

Mass flux of a binary mixture of Maxwell molecules under shear flow

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Abstract

Transport coefficients associated with the mass flux of a binary mixture of Maxwell molecules under uniform shear flow are exactly determined from the Boltzmann kinetic equation. A normal solution is obtained via a Chapman–Enskog-like expansion around a local shear flow distribution that retains all the hydrodynamics orders in the shear rate. In the first order of the expansion the mass flux is proportional to the gradients of mole fraction, pressure, and temperature but, due to the anisotropy induced in the system by the shear flow, mutual diffusion, pressure diffusion and thermal diffusion tensors are identified instead of the conventional scalar coefficients. These tensors are obtained in terms of the shear rate and the parameters of the mixture (particle masses, concentrations, and force constants). The description is made both in the absence and in the presence of an external thermostat introduced in computer simulations to compensate for the viscous heating. As expected, the analysis shows that there is no simple relationship between the results with and without the thermostat. The dependence of the three diffusion tensors on the shear rate is illustrated in the tracer limit case, the results showing that the deviation of the generalized transport coefficients from their equilibrium forms is in general quite important.

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1. Introduction

The description of transport properties for states close to equilibrium in gaseous binary mixtures is well established. In these situations, the Curie principle [1] states that the presence of a velocity gradient (second-rank tensorial quantity) cannot modify a vectorial quantity such as the mass flux \mathbf{j}_1 , which is generated by gradients of mole fraction x_1 , pressure p , and temperature T . As a consequence, the mutual-diffusion coefficient D (which couples the mass current with ∇x_1), the pressure diffusion coefficient D_p (which couples the mass current with ∇p) and the thermal diffusion coefficient D_T (which couples the mass current with ∇T) do not depend on the velocity gradient. However, when the shear rate applied is large, non-Newtonian effects are important so that the Curie principle does not hold and the coefficients associated with the mass transport are affected by the presence of shear flow. In particular, if the spatial gradients ∇x_1 , ∇p , and ∇T are weak, one expects that the flux \mathbf{j}_1 is still linear in these gradients but the standard scalar coefficients $\{D, D_p, D_T\}$ must be replaced by the shear-rate dependent second-rank tensors $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$.

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It is theoretically known that the presence of shear flow affects the microscopic diffusion [2–5]. On a molecular scale, nonequilibrium molecular dynamics simulations have shown an anisotropy of self-diffusion under shear [6–9]. In the case of colloidal systems this anisotropy has been measured experimentally by neutron scattering [10–12] and also in computer simulations [13]. However, the shearing effects on diffusion observed in liquids are qualitatively different from those observed in gas phase systems. In this paper, to gain some insight into this phenomenon, a gaseous binary mixture in the low-density regime will be considered to determine the dependence of the diffusion tensors $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ on the shear rate. For a low-density gas, the Boltzmann equation [14] is the master equation and describes the time evolution of the one-particle distribution function.

We are interested in a situation where *weak* spatial gradients of mole fraction, pressure, and temperature coexist with a *strong* shear rate. Under these conditions, the application of the conventional Chapman–Enskog expansion [15] around the local equilibrium state to obtain higher-order hydrodynamic effects (Burnett, super-Burnett, etc.) to the mass flux turns out to be extremely difficult. This gives rise for the need to look for alternative approaches. A possibility is to expand around a more relevant reference state than the local equilibrium. Since we want to compute the mass transport in a strongly sheared mixture, the so-called uniform shear flow (USF) state can be chosen as the reference state. The USF state is characterized by constant mole fractions, a uniform temperature, and a linear velocity profile $u_x = ay$, where a is the constant shear rate. Due to its simplicity, this state has been widely used in the past to shed light on the complexities associated with the *nonlinear* response of the system to the action of strong shearing. In addition, the USF state is one of the rare exceptions for which the hierarchy of moments of the Boltzmann equation admits an exact solution for single [16] and multicomponent gases [17] of Maxwell molecules (repulsive potential of the form r^{-4}). In this case, explicit expressions of the pressure tensor (which is the relevant irreversible flux of the problem) have been obtained for *arbitrary* values of the shear rate and the parameters of the system (masses, concentrations and force constants).

As said before, here we want to compute the mass transport under USF for Maxwell molecules. Since the mixture is slightly perturbed from the USF, the Boltzmann equation can be solved by an expansion in small gradients around the (local) shear flow distribution instead of the (local) equilibrium. This is the main feature of the expansion since the reference state is not restricted to small values of the shear rate. In the first order of the expansion, the set of generalized transport coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ is identified from the mass flux \mathbf{j}_1 as nonlinear functions of the shear rate and the parameters of the mixture. This Chapman–Enskog-like expansion has been used to analyze transport properties in spatially inhomogeneous states near USF in the case of ordinary gases [18] and more recently in the context of granular gases [19–23]. On the other hand, although the results derived in this paper are restricted to Maxwell molecules, one expects that the influence of the interaction potential on the nonlinear transport properties is only residual, once the relevant transport properties are conveniently nondimensionalized. This expectation has been clearly confirmed by computer simulations [24,25] for non-Maxwell interaction potentials where it has been shown that the rheological properties of the USF problem are indeed practically insensitive to the interaction law. A comparison between the exact results derived here for Maxwell molecules with those obtained by performing Monte Carlo simulations for hard spheres could assess the influence of the interaction potential on the shear-rate dependence of the coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$. Although this is an interesting issue, it is beyond the aim of the present paper.

Some previous attempts to determine the above coefficients have been carried out earlier by the author and coworkers [5,26] in the case of the diffusion tensor D_{ij} . However, all these studies have been restricted to perturbed *steady* states with the constraints $p = \text{const}$ and $T = \text{const}$. Although steady states are in general desirable for practical purposes, especially in computer simulations [27], here we extend the above studies to a general time and space dependence of the hydrodynamic fields. This allows us to evaluate new contributions to the mass flux (those proportional to ∇p and ∇T), which were not taken into account in the previous studies.

2. A binary mixture under uniform shear flow

We consider a *dilute* binary mixture where $f_s(\mathbf{r}, \mathbf{v}; t)$ is the one-particle velocity distribution function of species s ($s = 1, 2$). The time evolution of the distributions f_s is given by the set of two coupled nonlinear Boltzmann equations:

$$\left(\partial_t + \mathbf{v} \cdot \nabla + \frac{\partial}{\partial \mathbf{v}} \cdot \frac{\mathbf{F}_s}{m_s} \right) f_s(\mathbf{r}, \mathbf{v}, t) = \sum_{r=1}^2 J_{sr}[\mathbf{v}|f_s(t), f_r(t)], \quad (2.1)$$

where m_s is the mass of a particle of species s , \mathbf{F}_s is a possible external force acting on particles of species s , and $J_{sr}[\mathbf{v}|f_s, f_r]$ is the Boltzmann collision operator [15]. The basic moments of f_s are the species number densities n_s , the mean velocity \mathbf{u}_s , and the partial kinetic temperatures T_s . These quantities define the total number density $n = \sum_s n_s$, the flow velocity $\mathbf{u} = \sum_s \rho_s \mathbf{u}_s / \rho$ and the temperature $nk_B T = \sum_s n_s k_B T_s$. Here, $\rho_s = m_s n_s$ is the mass density of species s , $\rho = \sum_s \rho_s$ is the total mass density, and k_B is the Boltzmann constant. Moreover, in a dilute gas the hydrostatic pressure p is given by $p = nk_B T$. The quantities n_s , \mathbf{u} , and T are associated with the densities of conserved quantities (mass of each species, total momentum, and total energy). The corresponding balance equations define the dissipative fluxes of mass

$$\mathbf{j}_s = m_s \int d\mathbf{v} \mathbf{V} f_s, \quad (2.2)$$

momentum (pressure tensor),

$$\mathbf{P} = \sum_s \mathbf{P}_s = \sum_s m_s \int d\mathbf{v} \mathbf{V} \mathbf{V} f_s, \quad (2.3)$$

and energy (heat flux)

$$\mathbf{q} = \sum_s \mathbf{q}_s = \sum_s \frac{m_s}{2} \int d\mathbf{v} \mathbf{V}^2 \mathbf{V} f_s. \quad (2.4)$$

The expressions of the partial contributions \mathbf{P}_s and \mathbf{q}_s can be easily identified from the second equalities in Eqs. (2.3) and (2.4), respectively. The fact that the mass flux \mathbf{j}_s is defined with respect to the local center-of-mass velocity \mathbf{u} implies that $\sum_s \mathbf{j}_s = \mathbf{0}$.

The USF state is macroscopically defined by constant densities n_s , a spatially uniform temperature $T(t)$ and a linear velocity profile $\mathbf{u}(y) = \mathbf{u}_1(y) = \mathbf{u}_2(y) = ay\hat{\mathbf{x}}$, where a is the *constant* shear rate. Since n_s and T are uniform, then $\mathbf{j}_s = \mathbf{q} = \mathbf{0}$, and the transport of momentum (measured by the pressure tensor) is the relevant phenomenon. In the USF problem, the temperature tends to increase in time due to viscous heating. Usually, an external force (thermostat) is introduced in computer simulations to remove this heating effect and to keep the temperature constant [27]. The simplest choice is a Gaussian isokinetic thermostat given by $\mathbf{F}_s = -m_s \alpha \mathbf{V}$, where $\mathbf{V} = \mathbf{v} - \mathbf{u}$ is the peculiar velocity. The thermostat parameter α is a function of the shear rate adjusted so as to keep the temperature constant. The implicit assumption behind the introduction of these forces is that they play a neutral role in the transport properties, so that the latter are the same with and without a thermostat, when conveniently scaled with the thermal speed. Nevertheless, this expectation is not in general true, except for some specific situations and/or interaction potentials [28,29].

The hierarchy of velocity moments associated with the Boltzmann equation in the USF state can be recursively solved in the particular case of Maxwell molecules, i.e., when particles of species r and s interact through a potential of the form $V_{rs}(r) = \kappa_{rs} r^{-4}$. The key point is that for this interaction the collision rate is independent of the relative velocity and so the collisional moments of order k only involve moments of degree smaller than or equal to k . Thanks to the above property, exact expressions of the pressure tensor \mathbf{P} for a binary mixture of Maxwell molecules under USF were obtained some time ago [17]. The nonzero elements of \mathbf{P} are related to the rheological properties of the mixture, namely, the nonlinear shear viscosity and the viscometric functions. In reduced units, they turn out to be nonlinear functions of the (reduced) shear rate $a^* = a/\zeta$ (where ζ is a convenient time unit defined below) and the parameters of the mixture: the mass ratio $\mu = m_1/m_2$, the mole fraction $x_1 = n_1/n$ and the force constant ratios κ_{11}/κ_{12} and κ_{22}/κ_{12} . As expected, the results also show that the temperature ratio T_1/T_2 is clearly different from 1 and so, the total kinetic energy is not equally distributed between both species (breakdown of the equipartition theorem). The temperature ratio T_1/T_2 does not present a monotonic dependence on the shear rate and so, both partial temperatures coincide at a certain value of a^* , which depends on the parameters of the system. Regarding the influence of thermostat, it must be noted that in the particular case of Maxwell molecules there is an exact equivalence between the USF results with and without the Gaussian thermostat. As will be shown below, beyond the USF problem, the presence of the thermostat does not play a neutral role in the results and a certain influence may exist.

3. Mass flux under shear flow

Let us disturb the USF state by small spatial perturbations. The response of the system to those perturbations gives rise to contributions to the mass flux that can be characterized by generalized transport coefficients. In order to analyze this problem we have to start from the set of Boltzmann Eq. (2.1) with a general time and space dependence. Let $\mathbf{u}_0 = \mathbf{a} \cdot \mathbf{r}$ be the flow velocity of the *undisturbed* USF state, where the elements of the tensor \mathbf{a} are $a_{ij} = a\delta_{ix}\delta_{jy}$. In the *disturbed* state, however the true velocity \mathbf{u} is in general different from \mathbf{u}_0 , i.e., $\mathbf{u} = \mathbf{u}_0 + \delta\mathbf{u}$, $\delta\mathbf{u}$ being a small perturbation to \mathbf{u}_0 . As a consequence, the true peculiar velocity is now $\mathbf{c} \equiv \mathbf{v} - \mathbf{u} = \mathbf{V} - \delta\mathbf{u}$, where $\mathbf{V} = \mathbf{v} - \mathbf{u}_0$. In the Lagrangian frame moving with \mathbf{u}_0 , the Boltzmann Eq. (2.1) can be written as

$$\frac{\partial}{\partial t} f_1 - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_1 + (\mathbf{V} + \mathbf{u}_0) \cdot \nabla f_1 + \alpha \delta\mathbf{u} \cdot \frac{\partial f_1}{\partial \mathbf{V}} = J_{11}[f_1, f_1] + J_{12}[f_1, f_2], \quad (3.1a)$$

$$\frac{\partial}{\partial t} f_2 - \frac{\partial}{\partial V_i} (a_{ij} V_j + \alpha V_i) f_2 + (\mathbf{V} + \mathbf{u}_0) \cdot \nabla f_2 + \alpha \delta\mathbf{u} \cdot \frac{\partial f_2}{\partial \mathbf{V}} = J_{22}[f_2, f_2] + J_{21}[f_2, f_1], \quad (3.1b)$$

where the derivative ∇f_s is taken at constant \mathbf{V} . In addition, in Eqs. (3.1a) and (3.1b) the thermostat force has been assumed to be proportional to the actual peculiar velocity, $\mathbf{F}_s = -m_s \alpha (\mathbf{V} - \delta\mathbf{u})$ where now the parameter α is in general a function of \mathbf{r} and t through their functional dependence on the hydrodynamic fields n_s and T . The generalization of α to the inhomogeneous case is essentially a matter of choice. Here, for the sake of simplicity, we will take two different choices for α : (i) $\alpha = 0$, so that the temperature grows in time, and (ii) the same expression obtained in the (pure) USF problem, except that the densities and temperature are replaced by those of the general inhomogeneous state.

We assume that the deviations from the USF state are small. This means that the spatial gradients of the hydrodynamic fields are small. For systems near equilibrium, the specific set of gradients contributing to each flux is restricted by fluid symmetry, Onsager relations, and the form of entropy production [1]. However, in far from equilibrium situations (such as the one considered in this paper), only fluid symmetry applies and so there is more flexibility in the representation of the heat and mass fluxes since they can be defined in a variety of equivalent ways depending on the choice of hydrodynamic gradients used. Here, as in previous works in granular mixtures [22,31], the mole fraction x_1 , the pressure p , the temperature T , and the local flow velocity $\delta\mathbf{u}$ are chosen as hydrodynamic fields. Since the system is strongly sheared, a solution to the set of Boltzmann equations (3.1a) and (3.1b) can be obtained by means of a generalization of the conventional Chapman–Enskog method [15] in which the velocity distribution function is expanded around a *local* shear flow reference state in terms of the small spatial gradients of the hydrodynamic fields relative to those of USF. This is the main new ingredient of the expansion. This type of Chapman–Enskog-like expansion has been already considered to obtain the set of shear-rate dependent transport coefficients in thermostatted shear flow problems [18] and it has also been recently developed for inelastic gases [19–23]. More technical details on the application of this perturbative scheme to obtain the mass flux in a binary mixture of Maxwell molecules can be found in Ref. [30].

The first-order contribution to the mass flux $\mathbf{j}_1^{(1)}$ can be written as

$$j_{1,i}^{(1)} = -\frac{m_1 m_2 n}{\rho} D_{ij} \frac{\partial x_1}{\partial r_j} - \frac{\rho}{p} D_{p,ij} \frac{\partial p}{\partial r_j} - \frac{\rho}{T} D_{T,ij} \frac{\partial T}{\partial r_j}, \quad (3.2)$$

where the set of *generalized* transport coefficients D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ are nonlinear functions of the shear rate and the parameters of the mixture. As expected, the mass flux is expressed in terms of a diffusion tensor D_{ij} , a pressure diffusion tensor $D_{p,ij}$, and a thermal diffusion tensor $D_{T,ij}$. As will be shown below, when $a^* = 0$, one recovers the usual Navier–Stokes description, namely, $D_{ij} = D_0 \delta_{ij}$, $D_{p,ij} = D_{p,0} \delta_{ij}$ and $D_{T,ij} = 0$. However, for nonvanishing shear rates, it is apparent that the anisotropy induced by the presence of shear flow gives rise to new transport coefficients which are zero when the mixture is close to equilibrium (say for instance, the off-diagonal coefficients $D_{xy} \neq D_{yx} \neq D_{p,xy} \neq D_{p,yx} \neq D_{T,xy} \neq D_{T,yx} \neq 0$). Note that although the partial temperatures of each species are different ($T_1 \neq T_2$), there are no additional hydrodynamic degrees of freedom in the problem since the temperatures T_i can be still expressed in terms of the global temperature T , which is the relevant one at a hydrodynamic level. As a consequence, the mass flux (3.2) can be represented in terms of the gradients of the hydrodynamic fields x_1 , p , and T .

3.1. Unthermostatted USF state

In the absence of an external thermostat ($\alpha = 0$), the generalized transport coefficients D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ obey the following set of coupled algebraic equations:

$$\left[\left(\frac{\rho\lambda_{12}}{m_1m_2} - \frac{2}{3}aP_{xy}^* \right) \delta_{ik} + a_{ik} \right] D_{kj} = \frac{\rho k_B T}{m_1m_2} \left(\partial_{x_1} P_{1,ij}^* - \frac{\rho_1}{\rho} \partial_{x_1} P_{ij}^* \right) + \frac{2a\rho^2}{3m_1m_2n} (\partial_{x_1} P_{xy}^*) (D_{p,ij} + D_{T,ij}), \quad (3.3)$$

$$\left[\left(\frac{\rho\lambda_{12}}{m_1m_2} - \frac{2a}{3p}(1 - a^*\partial_{a^*})P_{xy}^* \right) \delta_{ik} + a_{ik} \right] D_{p,kj} = \frac{p}{\rho}(1 - a^*\partial_{a^*}) \left(P_{1,ij}^* - \frac{\rho_1}{\rho} P_{ij}^* \right) - \frac{2a}{3}a^*D_{T,ij}(\partial_{a^*}P_{xy}^*), \quad (3.4)$$

$$\left[\left(\frac{\rho\lambda_{12}}{m_1m_2} - \frac{2a}{3}(1 + a^*\partial_{a^*})P_{xy}^* \right) \delta_{ik} + a_{ik} \right] D_{T,kj} = \frac{p}{\rho}a^*\partial_{a^*} \left(P_{1,ij}^* - \frac{\rho_1}{\rho} P_{ij}^* \right) + \frac{2a}{3}a^*D_{p,ij}(\partial_{a^*}P_{xy}^*). \quad (3.5)$$

Here, $\mathbf{P}^* = \mathbf{P}^{(0)}/p$ and $\mathbf{P}_s^* = \mathbf{P}_s^{(0)}/p$ are the (reduced) pressure tensors of the USF and $\lambda_{sr} = 1.69\pi\sqrt{\kappa_{sr}m_s m_r/(m_s + m_r)}$. In addition, $a^* = a/\zeta$, where $\zeta = (2p/k_B T)[\lambda'_{12}/(m_1 + m_2)]$ with $\lambda'_{sr} = 2.61\pi\sqrt{\kappa_{sr}m_s m_r/(m_s + m_r)}$. The solution to Eqs. (3.3)–(3.5) provides the forms of the tensors D_{ij} , $D_{p,ij}$ and $D_{T,ij}$ in the unthermostatted shear flow state.

In the absence of shear field ($a = 0$), then $P_{s,ij}^* = x_s \delta_{ij}$, and $P_{ij}^* = \delta_{ij}$, so that Eqs. (3.3)–(3.5) have the solutions $D_{ij} = D_0 \delta_{ij}$, $D_{p,ij} = D_{p,0} \delta_{ij}$, and $D_{T,ij} = 0$, where D_0 and $D_{p,0}$ are the conventional Navier–Stokes transport coefficients for Maxwell molecules [15]. Their expressions are $D_0 = k_B T/\lambda_{12}$ and $D_{p,0} = D_0(m_2 - m_1)(\rho_1 \rho_2/\rho^3)$. The fact that the thermal diffusion coefficient vanishes when $a^* = 0$ is due to the interaction potential considered (Maxwell molecules) since this coefficient is different from zero for more general interaction potentials [15]. However, when the mixture is strongly sheared, the Boltzmann equation leads to contributions to the mass flux proportional to the thermal gradient, even for Maxwell molecules. In the case of mechanically equivalent particles ($\mu = 1$, $\kappa_{11} = \kappa_{22} = \kappa_{12}$), $P_{1,ij}^* = x_1 P_{ij}^*$, $\partial_{x_1} P_{1,ij}^* = P_{1,ij}^*/x_1 = P_{xy}^{(0)}$, and so $D_{p,ij} = D_{T,ij} = 0$ and the expression for D_{ij} is consistent with previous results derived for the self-diffusion tensor [32,33]. Furthermore, known results for the diffusion tensor [26] are also recovered in the tracer limit ($x_1 \rightarrow 0$).

3.2. Thermostatted USF state

In the thermostatted case, $\alpha = -aP_{xy}^{(0)}/3p$, and the explicit expressions for D_{ij} , $D_{p,ij}$, and $D_{T,ij}$ are given by

$$D_{ij} = \frac{\rho k_B T}{m_1m_2} \frac{1}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \right) \left(\partial_{x_1} P_{1,kj}^* - \frac{\rho_1}{\rho} \partial_{x_1} P_{kj}^* \right), \quad (3.6)$$

$$D_{p,ij} = \frac{p}{\rho} \frac{1}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \right) (1 - a^*\partial_{a^*}) \left(P_{1,kj}^* - \frac{\rho_1}{\rho} P_{kj}^* \right), \quad (3.7)$$

$$D_{T,ij} = \frac{p}{\rho} \frac{a^*}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \left(\delta_{ik} - \frac{a_{ik}}{\alpha + \frac{\rho\lambda_{12}}{m_1m_2}} \right) \partial_{a^*} \left(P_{1,kj}^* - \frac{\rho_1}{\rho} P_{kj}^* \right). \quad (3.8)$$

The expression (3.6) for the diffusion tensor D_{ij} coincides with the one derived before [5] in a stationary state with the constraints $p = \text{const}$ and $T = \text{const}$. Finally, it is also apparent that, except for vanishing shear rates, the expressions of the generalized transport coefficients (3.6)–(3.8) in the thermostatted state differ from the ones derived in the absence of a thermostat, Eqs. (3.3)–(3.5). This shows again that the presence of the thermostat affects the *nonlinear* transport properties of the system.

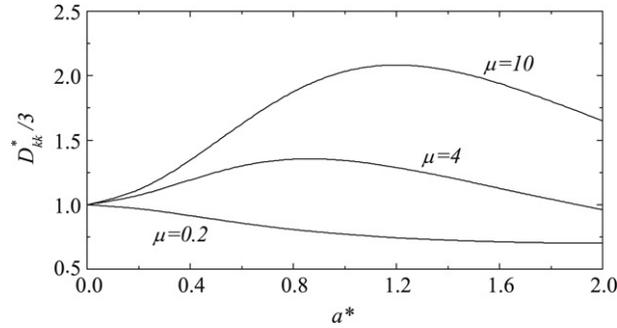


Fig. 1. Shear-rate dependence of the trace $\frac{1}{3}D_{kk}^*$ of the mutual-diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

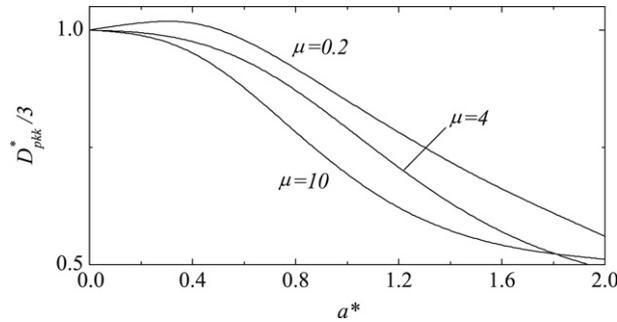


Fig. 2. Shear-rate dependence of the trace $\frac{1}{3}D_{pkk}^*$ of the pressure diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

4. Illustrative examples in the tracer limit

The results obtained in the preceding Section give all the relevant information on the influence of shear flow on the mass transport. In general, the elements D_{ij} , $D_{p,ij}$ and $D_{T,ij}$ present a complex dependence on the shear rate and the parameters of the mixture without any restriction on their values. However, although the solution to Eqs. (3.3)–(3.5) (in the unthermostatted case) and Eqs. (3.6)–(3.8) (in the thermostatted case) is simple, it involves quite a tedious algebra due to the complex dependence of the partial pressure tensors $\mathbf{P}_{s,ij}^{(0)}$ and the thermostat parameter α on the mole fraction x_1 and the reduced shear rate a^* . To show the shear-rate dependence of the tensors $T_{ij} \equiv \{D_{ij}, D_{p,ij}, D_{T,ij}\}$ in a clearer way, the tracer limit ($x_1 \rightarrow 0$) will be considered here in detail. In addition, to make some contact with computer simulation results, the thermostatted case will be studied. In the tracer limit case, $\mathbf{P}^{(0)} \simeq \mathbf{P}_2^{(0)}$ and the partial pressure tensors $\mathbf{P}_1^{(0)}$ and $\mathbf{P}_2^{(0)}$ have a more simplified forms [26]. In particular, $\partial_{x_1} P_{ij}^{(0)} = 0$ and $\partial_{x_1} P_{1,ij}^{(0)} = P_{1,ij}^{(0)}/x_1$.

As expected, $T_{xz} = T_{zx} = T_{yz} = T_{zy} = 0$, in agreement with the symmetry of the problem. As a consequence, there are five relevant elements: the three diagonal (T_{xx} , T_{yy} , and T_{zz}) and two off-diagonal elements (T_{xy} and T_{yx}). In addition, $T_{xx} \neq T_{yy} = T_{zz}$ and $T_{xy} \neq T_{yx}$. The equality $P_{s,yy}^{(0)} = P_{s,zz}^{(0)}$ implies $T_{yy} = T_{zz}$. This property is a consequence of the interaction model considered since for non-Maxwell molecules computer simulations show that the yy and zz elements of the pressure tensor are different [25]. In Figs. 1–6, the relevant elements of tensors D_{ij}^* , $D_{p,ij}^*$ and $D_{T,ij}^*$ are plotted as functions of the reduced shear rate a^* for $\kappa_{12} = \kappa_{22}$ and several values of the mass ratio μ . Here, the tensors have been reduced with respect to their Navier–Stokes values (except $D_{T,ij}$), namely, $D_{ij}^* = D_{ij}/D_0$, $D_{p,ij}^* = D_{p,ij}/D_{p,0}$ and $D_{T,ij}^* = D_{T,ij}/x_1 D_0$. One third of the trace of these tensors is plotted in Figs. 1–3, while the xy element is plotted in Figs. 4–6. We observe that in general the influence of shear flow on the mass transport is quite important. It is also apparent that the anisotropy of the system, as measured by the traces $\frac{1}{3}D_{kk}^*$, $\frac{1}{3}D_{p,kk}^*$, and $\frac{1}{3}D_{pTkk}^*$, grows with the shear rate. This anisotropy is more significant when the impurity is heavier than the particles of the gas. Moreover, the shear field induces cross effects in the diffusion of particles. This is measured by the (reduced) off-diagonal elements D_{xy}^* , $D_{p,xy}^*$, and $D_{T,xy}^*$. These coefficients give the transport of mass along the x axis due to gradients parallel to the y axis. While D_{xy}^* and $D_{p,xy}^*$ are negative, the coefficient $D_{T,xy}$ can be

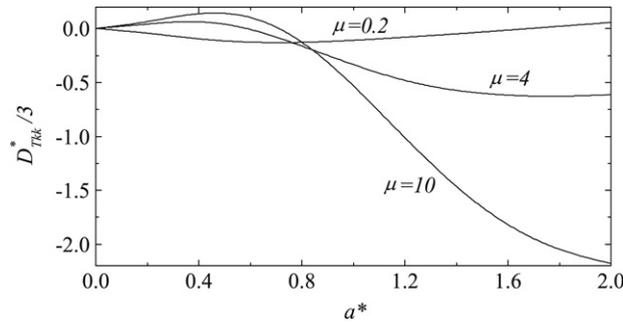


Fig. 3. Shear-rate dependence of the trace $\frac{1}{3}D_{T,kk}^*$ of the thermal diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

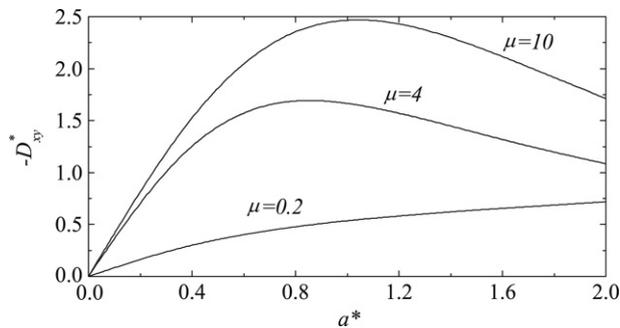


Fig. 4. Shear-rate dependence of the off-diagonal element $-D_{xy}^*$ of the mutual-diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

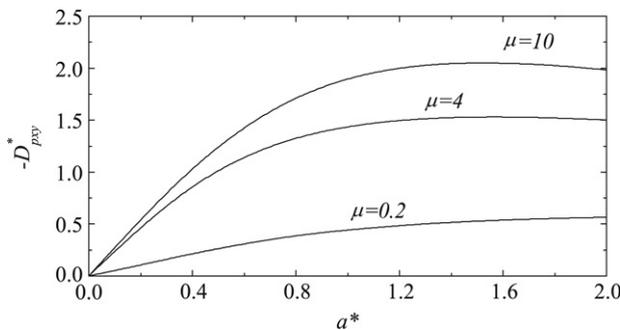


Fig. 5. Shear-rate dependence of the off-diagonal element $-D_{p,xy}^*$ of the pressure diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

positive in the region of small shear rates. We observe that, regardless of the mass ratio, the shapes of D_{xy}^* and $D_{p,xy}^*$ are quite similar: there is a region of values of a^* for which $-D_{xy}^*$ and $-D_{p,xy}^*$ increase with increasing shear rate, while the opposite happens for larger shear rates. The magnitude of $D_{T,xy}^*$ is smaller than that of the elements $-D_{xy}^*$ and $-D_{p,xy}^*$, especially when the tracer particles are lighter than the particles of the gas. In this latter case, $D_{T,xy}^*$ is practically negligible.

5. Discussion

Diffusion of particles in a binary mixture in non-Newtonian regimes is a subject of great interest from fundamental and practical points of view. If the mixture is strongly sheared, the mass flux \mathbf{j}_1 can be significantly affected by the presence of shear flow so that the corresponding transport coefficients may differ significantly from their equilibrium values. In order to gain some insight into this complex problem, a dilute binary mixture of Maxwell molecules under USF has been considered. This is perhaps the only interaction potential for which the Boltzmann equation can be

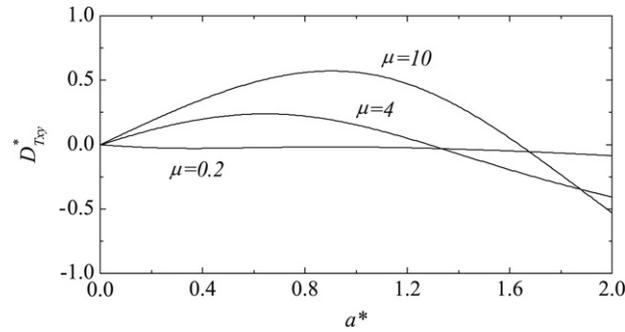


Fig. 6. Shear-rate dependence of the off-diagonal element $D_{T,xy}^*$ of the thermal diffusion tensor for $x_1 = 0$, $\kappa_{22} = \kappa_{12}$ and several values of the mass ratio $\mu = m_1/m_2$.

exactly solved in some specific nonhomogeneous situations, such as in the case of the USF problem. This exact solution is of great significance in providing insight into the type of phenomena that can occur in conditions far away from equilibrium. In this paper, the interest has been focused on situations that slightly deviate from the USF by small spatial gradients. Under these conditions, a generalized Chapman–Enskog method [18,20–23] around the shear flow distribution has been used to determine mass transport in the first order of the deviations of the hydrodynamic field gradients from their values in the reference shear flow state $f_s^{(0)}$. In this case, the mass flux $\mathbf{j}_1^{(1)}$ is given by Eq. (3.2), where the corresponding set of generalized transport coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ is the solutions of the coupled algebraic equations (3.3)–(3.5) in the unthermostatted case, while they are explicitly given by Eqs. (3.6)–(3.8) in the presence of a Gaussian thermostat [27]. This type of external forces are usually employed in nonequilibrium molecular dynamics simulations to compensate exactly for the viscous increase of temperature.

As expected, the results show that the coefficients $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ present a complex dependence on the shear rate and on the masses, mole fractions, and force constants. This is clearly illustrated in Figs. 1–6 for the tracer limit case ($x_1 \rightarrow 0$). The deviations of $\{D_{ij}, D_{p,ij}, D_{T,ij}\}$ from their equilibrium values are basically due to three different reasons. First, the presence of shear flow modifies the collision frequency of the conventional diffusion problem ($\rho\lambda_{12}/m_1m_2$) by a shear-rate dependent term. Second, given that the binary mixture is in general constituted by particles mechanically different, the reference shear flow states $f_1^{(0)}$ and $f_2^{(0)}$ are completely different. This effect gives rise to terms proportional to $P_{1,ij}^* - (\rho_1/\rho)P_{ij}^*$. Third, in the unthermostatted case, the generalized coefficients are coupled due to the inherent non-Newtonian features of the USF state. Each one of the three effects is a different reflection of the extreme nonequilibrium conditions present in the mixture.

It is apparent that the results presented here in the particular case of Maxwell molecules may be relevant for interpreting computer simulation results. As said in the Introduction, Sarman, Evans, and Baranyai [7] carried out some time ago molecular dynamics simulations in a strongly sheared Lennard-Jones binary mixture to evaluate the self- and mutual-diffusion tensor by means of Green–Kubo formulae [34]. They considered an equimolar Lennard-Jones mixture at two different densities and the parameters in the potential were adjusted to model an argon–krypton mixture, which means that the two components are fairly similar. As already said in Ref. [5], when one considers this type of mixture ($x_1 = 0.5$, $m_1/m_2 = 0.48$, $\kappa_{11} = \kappa_{22} = \kappa_{12}$) in the thermostatted case, the general qualitative dependence of the (reduced) mutual-diffusion tensor $D_{ij}(a^*)/D_0$ on the (reduced) shear rate agrees quite well with computer simulations. Thus, theory and simulation predict that in general, the xx element increases to a maximum and then it decreases again, while the yy element decreases with increasing shear rate. The off-diagonal elements xy and yx are negative and their magnitude increases with a^* for not very large values of the shear rate. However, the kinetic theory predicts that $|D_{xy}| > |D_{yx}|$, while the opposite happens in computer simulations. On the other hand, a quantitative comparison is prevented by the difficulties involved in mapping the Lennard-Jones parameters of the mixture onto the force constants for Maxwell interactions, as well as by the fact that the simulations were performed for densities beyond the range of applicability of the Boltzmann equation. An alternative to overcome these difficulties is to use the well-known direct simulation Monte Carlo method [35] for dilute gases. I hope that the results derived here for Maxwell molecules for D_{ij} , $D_{p,ij}$ and $D_{T,ij}$ stimulate the performance of Monte Carlo simulations to assess the reliability of the Maxwell results to describe mass transport in strongly sheared mixtures for more realistic interaction potentials.

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