

Kinetic models for diffusion in shear flow

V. Garzó^{ab} and M. López de Haro

Laboratorio de Energía Solar, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apdo. Postal 34, Temixco 62580, Mor., Mexico

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The kinetic models proposed by Garzó *et al.* [Phys. Fluids A **1**, 380 (1989)] and Gross and Krook [Phys. Rev. **102**, 593 (1956)] are used to study diffusion in uniform shear flow. The kinetic equations are solved by means of a generalized Chapman–Enskog expansion for Maxwell molecules. The main peculiarity of the method is that the successive approximations to the velocity distribution functions retain all orders in the shear rate. Two cases are considered, namely the self-diffusion and the tracer diffusion in a system under shear flow. The relevant transport properties and the distribution functions are explicitly obtained. A comparison with previous results derived from the Boltzmann equation and between both models is carried out.

I. INTRODUCTION

The theoretical description of transport processes in dilute binary gas mixtures is well developed for states near equilibrium. For such states, the Boltzmann equations may be solved for a general interaction law by using the standard Chapman–Enskog method,¹ except probably in the case of disparate masses, where a slight modification of the method is required.² The results obtained within the linear regime indicate, in agreement with linear irreversible thermodynamics,³ that a physical problem in which the mixture is simultaneously subjected to velocity and concentration gradients, the diffusive flux that obeys Fick's law is not affected by the presence of the velocity gradient. However, much less is known concerning diffusion in far-from-equilibrium states and the question arises as to whether outside the realm of linear response diffusive motion may be disturbed, for instance, by shearing motion.

Recently, it has been shown by different means that the above question may be answered affirmatively. On the one hand, in the case of mechanically identical Maxwell molecules and in the uniform shear flow state, Marchetti and Dufty⁴ and Garzó *et al.*,⁵ derived from the Boltzmann equation an expression for the nonlinear shear-rate-dependent self-diffusion tensor. Subsequently, Garzó and López de Haro⁶ generalized such an expression for binary mixtures of Maxwell molecules with one component in tracer concentration. Their expression was also shown to reduce to previous results derived with a Green–Kubo formalism⁷ in the Fokker–Planck limit.⁸ On the other hand, Cummings *et al.*⁹ have obtained a strain-rate-dependent diffusion tensor from molecular dynamics simulations in a Lennard–Jones fluid in shear flow.

In contrast with what occurs in the linear regime, for uniform shear flow it is a very difficult task to find explicit solutions to the Boltzmann equations even if one restricts oneself to the case of the Maxwell interaction law. Therefore,

since the general description of transport processes in the mixture requires knowledge of the velocity distribution functions, a possible way to avoid the mathematical difficulties embodied in the Boltzmann description is to use kinetic models. While keeping the main physical properties of the Boltzmann equations, in addition these models should allow for the explicit derivation of the distribution function. This idea has been widely exploited in the past and the usefulness of such an approach has been demonstrated¹⁰ in the case of a single component with the Bhatnagar–Gross–Krook (BGK) equation.

The aim of this paper is twofold. On the one hand, we will assess the virtues of two kinetic models^{11,12} for dilute gas mixtures of Maxwell molecules to describe self- and tracer diffusion in uniform shear flow. This will be achieved by comparing with the exact results derived previously from the Boltzmann equations. The motivation for considering these two models is that one is thought to be suitable for particles of similar masses while the other seems to be more adequate for disparate masses. On the other hand, in addition, we will find explicitly for both models the velocity distribution functions and compute the contribution of the tracer to the heat flux.

The paper is organized as follows. In Sec. II, we provide a brief account of the description of uniform shear flow at the level of the BGK equation. In Sec. III, we present the two kinetic models to be used in the rest of the paper. Section IV deals with the problem of self-diffusion under uniform shear flow while Sec. V addresses the case of tracer diffusion. Finally, we close the paper in Sec. VI with a discussion of the results and some concluding remarks.

II. UNIFORM SHEAR FLOW

Let us consider a single gas under uniform shear flow (USF). This state is characterized by a linear profile of the x component of the local velocity \mathbf{u} along the y axis, a constant density n , and a uniform temperature T :

$$u_x = a_{ij}r_j, \quad a_{ij} = a\delta_{ix}\delta_{jy}, \quad (1)$$

^{ab} On leave from Departamento de Física, Universidad de Extremadura, 06071–Badajoz, Spain.

$$n = \text{const}, \quad (2)$$

$$\nabla T = 0, \quad (3)$$

where a is the (constant) shear rate. The USF can be maintained in the system, provided that the temperature increases in time (viscous heating) according to the equation

$$\frac{dT}{dt} + \frac{2}{3nk_B} a P_{xy} = 0, \quad (4)$$

where P_{xy} is the xy component of the pressure tensor

$$\mathbf{P} = m \int d\mathbf{v} (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u}) f. \quad (5)$$

Here, m is the molecular mass and f is the velocity distribution function (VDF). The USF is simple enough to allow for a complete description when the BGK equation¹³ is used. It is adequate for this state to introduce the velocity rest frame defined by

$$\mathbf{V} = \mathbf{v} - \mathbf{a}\cdot\mathbf{r}. \quad (6)$$

In this new frame, the BGK equation corresponding to this problem is given by

$$\left(\frac{\partial}{\partial t} - a_{ij} V_j \frac{\partial}{\partial V_i} \right) f = -\nu(f - f_{LE}), \quad (7)$$

where now the USF is described by a homogeneous distribution function. It must be pointed out that this feature is particular to the USF problem and, of course, serves to greatly simplify the analysis. In Eq. (7), f_{LE} is the local equilibrium distribution function defined as

$$f_{LE} = n(m/2\pi k_B T)^{3/2} \exp(-mV^2/2k_B T) \quad (8)$$

and ν is an effective velocity-independent collision frequency. In the particular case of Maxwell molecules, for which ν only depends on the density n , the USF has a clearer meaning as an arbitrary far from equilibrium state. Therefore, in the following, we shall restrict ourselves to the Maxwell interaction. Moreover, of the many solutions that, undoubtedly, an equation as highly nonlinear as Eq. (7) has, we will only be concerned with the so-called normal ones in which there is no dependence on the initial conditions and the time dependence of the VDF is governed by the time dependence of the temperature T . The main transport coefficients in this problem are related with the nonzero components of the pressure tensor. Taking moments in Eq. (7), one obtains in the long time limit (hydrodynamic regime)¹⁴

$$P_{xx} = p(1 + 3\lambda)/(1 + \lambda), \quad (9)$$

$$P_{yy} = P_{zz} = p/(1 + \lambda), \quad (10)$$

$$P_{xy} = P_{yx} = -\frac{3}{2}p(\lambda/a^*), \quad (11)$$

where $p = nk_B T$ is the pressure, $a^* = a/\nu$ is the reduced shear rate, and

$$\lambda(a^*) = \frac{4}{3} \sinh^2 \left[\frac{1}{6} \cosh^{-1}(1 + 9a^{*2}) \right]. \quad (12)$$

These results are identical to those given by the Boltzmann equation.¹⁵ In addition, the BGK equation allows us to explicitly obtain the VDF representing the normal solution. Thus one expects that, after a transient period, the VDF reaches a form independent of the initial conditions. In the long time limit, the solution to Eq. (7) can be written in the form

$$f(\mathbf{V}, t) = (1/n) [2k_B T(t)/m]^{3/2} f^*(\xi), \quad (13)$$

where a natural velocity scale is introduced by the temperature

$$\xi = (2k_B T/m)^{-1/2} \mathbf{V}, \quad (14)$$

and the reduced VDF f^* is constant in time and represents the normal solution to the BGK equation for Maxwell molecules under USF. It is given by

$$f^*(\xi; a^*) = \pi^{-3/2} \int_0^\infty d\tau \exp \left[- \left(1 - \frac{3}{2} \lambda \right) \tau \right] \times \exp(-e^{\lambda\tau} \xi \cdot \Gamma_\tau \cdot \xi), \quad (15)$$

where Γ_τ is the matrix of components

$$\Gamma_{ij} = \delta_{ij} + a^2 \tau^2 \delta_{iy} \delta_{jy} + a\tau (\delta_{ix} \delta_{jy} + \delta_{iy} \delta_{jx}). \quad (16)$$

According to Eq. (15), one may conclude that, in the USF case, the normal state can be seen as equivalent to a steady state. The results derived in this section will be used later when diffusion takes place.

III. KINETIC MODELS

We consider now a binary mixture. In the low-density limit, the time evolution of the system is usually described by the set of two coupled nonlinear Boltzmann equations:¹

$$\begin{aligned} \frac{df_1}{dt} + \mathbf{v} \cdot \nabla f_1 &= K_{11}[f_1, f_1] + K_{12}[f_1, f_2], \\ \frac{df_2}{dt} + \mathbf{v} \cdot \nabla f_2 &= K_{22}[f_2, f_2] + K_{21}[f_2, f_1], \end{aligned} \quad (17)$$

where $f_i(\mathbf{r}, \mathbf{v}, t)$ is the one-particle distribution of species i and $K_{ij}[f_i, f_j]$ ($i, j = 1, 2$) is the nonlinear Boltzmann collision operator. The terms that appear on the right-hand side of Eq. (17) represent the self- and cross-collisions, respectively. They conserve the number of particles of each species, the total momentum, and the total energy. In terms of the distribution functions, the densities of these quantities are defined by

$$n_i = \int d\mathbf{v} f_i \quad (i = 1, 2), \quad (18)$$

$$\rho \mathbf{u} = \sum_{i=1}^2 \int d\mathbf{v} m_i \mathbf{v} f_i = \sum_{i=1}^2 \rho_i \mathbf{u}_i, \quad (19)$$

$$\frac{3}{2} nk_B T + \frac{1}{2} \rho u^2 = \sum_{i=1}^2 \int d\mathbf{v} \frac{m_i}{2} v^2 f_i, \quad (20)$$

where m_i is the mass of a particle of species i . Here, $\rho_i = m_i n_i$ is the mass density of species i , $\rho = \rho_1 + \rho_2$ is the total mass density, and $n = n_1 + n_2$ is the total number density. Further, Eqs. (19) and (20) define the local velocity \mathbf{u} and the local temperature T of the mixture, respectively. From Eq. (20), one may define also a local "temperature" T_i for each species in the form

$$\frac{3}{2} n_i k_B T_i = \int d\mathbf{v} \frac{m_i}{2} (\mathbf{v} - \mathbf{u}_i)^2 f_i \quad (i = 1, 2). \quad (21)$$

It must be noticed that the bilinear character of the Boltzmann collision operator allows that the total distribution

function $f = \sum_i f_i$ obeys itself the familiar Boltzmann equation when a system of mechanically identical particles (e.g., in the case of self-diffusion) is considered.

However, due to the complex structure of Eqs. (17), for a general interaction law between the particles it is a very hard task to solve explicitly for the f_i . This question has motivated the search of several model kinetic equations that preserve the main physical properties of the full Boltzmann equations and whose solution can be obtained. As we said previously, for a single-component gas, the BGK equation has been shown to be very useful. In the same way, for a binary mixture the general idea is to replace the correct collision integrals K_{ij} by a simple relaxation term of the form

$$- \nu_{ij} (f_i - f_{ij}^R), \quad (22)$$

where ν_{ij} is an effective collision frequency of a particle of species i with a particle of species j . It has the general property $n_i \nu_{ij} = n_j \nu_{ji}$. On the other hand, f_{ij}^R is a reference distribution function to be determined by requiring that Eq. (22) keeps the relevant physical properties of the Boltzmann operator. One of the most widely used kinetic equations is the model proposed by Gross and Krook (GK model),¹¹ where f_{ij}^R is defined by

$$f_{ij}^R = n_i (m_i / 2\pi k_B T_{ij})^{3/2} \times \exp[-(m_i / 2k_B T_{ij})(\mathbf{v} - \mathbf{u}_{ij})^2], \quad (23)$$

where \mathbf{u}_{ij} and T_{ij} are given by

$$\mathbf{u}_{ij} = (m_i \mathbf{u}_i + m_j \mathbf{u}_j) / (m_i + m_j), \quad (24)$$

$$T_{ij} = T_i + 2[m_i m_j / (m_i + m_j)^2] [(T_j - T_i) + (m_j / 6k_B)(\mathbf{u}_i - \mathbf{u}_j)^2]. \quad (25)$$

It is worth remarking that the above terms are explicitly obtained when one requires that the collisional transfer of momentum and energy given by Eq. (22) are the same as those of the Boltzmann equation for Maxwell molecules.¹⁶ This suggests that one may identify the effective collision frequency ν_{ij} by

$$\nu_{ij} = A n_j [K_{ij} (m_i + m_j) / m_i m_j]^{1/2}, \quad (26)$$

where A is a pure number and K_{ij} is a proportionality constant in the force law. Here, we will assume for simplicity that K_{ij} is the same for all possible interactions. Models¹⁷ based on Eq. (23) have been usually used to study linear transport properties in the case of disparate-mass binary mixtures. The form (23) satisfies the conservation laws, but it, however, does not reduce to a closed equation (BGK model) for the total distribution function f in the case of mechanically identical particles ($m_1 = m_2$). This deficiency is due basically to the highly nonlinear character of f_{ij}^R in Eq. (23).

In order to avoid the above problem, recently Garzó *et al.* (GSB model)¹² have suggested a model in which a new f_{ij}^R is proposed, namely

$$f_{ij}^R = n_i (m_i / 2\pi k_B T)^{3/2} \times \exp(-m_i V^2 / 2k_B T) (1 + A_{ij} + \mathbf{B}_{ij} \cdot \mathbf{V} + C_{ij} V^2), \quad (27)$$

where $\mathbf{V} = \mathbf{v} - \mathbf{u}$ is the peculiar velocity. The parameters A_{ij} , \mathbf{B}_{ij} , and C_{ij} are determined by requiring the same conditions as those of the GK model. However, now the conservation conditions are sufficient to assure that the GSB model yields to the BGK equation in the mechanically identical particles case. To this end, it is only necessary that the collision frequency ν_{ij} verifies the identity

$$\nu = \sum_{j=1}^2 \nu_{ij}, \quad (28)$$

for $i = 1, 2$. Relation (28), which defines the total collision frequency of the system introduced in Eq. (7), is satisfied in the case of Maxwell molecules. Further, from the Boltzmann collisional transfer of momentum and energy for Maxwell molecules, one obtains

$$A_{ij} = -3(k_B T / m_i) C_{ij}, \quad (29)$$

$$\mathbf{B}_{ij} = (m_i / k_B T) (\mathbf{u}_{ij} - \mathbf{u}), \quad (30)$$

$$C_{ij} = \frac{m_i}{2k_B T} \left(\frac{T_{ij} - T}{T} + \frac{m_i}{3k_B T} (\mathbf{u}_{ij} - \mathbf{u})^2 \right), \quad (31)$$

where \mathbf{u}_{ij} and T_{ij} are defined by Eqs. (24) and (25). The GSB model resembles some kind of linearization around a local equilibrium defined by the hydrodynamic fields of the mixture seen as a whole. Thus the global effect of the collisions on particles of species i is to drive the system toward the local equilibrium state of the mixture. The details of the collisions with species j are considered through the parameters defined in Eqs. (29)–(31). In this way, although the model is not *a priori* restricted to any range of mass ratio, one expects that it is suitable for systems of like particles.

The combination of the GK and GSB models may be useful to study general transport problems when no restriction on the mass ratio must be taken into account. Here, both models will be used as a starting point to compare our results with those previously derived from the Boltzmann equation.

IV. SELF-DIFFUSION IN USF

We assume now that we have a system of mechanically equivalent particles, some of which are tagged. This situation is appropriate for studying a self-diffusion problem. We further consider that our system, as a whole, is in USF, i.e., it is in a state arbitrarily far from equilibrium. This implies that the VDF f corresponding to this system obeys Eq. (7). Let $f_1(\mathbf{r}, \mathbf{v}; t)$ be the VDF of tagged particles. Since, as mentioned in Sec. II, for the particular situation we want to deal with the GK model presents some problems, we will only treat the GSB model here. According to Eqs. (27)–(31), in the rest frame of reference and for identical masses, after some algebra, we find that f_1 satisfies the equation

$$\frac{\partial}{\partial t} f_1 + (V_i + a_{ij} r_j) \frac{\partial}{\partial r_i} f_1 - a_{ij} V_j \frac{\partial}{\partial V_i} f_1 = -\nu (f_1 - \phi), \quad (32)$$

where ν is defined by Eq. (28) and ϕ is a reference function given by

$$\phi = \left[\frac{n_1}{n} + \frac{m}{2p} \mathbf{V} \cdot \mathbf{j}_1 + \frac{1}{2p} \left(\frac{mV^2}{2k_B T} - \frac{3}{2} \right) \times (p_1 - n_1 k_B T) \right] f_{LE}. \quad (33)$$

Here,

$$\mathbf{j}_1 = \int d\mathbf{v} \mathbf{V} f_1 \quad (34)$$

is the flux of tagged particles and

$$p_1 = \frac{1}{3} \int d\mathbf{v} m V^2 f_1 \quad (35)$$

is a partial pressure of tagged particles.

It is worth remarking that the kinetic equation (32) holds for any relative number of tagged particles. On the other hand, the collision term (right-hand side) in Eq. (32) mimics well the Boltzmann operator for the same problem since it only depends on the variables of tagged particles and of the mixture as a whole. Thus, since the function f given by Eq. (13) is known, Eq. (32) becomes a linear equation in f_1 . Our aim here is to determine the self-diffusion coefficient.

In order to solve Eq. (32), we will use a perturbative scheme similar to the Chapman–Enskog method, but taking the USF state given by Eqs. (13) and (15) as the zeroth-order reference state.⁵ In this way, the successive approximations will be highly nonlinear functions of the shear rate. Assuming that the system has reached the hydrodynamic state, we look for solutions of the form

$$f_1 = f_1^{(0)} + \epsilon f_1^{(1)} + \epsilon^2 f_1^{(2)} + \dots, \quad (36)$$

where ϵ is an auxiliary parameter related with the gradient of the concentration of tagged particles. It is worth emphasizing again that the different approximations $f_1^{(k)}$ are of order k in ϵ , but retain all hydrodynamic orders in the shear rate. Similarly, the time derivatives on the left-hand side of Eq. (32) can be computed from the hydrodynamic balance equations. They are given by

$$\frac{\partial}{\partial t} n_1 + a_{ij} r_j \frac{\partial}{\partial r_i} n_1 = 0, \quad (37a)$$

$$\frac{\partial}{\partial t} T - \lambda \nu T = 0 \quad (37b)$$

in the zeroth-order approximation, and

$$\frac{\partial}{\partial t} n_1 = -\nabla \cdot \mathbf{j}_1^{(k-1)}, \quad k \geq 1, \quad (38a)$$

$$\frac{\partial}{\partial t} T = 0, \quad k \geq 1 \quad (38b)$$

in the k th approximation. Moreover, the function ϕ is expanded in a similar way as

$$\phi^{(0)} = \left[\frac{n_1}{n} + \frac{m}{2p} \mathbf{V} \cdot \mathbf{j}_1^{(0)} + \frac{1}{2p} \left(\frac{mV^2}{2k_B T} - \frac{3}{2} \right) (p_1^{(0)} - n_1 k_B T) \right] f_{LE}, \quad (39a)$$

$$\phi^{(k)} = \left[\frac{m}{2p} \mathbf{V} \cdot \mathbf{j}_1^{(k)} + \frac{1}{2p} \left(\frac{mV^2}{2k_B T} - \frac{3}{2} \right) p_1^{(k)} \right] f_{LE}, \quad k \geq 1. \quad (39b)$$

Here, $\mathbf{j}_1^{(k)}$ and $p_1^{(k)}$ are the k th approximations to \mathbf{j}_1 and p_1 computed from $f_1^{(k)}$. Notice that, upon writing Eqs. (37) and (38), we have again considered that the system seen as a whole is in USF. Following the well-known procedure of the Chapman–Enskog method, one obtains in the lowest order the solution⁵

$$f_1^{(0)}(\mathbf{r}, \mathbf{V}; t) = [n_1(\mathbf{r}, t)/n] f(\mathbf{V}, t), \quad (40)$$

where f is given by Eq. (13). From Eq. (40), it follows that $\mathbf{j}_1^{(0)} = \mathbf{0}$, and $p_1^{(0)} = n_1 k_B T$. To first order, one obtains the equation

$$\begin{aligned} \frac{\partial}{\partial t} f_1^{(1)} + a_{ij} r_j \frac{\partial}{\partial r_i} f_1^{(0)} - a_{ij} V_j \frac{\partial}{\partial V_i} f_1^{(1)} + \mathbf{v} f_1^{(1)} \\ = \mathbf{v} f_{LE} \left[\frac{m}{2p} \mathbf{V} \cdot \mathbf{j}_1^{(1)} + \frac{1}{2p} \left(\frac{mV^2}{2k_B T} - \frac{3}{2} \right) p_1^{(1)} \right] \\ - f \mathbf{V} \cdot \nabla \left(\frac{n_1}{n} \right). \end{aligned} \quad (41)$$

Taking moments in Eq. (41), one obtains $p_1^{(1)} = 0$ and the flux of tagged particles obeys the differential equation

$$\frac{P_{ik}}{m} \frac{\partial}{\partial r_k} \frac{n_1}{n} + \lambda \nu T \frac{\partial}{\partial T} j_{ii}^{(1)} + a_{ik} j_{ik}^{(1)} = -\frac{\nu}{2} j_{ii}^{(1)}, \quad (42)$$

where we have used Eqs. (37a) and (37b) and P_{ik} is given by Eqs. (9)–(11). The hydrodynamic solution (long time limit) to Eq. (42) can be written in the form

$$j_{ii}^{(1)} = -D_{ik} \frac{\partial}{\partial r_k} n_1, \quad (43)$$

where a self-diffusion tensor, rather than a scalar, appears. It is given by

$$D_{ik} = \frac{2k_B T}{m\nu} \frac{1}{1+2\lambda} \left(\delta_{ik} - \frac{2a_{ik}^*}{1+2\lambda} \right) P_{kj}^*, \quad (44)$$

where $P_{kj}^* = P_{kj}/p$. Expression (44) is a generalization of the usual Fick's law (valid in the absence of shear), since it has been derived keeping the first order in the gradient of the concentration of tagged particles while retaining all the orders in the shear rate. The effect of the shear flow is to induce anisotropy in the self-diffusion of particles. For $a = 0$, $D_{ij} = D\delta_{ij}$, with $D = 2k_B T/m\nu$, i.e., we recover the usual self-diffusion coefficient given by the GSB equation.¹²

In an attempt to carry out a comparison with the Boltzmann equation results, in Fig. 1 we have plotted $D_{kk}^*/3$ vs a^* . Here, to parallel Ref. 5, $D_{ij}^* = D_{ij}/D$. Figure 1 shows a qualitative agreement between both results, in particular it is worth noticing that the value of this coefficient decreases as the shear rate increases. This assertion contrasts with recent results obtained from molecular dynamics simulations in a Lennard-Jones fluid, where the opposite behavior is observed.⁹ The latter may be due to the fact that the Lennard-Jones interaction includes an attractive part or that the simulations were carried out far from the dilute gas limit, where the applicability of the Boltzmann and GSB equations is not valid, or to the combination of both aspects.

It still remains to obtain the first Chapman–Enskog approximation $f_1^{(1)}$. Here, we are interested in the long time limit solution to Eq. (41). For simplicity, we take the gradient of concentration orthogonal to the shear rate

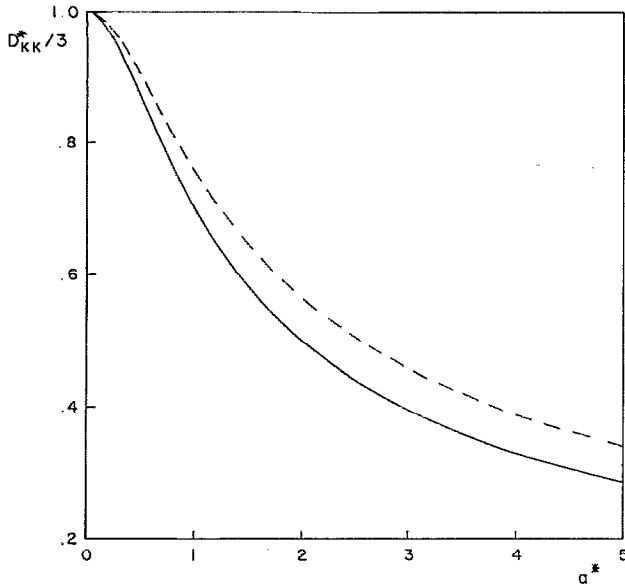


FIG. 1. Shear rate dependence of the trace $D_{kk}^*/3$ of the dimensionless self-diffusion tensor. The solid line corresponds to the GSB model and the dashed line refers to the Boltzmann equation.

($\partial n_1/\partial x = 0$), and so, according to the balance equation (37a), n_1 is a time-independent variable. In the following, we will restrict ourselves to this geometry. Neglecting the term involving the initial conditions, the solution is

$$f_1^{(1)}(\mathbf{r}, \mathbf{V}; t) = - \int_0^t d\tau \exp[-\nu(t-\tau)] \times \exp\left((t-\tau)a_{ij}V_j \frac{\partial}{\partial V_i}\right) \times [f_{LE}(\mathbf{V}; \tau)V_i D_{ij}^* + f(\mathbf{V}, \tau)V_j] \frac{\partial}{\partial r_j} \frac{n_1}{n}. \quad (45)$$

Equation (45) provides the general solution and not just the normal solution. To obtain the latter, we must take the limit $t \rightarrow \infty$ accounting for the temporal behavior of the temperature. For that purpose, it is convenient to introduce the dimensionless velocity ξ defined by Eq. (14) and the reduced function $h^*(\mathbf{r}, \mathbf{V}; t)$ given by

$$h^*(\mathbf{r}, \mathbf{V}; t) = (1/n_1) [2k_B T(t)/m]^{3/2} f_1^{(1)}(\mathbf{r}, \mathbf{V}; t). \quad (46)$$

Inserting now the expression (45) in Eq. (46), and after some algebra, one obtains

$$\lim_{t \rightarrow \infty} h^*(\mathbf{r}, \mathbf{V}; t) = \varphi(\xi; a^*) \cdot \epsilon^*, \quad (47)$$

where we have introduced the dimensionless gradient

$$\epsilon^* = \left(\frac{2k_B T(t)}{m}\right)^{1/2} \frac{1}{\nu} \nabla \left(\frac{n_1}{n}\right), \quad (48)$$

and the vectorial function φ given by

$$\varphi_i(\xi; a^*) = -\pi^{-3/2} \int_0^\infty d\tau \exp\left[-\left(1 - \frac{3}{2}\lambda\right)\tau\right] \times (\xi_j + a_{jk}^* \xi_k \tau) D_{ji}^* \exp(-e^{\lambda\tau} \xi \cdot \Gamma_\tau \cdot \xi). \quad (49)$$

Here, we have made use of the identity

$$\exp\left(\tau a_{ij} V_j \frac{\partial}{\partial V_i}\right) g(V_x, V_y, V_z) = g(V_x + a\tau V_y, V_y, V_z). \quad (50)$$

Equation (49) can be seen as the normal (stationary) representation of the Chapman-Enskog first approximation. Furthermore, it may be considered as a generalization of the Navier-Stokes distribution function in the self-diffusion problem. As a matter of fact, when $a = 0$, one recovers the usual results given by the linear BGK transport theory.

V. TRACER DIFFUSION IN USF

We will now consider a binary mixture in USF in which the masses of both species are arbitrary. Our aim is to generalize the results derived in Sec. IV to this kind of system. However, due to the mathematical difficulties embodied in this problem, it does not seem possible to obtain a general description of diffusion in far-from-equilibrium situations. Thus we have chosen a case that shares the simplicity of the self-diffusion problem and yet introduces a new ingredient into the dynamics (the mass ratio). This case corresponds to the limit in which one of the components, say 1, is present in tracer concentration, i.e., $n_1 \ll n_2 \simeq n$ or $n_1/n_2 \ll 1$. Our choice is mainly motivated by the recent results obtained in this limit from the Boltzmann equation.^{6,18}

In the tracer limit, one expects that the excess component 2 is not appreciably perturbed by the collisions with particles of component 1, and so one may assume that it is always in USF. On the other hand, the particles of species 1 are so few that their mutual interactions can be neglected. With these assumptions, the kinetic equations governing the nonequilibrium dynamics^{6,8} reduce to

$$\frac{\partial}{\partial t} f_1 + (V_i + a_{ij}r_j) \frac{\partial}{\partial r_i} f_1 - a_{ij}V_j \frac{\partial}{\partial V_i} f_1 = -\nu_{12}(f_1 - f_{12}^R) \quad (51)$$

for component 1, and

$$\frac{\partial}{\partial t} f_2 + (V_i + a_{ij}r_j) \frac{\partial}{\partial r_i} f_2 - a_{ij}V_j \frac{\partial}{\partial V_i} f_2 = -\nu_{22}(f_2 - f_{22}^R) \simeq -\nu_{22}(f_2 - f_2^{LE}) \quad (52)$$

for component 2. In Eq. (52), we have introduced

$$f_2^{LE} = n_2 (m_2/2\pi k_B T)^{3/2} \exp(-m_2 V^2/2k_B T), \quad (53)$$

and the last identity comes from the fact that, in the tracer limit, \mathbf{u}_2 and T_2 coincide with the velocity and the temperature of the mixture seen as a whole. Therefore, from the mathematical point of view, the problem is analogous to the one involving tagged particles since f_2 verifies the BGK equation corresponding to USF and its explicit expression is known. The task now is to solve Eq. (51) using the GSB and GK models.

A. Results from the GSB model

As pointed out above, the GSB model is introduced into Eq. (51) by taking as the reference function the one given by Eq. (27). In the same way as in the case of the self-diffusion calculations, to solve Eq. (51) we shall carry out a Chapman-Enskog-like expansion around a time nonequilibrium state with arbitrary a . However, now the reference state does not correspond to the usual USF. This is due to the fact that the collision frequency ν_{12} depends on the mass ratio $\mu = m_2/m_1$ and consistently one must take different temperatures for both species in the lowest order. By expanding the VDF and collecting terms of the same order in the gradient concentration, one obtains up to first order the equations

$$\begin{aligned} \frac{\partial}{\partial t} f_1^{(0)} - a_{ij} V_j \frac{\partial}{\partial V_i} f_1^{(0)} + \nu_{12} f_1^{(0)} \\ = \nu_{12} \frac{n_1}{n} f_1^{\text{LE}} \left[1 + \left(\frac{m_1 V^2}{2k_B T} - \frac{3}{2} \right) \left(\frac{T_1 - T}{T} \right) (1 - 2M) \right], \end{aligned} \quad (54)$$

$$\begin{aligned} \frac{\partial}{\partial t} f_1^{(1)} + (V_i + a_{ij} r_j) \frac{\partial}{\partial r_i} f_1^{(0)} - a_{ij} V_j \frac{\partial}{\partial V_i} f_1^{(1)} \\ + \nu_{12} f_1^{(1)} = \nu_{12} \frac{f_1^{\text{LE}}}{1 + \mu} \frac{m_1}{p} \mathbf{V} \cdot \mathbf{j}_1^{(1)}, \end{aligned} \quad (55)$$

where $M = m_1 m_2 / (m_1 + m_2)^2 = \mu / (1 + \mu)^2$. It must be pointed out that the form of the right-hand sides of Eqs. (54) and (55) has been suggested by the parallel recent results derived using the Boltzmann equation.⁶ Clearly, these assumptions must be verified later. Further, in the tracer limit one has $T_2(t) \simeq T(t) \exp(\lambda \nu_{22} t)$ with λ given by an expression similar to Eq. (12) in which now $a^* = a/\nu_{22}$.

For long times, the formal solution to Eq. (54) is given by

$$\begin{aligned} f_1^{(0)}(\mathbf{r}, \mathbf{V}; t) = n_1 \nu_1 \int_0^t d\tau \exp[-\nu_1(t - \tau)] \left(\frac{m_1}{2\pi k_B T} \right)^{3/2} \\ \times \left[1 + \left(\frac{m_1}{2k_B T} \mathbf{V} \cdot \boldsymbol{\Gamma}_{t-\tau} \cdot \mathbf{V} - \frac{3}{2} \right) \right. \\ \times \left(\frac{T_1 - T}{T} \right) (1 - 2M) \left. \right] \\ \times \exp\left(-\frac{m_1}{2k_B T} \mathbf{V} \cdot \boldsymbol{\Gamma}_{t-\tau} \cdot \mathbf{V} \right), \end{aligned} \quad (56)$$

where, for simplicity, from now on we will set $\nu_1 \equiv \nu_{12}$ (and also $\nu_{22} \equiv \nu_2$), and the temperatures are evaluated in the instant $t = \tau$. It is easy to check that $f_1^{(0)}$ is a self-consistent solution, i.e.,

$$\int d\mathbf{v} \begin{Bmatrix} 1 \\ \mathbf{V} \end{Bmatrix} f_1^{(0)} = \begin{Bmatrix} n_1 \\ \mathbf{0} \end{Bmatrix}, \quad (57)$$

and it leads to the following linear integral equation for the temperature T_1 :

$$\begin{aligned} T_1(t) = \frac{1}{3} \nu_1 \int_0^t d\tau \exp[-\nu_1(t - \tau)] \\ \times [3 + a^2(t - \tau)^2] [T_1 + 2M(T - T_1)]. \end{aligned} \quad (58)$$

Three successive derivatives transform Eq. (58) into an inhomogeneous differential equation:

$$\left(\frac{d^3}{dt^3} + \alpha \frac{d^2}{dt^2} + \beta \frac{d}{dt} + \gamma \right) T_1 = \theta T, \quad (59)$$

where

$$\alpha = \sqrt{2}(1 + \mu)^{1/2}(1 + M)\nu_2, \quad (60)$$

$$\beta = [(1 + \mu)/2](1 + 4M)\nu_2^2, \quad (61)$$

$$\gamma = \frac{(1 + \mu)^{3/2}}{\sqrt{2}} \left[\left(1 + \frac{4}{3} \frac{a^{*2}}{1 + \mu} \right) M - \frac{2}{3} \frac{a^{*2}}{1 + \mu} \right] \nu_2^3, \quad (62)$$

$$\begin{aligned} \theta = 2M \left[\left(\frac{1 + \mu}{2} \right)^{1/2} \lambda^2 + (1 + \mu)\lambda \right. \\ \left. + \left(\frac{1 + \mu}{2} \right)^{3/2} \left(1 + \frac{4}{3} \frac{a^{*2}}{1 + \mu} \right) \right] \nu_2^3. \end{aligned} \quad (63)$$

In the long time limit, the dominant contribution to the general solution to Eq. (59) can be written in the form

$$T_1(t) = (C e^{-(\lambda - k)\nu_2 t} + \chi) T(t), \quad (64)$$

where we have neglected the contributions that exponentially decay in time for all values of μ and a^* . Here, we have introduced the quantities

$$\begin{aligned} k = \frac{2}{3} \left(\frac{1 + \mu}{2} \right)^{1/2} \left[[1 - 4M(1 - M)]^{1/2} \right. \\ \left. \times \cosh\left(\frac{\psi}{3} \right) - (1 + M) \right], \end{aligned} \quad (65)$$

$$\chi(\mu, a^*) = \theta / [(\lambda \nu_2)^3 + \alpha(\lambda \nu_2)^2 + \beta(\lambda \nu_2) + \gamma], \quad (66)$$

C is a constant to be determined from the initial conditions and ψ is given by

$$\begin{aligned} \cosh \psi = 9[1 - 4M(1 - M)]^{-3/2} \\ \times \left[\frac{1}{9} - \frac{2}{3} M \left(1 - 2M + \frac{4}{3} M^2 \right) \right. \\ \left. + \frac{2a^{*2}}{1 + \mu} (1 - 2M) \right]. \end{aligned} \quad (67)$$

A hydrodynamic expression for the temperature T_1 is expected to hold after a transient period. For that, it is necessary that the first term on the right-hand side of Eq. (64) be neglected. Therefore the system reaches a hydrodynamic regime when $\lambda > k$ for all values of μ, a^* . The opposite situation happens when $\lambda < k$, for which a hydrodynamic solution cannot be obtained. In Fig. 2, we have determined the region of validity of the hydrodynamic solution (below the solid line). Below $a^* \simeq 7.0$, Eq. (64) always admits a hydrodynamic solution for any μ , while for $\mu \leq 1$, this region extends up to arbitrary shear rates. In general, the number of states allowed by the GSB model is smaller than the one given by the Boltzmann equation (dashed line).⁶ Anyway, in view of Fig. 2, for practical purposes, one may conclude that the system described by the GSB model reaches the normal stage for reasonable values of the shear rate and all mass ratios. When this stage is attained, the temperature of the tracer species is given by

$$T_1(t) = \chi(\mu, a^*) T(t), \quad (68)$$

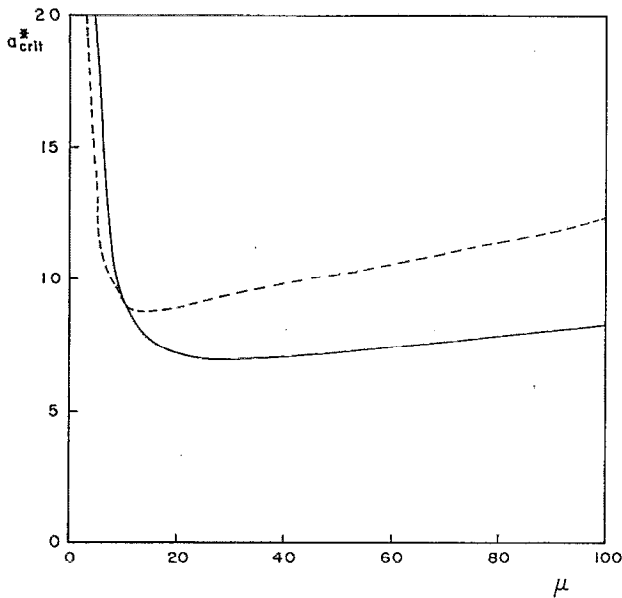


FIG. 2. Plane $a_{crit}^* - \mu$ showing the region of validity of the hydrodynamic solution to Eq. (64). In the case of the GSB model, this region corresponds to the one delimited by the solid curve while for the Boltzmann equation it is the one below the dashed line.

where χ is a highly nonlinear function of the mass ratio and the shear rate. The shape of this function is plotted in Fig. 3 for several values of μ . For $\mu = 1$, $\chi = 1$ for any value of a^* and so one recovers the self-diffusion results. In the region where $\mu \simeq 1$, for small values of a^* one may take the same temperature for both species and the conventional Chapman-Enskog theory holds.¹ However when the species masses are very different from each other, even for small a^* , one needs a description that includes different temperatures for the components of the mixture. Such a description is not

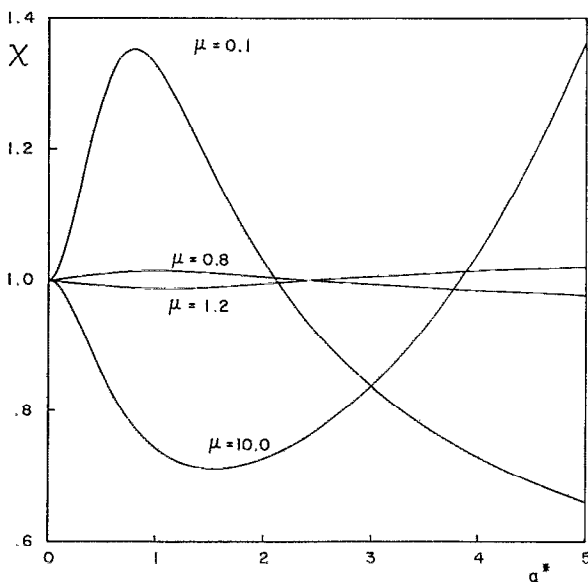


FIG. 3. Shear rate dependence of the function $\chi(\mu, a^*)$ for several values of the mass ratio μ .

allowed by the standard Chapman-Enskog theory, and one uses the so-called two-fluid theory. These conclusions are identical to those given in the linear transport theory when the applicability of the standard Chapman-Enskog theory is discussed.² Here, it is clear that, for arbitrary shear rates, it is necessary to take separate species temperatures. However, it must be pointed out that there exist particular combinations of μ and a^* for which $\chi = 1$. In fact, from Eq. (66) it is easy to show that this will happen when

$$a^{*2} = \frac{3}{2} \left(\frac{1+\mu}{2} \right)^{1/4} \left[1 + \left(\frac{1+\mu}{2} \right)^{1/4} \right] \quad (69)$$

and so, for these particular situations, the usual Chapman-Enskog theory (with only one temperature) can be adequate to describe the transport even for the disparate-mass binary mixture case. In this way, one expects that the GSB model is suitable in the range where a two-fluid theory² is not necessary, namely for $\chi \simeq 1$.

By using Eq. (68), the pressure tensor of the tracer species can be computed. In the hydrodynamic regime, its non-zero components are given by

$$\begin{aligned} P_1^{(0)} &= \int d\mathbf{v} m_1 \mathbf{v} \mathbf{v} f_1^{(0)} \\ &= \left(\frac{1+\mu}{2} \right)^{1/2} v_2 n_1 k_B T [(1-2M)\chi + 2M] \\ &\quad \times \lim_{t \rightarrow \infty} \int_0^t d\tau \Gamma_{t-\tau}^{-1} \exp \left\{ -v_2(t-\tau) \right. \\ &\quad \left. \times \left[\left(\frac{1+\mu}{2} \right)^{1/2} + \lambda \right] \right\} \\ &= n_1 k_B T [(1-2M)\chi + 2M] \Lambda, \end{aligned} \quad (70)$$

where the components of the tensor Λ are given by

$$\begin{aligned} \Lambda_{ij} &= \frac{1}{1+\lambda_0} \left(\delta_{ij} + \frac{2}{(1+\lambda_0)^2} a_{ik}^* a_{jk}^* \right. \\ &\quad \left. - \frac{1}{1+\lambda_0} (a_{ij}^* + a_{ji}^*) \right), \end{aligned} \quad (71)$$

with $\lambda_0 = (2/1+\mu)^{1/2} \lambda$, $a_{ij}^* = (2/1+\mu)^{1/2} a^* \delta_{ix} \delta_{jy}$, $= a^* \delta_{ix} \delta_{jy}$.

When the temporal dependence of the temperature T_1 is introduced in the VDF $f_1^{(0)}$, by scaling the velocities one may obtain a stationary or normal representation of the corresponding distribution. Performing similar algebra to that outlined in Sec. III, the reduced distribution g^* defined by

$$g^*(\xi; \mu, a^*) = (1/n_1) (2k_B T/m_1)^{3/2} f_1^{(0)} \quad (72)$$

can be cast in the form

$$\begin{aligned} g^*(\xi; \mu, a^*) &= \pi^{-3/2} \int_0^\infty d\tau \exp \left[-\tau \left(1 - \frac{3}{2} \lambda_0 \right) \right] \\ &\quad \times \left[1 + \left(e^{\lambda_0 \tau} \xi \cdot \Gamma_{[2/(1+\mu)]^{1/2} \tau} \cdot \xi - \frac{3}{2} \right) \right. \\ &\quad \left. \times (\chi - 1) (1 - 2M) \right] \\ &\quad \times \exp \left(-e^{\lambda_0 \tau} \xi \cdot \Gamma_{[2/(1+\mu)]^{1/2} \tau} \cdot \xi \right), \end{aligned} \quad (73)$$

where ξ is defined as in Eq. (14), replacing m by m_1 and the product

$$\xi \cdot \Gamma_{(2/1+\mu)^{1/2} \tau} \cdot \xi = \xi^2 + 2\xi_x \xi_y a^* \tau + \xi_y^2 a^{*2} \tau^2.$$

For $\mu = 1$, Eq. (73) reduces to the VDF corresponding to the USF state, Eq. (15). Equation (73) gives the reference state for the tracer particles when the concentration gradient has not been introduced and the only nonuniformity is due to the shear rate.

In order to obtain the first-order distribution $f_1^{(1)}$, one has to know the flux of tracer particles. Thus, from Eq. (55), one obtains

$$\lambda T \frac{\partial}{\partial t} j_{ii}^{(1)} + a_{ik} j_{ik}^{(1)} + \frac{\mu}{1+\mu} v_1 j_{ii}^{(1)} = - \frac{P_{1,ik}^{(0)}}{m_1} \frac{1}{n_1} \frac{\partial}{\partial r_k} n_1, \quad (74)$$

where once again we have taken into account Eqs. (37a) and (37b). The hydrodynamic solution to Eq. (74) can be written in the form

$$j_{ii}^{(1)} = - D_{ik} \frac{\partial}{\partial r_k} n_1, \quad (75)$$

where now the diffusion tensor is a highly nonlinear function of both the mass ratio and the shear rate. It is given by

$$D_{ik} = \frac{k_B T}{m_1 v_2} \left(\frac{2}{1+\mu} \right)^{1/2} \frac{1}{\lambda_0 + \mu/(1+\mu)} \times \left(\delta_{ii} - \frac{a_{ii}^*}{\lambda_0 + \mu/(1+\mu)} \right) \times [(1-2M)\chi + 2M] \Lambda_{1,ik}. \quad (76)$$

If $\mu = 1$, Eq. (76) reduces to the self-diffusion tensor. For $a^* = 0$, $D_{ik} = D_0 \delta_{ik}$, with

$$D_0 = (k_B T / m_1 v_2) \sqrt{2} [(1+\mu)^{1/2} / \mu], \quad (77)$$

where D_0 is the diffusion coefficient for the tracer component when the excess component is in total equilibrium. In Fig. 4, we have plotted $D_{kk}^*/3$ vs a^* for different values of the mass ratio. Here, $D_{kk}^* = D_{ik}/D_0$. For small μ , the agreement between the Boltzmann and GSB results increases as a^* decreases. For large μ , the opposite situation happens.

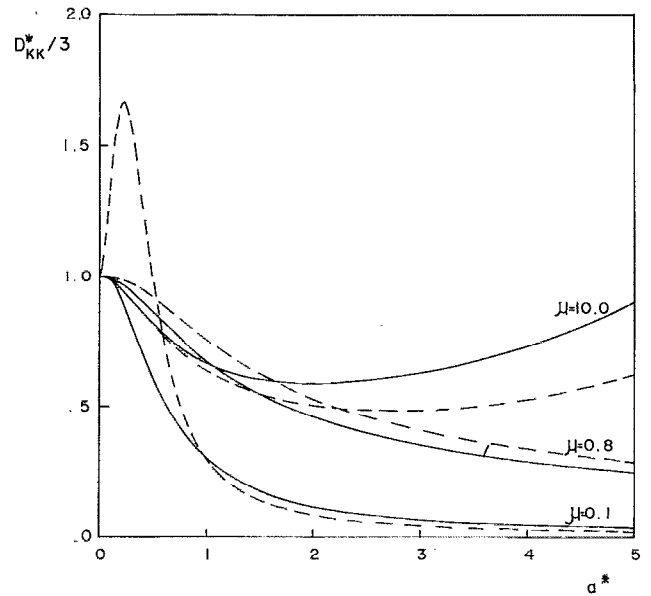


FIG. 4. Shear rate dependence of the trace $D_{kk}^*/3$ of the dimensionless tracer diffusion tensor for several values of μ . Solid lines indicate GSB results and dashed lines Boltzmann results.

From Eq. (55), the first-order approximation to the normal solution can be derived. The procedure is analogous to the one described in the self-diffusion section. Therefore, by introducing the corresponding dimensionless concentration gradient ϵ^* ,

$$\epsilon^* = \left(\frac{2k_B T}{m_1} \right)^{1/2} \frac{1}{v_2} \frac{1}{n_1} \nabla n_1, \quad (78)$$

and after tedious manipulations the reduced function $h^* = n_1^{-1} (2k_B T / m_1)^{3/2} f_1^{(1)}$ can be written in the long time limit as

$$\lim_{t \rightarrow \infty} h^*(\mathbf{r}, \mathbf{V}; t) = \varphi(\xi; \mu, a^*) \cdot \epsilon^*, \quad (79)$$

where the normal solution φ is given by

$$\varphi_1(\xi; \mu, a^*) = - \pi^{-3/2} \left(\frac{2}{1+\mu} \right)^{1/2} \int_0^\infty d\tau \exp \left[- \left(1 - \frac{3}{2} \lambda_0 \right) \tau \right] \left\{ \frac{1}{\mu} (\xi_j + a_{jk}^* \xi_k \tau) D_{ji}^* + \xi_i \tau \right. \\ \left. \times \left[1 + \left(e^{\lambda_0 \tau} \xi \cdot \Gamma_{[2/(1+\mu)]^{1/2} \tau} \cdot \xi - \frac{3}{2} \right) (\chi - 1) (1 - 2M) \right] \right\} \exp \left(- e^{\lambda_0 \tau} \xi \cdot \Gamma_{[2/(1+\mu)]^{1/2} \tau} \cdot \xi \right). \quad (80)$$

Equation (80) shows a very complicated dependence of φ on μ and a^* that yields a generalization of the “Navier–Stokes” approximation for tracer diffusion in USF.

By using Eqs. (79) and (80), all velocity moments may be computed. The next nontrivial moment is the heat flux, defined by

$$\mathbf{q}_1^{(1)} = \int d\mathbf{v} \frac{m_1}{2} v^2 \mathbf{V} f_1^{(1)}. \quad (81)$$

The evaluation of $\mathbf{q}_1^{(1)}$ is not straightforward and it is performed in the Appendix. It is given by

$$\mathbf{q}_1^{(1)} = - (2k_B^2 T^2 / m_1 v_2) \Sigma \cdot \nabla n_1, \quad (82)$$

where the tensor Σ is a highly nonlinear function of μ and a^* and its explicit form is also given in the Appendix. Equation (82) can be seen as the cross contribution to the “heat flux” of the tracer particles due to the gradient of concentration. It may be identified as a kind of Dufour effect³ in the tracer limit when the contribution to the total heat flux due to the excess component is neglected. We will return to this point in the discussion where a comparison with the GK results is carried out.

B. Results from the GK model

The GK model is defined from Eq. (51) inserting the reference function given by Eq. (23). According to the collision term proposed, one expects that this model is useful when the mass ratio is not of the order of one. Our aim here is to solve it following the same kind of techniques that we have used in the previous section. In this way, up to first order in the concentration of the tracer particles, one obtains the equations

$$\frac{\partial}{\partial t} f_1^{(0)} - a_y V_j \frac{\partial}{\partial V_i} f_1^{(0)} + v_j f_1^{(0)} = v_j f_{12}^{(0)}, \quad (83)$$

$$\begin{aligned} \frac{\partial}{\partial t} f_1^{(1)} + (V_i + a_y v_j) \frac{\partial}{\partial r_i} f_1^{(0)} \\ - a_y V_j \frac{\partial}{\partial V_i} f_1^{(1)} + v_j f_1^{(1)} = v_j f_{12}^{(1)}, \end{aligned} \quad (84)$$

where

$$f_{12}^{(0)} = n_1 (m_1/2\pi k_B T_{12})^{3/2} \exp(-m_1 V^2/2k_B T_{12}), \quad (85)$$

$$f_{12}^{(1)} = m_1 [f_{12}^{(0)}/(1+\mu)] [(V \cdot j_i^{(1)})/n_1 k_B T_{12}]. \quad (86)$$

For the zeroth-order approximation we obtain

$$\begin{aligned} f_1^{(0)}(\mathbf{r}, \mathbf{V}; t) = n_1 v_1 \int_0^t d\tau \\ \times \exp[-v_1(t-\tau)] \left(\frac{m_1}{2\pi k_B T_{12}} \right)^{3/2} \\ \times \exp\left(-\frac{m_1}{2k_B T_{12}} \mathbf{V} \cdot \mathbf{\Gamma}_{t-\tau} \cdot \mathbf{V} \right). \end{aligned} \quad (87)$$

From Eq. (87), it is straightforward to show that its first moments are identical to those given by the GSB model. These moments refer to the temperature T_1 , Eq. (64), and the pressure tensor, Eq. (70). However, the VDF is different. After some algebra, the stationary representation of the function $f_1^{(0)}$ can be written as

$$\begin{aligned} g^*(\xi; \mu, \mathbf{a}^*) = \pi^{-3/2} \int_0^\infty d\tau \exp\left[-\left(1 - \frac{3}{2}\lambda_0\right)\tau \right] [(1-2M)\chi + 2M]^{-3/2} \\ \times \exp\left(-\frac{e^{\lambda_0\tau}}{(1-2M)\chi + 2M} \xi \cdot \mathbf{\Gamma}_{[2/(1+\mu)]^{1/2}\tau} \cdot \xi \right), \end{aligned} \quad (88)$$

where all of the parameters and notation are as previously defined.

In the first-order approximation, it is easy to show that Eq. (84) leads to the same expression for the diffusion tensor as that given by the GSB model, Eqs. (75) and (76). Therefore, in the long time limit, the vectorial normal solution can be identified as

$$\begin{aligned} \varphi_1(\xi; \mu, \mathbf{a}^*) = -\pi^{-3/2} \left(\frac{2}{1+\mu} \right)^{1/2} \int_0^\infty d\tau \exp\left[-\left(1 - \frac{3}{2}\lambda_0\right)\tau \right] [(1-2M)\chi + 2M]^{-3/2} \\ \times \left(\frac{1}{(1-2M)\chi + 2M} \frac{1}{\mu} (\xi_j + \mathbf{a}_{jk}^* \xi_k \tau) D_{ji}^* + \xi_i \tau \right) \exp\left(-\frac{e^{\lambda_0\tau}}{(1-2M)\chi + 2M} \xi \cdot \mathbf{\Gamma}_{[2/(1+\mu)]^{1/2}\tau} \cdot \xi \right). \end{aligned} \quad (89)$$

By using Eq. (89), one obtains the heat flux whose expression is similar to Eq. (82) but now the tensor Σ is different. Its form is also given in the Appendix. The heat flux is the first interesting moment that is different in both models. Before closing this section it is adequate to remark that the results given by the GSB and GK models are exactly identical for $\chi = 1$. This means that, in the tracer limit, because of the simple mathematical form of the GK collision term, this model can also be adequate to study transport properties where a two-fluid theory is not necessary. For more general situations, one expects that both models may yield different results in the range of μ close to unity.

VI. DISCUSSION

In this paper, we have addressed the problem of diffusion in shear flow by using two different kinetic models (GSB and GK) for dilute binary mixtures of Maxwell molecules and considering the case of mechanically similar particles and the tracer limit. The results presented in previous sections provide grounds for further elaboration.

We begin with self-diffusion. For this problem, our starting point was the GSB model alone since the GK model is not adequate in the sense that it does not yield to a closed kinetic equation for the VDF of the system seen as a whole. The main advantage of using a kinetic model (which reduces to the BGK equation) rather than the Boltzmann equation resides on the fact that one is able not only to explicitly write the VDF corresponding to the USF for the full system but also the VDF of the tagged particles. Using this latter distribution, one may compute all the velocity moments. And since for this particular problem the shear-dependent self-diffusion tensor has been obtained from the Boltzmann equation,⁵ a comparison between both calculations is feasible. This we have done and the agreement is rather satisfactory. Two points are worth emphasizing. First, our results hold for any number density ratio of tagged particles. Second, in contrast to what has been found in molecular dynamics simulations of Lennard-Jones fluids,⁹ but in agreement with what has been found for Maxwell molecules using the Boltzmann equation,⁵ the self-diffusion tensor decreases with increasing shear rate.

Concerning the tracer limit, we have computed, using both the GSB and GK models, the main transport properties as well as the VDF of the tracer particles for arbitrary mass ratio. This is the simplest extension of the tagged particles problem (to which the present results reduce for the GSB model when $\mu = 1$) since we may still assume that the VDF of the excess component is that of USF. We find that the first few moments of the VDF of the tracer particles turn out to be identical for both models although these distribution functions are, in general, different for each model. In terms of the aforementioned moments, in the tracer limit two temperatures corresponding to each individual species arise naturally in our formulation, which are related through a highly nonlinear function $\chi(\mu, a^*)$. Thus a two-fluid description, similar to the ones employed in the linear regime² for disparate-mass mixtures, seems to be, in principle, required. Nevertheless, it must be stressed that, if $\chi = 1$ [which occurs when either $\mu = 1$ or $a^* = 0$ or when Eq. (69) holds], $T_1 = T_2 = T$ and the standard Chapman–Enskog description is valid. This conclusion might not have been anticipated on the basis of the results derived in the linear regime.

On the other hand, the expression for the shear-dependent diffusion tensor for any value of the mass ratio is also identical in the GSB and GK models. A comparison with related results derived from the Boltzmann equation⁶ again indicates a reasonably good agreement. The first moment that is different in both models is the heat flux [cf. Eqs. (82), (A4), and (A6)], which arises from the cross effect of the gradient of concentration of the tracer particles. In an attempt to make contact with the phenomenological approach of linear irreversible thermodynamics,³ we may define a “generalized” Dufour tensor L_{q1} such that

$$\begin{aligned} \mathbf{j}_q &= \mathbf{q}_1^{(1)} - \frac{5}{2} k_B T \mathbf{j}_1^{(1)} \\ &= -\frac{5}{2} \frac{n_1 k_B T^2}{\nu_2} L_{q1}(\mu, a^*) \cdot \left(\frac{\nabla \mu_1}{T} \right)_T, \end{aligned} \quad (90)$$

where

$$\mu_1 = \left(\frac{k_B T}{m_1} \right) \left(\log n_1 - \frac{3}{2} \log \frac{2k_B T}{m_1} \right)$$

is the chemical potential of the tracer species per mass unit. It must be pointed out that $L_{q1}(\mu, 0) = 0$, in agreement with the results derived for Maxwell molecules in the linear regime both from the Boltzmann¹ and the kinetic models.^{5,11} In order to gain some insight of the behavior of the “generalized” Dufour tensor, for simplicity we consider a geometry in which the gradient of concentration of tracer particles is parallel to the z axis. Hence, the zz component of the Dufour tensor, which we shall denote by L_{q1} , is the only relevant component in Eq. (90). In Figs. 5 and 6, we show the shear rate dependence of L_{q1} for illustrative values of μ and for both kinetic models. For $\mu = 1$, the value of L_{q1} is the same in the GSB and GK models. In the case where $\mu = 10$, although the two models may yield slightly different numerical values, the overall trends are similar. On the other hand, if $\mu = 0.1$ the numerical differences are much greater up to

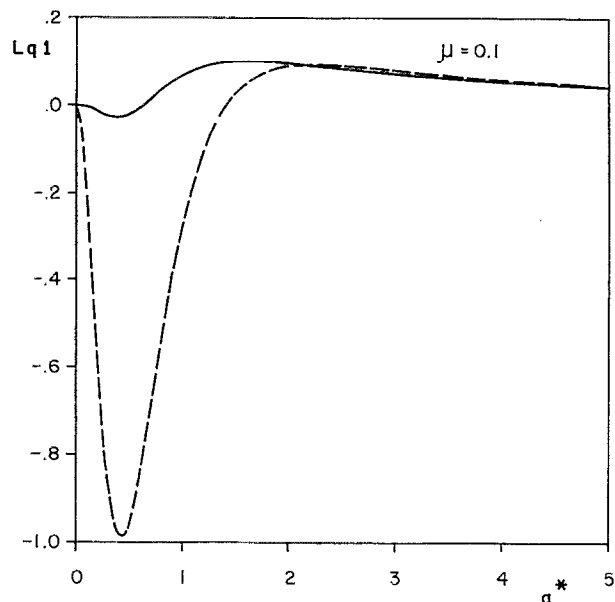


FIG. 5. Shear rate dependence of the generalized Dufour coefficient for $\mu = 0.1$. The solid line is the result of the GSB model and the dashed line refers to the GK model.

$a^* \approx 2$ in both models, while for $a^* > 2$, the results are almost identical.

As already pointed out, the VDF in both models is different, except when $\chi = 1$. The conditions where the latter happens have been stated above and there are, of course, infinite ways to combine a^* and μ so that Eq. (69) is satisfied. Moreover, for the far-from-equilibrium states considered in this paper, the parameter χ seems to play a similar role to the one played by μ in the linear theory. In this sense, one would expect that, for $\chi \approx 1$, a two-temperature theory is

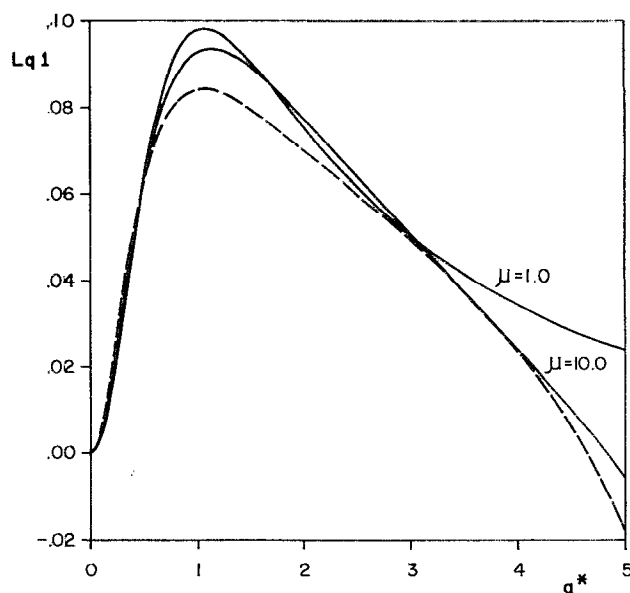


FIG. 6. The same as in Fig. 5 but for $\mu = 1, 10$. The GSB and GK results coincide for $\mu = 1$.

not required, while outside the region defined by this condition the opposite happens. Notice that the VDF in the GSB model depends linearly on $(\chi - 1)$, while in the GK model a highly nonlinear dependence on this parameter is obtained. If an expansion in $(\chi - 1)$ of the VDF in this latter model is performed, the resulting function up to first order in the expansion parameter is similar (but still different) to the one corresponding to the GSB model. Therefore one might reasonably conjecture that, in the tracer limit, either the GSB model or the GK model would be appropriate when $\chi \simeq 1$ and only the GK model otherwise. However, because of the conceptual difficulties inherent to the GK model concerning the way the collisions are modeled, we favor the use of the GSB model for values of χ in the neighborhood of 1.

For the sake of illustration of the behavior of the VDF obtained from the kinetic models, we have considered it adequate to restrict ourselves to the zeroth-order approximations (reference states) to the normal solutions given by Eqs. (73) and (88). We find it convenient to introduce the reduced distributions

$$\tilde{g}^*(\xi_y; \mu, a^*) = \int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_z g^*(\xi; \mu, a^*) \quad (91)$$

in order to compare the results from both models. For a fixed value of $a^* = 2$ (which, of course, implies a state far away from equilibrium), in Figs. 7 and 8 we display the behavior of the \tilde{g}^* with ξ_y for two extreme values of μ . In the first case ($\mu = 0.1$), we are in a region where $\chi \simeq 1$ and the results of both models are clearly seen to coincide. On the other hand, for $\mu = 10$, $\chi \simeq 0.7$ and a slight discrepancy is observed. This is in agreement with the statements put forward above, but the small numerical differences suggest that the GSB model may also be useful when χ is not of the order of 1.

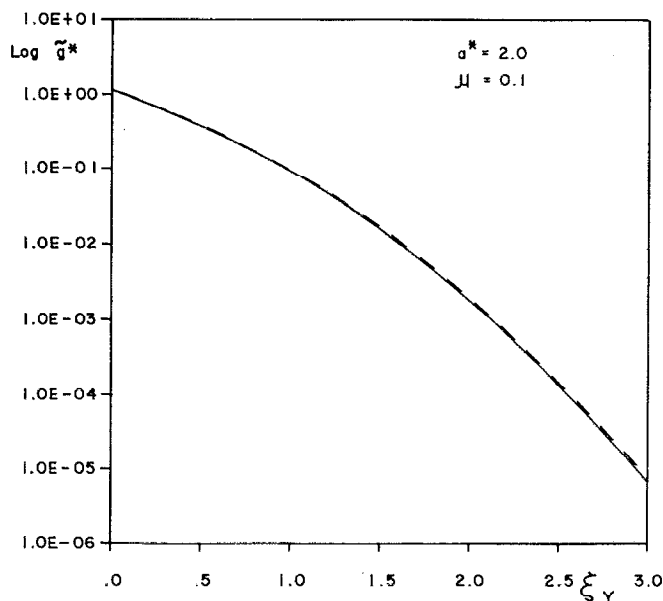


FIG. 7. Reduced distribution function \tilde{g}^* vs ξ_y , for $\mu = 0.1$ and $a^* = 2$. The solid line is the GSB result while the dashed line corresponds to the GK model.

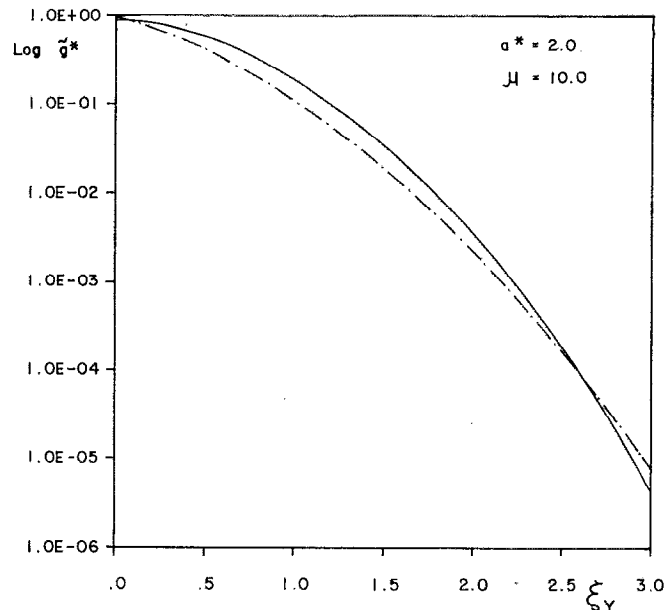


FIG. 8. The same as in Fig. 7 but now for $\mu = 10$ and $a^* = 2$.

It should be apparent that the derivation of explicit expressions for the fluxes and the VDF's involved in a given nonequilibrium problem (such as the one carried out here) may prove to be useful for interpreting computer simulations of systems far from equilibrium. While this approach in the case of a single-component gas in USF has been successfully exploited, for instance in Ref. 10, we are not aware of the availability of similar simulation results for binary mixtures, not even in the tracer limit. In this respect, we hope that our work may serve to encourage the performance of simulations of self- and tracer diffusion in USF.

Finally, in view of the results derived in this paper, it seems worthwhile to investigate the usefulness of the kinetic models in the tracer limit for other nonequilibrium situations and the possibility to eliminate the restrictions imposed by such a limit. Work along this line is already in progress.

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APPENDIX: DERIVATION OF EXPRESSIONS FOR THE TENSOR Σ

In order to compute the heat flux vector in the GSB and the GK models, one needs the result

$$\int d\xi_x \xi_x^2 \xi_y \exp\left(b\xi_y \frac{\partial}{\partial \xi_x}\right) e^{-c\xi^2} = \frac{\pi^{3/2}}{4} c^{-7/2} A_{ij}(b), \quad (\text{A1})$$

where we have introduced the tensor A whose components are

$$A_{ij}(b) = (5 + 10b^2 + 3b^4)\delta_{ix}\delta_{jx} + (5 + 3b^2)\delta_{iy}\delta_{jy} + (5 + b^2)\delta_{ix}\delta_{jy} - b(7 + 3b^2)(\delta_{ix}\delta_{jy} + \delta_{jx}\delta_{iy}). \quad (\text{A2})$$

In this way, from the GSB model, one gets for the tensor Σ the expression

$$\Sigma_{ij}(\mu, a^*) = \frac{1}{4} \left(\frac{2}{1+\mu} \right)^{1/2} \int_0^\infty d\tau \exp[-(1+2\lambda_0)\tau] \times \left(\frac{1}{\mu} [A_{ik}(a^*\tau) + A_{il}(a^*\tau)a_{kl}^*\tau] D_{kj}^* + A_{ij}(a^*\tau)\tau[1+2(\chi-1)(1-2M)] \right). \quad (\text{A3})$$

Performing the integration over τ , one finally arrives at

$$\Sigma_{ij}(\mu, a^*) = \frac{1}{4} \left(\frac{2}{1+\mu} \right)^{1/2} \left[\frac{1}{\mu} \left(B_{ik} - \frac{a_{kl}^*}{2} \frac{\partial B_{il}}{\partial \lambda_0} \right) D_{kj}^* - \frac{1}{2} \frac{\partial B_{ij}}{\partial \lambda_0} [1+2(\chi-1)(1-2M)] \right]. \quad (\text{A4})$$

Here, we have introduced the tensor

$$B_{ij}(\lambda_0, a^*) = \int_0^\infty d\tau \exp[-(1+2\lambda_0)\tau] A_{ij}(a^*\tau) = \frac{1}{(1+2\lambda_0)} \left\{ \left(5 + 20 \frac{a^{*2}}{(1+2\lambda_0)^2} + 72 \frac{a^{*4}}{(1+2\lambda_0)^4} \right) \delta_{ix}\delta_{jx} + \left(5 + 6 \frac{a^{*2}}{(1+2\lambda_0)^2} \right) \delta_{iy}\delta_{jy} + \left(5 + 2 \frac{a^{*2}}{(1+2\lambda_0)^2} \right) \delta_{ix}\delta_{jy} - \left(7 \frac{a^*}{(1+2\lambda_0)} + 18 \frac{a^{*3}}{(1+2\lambda_0)^3} \right) (\delta_{ix}\delta_{jy} + \delta_{iy}\delta_{jx}) \right\}, \quad (\text{A5})$$

and its derivatives with respect to λ_0 can be easily obtained.

In a similar way, in the GK model, one gets the expression

$$\Sigma_{ij}(\mu, a^*) = \frac{1}{4} \left(\frac{2}{1+\mu} \right)^{1/2} [(1-2M)\chi + 2M]^2 \times \left[\frac{1}{\mu} \frac{1}{(1-2M)\chi + 2M} \left(B_{ik} - \frac{a_{kl}^*}{2} \frac{\partial B_{il}}{\partial \lambda_0} \right) \times D_{kj}^* - \frac{1}{2} \frac{\partial B_{ij}}{\partial \lambda_0} \right], \quad (\text{A6})$$

which is, in general, different from that given by the GSB model, except in the case $\chi = 1$.

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