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Mutual diffusion in a binary mixture under shear flow

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Mass transport in a dilute binary mixture of Maxwell molecules under steady shear flow is studied. The analysis is made from an exact perturbation solution of the Boltzmann equation through first order in the concentration gradient. The reference state (zeroth order approximation) corresponds to the exact recent solution [Phys. Rev. E **52**, 3812 (1995)] of the Boltzmann equation in the uniform shear flow, which holds for arbitrary values of the shear rate. The results show that the mass flux obeys a generalized Fick's law where, due to the anisotropy of the problem, a mutual diffusion tensor is defined. This tensor is a highly nonlinear function of the shear rate and the parameters of the mixture (particle masses, concentrations, and force constants). The calculations presented here extend previous results derived in the limit cases of self-diffusion and tracer particles. [S1063-651X(98)02601-4]

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I. INTRODUCTION

The description of transport processes taking place in fluid mixtures 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 mass flux (vector quantity) that obeys Fick's law is not affected by the presence of the velocity gradient (second-rank tensorial quantity). Nevertheless, beyond the linear domain Curie's principle does not apply, and the mass flux can be modified by the shear flow even if the concentration gradient is small.

In order to capture the essential aspects of such a nonlinear problem, we consider a binary mixture in the low density regime as a prototype fluid, which lends itself to a detailed description by means of the nonlinear Boltzmann equation [2]. However, due to the complexity of its collision term, it is a very hard task to get explicit results in far from equilibrium situations, especially in the case of multicomponent systems. One of the few *inhomogeneous* states for which exact results can be obtained is the uniform shear flow (USF). In this state, the only nonzero gradient is $\partial u_x/\partial y = a = \text{const}$, where $\mathbf{u}(\mathbf{r})$ is the flow velocity of the mixture. Recently, rheological properties (such as the shear viscosity and viscometric functions) of a dilute binary mixture under shear flow have been *exactly* obtained in terms of the shear rate a and the parameters of the mixture [3]. The solution is restricted to the Maxwell potential, i.e., particles of species r and s interact through a potential of the form $\Phi_{rs} = \kappa_{rs} r^{-4}$. Apart from the limitation to the interaction considered, the solution applies to arbitrary values of masses, concentrations, and force constants. In the particular case of mechanically equivalent particles (single gas), the well-known solution given years ago by Ikenberry and Truesdell [4] is recovered.

The aim of this paper is to study a diffusion problem in a strongly sheared binary mixture. The physical situation is such that an *arbitrary* shear rate coexists with a *weak* concentration gradient. Under these conditions, one expects that the mass flux verifies a generalized Fick's law where, due to the anisotropy of the problem, a mutual diffusion tensor rather than a scalar can be identified. Our goal is to get the explicit expression of this tensor in the case of Maxwell molecules. Such an expression generalizes previous results derived in the cases of tagged particles (self-diffusion) [5–7] and tracer particles [8,9].

In the context of dense fluids, Evans and co-workers [10,11] have derived a Green-Kubo formula for the mutual diffusion tensor in fluids undergoing strong shear. In a similar manner as in equilibrium, the mutual diffusion tensor of a thermostated shearing steady state is related to fluctuations in the steady mass flux. This expression has been used to evaluate the influence of the shear rate on the diffusion tensor in a binary Lennard-Jones mixture by means of computer simulations [11]. In their simulations they do not observe a significant shear rate dependence of the diffusion tensor. This is probably due to the fact that the shear rates considered in the simulation are not sufficiently large to observe non-Newtonian effects.

The plan of the paper is as follows. In Sec. II we give a brief summary of the results derived from the Boltzmann equation for a binary mixture under uniform shear flow. Section III is concerned with the evaluation of the mutual diffusion tensor. By performing a perturbation expansion around the shear flow solution, we get an explicit expression for the mass flux up to first order in the concentration gradient. The nonzero elements of the diffusion tensor happen to be nonlinear functions of the shear rate and the parameters of the mixture (mass ratio, concentration ratio, and force constant ratios). Finally, in Sec. IV the results are discussed and compared with previous simulation results.

II. DILUTE BINARY MIXTURE UNDER SHEAR FLOW

Let us consider a binary mixture. In the low-density regime, the evolution of the system is described by the set of two coupled nonlinear Boltzmann equations [2]:

$$\frac{\partial}{\partial t} f_1 + \mathbf{v}\cdot\boldsymbol{\nabla} f_1 + \frac{\partial}{\partial \mathbf{v}}\cdot\frac{\mathbf{F}_1}{m_1} f_1 = J_{11}[f_1,f_1] + J_{12}[f_1,f_2], \tag{1a}$$

$$\frac{\partial}{\partial t} f_2 + \mathbf{v}\cdot\nabla f_2 + \frac{\partial}{\partial \mathbf{v}}\cdot\frac{\mathbf{F}_2}{m_2} f_1 = J_{21}[f_2,f_1] + J_{22}[f_2,f_2], \tag{1b}$$

where m_s is the mass of a particle of species s, $\mathbf{F}_s$ is the external force acting on particles of species s, f_s is the one-particle velocity distribution function of species s, and $J_{sr}[f_s,f_r]$ is the Boltzmann collision term, which in standard notation reads [2]

$$J_{sr}[f_s,f_r] = \int d\mathbf{v}_1 \int d\Omega |\mathbf{v}-\mathbf{v}_1| \sigma_{rs}(\mathbf{v}-\mathbf{v}_1,\theta)[f_s(\mathbf{v}')f_r(\mathbf{v}_1') - f_s(\mathbf{v})f_r(\mathbf{v}_1)]. \tag{2}$$

In terms of f_s, the densities of conserved quantities (mass of each species, total momentum, and total energy) can be defined. They are given by

$$n_s = \int d\mathbf{v} f_s, \tag{3}$$

$$\rho \mathbf{u} = \sum_{s=1}^{2} \int d\mathbf{v} m_s \mathbf{v} f_s = \sum_{s=1}^{2} \rho_s \mathbf{u}_s, \tag{4}$$

$$n k_B T = \sum_{s=1}^{2} \frac{m_s}{3} \int d\mathbf{v} (\mathbf{v}-\mathbf{u})^2 f_s, \tag{5}$$

where k_B is the Boltzmann constant. Here, n_s is the number density of species s, $\rho_s = m_s n_s$ is the mass density of species s, $\rho = \rho_1 + \rho_2$, $n = n_1 + n_2$, $\mathbf{u}$ is the flow velocity of the mixture, and T is the temperature of the mixture. The corresponding balance equations associated with n_s, $\mathbf{u}$, and T define the dissipative flux of mass

$$\mathbf{j}_s = \int d\mathbf{v} m_s (\mathbf{v}-\mathbf{u}) f_s = \rho_s(\mathbf{u}_s - \mathbf{u}), \tag{6}$$

momentum (pressure tensor)

$$\mathsf{P} = \sum_{s=1}^{2} \int d\mathbf{v} m_s (\mathbf{v}-\mathbf{u})(\mathbf{v}-\mathbf{u}) f_s = \sum_{s=1}^{2} \mathsf{P}_s, \tag{7}$$

and energy (heat flux)

$$\mathbf{q} = \sum_{s=1}^{2} \int d\mathbf{v} \frac{m_s}{2} (\mathbf{v}-\mathbf{u})^2 (\mathbf{v}-\mathbf{u}) f_s. \tag{8}$$

From the partial pressure of species s, one may also define a partial "temperature" T_s as $p_s = n_s k_B T_s = \frac{1}{3}\text{tr}\mathsf{P}_s$.

The USF state is macroscopically characterized by a constant density n_s, uniform temperature, and a linear profile of the x component of the flow velocities along the y direction:

$$u_{s,i} = u_i = a_{ij} r_j, \quad a_{ij} = a\,\delta_{ix}\delta_{jy}, \tag{9}$$

a being the constant shear rate. The shear flow produces viscous heating so that the temperature increases in time. From a computer simulation point of view, it is desirable to measure the transport properties of the mixture in a steady state. For this reason, usually a thermostat force is introduced to keep the temperature constant [12]. The simplest choice is

$$\mathbf{F}_s = -m_s \alpha \mathbf{V}, \tag{10}$$

where $V_i = v_i - a_{ij} r_j$. Here, to parallel the results previously obtained from computer simulations [11], we also include a thermostat force of the form (10) to remove this heating effect [13]. For Maxwell molecules, it is important to remark that in the USF problem there is an exact equivalence between the results obtained with and without a thermostat force [14]. Furthermore, the USF becomes spatially homogeneous in the frame moving with the flow velocity $\mathbf{u}$. In this local frame, the velocity distribution function adopts the form $f_s(\mathbf{r},\mathbf{v}) = f_s(\mathbf{V})$. Under these conditions, Eqs. (1) can be written as

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

and a similar equation for f_2. In the particular case of Maxwell molecules, Eq. (11) can be recursively solved by the moment method. The key point is that for this interaction 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 [4].

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 [3]. These elements define the main transport coefficients of the problem, namely, the shear viscosity and the viscometric functions. They are nonlinear functions of the dimensionless shear rate $a^* = a/\zeta$ and the parameters of the mixture: the mass ratio $\mu = m_1/m_2$, the concentration ratio $\nu = n_1/n_2$ and the force constant ratios κ_{11}/κ_{12} and κ_{22}/κ_{12}. Here, ζ^{-1} is a convenient time unit defined in the Appendix. The explicit expressions of the partial pressure tensors are also quoted in the Appendix.

Since the USF state is well characterized through the first nontrivial moments, we are now in conditions to study the influence of the shear field on the mass flux in a dilute binary mixture. This will be done in the next section.

III. DIFFUSION UNDER SHEAR FLOW

We are interested in analyzing the effect of the shear flow on diffusive motion in the limit of small concentration gradients. In this situation, symmetry arguments suggest that the mass flux is still proportional to the concentration gradient but a shear-rate-dependent mutual diffusion tensor can be identified. As stated in the Introduction, the evaluation of this tensor is the main goal of this paper. To this end, let us assume that we perturb the USF state by introducing a weak concentration gradient $\boldsymbol{\nabla}\nu$. On physical grounds, we also assume that the total density n is constant so that $\boldsymbol{\nabla} n_1 = -\boldsymbol{\nabla} n_2$. These are the usual experimental conditions for measuring the mutual diffusion coefficient at equilibrium. In this case, the corresponding steady Boltzmann equations for the mixture are given by

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

and similarly for f_2. 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. Since the concentration ratio is slightly nonuniform, we solve Eq. (12) by means of a perturbation expansion around the uniform shear flow state. In this expansion, the different aproximations are nonlinear functions of the shear rate. Therefore, we write

$$f_1=f_1^{(0)}+f_1^{(1)}+\cdots, \tag{13}$$

where $f_1^{(k)}$ is of order k in $\nabla\nu$ but retains all the orders in a. The zeroth-order approximation $f_1^{(0)}$ corresponds to the USF distribution but taking into account now the local dependence of the densities n_s. Although the explicit form of $f_1^{(0)}$ is not known, only the knowledge of its second-degree moments (related to the pressure tensor) is necessary to get the mutual diffusion tensor. Here, we will restrict our calculations to first order in the expansion. In this approximation, and assuming that the system has reached a stationary state, one gets

$$-\frac{\partial}{\partial V_i}(a_{ij}V_j+\alpha V_i)f_1^{(1)}+(V_i+a_{ij}r_j)\frac{\partial}{\partial r_i}f_1^{(0)}=J_{11}^{(1)}+J_{12}^{(1)}, \tag{14}$$

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. (14) and its counterpart for $f_2^{(1)}$. First, the mass balance implies that $a_{ij}r_j(\partial n_1/\partial r_i)=0$ and consequently $\partial n_1/\partial x=0$. This means that, in order to maintain the mixture in a steady state, the concentration gradient must be orthogonal to the direction of the shear flow. On the other hand, the total momentum balance equation leads to

$$a_{ik}u_k^{(1)}+\alpha u_i^{(1)}=-\frac{1}{\rho}\frac{\partial}{\partial r_k}P_{ik}^{(0)}, \tag{15}$$

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

$$\mathbf{u}^{(1)}=\frac{1}{\rho}\sum_{s=1}^{2}\int d\mathbf{v}m_s\mathbf{V}f_s^{(1)}, \tag{16}$$

and $\mathsf{P}^{(0)}$ is the total pressure tensor in the uniform shear flow state. According to Eq. (15), 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 $a=0$, $P_{ij}^{(0)}=nk_BT\delta_{ij}=$const, so $\mathbf{u}^{(1)}=0$. For nonzero shear rates, there are only two limit cases for which $\mathsf{P}^{(0)}$ is constant: the case of mechanically equivalent particles ($\mu=1$, $\kappa_{11}=\kappa_{22}=\kappa_{12}$) [7] and the tracer limit ($n_1\ll n_2$) [9]. In both cases, $P_{ij}^{(0)}=nk_BTF(a^*)$, $F(a^*)$ being a nonlinear function of the *constant* shear rate a^*. Beyond these limit cases the pressure tensor depends on space through its dependence on ν, so that the concentration gradient not only induces a mass flux but it also disturbs the linear shear flow. The solution to Eq. (15) is

$$u_i^{(1)}=-\frac{1}{\rho\alpha}\left(\delta_{ik}-\frac{a_{ik}}{\alpha}\right)\frac{\partial}{\partial r_j}P_{kj}^{(0)}. \tag{17}$$

We are interested in computing the mass flux $\mathbf{j}_1^{(1)}$ across the system. Taking into account the relation (6), the mass flux at this order can be written as

$$\mathbf{j}_1^{(1)}=m_1\int d\mathbf{v}\mathbf{V}f_1^{(1)}-\rho_1\mathbf{u}^{(1)}\equiv\tilde{\mathbf{j}}_1^{(1)}-\rho_1\mathbf{u}^{(1)}, \tag{18}$$

where $\tilde{\mathbf{j}}_1^{(1)}$ is the mass flux defined with respect to the Lagrangian frame moving with the unperturbed velocity $u_i^{(0)}=a_{ij}r_j$. The quantity $\tilde{\mathbf{j}}_1^{(1)}$ can be obtained from the Boltzmann equation (14) after multiplying it by m_1V_i and integrating over $\mathbf{V}$. Thus, one finds that

$$a_{ik}\tilde{j}_{1,k}^{(1)}+\alpha\tilde{j}_{1,i}^{(1)}+\frac{\rho\lambda_{12}}{m_1m_2}\tilde{j}_{1,i}^{(1)}=\frac{\rho\lambda_{12}}{m_1m_2}\rho_1u_i^{(1)}-\frac{\partial}{\partial r_k}P_{1,ik}^{(0)}, \tag{19}$$

where λ_{12} is defined in Eq. (A1) and we have used the relation [15]

$$\int d\mathbf{v}m_1V_i(J_{11}^{(1)}+J_{12}^{(1)})=-\frac{\rho\lambda_{12}}{m_1m_2}(\tilde{j}_{1,i}^{(1)}-\rho_1u_i^{(1)}). \tag{20}$$

The solution to Eq. (19) is

$$\tilde{j}_{1,i}^{(1)}=-\frac{1}{\alpha+(\lambda_{12}/m_1m_2)\rho}\left(\delta_{ik}-\frac{a_{ik}}{\alpha+(\lambda_{12}/m_1m_2)\rho}\right)$$
$$\times\left(\frac{\partial}{\partial r_j}P_{1,kj}^{(0)}-\frac{\lambda_{12}\rho_1}{m_1m_2}\rho u_k^{(1)}\right). \tag{21}$$

From Eqs. (17), (18), and (21), one can write the explicit expression of $\mathbf{j}_1^{(1)}$. After some manipulations, it is easy to show that the mass flux can be cast in the form of a generalized Fick's law:

$$j_{1,i}^{(1)}=-\frac{m_1m_2n}{\rho}D_{ij}\frac{\partial}{\partial r_j}n_1 \tag{22}$$

with the mutual diffusion tensor given by

$$D_{ij}=\frac{k_BT}{n\lambda_{12}}\frac{(1+\mu\nu)(1+\nu)^2}{\mu\nu}\tau\left\{\frac{1}{\alpha^*+\beta}\left(\delta_{ik}-\frac{a_{ik}^*}{\alpha^*+\beta}\right)\right.$$
$$\left.\times\left[\frac{\partial}{\partial\nu}P_{1,kj}^{*(0)}+\tau\Lambda_{kj}\right]-\frac{\mu\nu}{1+\mu\nu}\Lambda_{ij}\right\}, \tag{23}$$

where

$$\Lambda_{ij}=\frac{1}{\alpha^*}\left(\delta_{ik}-\frac{a_{ik}^*}{\alpha^*}\right)\frac{\partial}{\partial\nu}P_{kj}^{*(0)}, \tag{24}$$

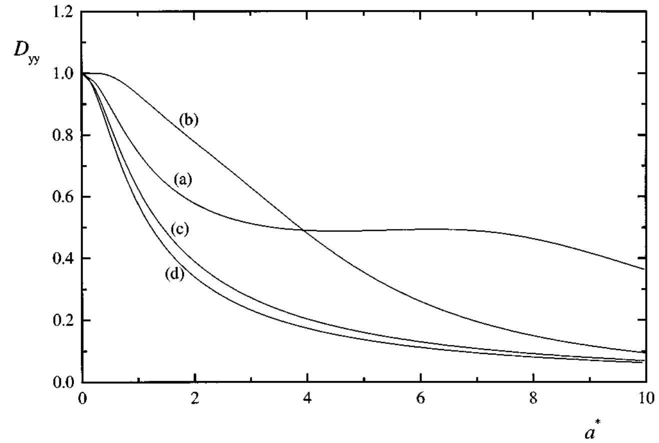

FIG. 1. Plot of the reduced diagonal element of the difusion tensor $\mathcal{D}_{yy}=D_{yy}/D_0$ vs the reduced shear rate $a^*=a/\zeta$ for $\kappa_{11}=\kappa_{22}=\kappa_{12}$, and several values of the concentration ratio $\nu=n_1/n_2$ and the mass ratio $\mu=m_1/m_2$: (a) $\nu=3$, $\mu=10$; (b) $\nu=3$, $\mu=0.1$, (c) the mixture considered in Ref. [11], i.e., $\nu=1$, $\mu=0.48$; and (d) $\mu=1$.

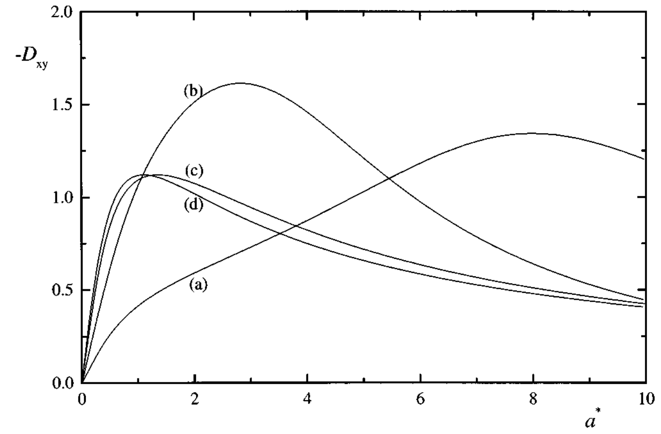

FIG. 2. Plot of the reduced off-diagonal element of the difussion tensor $-\mathcal{D}_{xy}=-D_{xy}/D_0$ vs the reduced shear rate $a^*=a/\zeta$ for $\kappa_{11}=\kappa_{22}=\kappa_{12}$, and several values of the concentration ratio $\nu=n_1/n_2$ and the mass ratio $\mu=m_1/m_2$: (a) $\nu=3$, $\mu=10$; (b) $\nu=3$, $\mu=0.1$, (c) the mixture considered in Ref. [11], i.e., $\nu=1$, $\mu=0.48$; and (d) $\mu=1$.

and we have introduced the dimensionless quantities $a_{ik}^*=a_{ik}/\zeta$, $\alpha^*=\alpha/\zeta$, and $\mathsf{P}_{ij}^{*(0)}=\mathsf{P}_{ij}^{(0)}/nk_BT$. Furthermore,

$$\beta=\frac{\gamma_{12}}{2}\frac{(1+\mu)(1+\mu\nu)}{\mu(1+\nu)}, \tag{25}$$

$$\tau=\frac{\gamma_{12}}{2}\frac{\nu(1+\mu)}{1+\nu}, \tag{26}$$

and $\gamma_{12}=0.648$ is defined in the Appendix.

Equations (22)–(24) represent the major result of this paper. They provide an explicit expression of the mutual diffusion tensor of a dilute binary mixture of Maxwell molecules under shear flow. The components of this tensor give all the information on the physical mechanisms involved in the mass transport in a strongly sheared mixture. They have been derived keeping the first order in the gradient of concentration, but no restriction on the values of the shear rate, the mass ratio, the concentration ratio, and/or the force constant ratios have been considered. In the limits of tagged particles and tracer particles we recover previous results derived for the self-diffusion [7] and tracer diffusion tensors [9], respectively.

In the absence of the shear field ($a=0$), $D_{ij}=D_0\delta_{ij}$, $D_0=k_BT/n\lambda_{12}$ being the mutual diffusion coefficient given by the Chapman-Enskog method [16]. Furthermore, according to Eq. (23), $D_{xz}=D_{yz}=D_{zy}=0$, 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 elements 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 obtained for a Lennard-Jones mixture [11], where $D_{yy}>D_{zz}$. In Figs. 1 and 2 we have plotted the reduced diffusion tensor $\mathcal{D}_{ij}=D_{ij}/D_0$ as a function of the reduced shear rate a^* for $\nu=3$, $\kappa_{11}=\kappa_{22}=\kappa_{12}$, and several values of the mass ratio. Although we have only considered $\nu>1$, the corresponding behavior for $\nu<1$ can be easily inferred when one takes into account that the diffusion tensor is invariant under the changes $\mu\leftrightarrow\mu^{-1}$, $\nu\leftrightarrow\nu^{-1}$, and $\kappa_{11}\leftrightarrow\kappa_{22}$. In the region of shear rates analyzed, non-Newtonian effects are important since, for instance, at $a^*\simeq 5$ in the case of $\mu=1$, the shear viscosity is about 88% smaller than its Navier-Stokes value. We observe that in general the influence of the shear flow on the mass transport is quite important. Figure 1 shows that the value of D_{yy} decreases relative to its value in the absence of shear for all shear rates. Consequently, the shear flow inhibits the mass transport along the direction of the gradient of the flow velocity (y axis). Furthermore, this inhibition becomes more significant when the mass ratio is different from 1 than in the case of identical particles (self-diffusion). The shear flow induces cross effects in the diffusion of particles. This is measured by the off-diagonal element $\mathcal{D}_{xy}$. It gives the transport of mass along the x axis due to a concentration gradient parallel to the y axis. This element is negative and, independently of the mass ratio, its shape is quite similar: there is a region of values of a^* for which $-\mathcal{D}_{xy}$ increases with the shear rate while the opposite happens for larger shear rates. Once the shear-rate dependence of the elements of the diffusion tensor has been studied, it is also interesting to analyze the global effect of the shear field on the mass transport. In order to illustrate this effect, we assume that $\partial n_s/\partial z=0$ and plot the magnitude of the mass flux relative to its Navier-Stokes value, namely, $\Phi_1(a^*)\equiv|\mathbf{j}_1^{(1)}(a^*)|/|\mathbf{j}_1^{(1)}(0)|$. This is done in Fig. 3 for the same cases as in previous figures. We see that, for not too larges shear rates (say $a^*\simeq 1$), the presence of shear flow enhances the total mass flux when the deffect species are lighter than the excess species while the opposite happens when the mass ratio is larger than one. Anyway, in the limit of large shear

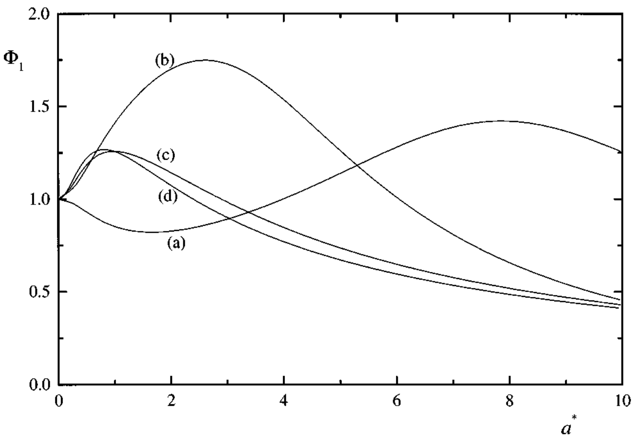

FIG. 3. Plot of the magnitude of the mass flux relative to its Navier-Stokes value $\Phi_1=|\mathbf{j}_1^{(1)}(a^*)|/|\mathbf{j}_1^{(1)}(0)|$ vs the reduced shear rate $a^*=a/\zeta$ for $\kappa_{11}=\kappa_{22}=\kappa_{12}$, and several values of the concentration ratio $\nu=n_1/n_2$ and the mass ratio $\mu=m_1/m_2$: (a) $\nu=3$, $\mu=10$; (b) $\nu=3$, $\mu=0.1$, (c) the mixture considered in Ref. [11], i.e., $\nu=1$, $\mu=0.48$; and (d) $\mu=1$.

rates, $|\mathbf{j}_1^{(1)}(a^*)|/|\mathbf{j}_1^{(1)}(0)|\sim a^{*-1/3}$ so that the mass flux is significantly reduced with respect to its Navier-Stokes value as the shear rate increases.

IV. DISCUSSION

The problem of diffusion of particles in a fluid under shear flow has been a subject of interest in the last few years. Usually, theoretical analysis as well as nonequilibrium computer simulations have been restricted to the special case in which all the particles are mechanically equivalent (self-diffusion). This situation involves only single-particle motion and is therefore somewhat simpler to treat. In this paper we have investigated the influence of shear flow on the mass flux in a binary mixture constituted by particles mechanically *different*. Specifically, we have considered a dilute binary mixture of Maxwell molecules described by the Boltzmann equation. The system is in a steady inhomogeneous state characterized by a constant pressure and temperature, nonuniform partial densities of each species and a linear profile of the x component of the flow velocity along the y direction. We are mainly interested in the physical situation where a weak concentration gradient simultaneously coexists with a strong shear rate. Under these conditions, the mass flux is still a linear function of the concentration gradient although a shear-rate-dependent mutual diffusion tensor rather than a scalar can be defined. The explicit determination of this tensor has been the goal of this paper. It is important to remark that our description has not been restricted to specific values of the parameters of the mixture (mass ratio, concentration ratio, and force constant ratios) and progress has been possible here due to previous results derived in the limit cases of self-diffusion [7] and tracer particles [9].

The Boltzmann equation has been solved by means of a perturbation expansion around the uniform shear flow state. The knowledge of the pressure tensor of the mixture in the pure shear flow state [3] allows one to get an explicit expression of the diffusion tensor D_{ij} in the first order of the expansion. According to the geometry of the problem, the elements $D_{yy}=D_{zz}$ and D_{xy} are the relevant transport coefficients. While the diagonal elements are even functions of the shear rate, D_{xy} is an odd function. In general, they exhibit a highly nonlinear dependence on the shear rate and the parameters of the mixture. The diagonal elements of D_{ij} can be interpreted as generalizations of the conventional mutual diffusion coefficient since they conjugate the ith component of the mass flux vector with the ith component of the concentration gradient. The off-diagonal element D_{xy} can be seen as a generalization of a nonlinear Burnett coefficient as it measures cross-coupling effects. With respect to the dependence of such elements on the shear rate, we conclude that the net effect of the shear flow on the mass transport is to produce an inhibition of the transport of particles along the direction of the gradient of the flow velocity (y axis). In the case of the x direction, $-D_{xy}$ presents a maximum at a given value of the shear rate. These results show that diffusion under shear flow is a very complex problem due basically to the anisotropy induced in the system by the presence of the shear field.

It is apparent that the derivation of explicit expressions for the transport properties involved in a nonequlibrium problem may be useful for interpreting computer simulations results. In this context, recently Sarman, Evans, and Baranyai [11] have performed simulations in a strongly shearing Lennard-Jones binary mixture to evaluate the mutual diffusion tensor by means of a Green-Kubo formula [10]. To the best of our knowledge, this is the only computer experiment in which mass transport under shear flow has been analyzed. They considered an equimolar Lennard-Jones mixture at two different densities and the parameters in the potential were chosen to model an argon-krypton mixture. Although the Lennard-Jones fluid has an attractive tail (absent in our model), in an attempt to make a comparison of theory and simulation, we have applied our results to this type of mixture. Specifically, we have taken $\nu=1$, $\mu=0.48$, and since the two components of the mixture are fairly similar we have also assumed that $\kappa_{11}=\kappa_{22}=\kappa_{12}$. According to the behavior of $\mathcal{D}_{ij}$ displayed in the figures, we observe that the general shear-rate dependence of the diffusion tensor agrees qualitatively well with the simulation results, at least for the lowest density considered [11]. As a matter of fact, for small shear rates, for this mixture one has that $\mathcal{D}_{yy}\approx 1-0.962a^{*2}$ and $\mathcal{D}_{xy}\approx -2.214a^*$. Nevertheless, as far as quantitative effects are concerned, simulation results predict an influence of the shear flow on the diffusion tensor more modest than the one obtained here, especially in the case of the diagonal elements. Perhaps these discrepancies are due to the fact that the shear rates applied in the simulation are not large enough to clearly observe nonlinear effects. For instance, if one extrapolates our definition of the collision frequency $\zeta=[2k_BT/\gamma_{12}(m_1+m_2)D_0]$ to dense fluids [18], one can estimate that the range of shear rates considered here is much larger than the one used in computer simulations. As an alternative to overcome the difficulties associated with molecular dynamics simulations in the low-density regime, one could perhaps use the direct simulation Monte Carlo method [19], which has been shown to be fruitful in the past years.

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APPENDIX

In this Appendix, we give the explicit expression of the partial pressure tensor P_1. Let us introduce the quantities

$$\lambda_{rs}=1.69\pi\left(\kappa_{rs}\frac{m_r m_s}{m_r+m_s}\right)^{1/2}, \tag{A1}$$

$$\lambda'_{rs}=2.61\pi\left(\kappa_{rs}\frac{m_r m_s}{m_r+m_s}\right)^{1/2}, \tag{A2}$$

and the effective collision frequency $\zeta=2n\lambda'_{12}/(m_1+m_2)$. We define ζ^{-1} as the time unit and we will use the dimensionless quantities $a^*=a/\zeta$, and $\alpha^*=\alpha/\zeta$. Henceforth, we will omit the asterisks. In terms of the mass ratio μ, the concentration ratio ν and the ratios $\gamma_{11}=\lambda'_{11}/\lambda'_{12}$, $\gamma_{22}=\lambda'_{22}/\lambda'_{12}$, and $\gamma_{12}=\lambda_{12}/\lambda'_{12}=0.648$, the nonzero elements of the tensor P_1 are given by [3]

$$\frac{P_{1,yy}}{p}=\frac{P_{1,zz}}{p}=\frac{Ma^2+N}{Ra^2+S}, \tag{A3}$$

$$\frac{P_{1,xy}}{p}=-\frac{Q}{Ra^2+S}a, \tag{A4}$$

$$\frac{P_{1,xx}}{p}=3\frac{Ka^2+L}{Ra^2+S}-2\frac{P_{1,yy}}{p}, \tag{A5}$$

where

$$M=2\,B_{12}(A_{12}A_{21}-A_{11}A_{22}), \tag{A6}$$

$$\begin{aligned}N={}&48\,A_{12}\alpha^4+24\,\alpha^3[2\,A_{12}(B_{11}+B_{22})-B_{12}(A_{11}+A_{22})]+12\,\alpha^2[A_{12}(B_{11}^2+B_{22}^2+4\,B_{11}B_{22})-A_{12}B_{12}(A_{21}+B_{21})]\\&+B_{12}A_{11}(A_{22}-B_{11}-2\,B_{22})-B_{12}A_{22}(B_{22}+2\,B_{11})+B_{12}^2A_{21}]+6\,\alpha[B_{11}B_{12}(A_{11}A_{22}-A_{12}A_{21}+A_{21}B_{12}+A_{12}B_{21}\\&-2\,A_{11}B_{22}-2\,A_{22}B_{22}-A_{22}B_{11})+B_{12}^2(A_{11}B_{21}+A_{22}B_{21}+A_{21}B_{22})+B_{12}B_{22}(A_{11}A_{22}-A_{12}A_{21}-A_{12}B_{21}-A_{11}B_{22})\\&+2\,A_{12}B_{11}B_{22}(B_{11}+B_{22})]+3(B_{12}B_{21}-B_{11}B_{22})[B_{12}(A_{12}A_{21}-A_{11}A_{22})+B_{11}(B_{12}A_{22}-A_{12}B_{22})\\&+B_{12}(A_{11}B_{22}-B_{12}A_{21})],\end{aligned} \tag{A7}$$

$$\begin{aligned}Q={}&-24\,A_{12}\alpha^3+12\,\alpha^2[B_{12}(A_{11}+2\,A_{22})-A_{12}(B_{11}+2\,B_{22})]+6\,\alpha[2\,B_{12}(A_{12}A_{21}-A_{11}A_{22})+A_{22}B_{12}(3B_{11}+B_{22})\\&-A_{12}(B_{22}^2+2\,B_{11}B_{22})+B_{12}(2\,A_{11}B_{22}-2\,A_{21}B_{12}-A_{12}B_{21})]+3\,[A_{12}A_{21}B_{12}(B_{11}+B_{22})-A_{22}B_{11}B_{12}(A_{11}-B_{11})\\&+B_{12}^2(A_{11}B_{21}-A_{21}B_{11})A_{12}B_{11}(B_{12}B_{21}+B_{22}^2)+A_{11}B_{12}B_{22}(B_{22}-A_{22})+B_{12}B_{22}(A_{22}B_{11}-A_{21}B_{12})],\end{aligned} \tag{A8}$$

$$K=8\,\alpha^2A_{12}+8\,\alpha(A_{12}B_{22}-A_{22}B_{12})+2\,A_{12}(B_{12}B_{21}+{B_{22}}^2)-2\,A_{22}B_{12}(B_{11}+B_{22}), \tag{A9}$$

$$L=3\,(A_{12}-B_{12})[4\,\alpha^2+2\,\alpha(B_{11}+B_{22})+B_{11}B_{22}-B_{12}B_{21}]^2, \tag{A10}$$

$$R=8\,\alpha^2(A_{12}-A_{11})+8\,\alpha[B_{12}(A_{21}-A_{22})+B_{22}(A_{12}-A_{11})]+2\,B_{12}(A_{21}-A_{22})(B_{11}+B_{22})+2\,(A_{12}-A_{11})(B_{12}B_{21}+{B_{22}}^2), \tag{A11}$$

$$S=3\,(2\,\alpha-A_{11}+A_{12}+B_{11}-B_{12})[4\,\alpha^2+2\,\alpha(B_{11}+B_{22})+B_{11}B_{22}-B_{12}B_{21}]^2. \tag{A12}$$

Here, we have introduced the coefficients

$$A_{11}=\frac{\gamma_{11}}{2}\,\frac{\nu}{\nu+1}\,\frac{\mu+1}{\mu}+\frac{1}{2\mu(\nu+1)}, \tag{A13}$$

$$A_{12}=\frac{1}{2}\,\frac{\nu}{\nu+1}, \tag{A14}$$

$$B_{11}=A_{11}+\frac{\gamma_{12}}{\nu+1}, \tag{A15}$$

$$B_{12}=A_{12}-\gamma_{12}\frac{\nu}{\nu+1}, \tag{A16}$$

while the remaining coefficients are obtained by the adequate changes ($\mu\leftrightarrow\mu^{-1}$, $\nu\leftrightarrow\nu^{-1}$, $\gamma_{11}\leftrightarrow\gamma_{22}$). The consistency condition $\frac{1}{3}\mathrm{tr}\mathsf{P}=nk_BT$ leads to a sixth-degree algebraic equation in α that, in general, must be solved numerically. This can be written as

$$\alpha^6+C_5\alpha^5+C_4\alpha^4+C_3\alpha^3+C_2\alpha^2+C_1\alpha+C_0=0, \tag{A17}$$

where the coefficients C_i are nonlinear functions of a, μ, ν, γ_{11}, and γ_{12}. Their explicit expressions are very large and will not be included here. The largest real root of Eq. (A17) gives the physical solution to the thermostat parameter α.

On the other hand, in the diffusion problem, the pressure tensor depends on space through its explicit dependence on ν and through $\alpha(\nu)$. The derivative $\partial\alpha/\partial\nu$ can be formally obtained from Eq. (A17) by derivating such equation with respect to ν, namely

$$\frac{\partial\alpha}{\partial\nu}=-\frac{\alpha^5\partial_\nu C_5+\alpha^4\partial_\nu C_4+\alpha^3\partial_\nu C_3+\alpha^2\partial_\nu C_2+\alpha\partial_\nu C_1+\partial_\nu C_0}{6\alpha^5+5\alpha^4 C_5+4\alpha^3 C_4+3\alpha^2 C_3+2\alpha C_2+C_1}. \tag{A18}$$

In this way, the elements of the mutual diffusion tensor can be analytically given in terms of α, a, and the parameters of the mixture.

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

[2] J. A. McLennan, *Introduction to Nonequilibrium Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1989).

[3] C. Marín, V. Garzó, and A. Santos, Phys. Rev. E **52**, 3812 (1995).

[4] C. Truesdell and R. Muncaster, *Fundamentals of Maxwell's Kinetic Theory of a Simple Monoatomic Gas* (Academic, New York, 1980), Chap. XIV.

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

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

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

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

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

[10] D. J. Evans, Phys. Rev. A **44**, 3630 (1991).

[11] S. Sarman, D. J. Evans, and A. Baranyai, Phys. Rev. A **46**, 893 (1992).

[12] D. J. Evans and G. P. Morriss, *Nonequilibrium Statistical Mechanics of Liquids* (Academic, London, 1990).

[13] The calculation of the mutual diffusion tensor in the absence of the thermostat force can be easily made from the results presented here. In the same way as in the self-diffusion case (Ref. [7]), the thermostated diffusion tensor does not exactly coincide with the corresponding one in the absence of thermostat, although the shear-rate dependence of both tensors is quite similar for not too large shear rates.

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

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

[16] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1970).

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

[18] A. Santos, V. Garzó, and J. J. Brey, Phys. Rev. A **46**, 8018 (1992).

[19] G. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon, Oxford, 1994).