

Tracer diffusion under shear flow for general repulsive interactions

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Tracer diffusion in a steady shear flow state is analyzed. A kinetic model incorporating a temperature dependence in the collision frequencies is used. This allows for the consideration of a general repulsive intermolecular interaction. A perturbative scheme is applied to get the shear rate dependence of the tracer diffusion tensor in terms of the mass ratio, the force constants ratio, and a parameter characterizing the interaction potential considered. In addition, the heat flux arising from the concentration gradient of the tracer species is also evaluated. The results are illustrated for the two extreme cases of Maxwell molecules and hard spheres. © 1995 American Institute of Physics.

I. INTRODUCTION

The irreversible thermodynamics description of systems in which different transport processes occur, is well understood in the linear regime. Within this regime and in the case of isotropic systems such as simple fluids, the tensorial nature of the transport processes determines the couplings between thermodynamic forces appearing in the dissipative fluxes (Curie's principle).¹ An example of such a situation corresponds to a fluid mixture simultaneously subjected to both weak concentration and velocity gradients in which case the mass flux (vector quantity) is not affected by the action of the velocity gradient (second-rank tensorial quantity). However, beyond the linear regime Curie's principle is not necessarily satisfied. In particular, if the velocity gradient is not small, even if the concentration gradient is weak the mass flux can be modified by the presence of the velocity gradient.

Recently, we have analyzed the problem of diffusion under shear flow using a kinetic theoretical approach. The studies were carried out for a dilute binary mixture in which one of the components is present in tracer concentration. We considered both the Boltzmann equation² and well-known kinetic models³ as points of departure and the entire range of mass ratios between the molecules of the tracer component and those of the excess one was covered. A key motivation was to examine the interplay between mass ratio and shear rate in determining the behavior of the transport phenomena. For the sake of simplicity, we assumed that the molecules interacted through repulsive forces inversely proportional to the fifth power of the distance (Maxwell molecules). Nevertheless, our results cannot be regarded as general, since the model of Maxwell molecules is not a very realistic representation of intermolecular interactions except in some particular conditions. For this reason, in this paper we extend our previous efforts by addressing the problem of tracer diffusion in shear flow for general repulsive intermolecular forces. The underlying motivation of such a study is twofold. On the one hand, we would like to assess to what extent the previous results derived for Maxwell molecules are indicative of what

happens in more realistic models. On the other hand, it is also of interest to evaluate the effect of the interaction potential on the transport properties in a situation where a direct comparison with computer simulations is more likely to occur.

The program outlined above cannot, unfortunately, be carried out analytically using the Boltzmann equation. Therefore, either one restores to numerical solutions or follows a route that has been proved to be very fruitful in other instances, namely to use a kinetic model. Here, we adopt the second approach by considering a generalization of the familiar Gross-Krook (GK) kinetic model⁴ for a binary mixture where the effective collision frequencies depend on the temperature of each species.

The plan of the paper is as follows. In Sec. II, we introduce the kinetic model and state the transport problem to be analyzed. Due to our interest in making connection with computer simulations where a steady state is achieved, we also incorporate thermostat forces acting on each species. Further, a brief summary of relevant results concerning the uniform shear flow problem is included. Section III contains the main results of the paper. Starting from the kinetic equation for the velocity distribution function of the tracer component, a perturbative scheme is introduced to explicitly get the shear rate dependence of the tracer diffusion tensor. In addition, we also compute the heat flux arising from the presence of a concentration gradient. Finally, in Sec. IV we close the paper with some concluding remarks.

II. DESCRIPTION OF THE PROBLEM

We consider a dilute binary gas mixture. If $f_r(\mathbf{r}, \mathbf{v}; t)$ denotes the one-particle velocity distribution function of species r ($r=1,2$), in the presence of external forces \mathbf{F}_r , the following system of two coupled Boltzmann equations is satisfied:

$$\frac{\partial}{\partial t} f_1 + \mathbf{v} \cdot \nabla f_1 + \frac{\partial}{\partial \mathbf{v}} \cdot \left(\frac{\mathbf{F}_1}{m_1} f_1 \right) = J_{11}[f_1, f_1] + J_{12}[f_1, f_2], \quad (1)$$

$$\frac{\partial}{\partial t} f_2 + \mathbf{v} \cdot \nabla f_2 + \frac{\partial}{\partial \mathbf{v}} \cdot \left(\frac{\mathbf{F}_2}{m_2} f_2 \right) = J_{22}[f_2, f_2] + J_{21}[f_2, f_1], \quad (2)$$

where m_r is the molecular mass of particles of species r and $J_{rs}[f_r, f_s]$ are the nonlinear Boltzmann collision operators. The terms appearing on the right-hand sides of Eqs. (1)–(2) represent the self- and cross-collisions, respectively. They conserve the number of particles of each species, the total momentum, and the total kinetic energy. The local number density and mean velocity of species r are defined as

$$n_r = \int d\mathbf{v} f_r, \quad (3)$$

$$n_r \mathbf{u}_r = \int d\mathbf{v} \mathbf{v} f_r. \quad (4)$$

We also define a “local temperature” T_r for each species through

$$\frac{3}{2} n_r k_B T_r = \frac{m_r}{2} \int d\mathbf{v} (\mathbf{v} - \mathbf{u}_r)^2 f_r, \quad (5)$$

with k_B the Boltzmann constant. The solution to Eqs. (1)–(2) is in general a very difficult task due to the complex structure of the collision operators. This is specially so for a general interaction law between the particles. Therefore, many attempts have been made to construct kinetic models that, while being mathematically simpler, preserve the main physical features of the Boltzmann equation. Perhaps the most successful is the one proposed by Gross and Krook (GK model)⁴ in which case the collision operators J_{rs} are replaced by simple relaxation terms of the form

$$- \nu_{rs} (f_r - f_{rs}), \quad (6)$$

where ν_{rs} is an effective collision frequency verifying the general property $n_r \nu_{rs} = n_s \nu_{sr}$ and f_{rs} is a reference distribution function given by

$$f_{rs} = n_r \left(\frac{m_r}{2\pi k_B T_{rs}} \right)^{3/2} \exp \left(- \frac{m_r}{2k_B T_{rs}} (\mathbf{v} - \mathbf{u}_{rs})^2 \right). \quad (7)$$

The parameters \mathbf{u}_{rs} and T_{rs} are such that the total momentum and energy of the mixture are conserved. In addition, since the above requirements are not sufficient to explicitly determine them, one further imposes that the first five collisional moments as computed with Eq. (6) be the same as those computed with the exact J_{rs} . However, this can only be exactly achieved in the case of Maxwell molecules which clearly restricts the usefulness of the GK model. In the case of non-Maxwell molecules, one may introduce approximate forms for the above collisional moments and hence derive the corresponding expressions for \mathbf{u}_{rs} and T_{rs} . For instance, for molecules interacting via a repulsive force law $\mathcal{F}_{rs} = \kappa_{rs}/r^\gamma$ ($\gamma=5, \dots, \infty$) and under adequate approximations it can be proved that \mathbf{u}_{rs} and T_{rs} have the same expressions as those obtained in the conventional GK model for Maxwell molecules ($\gamma=5$),⁵ i.e.,

$$\mathbf{u}_{rs} = \frac{m_r \mathbf{u}_r + m_s \mathbf{u}_s}{m_r + m_s}, \quad (8)$$

$$T_{rs} = T_r + 2 \frac{m_r m_s}{(m_r + m_s)^2} \left((T_s - T_r) + \frac{m_s}{6k_B} (\mathbf{u}_r - \mathbf{u}_s)^2 \right), \quad (9)$$

but now the effective collision frequency ν_{rs} can be identified as

$$\nu_{rs} = A(\beta) n_s \left(\kappa_{rs} \frac{m_r + m_s}{m_r m_s} \right)^{(1-\beta)/2} \left(\frac{2k_B T_r}{m_r} + \frac{2k_B T_s}{m_s} \right)^{\beta/2} \quad (10)$$

Here, $\beta = (\gamma - 5)/(\gamma - 1)$ and $A(\beta)$ is a constant for a given interparticle potential. The kinetic model defined by Eqs. (6)–(10) can be seen as an extension of the usual GK model for inverse power laws. It incorporates a temperature dependence of the collision frequency. Obviously, for $\gamma=5$, ν_{rs} becomes independent of the temperature and one recovers the usual GK model for the Maxwell interaction. Here, we will consider the general form of ν_{rs} given by Eq. (10) in order to offer a theory with wider applicability than just for Maxwell molecules.

We describe now the problem we are interested in. We consider a dilute binary mixture in which the masses of both species are arbitrary. Our aim is to analyze a diffusion problem in a far from equilibrium steady state. Nevertheless, due to the complexity of the general problem we choose a particular case that shares the simplicity of the description given for the single gas and yet introduces the ingredient of the mass ratio in the dynamics of the problem. This case corresponds to the so-called tracer limit in which one of the components, say 1, is present in tracer concentration, i.e., $n_1/n_2 \ll 1$. This choice is motivated by the recent results derived in this limit for Maxwell molecules taking independently the Boltzmann equation² as well as kinetic models.³ In the tracer limit, it is expected that the excess component 2 is not appreciably disturbed by the collisions with particles of species 1 so that the velocity distribution f_2 verifies a closed equation. Moreover, in this case such equation turns out to be the well-known BGK equation for a single gas⁶ as follows from Eq. (2). Further, the molar fraction of the tracer species 1 is so small that one may neglect their mutual interactions. On the other hand, our description applies in principle for arbitrary values of the mass and intermolecular force constants ratios.

Under the above conditions, we assume that the excess component 2 is in a steady shear flow state. From a macroscopic point of view, this state is characterized by a constant density n_2 and temperature T_2 , and a linear profile of the x component of the flow velocity along the y direction, i.e.,

$$u_{2,i} = a_{ij} r_j \quad (11)$$

with $a_{ij} = a \delta_{ix} \delta_{jy}$, a being the constant shear rate. This state is not stationary since the temperature increases in time due to viscous heating. For practical purposes, it would be desirable to compute the transport properties in a steady state. Consequently, an external force must be included to remove this heating effect and so achieve a steady state. The simplest choice, which may be derived from Gauss’ Principle of Least Constraint,⁷ is a nonconservative force proportional to the peculiar velocity $V_i = v_i - a_{ij} r_j$

$$\mathbf{F}_2 = -m_2 \alpha \mathbf{V}, \quad (12)$$

where α plays the role of a thermostat parameter to be determined as a function of the shear rate from the condition that the temperature T_2 remains constant. This kind of force is usually employed in nonequilibrium molecular dynamics simulations.⁸ Furthermore, the thermostating mechanism must be completely specified in far from equilibrium states since it does not play a neutral role in the transport properties of the system.⁹

The uniform shear flow state is one of the few inhomogeneous states for which an exact description can be given far from equilibrium, both using the full Boltzmann equation (Maxwell molecules) and kinetic models. This state becomes spatially homogeneous when the velocities of particles are referred to a Lagrangian frame moving with the flow velocity $\mathbf{u}(\mathbf{r})$. In this new frame, the distribution function has the form $f_2(\mathbf{r}, \mathbf{v}) \equiv f_2(\mathbf{V})$. For this reason, the uniform shear flow has been extensively studied theoretically¹⁰ and also by means of computer simulations.⁷

According to Eq. (10) the collision frequency ν_{22} is a constant in the steady shear flow state. This simplicity allows us to explicitly obtain the reduced velocity moments M_{k_1, k_2, k_3} of the velocity distribution f_2 . They are defined by

$$M_{k_1, k_2, k_3} = \frac{1}{n_2} \left(\frac{2k_B T_2}{m_2} \right)^{-(1/2)(k_1 + k_2 + k_3)} \times \int d\mathbf{V} V_x^{k_1} V_y^{k_2} V_z^{k_3} f_2. \quad (13)$$

The only nonvanishing moments correspond to $k_1 + k_2$ and k_3 even, in which case one gets¹¹

$$M_{k_1, k_2, k_3} = \sum_{\substack{q=0 \\ q+k_1=\text{even}}}^{k_1} (-a^*)^q \frac{k_1!}{(k_1 - q)!} \times [1 + \alpha^*(k_1 + k_2 + k_3)]^{-(q+1)} A_{k_1 - q, k_2 + q, k_3}, \quad (14)$$

where $a^* = a/\nu_{22}$, $\alpha^* = \alpha/\nu_{22}$, and

$$A_{k_1, k_2, k_3} = \pi^{-3/2} \Gamma\left(\frac{k_1 + 1}{2}\right) \Gamma\left(\frac{k_2 + 1}{2}\right) \Gamma\left(\frac{k_3 + 1}{2}\right). \quad (15)$$

The thermostat parameter α^* can be determined from the consistency condition $M_{200} + M_{020} + M_{002} = 3/2$. This relation yields a cubic equation for α^* whose real solution is

$$\alpha^* = \frac{2}{3} \sinh^2\left(\frac{1}{6} \cosh^{-1}(1 + 9a^*)\right). \quad (16)$$

In addition, and in contrast to what happens in the Boltzmann description, the use of the BGK kinetic model allows one to explicitly obtain the velocity distribution function f_2 . For that purpose, it is convenient to take into account the exact equivalence between the uniform shear flow solutions with and without a thermostat.⁹ Thus, in terms of the reduced velocity $\xi = (2k_B T_2/m_2)^{-1/2} \mathbf{V}$, the reduced velocity distribution function $g_2 = (1/n_2)(2k_B T_2/m_2)^{3/2} f_2$ happens to be identical

to the one obtained in the uniform shear flow problem in the absence of a thermostat force in the particular case of Maxwell molecules.⁹ Its expression is¹¹

$$g_2(\xi; a^*) = \pi^{-3/2} \int_0^\infty ds \exp[-(1 - 3\alpha^*)s] \times \exp[-e^{2\alpha^* s} \xi \cdot \Omega_s \cdot \xi], \quad (17)$$

where Ω_s is the matrix of elements

$$\Omega_{ij} = \delta_{ij} + a^{*2} s^2 \delta_{iy} \delta_{jy} + a^* s (\delta_{ix} \delta_{jy} + \delta_{iy} \delta_{jx}). \quad (18)$$

Since the distribution function f_2 is known, our goal now is to compute the main transport properties of the tracer component when diffusion takes place. This will be done in the next section.

III. TRACER DIFFUSION UNDER SHEAR FLOW

As stated above, in the tracer limit the state of particles of species 1 is mainly governed by the collisions with particles of species 2, so that the self-collisions between particles 1 can be neglected. Under these conditions, the steady kinetic equation governing the evolution of the velocity distribution function f_1 becomes

$$-a_{ij} V_j \frac{\partial}{\partial V_i} f_1 + (V_i + a_{ij} r_j) \frac{\partial}{\partial r_i} f_1 + \frac{\partial}{\partial V_i} \left(\frac{F_{1,i}}{m_1} f_1 \right) = -\nu_{12} (f_1 - f_{12}). \quad (19)$$

Here, \mathbf{F}_1 is the adequate thermostat force to keep the temperature T_1 of the tracer species constant. Once again, according to the Gauss' Principle of Least Constraint, this force has an expression similar to that of Eq. (12), namely

$$\mathbf{F}_1 = -m_1 \alpha \mathbf{V}, \quad (20)$$

where α is the thermostat parameter defined by Eq. (16). This form has also been used for the self-diffusion problem.¹²

We are interested in studying the effect of the shear flow on the diffusion of tracer particles in terms of the shear rate, the mass, and intermolecular force constants ratios. Of course, for zero shear rate the usual Fick's law, implying a linear relationship between the flux of tracer particles and the concentration gradient, is obeyed. This law defines the diffusion coefficient. For finite shear rate, one expects that a generalized Fick's law holds but now a diffusion tensor rather than a scalar should arise. Our aim here is to generalize previous expressions^{2,3} derived for this tensor to the case of a general repulsive interaction law in order to analyze the influence of the intermolecular potential on this transport problem.

To this end we must first solve Eq. (19). Following a similar approach as in our previous work, we shall use a perturbative expansion around a nonequilibrium state with arbitrary shear rate. In this scheme, the uniformity parameter of the expansion will be the gradient of concentration of the tracer particles. We therefore look for solutions of the form

$$f_1 = f_1^{(0)} + f_1^{(1)} + \dots, \quad (21)$$

where the superindex refers to the order in the expansion parameter considered. Note that the successive approximations to f_1 are nonlinear functions of the shear rate. Since we are interested in deriving an explicit expression for the tracer diffusion tensor, our calculations will go up to first order in the concentration gradient ∇n_1 . To get the main transport properties of the tracer particles it is convenient to define the reduced velocity moments $N_{k_1, k_2, k_3}^{(p)}$ corresponding to the approximation $f_1^{(p)}$ as

$$N_{k_1, k_2, k_3}^{(p)} = \frac{1}{n_1} \left(\frac{2k_B T_2}{m_1} \right)^{-(1/2)(k_1 + k_2 + k_3)} \times \int d\mathbf{V} V_x^{k_1} V_y^{k_2} V_z^{k_3} f_1^{(p)}. \quad (22)$$

Now we are ready to examine the first two approximations.

A. Zeroth-order approximation

This approximation concerns with a situation where no diffusion of the tracer particles takes place. In this case, $f_1^{(0)}$ verifies the kinetic equation

$$-a_{ij} V_j \frac{\partial}{\partial V_i} f_1^{(0)} - \alpha \frac{\partial}{\partial V_i} (V_i f_1^{(0)}) + \nu_{12} f_1^{(0)} = \nu_{12} f_{12}^{(0)}, \quad (23)$$

where

$$f_{12}^{(0)} = n_1 \left(\frac{m_1}{2\pi k_B T_{12}} \right)^{3/2} \exp\left(-\frac{m_1}{2k_B T_{12}} V^2 \right). \quad (24)$$

Taking velocity moments in Eq. (23) and after some manipulations, one gets

$$a_0 k_1 N_{k_1-1, k_2+1, k_3}^{(0)} + [1 + \alpha_0(k_1 + k_2 + k_3)] N_{k_1, k_2, k_3}^{(0)} = R_{k_1, k_2, k_3}^{(0)}, \quad (25)$$

where

$$R_{k_1, k_2, k_3}^{(0)} = [(1 - 2M)\chi + 2M]^{1/2(k_1 + k_2 + k_3)} A_{k_1, k_2, k_3} \quad (26)$$

for (k_1, k_2, k_3) even, being zero otherwise. Furthermore, we have introduced the mass ratio $\mu = m_2/m_1$, the temperature ratio $\chi = T_1/T_2$, and the dimensionless quantities $M = \mu/(1 + \mu)^2$, $a_0 = (\nu_{22}/\nu_{12})a^*$, and $\alpha_0 = (\nu_{22}/\nu_{12})\alpha^*$. In particular, the introduction of a temperature ratio is related to the fact that the system is in a nonequilibrium steady state so that the mean kinetic energy per particle may turn out to be different in each species.

The solution to Eq. (25) can be cast into the form (see the Appendix)

$$N_{k_1, k_2, k_3}^{(0)} = \sum_{q=0}^{k_1} (-a_0)^q \frac{k_1!}{(k_1 - q)!} \times [1 + \alpha_0(k_1 + k_2 + k_3)]^{-(q+1)} R_{k_1 - q, k_2 + q, k_3}^{(0)}. \quad (27)$$

Notice that in Eqs. (25) and (27) we assume that $R^{(0)}$ is identically zero when any of its indices is negative. On the other hand, the expression (27) depends on the interaction model considered through the ratio ν_{22}/ν_{12} . In the particular case of repulsive potentials of the form $r^{-\gamma}$, this ratio can be written as

$$\frac{\nu_{22}}{\nu_{12}} = \omega^{\beta-1} \left(\frac{2}{1 + \mu} \right)^{1/2} \left(\frac{1 + \mu}{1 + \mu\chi} \right)^{\beta/2} \quad (28)$$

with $\omega = (\kappa_{12}/\kappa_{22})^{1/2}$. This parameter can be interpreted as a measure of the size ratio σ_{12}/σ_{22} when one assigns an effective diameter σ_{rs} to the interaction between particles of species r and s . In this sense, it is interesting to point out that the same kinetic equations corresponding to the tracer limit would be obtained for a mixture where the size of species 2 is much bigger than that of species 1 even for comparable number densities of both components.

To close the problem at this stage of approximation, it still remains to determine the function χ . It can be obtained from the requirement $(3/2)\chi = (N_{200}^{(0)} + N_{020}^{(0)} + N_{002}^{(0)})$. This relation yields

$$\chi = \frac{1}{1 + 2\alpha_0} \left(1 + \frac{2}{3} \frac{a_0^2}{(1 + 2\alpha_0)^2} \right) [(1 - 2M)\chi + 2M]. \quad (29)$$

The solution of this equation gives χ as a function of a^* , μ , ω , and β . Nevertheless, as a_0 and α_0 are nonlinear functions of χ , Eq. (29) must be solved in general numerically. On the other hand, according to the results derived in Ref. 3 and taking into account the equivalence between the formulations with and without a thermostat in a homogeneous state, there may be combinations of the shear rate and the mass ratio for which the temperature of the tracer species does not reach a stationary value (cf. Fig. 2 in Ref. 3). Such combinations lead to unphysical solutions to Eq. (29) that obviously will not be considered here.

Despite the generally complex nature of Eq. (29) there are some limiting cases for which the behavior of χ can be ascertained analytically. For instance, for small shear rates

$$\chi \approx 1 + \frac{1}{3M} \left(\frac{2}{1 + \mu} \omega^{(\beta-1)/2} - 1 \right) a^{*2}, \quad (30)$$

whereas if one takes $\omega = 1$, the behavior of χ in the case of similar masses ($\mu \sim 1$) is governed by

$$\chi \approx 1 - 2a^{*2} \frac{(10\alpha^* + 3)(\mu - 1)}{2a^{*2}[2\beta(5\alpha^* + 1) + 4(2\alpha^* + 1)] + 3(2\alpha^* + 1)^2[2\beta\alpha^* + 8(2\alpha^{*2} + 3\alpha^* + 1)]} \quad (31)$$

Also, there is a particular interaction model for which (29) reduces to a simple linear algebraic equation. It corresponds to Maxwell molecules ($\beta=0$), in which case a_0 and α_0 are independent of χ . The solution is then

$$\chi^M = \frac{2M}{2M - 1 + \Lambda_M}, \quad (32)$$

where

$$\Lambda_M = \frac{1 + 2\alpha_{0M}}{1 + \frac{2}{3}[a_{0M}^2/(1 + 2\alpha_{0M})^2]} \quad (33)$$

and α_{0M} and a_{0M} follow from Eq. (28) with $\beta=0$. Inserting Eq. (33) into Eq. (27), one gets explicitly the dependence of the velocity moments on the shear rate, the mass ratio, and the force constants ratio. We note that these moments are identical to the ones obtained in the absence of thermostat forces.³

In order to gain insight into the effect of the intermolecular potential on the form of χ , in Fig. 1, we plot this quantity as a function of a^* for the two extreme cases of Maxwell molecules ($\beta=0$) and hard spheres ($\beta=1$). We have included two values of μ and for simplicity we have set $\omega=1$. As clearly seen in this figure, the general shear rate dependence of the temperature ratio is not greatly affected by the power of the repulsive law. Also, for both potentials there are combinations of μ and a^* for which $\chi=1$. For small shear rates, χ is insensitive to the interaction potential considered, while specially for large μ the differences become more noticeable as a^* increases. In addition, for a fixed value of the shear rate beyond the linear regime, the numerical value of χ decreases with increasing β if $\mu=0.1$, whereas the opposite happens for $\mu=10$.

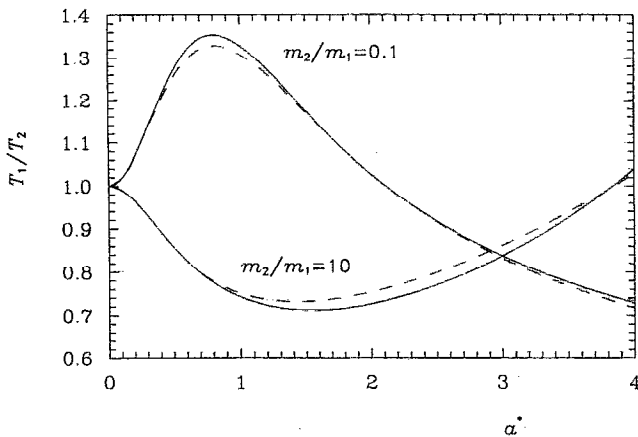


FIG. 1. Shear rate dependence of the ratio T_1/T_2 for $\omega=1$ and two values of the mass ratio m_2/m_1 . The solid line refers to Maxwell molecules and the dashed line refers to hard spheres.

Once χ has been determined, in order to close our analysis of the zeroth-order approximation, it remains to look into the velocity distribution function $f_1^{(0)}$. As a matter of fact, this function represents the reference state around which we construct the perturbation expansion. From a formal point of view, Eq. (23) is the same as the closed BGK equation for f_2 if one makes the changes $f_2 \rightarrow f_1^{(0)}$, $f_{22} \rightarrow f_{12}^{(0)}$, and $v_{22} \rightarrow v_{12}$. Therefore, the reduced distribution function $g_1 = (1/n_1)(2k_B T_2/m_1)^{3/2} f_1^{(0)}$ can be written at once as

$$g_1(\xi) = \pi^{-3/2} \int_0^\infty ds \exp[-(1-3\alpha_0)s] [(1-2M)\chi + 2M]^{-3/2} \times \exp\left(-\frac{e^{2\alpha_0 s}}{(1-2M)\chi + 2M}\right) \times (\xi^2 + 2\xi_x \xi_y a_0 s + \xi_y^2 a_0^2 s^2), \quad (34)$$

where $\xi = (m_1/2k_B T_2)^{1/2} \mathbf{V}$. Equation (34) gives the distribution of the tracer species when the concentration gradient does not yet play a role and the only nonuniformity parameter is the velocity gradient. For the sake of illustration, we have considered it convenient to introduce the reduced distribution $\varphi(\xi_y)$ in the form

$$\varphi(\xi_y) = \pi^{1/2} \exp(\xi_y^2) \int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_z g_1(\xi). \quad (35)$$

The behavior of $\varphi(\xi_y)$ with ξ_y is plotted in Figs. 2 and 3 for $a^*=1$, $\omega=1$, and for two values of μ . We consider again the Maxwell molecules and hard sphere cases. A distortion from local equilibrium is clearly observed in both interaction models. For $\mu=0.1$, the numerical value of φ for Maxwell molecules is smaller than the one corresponding to hard spheres in the region of small velocities. This tendency becomes op-

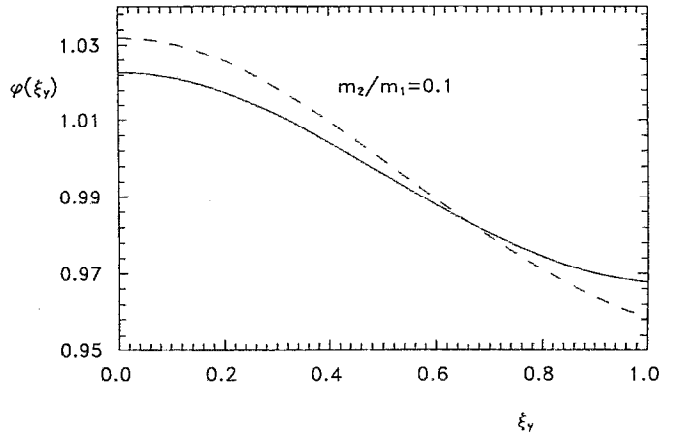


FIG. 2. Reduced velocity distribution function $\varphi(\xi_y)$ for $a^*=1$, $\omega=1$, and $m_2/m_1=0.1$. The solid line refers to Maxwell molecules and the dashed line refers to hard spheres.

posite as ξ_y increases. In the case of $\mu=10$, the opposite effect occurs as the number of particles with small velocities decreases as β decreases. Anyway, for this value of the shear rate, the influence of the repulsive interaction on the velocity distribution is more noticeable in the case of small mass ratios. This concludes our discussion of the zeroth-order stage where it is clear that no diffusion is considered.

B. First-order approximation

We assume now that we perturb the above state (zeroth-order approximation) by introducing a weak concentration gradient ∇n_1 . At this level of description we are mainly interested in obtaining the shear rate dependence of the diffusion tensor of the tracer species for a general repulsive power law. For that, we collect all the terms of first order in ∇n_1 in Eq. (19) to arrive at the following equation for $f_1^{(1)}$:

$$(V_i + a_{ij}r_j) \frac{\partial}{\partial r_i} f_1^{(0)} - \frac{\partial}{\partial V_i} (a_{ij}V_j + \alpha V_i) f_1^{(1)} + \nu_{12} f_1^{(1)} = \nu_{12} f_{12}^{(1)}, \quad (36)$$

where

$$f_{12}^{(1)} = \frac{m_1}{n_1 k_B T_{12}} \frac{1}{1 + \mu} \mathbf{V} \cdot \mathbf{j}_1^{(1)}, \quad (37)$$

and we have introduced the flux of tracer particles

$$\mathbf{j}_1^{(1)} = \int d\mathbf{V} \mathbf{V} f_1^{(1)}. \quad (38)$$

The mass conservation equation associated to Eq. (36) implies that $\partial n_1 / \partial x = 0$. It means that the concentration gradient must be orthogonal to the shear flow to maintain the stationarity of the state. In the following we will restrict ourselves to this geometry.

Taking velocity moments in Eq. (36), one gets the following hierarchy for the reduced moments $N_{k_1, k_2, k_3}^{(1)}$:

$$a_0 k_1 N_{k_1-1, k_2+1, k_3}^{(1)} + [1 + \alpha_0(k_1 + k_2 + k_3)] N_{k_1, k_2, k_3}^{(1)} = R_{k_1, k_2, k_3}^{(1)}, \quad (39)$$

where now

$$R_{k_1, k_2, k_3}^{(1)} = \frac{2}{1 + \mu} [(1 - 2M)\chi + 2M]^{-1/2} (R_{k_1+1, k_2, k_3}^{(0)} N_{100}^{(1)} + R_{k_1, k_2+1, k_3}^{(0)} N_{010}^{(1)} + R_{k_1, k_2, k_3+1}^{(0)} N_{001}^{(1)}) - \frac{\nu_{22}}{\nu_{12}} (N_{k_1, k_2+1, k_3}^{(0)} \epsilon_y + N_{k_1, k_2, k_3+1}^{(0)} \epsilon_z), \quad (40)$$

and we have introduced the dimensionless concentration gradient

$$\epsilon_j = \left(\frac{2k_B T_2}{m_1} \right)^{1/2} \frac{1}{\nu_{22}} \frac{\partial}{\partial r_j} \ln n_1. \quad (41)$$

In the same way as Eq. (25), Eq. (39) admits the solution

$$N_{k_1, k_2, k_3}^{(1)} = \sum_{q=0}^{k_1} (-a_0)^q \frac{k_1!}{(k_1 - q)!} \times [1 + \alpha_0(k_1 + k_2 + k_3)]^{-(q+1)} R_{k_1 - q, k_2 + q, k_3}^{(1)}. \quad (42)$$

Equation (42) is the major result of this paper since it provides an explicit expression for the velocity moments of the tracer species in a thermostated system of particles interacting via a general repulsive force and simultaneously subjected to an arbitrary shear rate and a weak concentration gradient. In particular, one may manipulate Eq. (42) to get explicitly the result for $\mathbf{j}_1^{(1)}$. This turns out to yield a generalized Fick's law of the form

$$\mathbf{j}_1^{(1)} = - \frac{k_B T_2}{m_1 \nu_{22}} \mathbf{D} \cdot \nabla n_1, \quad (43)$$

where the reduced tracer diffusion tensor \mathbf{D} is a highly non-linear function of the shear rate, the mass ratio, and the force constants ratio. Since no concentration gradient exists along the x direction, the relevant components in this problem are D_{yy} , D_{xy} , and D_{zz} . Explicitly, they are given by

$$D_{yy} = D_{zz} = \frac{\nu_{22}}{\nu_{12}} [(1 - 2M)\chi + 2M] \times \frac{1}{1 + 2\alpha_0} \frac{1}{\alpha_0 + [\mu/(1 + \mu)]}, \quad (44)$$

$$D_{xy} = - \frac{\alpha_0}{\alpha_0 + [\mu/(1 + \mu)]} D_{yy}. \quad (45)$$

Note that this model yields the equality $D_{yy} = D_{zz}$ also present when one deals with the exact Boltzmann equation for Maxwell molecules.² Whether this is a consequence of the GK model for other intermolecular potentials remains at this stage to be confirmed, specially in view of the results reported in Ref. 13. For $a^* = 0$, $D_{ij} = D_0 \delta_{ij}$, with $D_0 = \sqrt{2} \omega^{(\beta-1)} (\sqrt{(1 + \mu)}/\mu)$ the mutual diffusion coefficient for the tracer species in the linear regime.⁵ For small shear rates, these components behave as

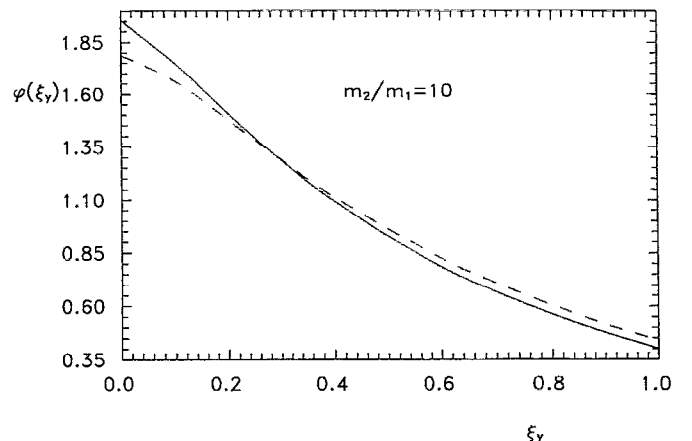


FIG. 3. The same as in Fig. 2 but for $m_2/m_1 = 10$.

$$D_{yy} \approx 1 - \frac{4\sqrt{2}(3\mu+2)\sqrt{1+\mu}\omega^\beta + \beta M \mu [2\omega^{(\beta+1)/2} - \omega(1+\mu)]}{6\omega(1+\mu)^2} a^{*2}, \quad (46)$$

$$D_{xy} \approx -\sqrt{2} \frac{\sqrt{1+\mu}}{\mu} \omega^{\beta-1} a^*. \quad (47)$$

In Figs. 4–6 we have plotted the relevant components of the tensor $\mathcal{D}_{ij}=D_{ij}/D_0$ for $\omega=1$ and two values of the mass ratio. We have considered again the cases of Maxwell molecules and hard-sphere interaction. In general, it is shown that the influence of the interaction law on the diffusion tensor is less sensitive in the case of small mass ratio. For large μ , given a fixed value of the shear rate, the numerical values of the \mathcal{D}_{yy} and $-\mathcal{D}_{xy}$ components increase as the interaction parameter β decreases. The diagonal component \mathcal{D}_{yy} decreases as the shear rate increases so that the mass transport along the y direction is inhibited by the presence of the shear flow. This effect becomes more significant as the mass ratio decreases. The component \mathcal{D}_{xy} is a measure of the anisotropy induced in the mass transport due to the presence of the shear flow. We find that for $\mu \geq 1$, the absolute value of this component increases as the shear rate increases whatever the interaction model considered is. On the other hand, for $\mu < 1$ there is a small region of shear rates ($\mu \leq 0.40$) for which $-\mathcal{D}_{xy}$ also increases with the shear rate while the opposite happens for larger values of a^* .

Recently, Sarman, Evans, and Baranyai¹³ have performed molecular dynamics simulations in a Lennard-Jones fluid to analyze the shear rate dependence of the mutual diffusion tensor. Although the Lennard-Jones fluid is not governed by a purely repulsive power law, to our knowledge this is the only system for which mutual diffusion under shear flow has been analyzed. It is interesting to point out that the conclusions in this paper concerning the shear rate dependence of D_{yy} , and D_{xy} agree, at least at a qualitative level, with our results since they observe that the yy component decreases with the shear rate while $-D_{xy}$ increases as a^*

increases. A comparison of components D_{xx} and D_{yx} is not feasible since in our case the stationarity condition ($\partial n_1/\partial x=0$) precludes the proper identification of these components. On the other hand, as pointed above, in the simulations $D_{zz} \neq D_{yy}$ in contrast with Eq. (44), but D_{zz} also decreases with the shear rate.

Once the flux of tracer particles has been determined, all the velocity moments in the first-order approximation can be explicitly obtained. In particular, an interesting moment corresponds to the cross contribution to the heat flux of the tracer particles due to the gradient of concentration. It is defined by

$$\mathbf{q}_1^{(1)} = \int d\mathbf{v} \frac{m_1}{2} v^2 \mathbf{v} f_1^{(1)}. \quad (48)$$

From Eq. (42) the heat flux can be easily computed. It can be written as

$$\mathbf{q}_1^{(1)} = -\frac{5}{2} \frac{k_B^2 T_2^2}{m_1 v_{22}} \sqrt{2} \frac{\sqrt{1+\mu}}{\mu} \omega^{\beta-1} \Sigma \cdot \nabla n_1, \quad (49)$$

where the dimensionless tensor Σ is a nonlinear function of the parameters of the problem. Its explicit form is not very illuminating and hence will be omitted. In Figs. 7 and 8 we

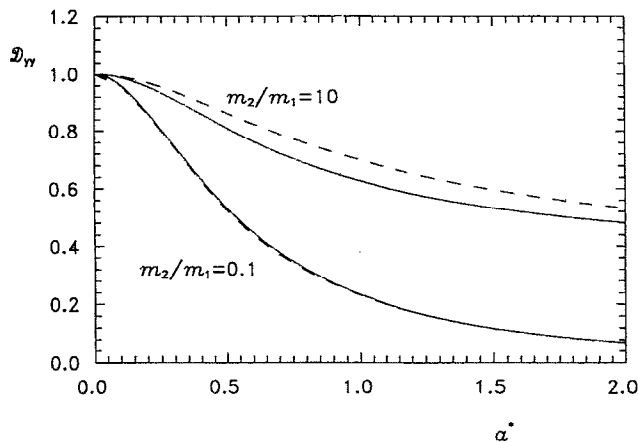


FIG. 4. Shear rate dependence of \mathcal{D}_{yy} for $\omega=1$ and two values of the mass ratio m_2/m_1 . The solid line refers to Maxwell molecules and the dashed line refers to hard spheres.

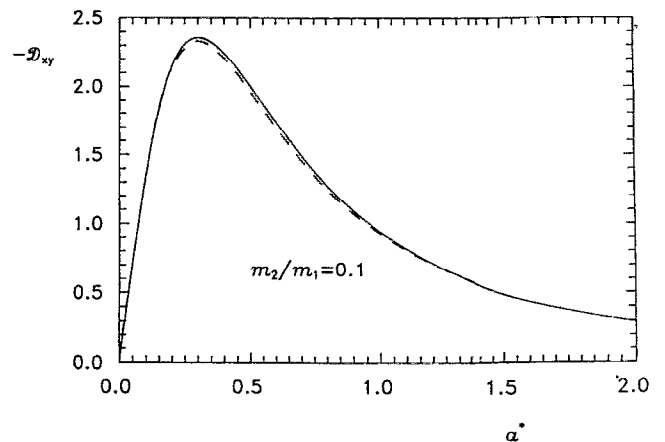


FIG. 5. Shear rate dependence of $-\mathcal{D}_{xy}$ for $\omega=1$ and $m_2/m_1=0.1$. The solid line refers to Maxwell molecules and the dashed line refers to hard spheres.

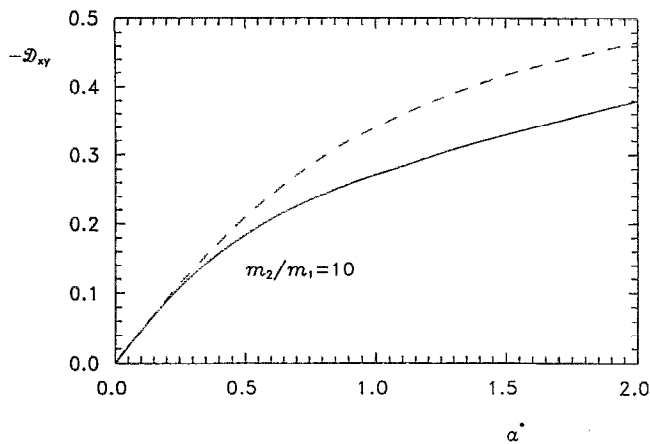


FIG. 6. The same as in Fig. 5 but for $m_2/m_1=10$.

plot Σ_{yy} as a function of a^* for the same cases as in previous figures. Again the numerical value of Σ_{yy} increases with the interaction parameter β . Furthermore, the influence of the potential model on the heat transport happens to be more important than it was for the lower degree moments in the range of values of shear rate studied. For instance, in the case of $\mu=10$, the relative difference between the Maxwell molecules and hard-sphere result is around 16% at $a^*\approx 2$ while in the case of $\mu=0.1$ this difference is around 22% at $a^*\approx 0.4$. According to this pattern, one would expect that the effect of the interaction potential will be more significant as the degree of moments considered increases.

IV. CONCLUDING REMARKS

In this paper we have addressed the problem of diffusion in a binary mixture under shear flow. The physical situation is such that a linear profile of the x component of the hydrodynamic velocity field along the y direction coexists with a weak concentration gradient. The shear rate is arbitrary so that the mass flux can be modified by the presence of the shear flow. The main transport property in this case is the mutual diffusion tensor whose shear rate dependence we

aimed at determining. For the sake of deriving analytical results, we considered a situation where the concentration of one of the components is much smaller than the concentration of the other one (tracer limit). In this limit only a model of Maxwell molecules allows one to obtain explicit results from the Boltzmann equation.² Since we are interested in analyzing the above problem for more realistic intermolecular interactions, we decided to use a kinetic model instead. Specifically, we took a generalization of the kinetic model proposed by Gross and Krook⁴ for repulsive law interactions. In this model all the details of the interaction potential are incorporated into the collision frequencies which may be temperature dependent. In this sense, this description extends our previous work on Maxwell molecules.³ Further, taking as a motivation that computer simulations are mainly performed under steady state conditions, we also introduced drag external forces for each species to remove viscous heating.

Although we have derived results which are valid for general repulsive potentials, to illustrate the main features we concentrated on the two extremes of Maxwell molecules and hard spheres. Concerning the results for such systems, discussed at length in Sec. III, the following conclusions may be drawn. The qualitative behavior of the shear rate dependent tracer diffusion tensor is not greatly affected by the power in the assumed interaction law. It is interesting to note that a similar conclusion applies in the case of the shear viscosity of a simple gas under uniform shear flow.¹⁴ The net consequence of the presence of the shear flow on the mass transport is to inhibit the diffusion of the tracer species. As far as the quantitative effects are concerned, we observe that they are more significant for mass ratios larger than one and the inhibition of diffusion increases as the intermolecular repulsion becomes softer. The numerical differences in the values of Σ_{yy} corresponding to Maxwell molecules and hard spheres suggest that as one goes up in the degree of moments the influence of the potential law becomes greater.

It should be clear that our results may be of relevance in connection with computer simulations. We have already mentioned the scarcity of simulation data for mutual diffusion under shear flow specially for low density. As an alternative to overcome the difficulties associated to molecular

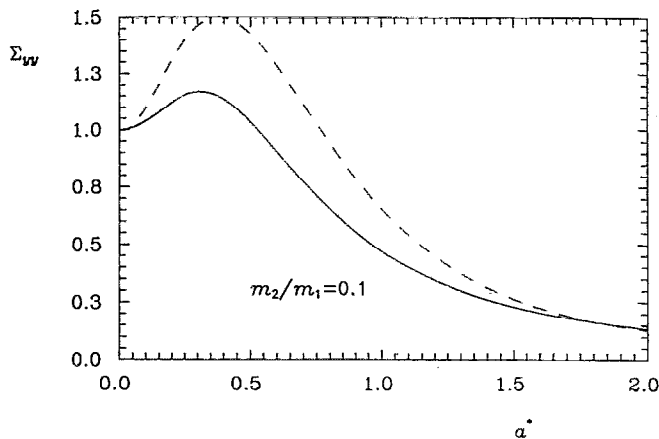


FIG. 7. Shear rate dependence of Σ_{yy} for $\omega=1$ and $m_2/m_1=0.1$. The solid line refers to Maxwell molecules and the dashed line refers to hard spheres.

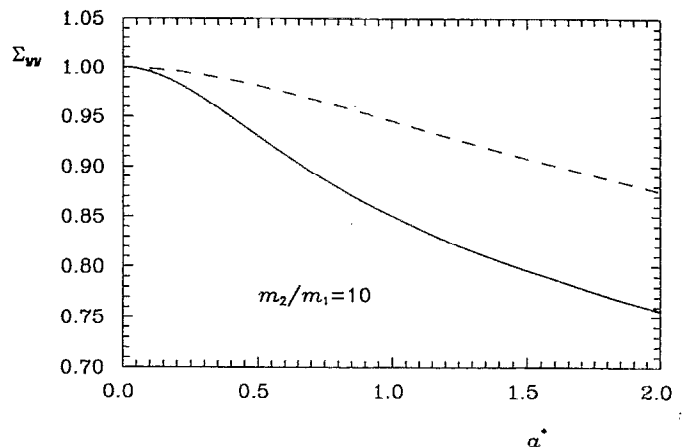


FIG. 8. The same as in Fig. 7 but for $m_2/m_1=10$.

dynamics simulations in this regime, one could perhaps use the direct Monte Carlo simulation method.¹⁵ On the other hand, we are fully aware that the tracer limit is certainly a restriction that one would like to get rid of. In this sense we expect that using the same kinetic model we will be able to analyze the more general situation of diffusion in shear flow when the molar fractions of both components are arbitrary. Work along this line is already in progress.

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APPENDIX: SOLUTION OF THE MOMENT EQUATIONS

Let us consider the equation

$$a_0 k_1 N_{k_1-1, k_2+1, k_3} + [1 + \alpha_0(k_1 + k_2 + k_3)] N_{k_1, k_2, k_3} = R_{k_1, k_2, k_3}, \quad (\text{A1})$$

which is similar to Eqs. (25) and (39) appearing in the text. To solve this equation we introduce the operators L_1 and L_2 acting on functions Ψ depending upon the indices (k_1, k_2, k_3) in the form

$$L_1 \Psi(k_1, k_2, k_3) = \Psi(k_1 - 1, k_2, k_3), \quad (\text{A2})$$

$$L_2 \Psi(k_1, k_2, k_3) = \Psi(k_1, k_2 + 1, k_3). \quad (\text{A3})$$

In this way, Eq. (A1) can be rewritten as

$$[a_0 k_1 L_1 L_2 + \alpha_0(k_1 + k_2 + k_3) + 1] N_{k_1, k_2, k_3} = R_{k_1, k_2, k_3}. \quad (\text{A4})$$

Its formal solution is

$$N_{k_1, k_2, k_3} = [a_0 k_1 L_1 L_2 + \alpha_0(k_1 + k_2 + k_3) + 1]^{-1} \times R_{k_1, k_2, k_3}. \quad (\text{A5})$$

In order to evaluate this formal expression one may use the identity

$$L_1 L_2 [\alpha_0(k_1 + k_2 + k_3) + 1] = \alpha_0(k_1 + k_2 + k_3) + 1, \quad (\text{A6})$$

which leads to the solution

$$N_{k_1, k_2, k_3} = \frac{1}{1 + \alpha_0(k_1 + k_2 + k_3)} \times \left(1 + \frac{a_0 k_1}{1 + \alpha_0(k_1 + k_2 + k_3)} L_1 L_2 \right)^{-1} R_{k_1, k_2, k_3} = \sum_{q=0}^{\infty} (-a_0)^q [1 + \alpha_0(k_1 + k_2 + k_3)]^{-(q+1)} \times (k_1 L_1 L_2)^q R_{k_1, k_2, k_3}. \quad (\text{A7})$$

In this equation it is easy to prove that

$$(k_1 L_1 L_2)^q R_{k_1, k_2, k_3} = \frac{k_1!}{(k_1 - q)!} R_{k_1 - q, k_2 + q, k_3} \quad (\text{A8})$$

if $q \leq k_1$, being zero otherwise. Therefore, one gets

$$N_{k_1, k_2, k_3} = \sum_{q=0}^{k_1} (-a_0)^q \frac{k_1!}{(k_1 - q)!} \times [1 + \alpha_0(k_1 + k_2 + k_3)]^{-(q+1)} R_{k_1 - q, k_2 + q, k_3} \quad (\text{A9})$$

which is the result we have used to arrive at Eqs. (27) and (42).

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