mass flux defined with respect to the linear shear field, i.e.,

$$\tilde{\mathbf{j}}_1^{(1)} = m_1 \int d\mathbf{v} \, \mathbf{V} f_1^{(1)} . \qquad (34)$$

The flux $\tilde{\mathbf{j}}_1^{(1)}$ can be obtained by multiplying both sides of Eq. (28) by $m_1 \mathbf{V}$ and integrating over $\mathbf{V}$. The result is

$$a_{ik} \tilde{j}_{1,k}^{(1)} + \alpha \tilde{j}_{1,i}^{(1)} + \frac{\rho \lambda_{12}}{m_1 m_2} \tilde{j}_{1,i}^{(1)} = \frac{\rho \lambda_{12}}{m_1 m_2} \rho_1 u_i^{(1)} - \frac{\partial}{\partial r_k} P_{1,ik}^{(0)} , \qquad (35)$$

where we have used the relation [16]

$$\int d\mathbf{v} \, \mathbf{V} (J_{11}^{(1)} + J_{12}^{(1)}) = -\frac{\rho \lambda_{12}}{m_1 m_2} (\tilde{j}_1^{(1)} - \rho_1 \mathbf{u}^{(1)}) . \qquad (36)$$

From the solution of Eq. (35), and taking into account Eqs. (32) and (33), the mass flux can be cast in the form of a generalized Fick's law, namely,

$$\mathbf{j}_1^{(1)} = -\frac{m_1 m_2 n}{\rho} \mathbf{D} \cdot \nabla n_1 , \qquad (37)$$

where the elements of the mutual diffusion tensor D_{ij} are

$$D_{ij} = D_0 \frac{(1+\mu\delta)(1+\delta)^2}{\mu\delta} \tau \left\{ \frac{1}{\alpha^* + \beta} \left(\delta_{ik} - \frac{a_{ik}^*}{\alpha^* + \beta} \right) \right.$$
$$\left. \times \left[\frac{\partial}{\partial \delta} P_{1,kj}^{*(0)} + \tau \Gamma_{kj} \right] - \frac{\mu\delta}{1+\mu} \Gamma_{ij} \right\} . \qquad (38)$$

Here, $D_0 \equiv k_B T / n \lambda_{12}$,

$$\Gamma_{ij} = \frac{1}{\alpha^*} \left(\delta_{ik} - \frac{a_{ik}^*}{\alpha^*} \right) \frac{\partial}{\partial \delta} P_{kj}^{*(0)} , \qquad (39)$$

and we have introduced the dimensionless quantities $P_{ij}^{*(0)} = P_{ij}^{(0)}/n k_B T$, $a_{ik}^* = a_{ik}/\gamma_{12}$, $\alpha^* = \alpha/\gamma_{12}$, with

$$\gamma_{12} = 5.22 \, \pi \, n \left(\kappa_{12} \frac{m_1 m_2}{(m_1 + m_2)^3} \right)^{1/2} \qquad (40)$$

being an effective collision frequency. Furthermore,

$$\beta = 0.324 \frac{(1+\mu)(1+\mu\delta)}{\mu(1+\delta)} , \qquad (41)$$

$$\tau = 0.324 \frac{\delta(1+\mu)}{1+\delta} . \qquad (42)$$

It must be recalled that Eq. (38) applies for *arbitrary* values of the shear rate and no restriction on the values of the mass ratio, the concentration ratio, and/or the force constant ratios have been considered. In the limits of tagged and tracer particles we recover previous results derived for the self-diffusion [7] and tracer diffusion tensors [9], respectively. As it was expected, in the absence of the shear field ($a = 0$), $D_{ij} = D_0 \delta_{ij}$, D_0 being the mutual diffusion coefficient given by the conventional Chapman-Enskog method [2]. Furthermore, according to Eq. (38), $D_{xz} = D_{yz} = D_{zy} = 0$, in agreement with the symmetry of the problem. Since no concentration gradient exists along the x direction, the only relevant components are $D_{yy} = D_{zz}$ and D_{xy}. Notice that the equality $P_{s,yy} = P_{s,zz}$ implies that $D_{yy} = D_{zz}$. This fact is probably a consequence of the particular interaction considered since only for Maxwell molecules the yy and zz of the pressure tensor are equal. For non-Maxwell molecules, recent simulation results performed in the case of a single dilute hard sphere gas show that these elements are in general different [17]. This is also consistent with the simulation results recently obtained for a Lennard-Jones mixture [18], where $D_{yy} > D_{zz}$.

Unfortunately, no explicit information on the shear-rate dependent Dufour tensor L can be obtained from the exact Boltzmann equation. For this reason, we resort to the well-known GK kinetic model.

3.2 Description based on the Gross-Krook equation

In the context of the GK model, $f_1^{(1)}$ verifies the steady equation

$$\frac{\partial}{\partial V_i}(a_{ij}V_j + \alpha V_i)f_1^{(1)} + (V_i + a_{ij}r_j)\frac{\partial}{\partial r_i}f_1^{(0)} + \nu_1 f_1^{(1)} = \nu_{11}f_{11}^{(1)} + \nu_{12}f_{12}^{(1)} \ , (43)$$

where

$$f_{11}^{(1)} = \frac{1}{n_1 k_B T_1}\mathbf{V}\cdot\vec{\mathbf{j}}^{(1)}f_{11}^{(0)} \ , \tag{44}$$

$$f_{12}^{(1)} = \frac{1}{n_1 k_B T_{12}}\left(\mu\frac{1-\delta}{1+\mu}\mathbf{V}\cdot\vec{\mathbf{j}}_1^{(1)} + \rho_1\frac{1+\mu\delta}{1+\mu}\mathbf{V}\cdot\mathbf{u}^{(1)}\right)f_{12}^{(0)} \ , \tag{45}$$

$$f_{ij}^{(0)} = n_i\left(\frac{m_i}{2\pi k_B T_{ij}}\right)^{3/2}\exp\left(-\frac{m_i V^2}{2k_B T_{ij}}\right) \ . \tag{46}$$

From Eqs. (43) and its counterpart for $f_2^{(1)}$, the velocity $\mathbf{u}^{(1)}$ can be obtained. It is easy to see that, in the same way as the Boltzmann equation, $\mathbf{u}^{(1)}$ is also given by Eq. (32) although the corresponding expressions for the thermostat parameter α and the pressure tensor $\mathsf{P}^{(0)}$ obtained from the GK model are different from those derived from the Boltzmann equation [4].

Let us introduce the dimensionless velocity moments $M_{k,\ell,m}^{(1)}$ corresponding to the approximation $f_1^{(1)}$ as

$$M_{k,\ell,m}^{(1)} = \frac{1}{n_1}\left(\frac{2k_B T}{m_1}\right)^{-\frac{k+\ell+m}{2}}\int d\mathbf{V}\, V_x^k V_y^\ell V_z^m f_1^{(1)}(\mathbf{V}) \ . \tag{47}$$

The hierarchy obeying these moments can be obtained by multiplying both sides of Eq. (43) by $V_x^k V_y^\ell V_z^m$ and integrating over the velocity space. Thus, one gets

$$akM_{k-1,\ell+1,m}^{(1)} + [\nu_1 + \alpha(k+\ell+m)]M_{k,\ell,m}^{(1)} = R_{k,\ell,m} \ , \tag{48}$$

where

$$R_{k,\ell,m} = -\zeta\left[1 + (1+\delta)\delta\frac{\partial}{\partial\delta}\right]$$
$$\times \left(M_{k,\ell+1,m}^{(0)}\epsilon_{1,y} + M_{k,\ell,m+1}^{(0)}\epsilon_{1,z}\right)$$
$$+2\nu_{11}\chi_1^{(g-1)/2}\left[A_{k+1,\ell,m}M_{1,0,0}^{(1)} + A_{k,\ell+1,m}M_{0,1,0}^{(1)} + A_{k,\ell,m+1}M_{0,0,1}^{(1)}\right]$$

$$+\frac{2\mu(1-\delta)}{1+\mu}\nu_{12}\chi_{12}^{(g-1)/2}\left[A_{k+1,\ell,m}M_{1,0,0}^{(1)} + A_{k,\ell+1,m}M_{0,1,0}^{(1)} + A_{k,\ell,m+1}M_{0,0,1}^{(1)}\right]$$
$$-\frac{\mu\delta(1+\delta)^2}{1+\mu}\nu_{12}\chi_{12}^{(g-1)/2}\left[(A_{k+1,\ell,m}\Lambda_{xy} + A_{k,\ell+1,m}\Lambda_{yy})\epsilon_{1,y} + A_{k,\ell,m+1}\Lambda_{zz}\epsilon_{1,z}\right] \ . \tag{49}$$

Here, $M_{k,\ell,m}^{(0)}$ refers to the moments of the pure USF state given in the reference [11], $\zeta = (n/n_2)\nu_{12}$, $g \equiv k+\ell+m$, $\chi_s \equiv T_s/T$, $\chi_{sr} \equiv T_{sr}/T$, and we have introduced the reduced concentration gradient

$$\epsilon_1 = \left(\frac{2k_B T}{m_1}\right)^{1/2}\frac{1}{\zeta}\nabla\ln n_1 \ , \tag{50}$$

and the dimensionless tensor

$$\Lambda_{ij} = \frac{\zeta}{\alpha}(\delta_{ik} - \frac{a_{ik}}{\alpha})\frac{\partial}{\partial\delta}P_{kj}^{*(0)} \ . \tag{51}$$

The solution to Eq. (48) can be written as

$$M_{k,\ell,m}^{(1)} = \sum_{q=0}^{k}\frac{k!}{(k-q)!}(-a)^q[\nu_1 + (k+\ell+m)\alpha]^{-(1+q)}$$
$$\times R_{k-q,\ell+q,m} \ . \tag{52}$$

Equation (52) is still formal since we need to know the first-degree moments. After some algebra, it is easy to see that these moments can be written as

$$M_{0,1,0}^{(1)} = -\tilde{D}_{yy}\epsilon_{1,y} \ , \tag{53}$$

$$M_{0,0,1}^{(1)} = -\tilde{D}_{zz}\epsilon_{1,z} \ , \tag{54}$$

$$M_{1,0,0}^{(1)} = -\tilde{D}_{zz}\epsilon_{1,z} \ , \tag{55}$$

where

$$\tilde{D}_{yy} = \tilde{D}_{zz} = \frac{1}{(1+\mu)\alpha + \nu_{12}(1+\delta\mu)}$$
$$\times \left\{(1+\mu)\zeta\left[1 + (1+\delta)\delta\frac{\partial}{\partial\delta}\right]M_{0,2,0}^{(0)} + \frac{1}{2}\delta\mu(1+\delta)^2\nu_{12}\Lambda_{yy}\right\} , \tag{56}$$

$$\tilde{D}_{xy} = \frac{1}{2[(1+\mu)\alpha + \nu_{12}(1+\delta\mu)]}$$
$$\times \left\{\delta(1+\delta)^2\mu\nu_{12}\Lambda_{xy} - 2a(1+\mu)\tilde{D}_{yy} + 2(1+\mu)\zeta\left[1 + (1+\delta)\delta\frac{\partial}{\partial\delta}\right]M_{1,1,0}^{(0)}\right\} . \tag{57}$$

From Eqs. (33), and (53)–(57), the mass flux $\mathbf{j}_1^{(1)}$ can be finally obtained. It can be written again in the form of

a generalized Fick's law, Eq. (37), where now the mutual diffusion tensor is given by

$$D_{ij} = D_0 \frac{1}{1+\mu}\left[2\frac{1+\mu\delta}{1+\delta}\widetilde{D}_{ij} - \mu\delta(1+\delta)\Lambda_{ij}\right] , \quad (58)$$

D_0 being the mutual diffusion coefficient at equilibrium. Just as it was obtained from the Boltzmann equation in the previous section, $D_{xz} = D_{yz} = D_{zy} = 0$, which is consistent with the symmetry of the problem.

Once the mass fluxes $\mathbf{j}_s^{(1)}$ have been obtained, all the velocity moments of $f_s^{(1)}$ can be explicitly determined from Eq. (52) and its corresponding counterpart for the component 2. We are now interested in calculating the total heat flux $\mathbf{q}^{(1)}$ given by

$$\mathbf{q}^{(1)} = \sum_{s=1}^{2}\frac{m_s}{2}\int d\mathbf{v}\,\mathbf{V}^2\mathbf{V}f_s^{(1)} - \frac{3}{2}p\mathbf{u}^{(1)} - \mathsf{P}^{(0)}\cdot\mathbf{u}^{(1)}$$

$$\equiv \sum_{s=1}^{2}\widetilde{\mathbf{q}}_s^{(1)} - \frac{3}{2}p\mathbf{u}^{(1)} - \mathsf{P}^{(0)}\cdot\mathbf{u}^{(1)}. \quad (59)$$

The fluxes $\widetilde{\mathbf{q}}_s^{(1)}$ can be obtained from Eq. (52). By collecting all the contributions coming from both species, the flux $\mathbf{j}_q^{(1)}$ can be obtained. After some algebra, $\mathbf{j}_q^{(1)}$ can be written as

$$\mathbf{j}_q^{(1)} = -\frac{k_B\rho}{\rho_1\rho_2}\mathsf{L}\cdot\nabla n_1 , \quad (60)$$

where the elements of the generalized Dufour tensor L_{ij} are

$$L_{ij} = \frac{k_B T^2}{m_1\zeta}\frac{\rho_1\rho_2}{\rho}\left[2(\Sigma_{1,ij} - \mu\Sigma_{2,ij}) - \frac{\mu(1+\delta)^3}{1+\mu\delta}\right.$$
$$\left.\times\left(\frac{3}{2}\Lambda_{ik} + P_{ik}^{(0)*}\right)\Lambda_{kj} - \frac{5}{2}\frac{(1-\mu^2)(1+\delta)}{1+\mu\delta}D_{ij}^*\right] .(61)$$

The nonzero elements of the tensor Σ_s are given by

$$\Sigma_{1,xy} = -\frac{\Delta}{z_1^4}\left[6a^3 M_{0,4,0}^{(0)} + az_1^2(M_{0,2,2}^{(0)} + M_{0,4,0}^{(0)} + 3M_{2,2,0}^{(0)})\right.$$
$$-z_1^3(M_{3,1,0}^{(0)} + M_{1,1,2}^{(0)}) - z_1(z_1^2 + 6a^2)M_{1,3,0}^{(0)}\bigg]$$
$$-A_1\frac{(7z_1^2 + 18a^2)a\widetilde{D}_{yy} - (5z_1^2 + 6a^2)z_1\widetilde{D}_{xy}}{2(1+\mu)z_1^4}$$
$$-B_1\frac{(7z_1^2 + 18a^2)a\Lambda_{yy} - (5z_1^2 + 6a^2)z_1\Lambda_{xy}}{4(1+\mu)z_1^4} , \quad (62)$$

$$\Sigma_{1,yy} = \frac{\Delta}{z_1}\left[M_{0,2,2}^{(0)} + M_{2,3,0}^{(0)} + \frac{2a^2 + z_1^2}{z_1^2}M_{0,4,0}^{(0)} - \frac{2a}{z_1}M_{1,3,0}^{(0)}\right]$$
$$+A_1\frac{(5z_1^2 + 6a^2)\widetilde{D}_{yy} - 2az_1\widetilde{D}_{xy}}{2(1+\mu)z_1^3}$$
$$+B_1\frac{(5z_1^2 + 6a^2)\Lambda_{yy} - 2az_1\Lambda_{xy}}{4(1+\mu)z_1^3} , \quad (63)$$

$$\Sigma_{1,zz} = \frac{\Delta}{z_1}\left[M_{2,0,2}^{(0)} + M_{0,0,4}^{(0)} + \frac{2a^2 + z_1^2}{z_1^2}M_{0,2,2}^{(0)} - \frac{2a}{z_1}M_{1,1,2}^{(0)}\right]$$
$$+A_1\frac{5z_1^2 + 2a^2}{2(1+\mu)z_1^3}\widetilde{D}_{zz} + B_1\frac{5z_1^2 + 2a^2}{4(1+\mu)z_1^3}\Lambda_{zz} . \quad (64)$$

Here, we have introduced the operator

$$\Delta[g(\delta)] = \left(1 + \delta(1+\delta)\frac{\partial}{\partial\delta}\right)g(\delta) , . \quad (65)$$

and the quantities $z_1 = \nu_1 + 3\alpha$, $A_1 = (1+\mu)\nu_{11}\chi_1 + (1-\delta)\mu\nu_{12}\chi_{12}$, $B_1 = \mu\nu_{12}\delta(1+\delta)^2\chi_{12}$.

In the same way as the diffusion tensor, the tensor L has three relevant elements: two diagonals L_{yy}, and L_{zz}, and one off-diagonal L_{xy}. However, in contrast to D its diagonal elements are different, which is a consequence of the high anisotropy induced by the shear field. For zero shear rate, one gets the well-known result for Maxwell binary mixtures near equilibrium, i.e., $L_{ij} = 0$ [2]. Also, if $\mu = 1$ $L_{ij} = 0$ even for $a \neq 0$.

3.3 SOME ILLUSTRATIVE EXAMPLES

The objective of this Section is to illustrate the shear-rate dependence of the diffusion and Dufour tensors for several values of the parameters of a mixture of Maxwell gases. We also compare the predictions made by the GK model with those obtained from the Boltzmann equation at the level of the diffusion tensor.

Figures 1 and 2 show the dependence of the reduced diffusion tensor $D_{ij}^* \equiv D_{ij}/D_0$ on the reduced shear rate .
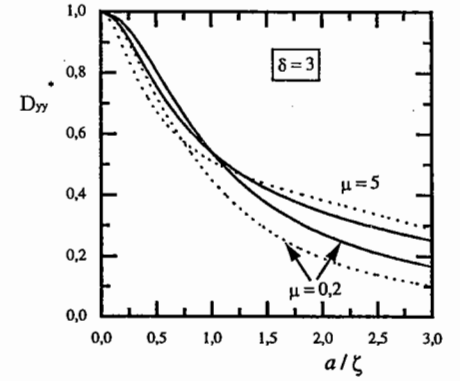

Figure 1: Plot of the reduced diagonal element of the diffusion tensor $D_{yy}^* = D_{yy}/D_0$ as a function of the reduced shear rate a/ζ for $\kappa_{11} = \kappa_{22} = \kappa_{12}$, $\delta = 3$, and $\mu = 5$, y $\mu = 0.2$. The solid lines correspond to the GK results while the dashed lines refer to the Boltzmann results.
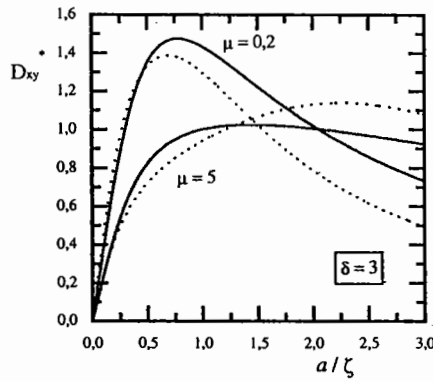
Figure 2: Plot of the reduced off-diagonal element of the diffusion tensor $D_{xy}^* = -D_{xy}/D_0$ as a function of the reduced shear rate a/ζ for $\kappa_{11} = \kappa_{22} = \kappa_{12}$, $\delta = 3$, y $\mu = 5$, and $\mu = 0.2$. The solid lines correspond to the GK results while the dashed lines refer to the Boltzmann results.

a/ζ for $\delta = 3$, $\kappa_{11} = \kappa_{22} = \kappa_{12}$ and $\mu = 5$ and 0.2. The behaviour for $\delta < 1$ can be easily inferred by taking into account that D_{ij} is invariant under the changes $\mu \leftrightarrow \mu^{-1}$, $\delta \leftrightarrow \delta^{-1}$, and $\kappa_{11} \leftrightarrow \kappa_{22}$. We observe that the GK predictions present a qualitative good agreement with the Boltzmann ones, especially when the mass of the excess component is larger than that of the defect component. The influence of the shear flow on the mass transport is quite significant in the region of shear rates analyzed. In the case of D_{yy}^*, we see that this element decreases as the shear rate increases so that the presence of the shear flow inhibits the mass transport along the direction of the gradient of the flow velocity (y axes). This inhibition becomes more significant when the defect species is heavier than the excess one. The shear flow induces cross effects in the diffusion of particles which are measured by the off-diagonal element D_{xy}. This component, which is zero in the absence of shear flow, gives the mass flux along the x direction due to a concentration gradient along the y direction. It can be seen as a measure of the anisotropy generated in the system by the action of the shear field. It is negative and its dependence on the shear rate is quite similar, regardless of which mass ratio considered: for small shear rates $-D_{xy}^*$ increases with a while the opposite happens for large shear rates. In general, the dependence of D_{ij} on a found here agrees qualitatively well with the one observed in molecular dynamics simulations [18] of a strongly shearing Lennard-Jones binary mixture.

In order to illustrate the dependence of the Dufour tensor on the shear rate and the parameters of the mixture, it is convenient to reduce it in a proper way. Here, we introduce the dimensionless Dufour tensor L_{ij}^* as

$$L_{ij}^* = \frac{m_1 m_2}{m_1 + m_2} \frac{\zeta}{k_B T^2} \frac{\rho}{\rho_1 \rho_2} L_{ij} \ . \tag{66}$$

The reduced tensor L_{ij}^* possesses the same invariant properties as the Dufour tensor L_{ij}. In Figs. 3, 4, and 5, we plot L_{yy}^*, L_{zz}^*, L_{xy}^*, as a function of the shear rate, respectively. We consider again $\delta = 3$, $\kappa_{11} = \kappa_{22} = \kappa_{12}$, and the
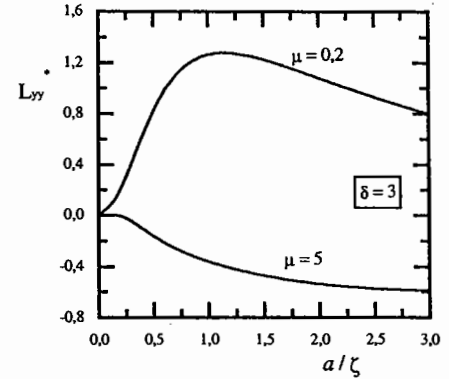

Figure 3: Plot of the reduced diagonal element of the Dufour tensor L_{yy}^* as a function of the reduced shear rate a/ζ for $\kappa_{11} = \kappa_{22} = \kappa_{12}$, $\delta = 3$, and $\mu = 5$, y $\mu = 0.2$.
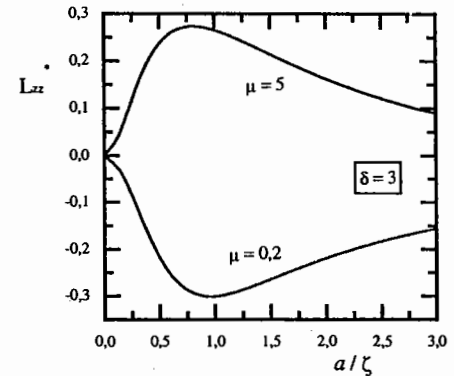

Figure 4: Plot of the reduced diagonal element of the Dufour tensor L_{zz}^* as a function of the reduced shear rate a/ζ for $\kappa_{11} = \kappa_{22} = \kappa_{12}$, $\delta = 3$, y $\mu = 5$, and $\mu = 0.2$.
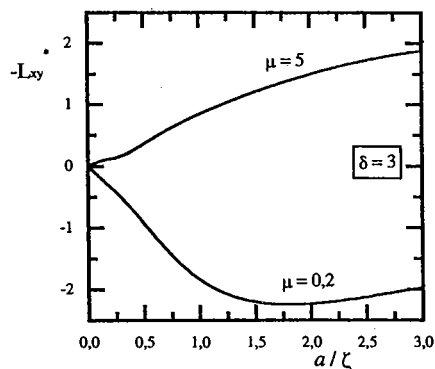
Figure 5: Plot of the reduced off-diagonal element of the Dufour tensor $-L_{xy}^*$ as a function of the reduced shear rate a/ζ for $\kappa_{11} = \kappa_{22} = \kappa_{12}$, $\delta = 3$, and $\mu = 5$, y $\mu = 0.2$.

same values of the mass ratio as before, namely, $\mu = 5$ and 0.2. To the best of our knowledge, we are not aware of any previous simulation or calculation of this tensor so that no comparison is possible at this stage. As Figs. 3–5 show, the nonzero components L_{ij}^* are nonmonotonic functions of a, reaching either a maximum or minimum for a given value of the shear rate. Note that depending on the value of the mass ratio, the shear-dependent components of the generalized Dufour tensor may either be negative or positive.

4 CONCLUDING REMARKS

Diffusion of particles in a fluid subjected to the uniform shear flow has been studied in the past few years from a theoretical point of view as well as from a computer simulation point of view. Usually, the different analyses have been made in the particular case in which all the particles are mechanically equivalent. This situation involves only single-particle motion and it is therefore somewhat simpler to treat. In this review we have investigated the influence of shear flow on the mass and heat fluxes in a binary mixture constituted by particles mechanically *different*. The reference frame is the Boltzmann equation which provides a controlled formulation of the problem. However, due to the complex mathematical structure of this equation, we have not been able to get the heat flux, so that a kinetic model has been used. Specifically, we have considered the GK model of the Boltzmann equation whose reability has been shown in the past years in different problems [9, 19, 20].

The physical situation is such that a linear profile of

the x component of the flow velocity along the y direction coexists with a weak concentration gradient. The strength of the velocity field is arbitrary so that the mass flux j_s and the heat flux j_q are disturbed by the shearing motion. In addition, in the same way as computer simulation studies, thermostat forces are introduced to remove the heat produced by viscous heating and get an stationary state. Under these conditions j_s and j_q are still proportional to the concentration gradient but the diffusion an Dufour coefficients become shear-rate dependent tensors. The determination of these tensors in the case of Maxwell molecules has been the objective of this review. Apart from the limitation of the interaction considered, our results apply to arbitrary values of masses, concentrations, and force constants.

The results show that the diffusion D_{ij} and Dufour L_{ij} tensors are highly disturbed with respect to their equilibrium values. As a matter of fact, both tensors present a complex nonlinear dependence on the shear rate a and the parameters of the mixture. Concerning the diffusion tensor, the relevant elements are $D_{yy} = D_{zz}$ and $D_{xy} < 0$. The net effect of the shear field on the transport of mass is to inhibit the transport of particles along the direction of the flow velocity (y axis). In the case of x direction, $-D_{xy}$ is not a monotonic function of the shear rate and has a maximum for a given value of a. With respect to the Dufour tensor, the results show that, for nonzero shear rates, $L_{yy} \neq L_{zz}$, that $L_{ij} = 0$ both for $a = 0$ or for equal masses, and that depending on the mass ratio the L_{ij}, which are nonmonotonic functions of the shear rate, may be either positive or negative, reaching a maximum or minimum for given a. As said before, to our knowledge this is the first derivation of an explicit expression of the shear-rate dependent diffusion and Dufour tensors for a binary mixture with arbitrary values of the mass ratio, the concentration ratios, and the force constant ratios.

The results reported here can also be of relevance in connection with computer simulations. As mentioned before Sarman, Evans, and Baranyai [18] performed molecular dynamics simulations to measure the influence of the shear rate on the diffusion tensor in a dense mixture. Nevertheless, the shear rates considered in their simulations are not large enough to clearly observe nonlinear effects. In the case of binary mixtures at low-density, one possibility to overcome the difficulties inherent to molecular dynamics to achieve large shear rates is to use the direct simulation Monte Carlo method [21]. We hope that the results derived here for the mutual diffusion and Dufour tensors stimulate the performance of computer simulations to check the accuracy of our predictions.

References

[1] de Groot, S. R., and Mazur, P. 1984, Nonequilibrium Thermodynamics, Dover, New York.

[2] Chapman, S., and Cowling, T. C. 1970, The Mathematical Theory of Nonuniform Gases, Cambridge University Press, Cambridge.

[3] Truesdell, C., and Muncaster, R. 1980, Fundamentals of Maxwell's Kinetic Theory of a Simple Monoatomic Gas, Academic, New York.

[4] Marín, C., Garzó, V., and Santos, A. 1995, Phys. Rev. E, 52, 3812.

[5] Marchetti, M. C., and Dufty, J. W. 1983, J. Stat. Phys., 32, 255.

[6] Dufty, J. W. 1984, Phys. Rev. A, 30, 1465.

[7] Garzó, V., Santos, A., and Brey, J. J. 1990, Physica A, 163, 651.

[8] Rodríguez, R. F., Salinas-Rodríguez, E., and Dufty, J. W. 1983, J. Stat. Phys., 32, 279.

[9] Garzó, V., and López de Haro, M. 1991, Phys. Rev. A, 44, 1397.

[10] Gross, E. P., and Krook, M. 1956, Phys. Rev., 102, 593.

[11] Marín, C., and Garzó, V. 1996, Phys. Fluids, 8, 2756.

[12] Marín, C., Garzó, V., and López de Haro, M. 2000, Phys. of Fluids, 12, 717.

[13] Marín, C., and Garzó, V. 1998, Phys. Rev. E, 57, 507.

[14] Dufty, J. W., Santos, A., Brey, J. J., and Rodríguez, R. F. 1986, Phys. Rev. A, 33, 459.

[15] Evans, D. E., and Morriss, G. P. 1990, Statistical Mechanics of Nonequilibrium Liquids, Academic, London.

[16] Holway, L. H. 1966, Phys. Fluids., 9, 1658.; Goldman, E., and Sirovich L. 1967, ibid, 10, 1928.

[17] Montanero, J. M., Santos, A., and Garzó, V. 1996, Phys. Fluids, 8, 1981.

[18] Sarman, S., Evans, D. J., and Baranyai, A. 1992, Phys. Rev. A, 46, 893.

[19] Garzó, V., and López de Haro, M. 1992, Phys. Fluids A, 4, 1057.

[20] Marín., C., Montanero, J. M., and Garzó, V. 1996, Physica A, 225, 235.

[21] Bird, G. 1994, Molecular Gas Dynamics and the Direct Simulation of Gas Flows, Clarendon, Oxford.