



Tracer diffusion under heat and momentum transport for general repulsive potentials

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Abstract

Tracer diffusion in a steady state with both velocity and temperature gradients is analyzed. The results are obtained from a kinetic model that incorporates a temperature dependence in the collision frequencies. This allows for the consideration of general r^{-l} -repulsive interactions. An explicit expression of the tracer diffusion tensor is obtained in terms of the shear rate, the mass ratio, the force constant ratio and a parameter characterizing the interaction model considered. This expression extends previous results derived in the case of Maxwell molecules ($l=5$).

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1. Introduction

An interesting problem in nonequilibrium statistical mechanics is the description of transport phenomena taking place in fluid mixtures. Nevertheless, the general study of these systems is certainly very complicated since the transport coefficients are not only functions of the nonequilibrium parameters (hydrodynamic gradients, external fields, ...), but also of parameters characterizing the mixture such as the mass ratios, the molar fractions and/or the size ratios. This complexity leads to consider tractable specific situations where a thorough description may be offered. Perhaps, one of the simplest cases is the so-called *tracer* limit, namely, a binary mixture with a solute molar fraction negligibly small. This limit shares the simplicity of the tagged particle problem but introduces the mass ratio as a new ingredient into the dynamics. In this situation, it is reasonable to assume that the state of the solvent component is not appreciably disturbed by the presence of the tracer particles, while collisions among tracer particles

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can be neglected. Very recently, we have analyzed a diffusion problem in a gaseous dilute solution under heat and momentum transport (steady Couette flow) in the low-density regime [1]. The results were derived from the Gross–Krook (GK) kinetic model [2] for binary mixtures, since no explicit solution of the Boltzmann equation for the steady Couette flow is known even for a single gas. The GK model is constructed in the same spirit as the Bhatnagar–Gross–Krook (BGK) model [3] of a single gas, for which an *exact* description of the planar Couette flow state has been given [4,5].

In the GK kinetic model all the details of the interaction potential are taken into account through effective collision frequencies ν_{ij} . For low-density mixtures, ν_{ij} is always proportional to the density n_j of species j . The dependence of ν_{ij} on the temperature comes from the specific scattering laws that one has in mind. The simplest interaction model corresponds to Maxwell molecules (particles interacting through repulsive forces inversely proportional to the fifth power of the distance), in which case ν_{ij} is independent of the temperature. For the sake of simplicity, our previous solution [1] was restricted to Maxwell molecules. Obviously, the model of Maxwell molecules cannot be considered as a very realistic example of intermolecular interactions except in some particular conditions. For this reason, in this paper we extend our previous efforts by addressing the same problem for general repulsive intermolecular forces.

The starting point is a kinetic model that generalizes the familiar Gross–Krook equation (originally proposed for Maxwell molecules) to inverse power laws. In the case of disparate-mass binary mixtures, it is well known [6] that even in the linear regime one needs a description which includes the possibility that the different components of the mixture have different temperatures. Since we are interested in describing tracer diffusion for arbitrary mass ratio, the effective collision frequencies ν_{ij} of the model must depend on the temperatures of each species T_i and T_j instead of the temperature of the mixture T . In this sense, one expects the model to be more suitable for systems of distinguishable particles. The reliability of this kinetic model has been recently assessed in the color conductivity problem [7].

As the state of the solvent component is well characterized (planar Couette flow) [4], our goal is to solve the corresponding kinetic equation for the solute component. This solution is constructed by means of a perturbation expansion in powers of the gradient of the molar fraction. The main difference of this perturbation method from the conventional Chapman–Enskog expansion [9] (valid for situations close to equilibrium) is that the zeroth-order approximation is not that of local equilibrium, but a nonequilibrium state with arbitrary values of the shear rate and the thermal gradient. In the first order of the expansion, one gets an explicit expression for the tracer diffusion tensor. This tensor turns out to be a nonlinear function of the shear rate, the mass ratio, the force constant ratio and also of a parameter characterizing the potential considered. This expression extends the one previously derived for Maxwell molecules [1]. It must be emphasized that, although the influence of the interaction potential is partially accounted for by a proper choice of scaled quantities, the extension to non-Maxwell molecules is not trivial at all since now the collision frequencies are also functions of

the nonequilibrium parameters of the problem. This implies that *new* terms appear *explicitly* in the expressions of the elements of the tracer diffusion tensor. The calculation of these terms is the main motivation of this work.

The plan of the paper is as follows. In Section 2 we introduce the model and describe the problem. Section 3 concerns with the two first approximations of the perturbation method. We obtain the main transport properties of the problem as well as the velocity distribution function of the tracer species. We complete the paper in Section 4 with some concluding remarks.

2. Kinetic model for tracer diffusion in steady Couette flow

Let us consider a binary mixture in the low-density regime, with $f_i(\mathbf{r}, \mathbf{v}; t)$ being the one-particle distribution function of species i ($i = 1, 2$). From this distribution, one defines the number density and mean velocity of species i , respectively, as

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

$$\mathbf{u}_i = \frac{1}{n_i} \int d\mathbf{v} \mathbf{v} f_i. \quad (2)$$

It is also convenient to define a temperature T_i for each species, which is a measure of its mean kinetic energy per particle. It is given by

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

where k_B is the Boltzmann constant and m_i is the mass of a particle of species i .

We are interested in analyzing a tracer diffusion problem in a far from equilibrium situation. In that case, it is a very hard task to solve the Boltzmann equation [9] even for simple interaction potentials. This prompts the use of a simple kinetic model. Here, we will start from a generalization of the familiar Gross–Krook (GK) model [2] (proposed for Maxwell molecules) to general repulsive intermolecular forces. Specifically, for particles interacting via a repulsive force law $\mathcal{F}_{ij} = \kappa_{ij} r^{-l} \hat{\mathbf{r}}$ ($l = 5, \dots, \infty$), the Boltzmann collision integrals $J_{ij}[f_i, f_j]$ are replaced by simple relaxation terms of the form

$$J_{ij}^{GK}[f_i, f_j] = -\nu_{ij} (f_i - f_{ij}), \quad (4)$$

where the expressions of the reference distribution functions f_{ij} are the same as those given in the conventional GK model for Maxwell molecules ($l = 5$) [2], i.e.

$$f_{ij} = n_i \left(\frac{m_i}{2k_B T_{ij}} \right)^{3/2} \exp \left(-\frac{m_i}{2k_B T_{ij}} (\mathbf{v} - \mathbf{u}_{ij})^2 \right), \quad (5)$$

with

$$\mathbf{u}_{ij} = \frac{m_i \mathbf{u}_i + m_j \mathbf{u}_j}{m_i + m_j}, \quad (6)$$

$$T_{ij} = T_i + 2 \frac{m_i m_j}{(m_i + m_j)^2} \left[(T_j - T_i) + \frac{m_j}{6k_B} (\mathbf{u}_i - \mathbf{u}_j)^2 \right]. \quad (7)$$

The influence of the interaction enters through the collision frequencies ν_{ij} , which can be identified as [8]

$$\nu_{ij} = A(\delta) n_j \left(\kappa_{ij} \frac{m_i + m_j}{m_i m_j} \right)^{(1-\delta)/2} \left(\frac{2k_B T_i}{m_i} + \frac{2k_B T_j}{m_j} \right)^{\delta/2}. \quad (8)$$

Here, $\delta = (l-5)/(l-1)$ and $A(\delta)$ is a constant for a given interparticle potential that is tabulated in Ref. [9]. The above expressions are obtained by requiring that the first five collisional moments as computed with Eq. (4) be the same as those computed with the Boltzmann operator $J_{ij}[f_i, f_j]$ for Maxwell molecules [10]. The kinetic model defined by Eqs. (4)–(8) can be considered as an extension of the GK model for Maxwell molecules since it generalizes the latter to harder repulsive intermolecular forces. One expects that the temperature dependence of ν_{ij} proposed in the model is sufficient (at least qualitatively) to explore the influence of the interaction potential on the transport properties. Recent results derived from it in the case of tracer diffusion under uniform shear flow [8] as well as in the color conductivity problem [7] confirm the above expectations.

We describe now the problem we are interested in. We consider a binary mixture in which one of the components, say 1, is present in tracer concentration, i.e., $n_1/n_2 \ll 1$. In the tracer limit, one expects that the state of the solvent component 2 is not significantly disturbed by collisions with tracer particles 1, so that the velocity distribution function f_2 satisfies a closed equation. This equation turns out to be the well-known Bhatnagar–Gross–Krook (BGK) kinetic model [3] for a single gas, i.e.

$$\frac{\partial}{\partial t} f_2 + \mathbf{v} \cdot \nabla f_2 = -\nu_{22}(f_2 - f_{22}). \quad (9)$$

Furthermore, the molar fraction $x_1 = n_1/n_2$ of the tracer species is so small that one can neglect their self-collisions. Consequently, f_1 verifies the equation

$$\frac{\partial}{\partial t} f_1 + \mathbf{v} \cdot \nabla f_1 = -\nu_{12}(f_1 - f_{12}). \quad (10)$$

On the other hand, the masses and sizes of both species are arbitrary. We assume that the solvent component is in steady planar Couette flow, namely, it is enclosed between two parallel plates (normal to the y axis) in relative motion (along the x axis) and kept at different temperatures. Consequently, profiles of density, velocity, and temperature exist across the system. In this state, no explicit solution of the Boltzmann equation valid for arbitrary values of the velocity and temperature gradients is known, although a perturbation solution through super-Burnett order has been recently obtained [11].

Nevertheless, an exact description can be given if one uses the BGK approximation. In this case, Eq. (9) becomes

$$v_y \frac{\partial}{\partial v_y} f_2 = -v_{22}(f_2 - f_{22}). \quad (11)$$

The solution is characterized by a uniform pressure and linear velocity and parabolic temperature profiles with respect to a scaled space variable, i.e.

$$p_2 \equiv n_2 k_B T_2 = \text{const.}, \quad (12)$$

$$\frac{1}{v_{22}(y)} \frac{\partial}{\partial y} u_{2,x} = a = \text{const.}, \quad (13)$$

$$\left[\frac{1}{v_{22}(y)} \frac{\partial}{\partial y} \right]^2 T_2 = -\frac{2m_2}{k_B} \gamma(a) = \text{const.} \quad (14)$$

Here, a is the constant shear rate and $\gamma(a)$ verifies the implicit equation [4]

$$a^2 = \gamma \frac{2F_2(\gamma) + 3F_1(\gamma)}{F_1(\gamma)}, \quad (15)$$

where $F_r(x) \equiv [(d/dx)x]^r F_0(x)$ and

$$F_0(x) = \frac{2}{x} \int dt t \exp(-t^2/2) K_0(2x^{-1/4} t^{1/2}), \quad (16)$$

K_0 being the zeroth-order modified Bessel function. The asymptotic series expansion of F_r is [4]

$$F_r(x) = \sum_{k=0}^{\infty} (k+1)^r (2k+1)! (2k+1)!! (-x)^k. \quad (17)$$

From the profiles (12)–(14), the local conservation equations provide the main transport properties. In particular, when conveniently scaled, the reduced shear viscosity and the reduced thermal conductivity happen to be *universal* functions of the shear rate, independently of the potential model. Furthermore, an explicit expression for the velocity distribution function f_2 has been also derived [5]. Now, our objective is to solve the kinetic equation for f_1 when tracer diffusion appears in the system.

3. Transport properties of the solute component

Let us assume that a weak molar fraction gradient ∇x_1 is introduced in the system. We are interested in deriving an explicit expression for the mutual diffusion tensor when only terms through first order in ∇x_1 are considered. In this approximation, and taking into account the mass balance equation of the solute component, one needs to take the concentration gradient parallel to both velocity and temperature gradients

to preserve the stationarity of the state, i.e., $\nabla x_1 \equiv (\partial x_1 / \partial y) \hat{\mathbf{y}}$. Therefore, under this geometry Eq. (10) becomes the steady equation

$$v_y \frac{\partial}{\partial y} f_1 = -v_{12}(f_1 - f_{12}). \tag{18}$$

In the same way as in Ref. [1], we shall solve Eq. (18) by expanding f_1 around a nonequilibrium state with arbitrarily large velocity and temperature gradients. The gradient of the molar fraction $x_1 = n_1/n_2$ will be taken as the perturbation parameter. Thus,

$$f_1 = f_1^{(k)} + \mathcal{O}(\nabla^{k+1} x_1), \tag{19}$$

where the approximation $f_1^{(k)}$ contains all the contributions up to order k in ∇x_1 , although it is a highly nonlinear function of the shear rate and the thermal gradient. As a consequence, the transport coefficients obtained from this method will be nonlinear functions of both nonequilibrium parameters. The corresponding hydrodynamic fields \mathbf{u}_{12} and T_{12} , as well as the collision frequency v_{12} must also be expanded in a similar way. By substituting these expansions into Eq. (18), one gets a hierarchy of equations for the different distributions $f_1^{(k)}$. In this paper, we only consider the two first approximations.

3.1. Zeroth-order approximation

On physical grounds, one expects that this approximation is characterized by a constant molar fraction, the absence of diffusion, i.e. $\mathbf{u}_1^{(0)} = \mathbf{u}_{12}^{(0)} = \mathbf{u}_2$, and a constant temperature ratio $\chi = T_1^{(0)}/T_2$. This parameter, which is the crucial quantity at this level of description, must be a function of the shear rate a , the mass ratio $\mu = m_2/m_1$, the force ratio $\omega \equiv \kappa_{12}/\kappa_{22}$, and the interaction parameter δ . The parameter ω can be interpreted as a measure of the size ratio σ_{12}/σ_{22} when one assigns an effective diameter σ_{ij} to the interaction between particles i and j .

In order to scale the influence of the interaction potential on the collision frequency $v_{12}^{(0)}$, it is convenient to introduce a space variable s through the relation $ds = v_{12}^{(0)}(y) dy$, where

$$v_{12}^{(0)}(y) = \omega^{(1-\delta)/2} \left(\frac{1+\mu}{2} \right)^{1/2} \left(\frac{1+\mu\chi}{1+\mu} \right)^{\delta/2} v_{22}(y). \tag{20}$$

In terms of s , we propose the same hydrodynamic profiles as the ones assumed in the case of Maxwell molecules [12], namely

$$p_{12}^{(0)} \equiv n_2 k_B T_{12}^{(0)} = \text{const.}, \tag{21}$$

$$\frac{\partial}{\partial s} u_{12,x}^{(0)} = \tilde{a} = \text{const.}, \tag{22}$$

$$\frac{\partial^2}{\partial s^2} T_{12}^{(0)} = -\frac{2m_1}{k_B} \tilde{\gamma} = \text{const.} \tag{23}$$

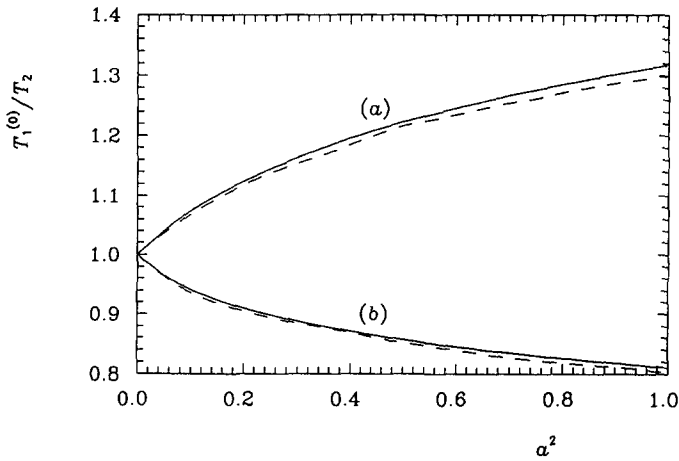


Fig. 1. Plot of the temperature ratio $\chi \equiv T_1^{(0)}/T_2$ versus the reduced shear rate for $\omega = 1$ and two values of the mass ratio $\mu \equiv m_2/m_1$: (a) $\mu = 0.5$, and (b) $\mu = 2$. The solid lines refer to Maxwell molecules ($\delta = 0$) and the dashed lines refer to hard spheres ($\delta = 1$).

These conditions imply that

$$\tilde{a} = \frac{a}{\omega^{(1-\delta)/2}[(1+\mu)/2]^{1/2}} \left(\frac{1+\mu}{1+\mu\chi} \right)^{\delta/2}, \quad (24)$$

$$\tilde{\gamma} = \frac{2\mu}{1+\mu} \frac{1}{\omega^{(1-\delta)}} [\chi + 2M(1-\chi)] \left(\frac{1+\mu}{1+\mu\chi} \right)^{\delta} \gamma, \quad (25)$$

where $M \equiv (\mu/(1+\mu)^2)$. The formal analogy between the equations for $f_1^{(0)}$ and for f_2 allows one to get the fluxes of $f_1^{(0)}$ [12]. In particular, the consistency of the solution gives $\tilde{\gamma}$ through the following implicit equation:

$$2\tilde{F}_2 + \left(3 - \frac{\tilde{a}^2}{\tilde{\gamma}} \right) \tilde{F}_1 = \frac{3}{\tilde{\gamma}} \beta, \quad (26)$$

where

$$\beta = \frac{M(1-\chi)}{\chi + 2M(1-\chi)}, \quad (27)$$

and $\tilde{F}_r \equiv F_r(\tilde{\gamma})$. Notice that in order to close Eq. (26) one must use the relations (24) and (25). The solution of the implicit equation (26) gives the temperature ratio χ as a function of a , μ , ω , and the interaction parameter δ . Even in the case of Maxwell molecules ($\delta = 0$), this solution must be obtained numerically except in some limiting cases. Thus, for small shear rates $\chi \approx 1 + \frac{2}{3} [(1-\mu^2)/\omega^{(1-\delta)}\mu]a^2$, while for large shear rates $\chi \approx 1/\mu$. These behaviors suggest that χ is hardly sensitive to the interaction potential. The temperature ratio χ is plotted in Fig. 1 as a function of the shear rate for the two extreme cases of Maxwell molecules ($\delta = 0$) and hard spheres ($\delta = 1$). We

have included two values of the mass ratio μ and for simplicity we have set $\omega = 1$. We observe that χ monotonically varies from 1 to m_1/m_2 as the shear rate increases whatever the interaction model considered is. Therefore, the mean-square velocities of each species tend to be equal (although the mean kinetic energies are different) as the mixture goes away from equilibrium. With respect to the influence of the repulsive force, Fig. 1 indicates that the general shear rate dependence of χ is not greatly affected by the power of the repulsive law, especially if $\omega \approx 1$. Beyond the linear regime and at a given value of a , we observe that the temperature ratio increases as the potential becomes softer.

Once χ is known, the velocity distribution function $f_1^{(0)}$ can be obtained. By exploiting again the formal analogy between Eqs. (18) (in the lowest order) and (11), it is easy to derive an explicit expression for $f_1^{(0)}$ from that of f_2 [5] by making the changes: $n_2 \rightarrow n_1$, $m_2 \rightarrow m_1$, $T_2 \rightarrow T_{12}^{(0)}$, and $v_{22} \rightarrow v_{12}^{(0)}$. This distribution can be written as $f_1^{(0)} = n_1(m_1/2\pi k_B T_2)^{3/2} \Phi(\xi)$, where

$$\begin{aligned} \Phi(\xi) = & \omega^{(1-\delta)/2} \left(\frac{1+\mu}{2\mu}\right)^{1/2} \left(\frac{1+\mu\chi}{1+\mu}\right)^{\delta/2} [\chi + 2M(1-\chi)]^{-3/2} \frac{2\alpha(1+\alpha)^{3/2}}{\varepsilon|\xi_y|} \\ & \times \int_{t_0}^{t_1} dt [2t - (1-\alpha)t^2]^{-5/2} \\ & \times \exp \left\{ -\omega^{(1-\delta)/2} \left(\frac{1+\mu}{2\mu}\right)^{1/2} \left(\frac{1+\mu\chi}{1+\mu}\right)^{\delta/2} \frac{2\alpha}{1+\alpha} \frac{1-t}{\varepsilon\xi_y} \right. \\ & \left. - [\chi + 2M(1-\chi)]^{-1} \frac{1+\alpha}{2t - (1-\alpha)t^2} \left[\left(\xi_x + \frac{2\alpha}{1+\alpha} \frac{1-t}{\mu^{1/2}\varepsilon} \right)^2 + \xi_y^2 + \xi_z^2 \right] \right\}. \end{aligned} \tag{28}$$

Here, $(t_0, t_1) = (0, 1)$ if $\xi_y > 0$ and $(t_0, t_1) = [1, 2/(1-\alpha)]$ if $\xi_y < 0$. Furthermore, $\xi = (m_1/2k_B T_2)^{1/2}(\mathbf{v} - \mathbf{u}_2)$,

$$\varepsilon = \frac{1}{v_{22}} \left(\frac{2k_B T_2}{m_2}\right)^{1/2} \frac{\partial}{\partial y} \ln T_2 \tag{29}$$

is the reduced temperature gradient and

$$\alpha = \frac{\varepsilon}{(\varepsilon^2 + 8\gamma)^{1/2}}. \tag{30}$$

Since this distribution depends on the three components of the velocity, for illustrative purposes it is convenient to define the (reduced) marginal distribution

$$\varphi(\xi_y) \equiv \frac{\int_{-\infty}^{\infty} d\xi_x \int_{-\infty}^{\infty} d\xi_z \Phi(\xi)}{\int_{-\infty}^{\infty} d\xi_x \int_{-\infty}^{\infty} d\xi_z e^{-\xi^2}}. \tag{31}$$

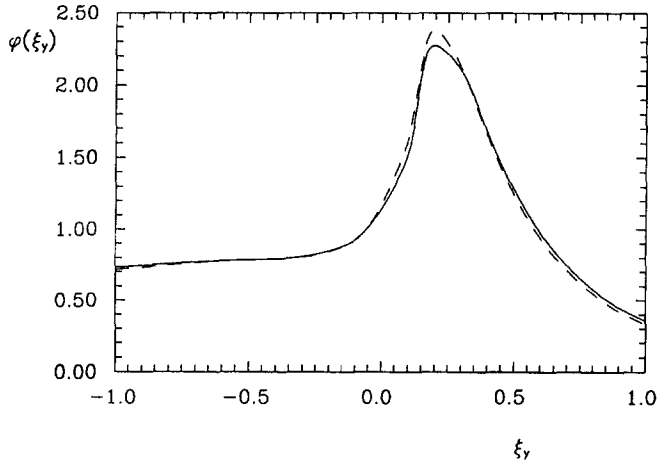


Fig. 2. Plot of the reduced distribution function $\varphi(\xi_y)$ for $a = 1$, $\varepsilon = 1$, $\omega = 1$, and $\mu = 2$. The solid line corresponds to Maxwell molecules ($\delta = 0$) and the dashed line corresponds to hard spheres ($\delta = 1$).

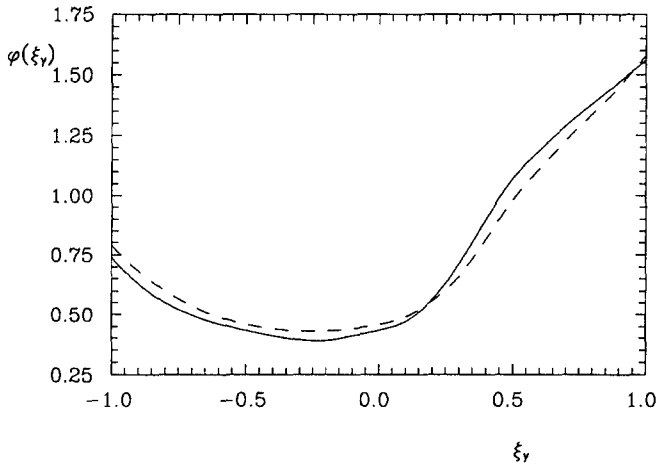


Fig. 3. The same as in Fig. 2 but for $\mu = 0.1$.

In Fig. 2 we plot $\varphi(\xi_y)$ for $\omega = 1$, $a = 1$, $\varepsilon = 1$, and $\mu = 2$, in the cases of Maxwell molecules and hard spheres. The distortion from local equilibrium [$\varphi(\xi_y) = 1$] is significant. Nevertheless, no important influence of the interaction potential on this distribution is observed. It might be due to the fact that the values considered for the nonequilibrium parameters are not sufficiently large and/or the mass ratio chosen is not very disparate. For this reason, in Fig. 3 we consider the case $\mu = 0.1$ for the same values as those in Fig. 2. For this case, $\chi \simeq 6.338$ for Maxwell molecules while $\chi \simeq 5.611$ for hard spheres. For a given interaction potential, we observe that the shape of this distribution is influenced by the value of the mass ratio. Further, it is evident that $\varphi(\xi_y)$ is more affected by the interaction considered. The discrepancies between both

distributions become more important in the region of high velocities. This concludes our discussion on this stage of approximation where no mutual diffusion is present in the mixture.

3.2. First-order approximation

The first-order approximation corresponds to a situation in which a weak molar fraction gradient coexists with arbitrarily large velocity and temperature gradients. The kinetic equation for $f_1^{(1)}$ can be written as

$$v_y \frac{\partial}{\partial s} f_1^{(1)} = -(f_1^{(1)} - f_{12}^{(1)}) - \left(\frac{v_{12}^{(1)}}{v_{12}^{(0)}} - 1 \right) (f_1^{(0)} - f_{12}^{(0)}), \tag{32}$$

where

$$\frac{v_{12}^{(1)}}{v_{12}^{(0)}} - 1 = \frac{\delta}{2} \frac{\mu}{1 + \mu\chi} \left(\frac{T_1^{(1)}}{T_2} - \chi \right), \tag{33}$$

$$f_{12}^{(1)} = \left[1 + \frac{m_1}{n_1 k_B T_{12}^{(0)}} \frac{1}{1 + \mu} \mathbf{V} \cdot \mathbf{j}_1^{(1)} + \left(\frac{m_1 V^2}{2k_B T_{12}^{(0)}} - \frac{3}{2} \right) \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right] f_{12}^{(0)}, \tag{34}$$

$$f_{12}^{(0)} = n_1 \left(\frac{m_1}{2\pi k_B T_{12}^{(0)}} \right)^{3/2} \exp \left(-\frac{m_1 V^2}{2k_B T_{12}^{(0)}} \right). \tag{35}$$

Here, $\mathbf{V} = \mathbf{v} - \mathbf{u}_2$,

$$\mathbf{j}_1^{(1)} = \int d\mathbf{v} \mathbf{V} f_1^{(1)} \tag{36}$$

is the flux of tracer particles, and

$$x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) = (1 - 2M) \frac{p_1^{(1)} - p_1^{(0)}}{p_{12}^{(0)}}, \tag{37}$$

where

$$p_1^{(k)} = \frac{m_1}{3} \int d\mathbf{v} V^2 f_1^{(k)} \tag{38}$$

is the partial pressure of tracer species.

The main goal of this paper is to derive the explicit expression of the tracer diffusion tensor in terms of the gradients and the parameters characterizing the mixture. This tensor is defined through $\mathbf{j}_1^{(1)}$. To evaluate this flux, let us consider the formal solution to Eq. (32) given by

$$f_1^{(1)} = \left(1 + v_y \frac{\partial}{\partial s} \right)^{-1} \left[f_{12}^{(1)} - \left(\frac{v_{12}^{(1)}}{v_{12}^{(0)}} - 1 \right) (f_1^{(0)} - f_{12}^{(0)}) \right]. \tag{39}$$

As the first term on the right-hand side of Eq. (39) does not explicitly depend on the interaction parameter δ , its contribution to the fluxes of $f_1^{(1)}$ will be formally the same as the one obtained for Maxwell molecules [1]. Consequently, beyond the Maxwell interaction, it is only necessary to evaluate the (*extra*) contributions to $\mathbf{j}_1^{(1)}$ and $p_1^{(1)}$ coming from the second term on the right-hand side of Eq. (39). This calculation is quite tedious but involves identical mathematical steps as those made in Ref. [1]. It is carried out in Appendix A. The final result is

$$j_{1,i}^{(1)} = -\frac{1 + \mu}{\mu} \frac{n_2 k_B T_2}{m_1 \tau_{12}} D_{ik}(a) \frac{\partial}{\partial r_k} x_1, \quad (40)$$

$$p_1^{(1)} - p_1^{(0)} = \frac{5}{6} \frac{(1 + \mu)^2 (1 + 2\mu)}{\mu^2} \frac{n_2 k_B^2 T_2}{m_1 \tau_{12}^2} \Omega(a) \frac{\partial T_2}{\partial y} \frac{\partial x_1}{\partial y}, \quad (41)$$

where $\tau_{12} \equiv \omega^{(1-\delta)/2} ((1 + \mu)/2)^{1/2} v_{22}$ and we have normalized the mutual diffusion tensor \mathbf{D} with respect to its Navier–Stokes value. The explicit expressions of the tensor \mathbf{D} and the function Ω are given in Appendix A.

Eq. (40) describes the mass transport of the solute (tracer) component when the solvent (bath) component is in a far from equilibrium situation. This expression can be considered as a generalization of the conventional Fick law (valid in the absence of velocity and thermal gradients). According to the symmetry of the problem, the relevant elements of the tracer diffusion tensor are D_{yy} and D_{xy} . They are given as functions of the shear rate, the mass ratio, the force constant ratio, and the interaction parameter. In the special case of Maxwell molecules ($\delta = 0$), the results derived in Ref. [1] are recovered. The fact that the mass flux does not depend on the thermal gradient (loss of thermodiffusion effect) is probably exact for Maxwell molecules (in the same way as in the linear regime), although for $\delta \neq 0$ one expects that there should exist a term proportional to ε in the expression of $\mathbf{j}_1^{(1)}$. This drawback of the model is perhaps related to the fact that the generalized GK model gives what Chapman and Cowling [9] call the first approximation to the determination of the transport coefficients. For small shear rates, the elements of the diffusion tensor behave as

$$D_{xy} \approx -\frac{1}{\omega^{(1-\delta)/2}} \left(\frac{2}{1 + \mu} \right)^{1/2} \frac{1 + 2\mu}{\mu} a, \quad (42)$$

$$D_{yy} \approx 1 - \frac{6(5\mu^2 + 18\mu + 11) - 5\delta(\mu - 7)(1 + \mu)}{15\omega^{(1-\delta)}(1 + \mu)} a^2. \quad (43)$$

Cross effects induced by the shear flow in the mass transport are measured through the off-diagonal element D_{xy} . In general, this coefficient is always negative and its magnitude increases as the mass of the tracer particles increases, irrespective of the model interaction considered. The influence of the repulsive power law is more significant as the mass of the tracer particles increases, as shown in Fig. 4 where $-D_{xy}$ is plotted versus a^2 for $\omega = 1$ and $\mu = 0.1$ in the cases of Maxwell molecules and hard spheres. As a matter of fact, $-D_{xy}$ increases as δ increases, especially in the region of small

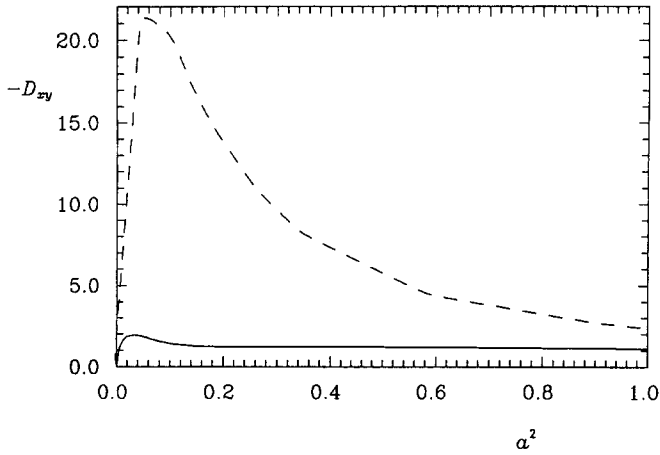


Fig. 4. Shear-rate dependence of the reduced element $-D_{xy}$ for $\omega = 1$ and $\mu = 0.1$ in the cases of Maxwell molecules (solid line) and hard spheres (dashed line).

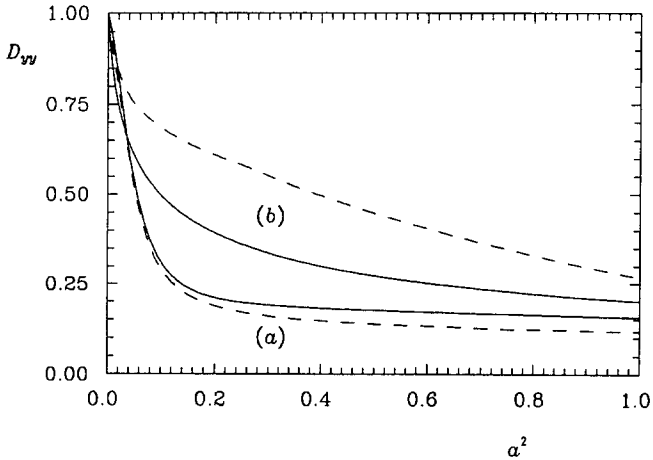


Fig. 5. Shear-rate dependence of the reduced element D_{yy} for $\omega = 1$ and two values of the mass ratio μ : (a) $\mu = 0.1$, and (b) $\mu = 10$. The solid lines refer to Maxwell molecules and the dashed lines refer to hard spheres.

shear rates. When $\mu > 1$ the value of $-D_{xy}$ is practically zero, independently of the interaction potential considered. The shear rate dependence of the diagonal element D_{yy} is plotted in Fig. 5 for the same cases as in previous figures and for two (disparate) values of the mass ratio. We observe that the mass transport along the y direction is inhibited by the presence of the shear flow. This inhibition becomes more noticeable as the mass of the solute particles is heavier than that of the solvent component. With respect to the influence of the interaction potential, we see that it is more important when the mass ratio is larger than 1. In this case and at a given value of the shear rate, D_{yy} decreases as the intermolecular repulsion becomes softer. For $\mu < 1$, the opposite

happens in the region of finite a although the effect of the power law is smaller than when $\mu > 1$.

4. Concluding remarks

In summary, we have analyzed a diffusion problem in a gaseous dilute binary mixture subjected to both velocity and temperature gradients. The starting point is a generalization of the GK model for a binary mixture where the collision frequencies ν_{ij} are in general functions of the temperatures of each species. This dependence allows one to consider general r^{-l} -intermolecular forces. The description is not restricted to any value of the mass ratio, the force constant ratio and the interaction parameter, and progress was possible here due to previous results derived for the simple case of Maxwell molecules [1], where ν_{ij} is independent of the temperature. The main transport property is the mutual diffusion tensor whose dependence on the nonequilibrium parameters and on the parameters of the mixture (mass ratio, force constant ratio, and interaction parameter) we aimed at determining.

Since the state of the solvent component is well characterized, our goal has been to solve the kinetic equation for the tracer species by means of a perturbation expansion in powers of the gradient of the molar fraction. The reference state of this expansion contains all the hydrodynamic orders in both the shear rate a and the thermal gradient ε , so that the corresponding transport coefficients are (in principle) highly nonlinear functions of a and ε . Our solution describes the two first approximations, and we have concentrated mainly in assessing the differences between our present results and those previously reported in the case of Maxwell molecules. These differences have been illustrated in the two extreme cases of Maxwell molecules and hard spheres.

Concerning the results for such systems, we conclude that the qualitative behavior of the shear-rate dependent tracer diffusion tensor is not significantly affected by the power of the interaction law considered. This conclusion is similar to the one obtained in the tracer diffusion problem under uniform shear flow [8]. At a quantitative level, it is interesting to remark that the influence of the interaction potential is more significant as the mass of the tracer species decreases, especially in the case of the off-diagonal element D_{xy} . This element measures the cross couplings due to the presence of the Couette flow. Besides, the inhibition of the mass transport along the y direction decreases as the interaction parameter increases.

Apart from obtaining the diffusion tensor, we have derived an explicit expression for the zeroth-approximation distribution function $f_1^{(0)}$. This function represents the reference state around which we perform our expansion. With respect to the dependence of $f_1^{(0)}$ on a and ε , we observe that this distribution is strongly distorted from its equilibrium value whatever be the interaction considered. Further, the influence of the interaction potential is hardly sensitive for systems of like particles. This influence increases significantly as the mass ratio differs from 1 (for instance $\mu = 0.1$).

The derivation of explicit expressions for the fluxes and the velocity distribution function involved in a certain nonequilibrium problem (such as the one analyzed here) may be of relevance in connection with computer simulations. Nevertheless, the scarcity of simulation data for mutual diffusion under steady planar Couette flow in the low-density regime does not allow a comparison with our predictions. We expect that the results presented in this paper can stimulate the performance of simulations of tracer diffusion in Couette flow.

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Appendix A. Extra contributions to the mass flux and partial pressure

In this appendix we calculate the (*extra*) contributions to $\mathbf{j}_1^{(1)}$ and $p_1^{(1)}$ coming from the second term on the right-hand side of Eq. (39). In the same way as the Maxwell description [1], we assume (to be verified later) that $\partial_s^2 x_1 (T_{12}^{(1)}/T_{12}^{(0)}) = 0$.

Let us start with the new contribution to the x component of the mass flux vector. It is proportional to the integral

$$\begin{aligned}
 & - \int d\mathbf{v} V_x (1 + v_y \partial_s)^{-1} \left(\frac{T_1^{(1)}}{T_2} - \chi \right) (f_1^{(0)} - f_{12}^{(0)}) \\
 & = \sum_{k=0}^{\infty} (-\partial_s)^k \int d\mathbf{v} \left(\frac{T_1^{(1)}}{T_2} - \chi \right) (V_x + u_{12,x}^{(0)}) V_y^k (f_1^{(0)} - f_{12}^{(0)}) \\
 & = \tilde{a} \sum_{k=0}^{\infty} (k+1) (-\partial_s)^k \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \int d\mathbf{v} V_y^{k+1} (f_1^{(0)} - f_{12}^{(0)}). \tag{A.1}
 \end{aligned}$$

The first piece of (A.1) is given by

$$\begin{aligned}
 & \sum_{k=0}^{\infty} (k+1) (-\partial_s)^k \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \int d\mathbf{v} V_y^{k+1} \sum_{l=0}^{\infty} (-\partial_s)^l V_y^l f_{12}^{(0)} \\
 & = \sum_{k=0}^{\infty} (k+1) \int d\mathbf{v} V_y^{k+1} \left\{ x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) (-\partial_s)^k \right. \\
 & \quad \left. - k \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] (-\partial_s)^{k-1} \right\} \sum_{l=0}^{\infty} (-\partial_s)^l V_y^l \varphi_{12}^{(0)}
 \end{aligned}$$

$$\begin{aligned}
 &= x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \sum_{k=0}^{\infty} (k+1)(2k+3)(2k+1)!! (-\partial_s)^{2k+1} n_2 (k_B T_{12}^{(0)}/m_1)^{k+1} \\
 &\quad - \frac{2}{3} \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \sum_{k=0}^{\infty} (2k+1)(2k^2+5k+3)(2k+1)!! \\
 &\quad \times \partial_s^{2k} n_2 (k_B T_{12}^{(0)}/m_1)^{k+1},
 \end{aligned} \tag{A.2}$$

where $\varphi_{12}^{(0)} \equiv f_{12}^{(0)}/x_1$ and only terms up to first order in $\partial_s x_1$ have been retained. Now, taking into account Eq. (23), one gets the result

$$\begin{aligned}
 &-\frac{2}{3} \frac{p_{12}^{(0)}}{m_1} \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \sum_{k=0}^{\infty} (2k^2+5k+3)(2k+1)!(2k+1)!! (-\tilde{\gamma})^k \\
 &= -\frac{2}{3} \frac{p_{12}^{(0)}}{m_1} (2\tilde{F}_2 + \tilde{F}_1) \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right],
 \end{aligned} \tag{A.3}$$

where use has been made of the functions $F_r(\tilde{\gamma})$ defined in Eqs. (16) and (17). Here, for the sake of brevity we have called $\tilde{F}_r \equiv F_r(\tilde{\gamma})$. Similarly, the second piece in Eq. (A.1) can be computed as

$$\begin{aligned}
 &\sum_{k=0}^{\infty} (k+1)(-\partial_s)^k x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \int d\mathbf{v} V_y^k \varphi_{12}^{(0)} \\
 &= -\partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \sum_{k=0}^{\infty} (2k+1)(2k+2)(2k+1)!! \partial_s^{2k} n_2 (k_B T_{12}^{(0)}/m_1)^{k+1} \\
 &= -2 \frac{p_{12}^{(0)}}{m_1} \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \sum_{k=0}^{\infty} (k+1)(2k+1)!(2k+1)!! (-\tilde{\gamma})^k \\
 &= -2 \frac{p_{12}^{(0)}}{m_1} \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \tilde{F}_1.
 \end{aligned} \tag{A.4}$$

Putting together *all* the contributions (those coming from the Maxwell case, Ref. [1], plus those given from Eqs. (A.3) and (A.4)), the x component of the mass flux can be written as

$$\begin{aligned}
 j_{1,x}^{(1)} &= \frac{1}{1+\mu} (1 - 2\tilde{\gamma}\tilde{F}_1) + 2 \frac{p_{12}^{(0)}}{m_1} \tilde{a} \tilde{F}_1 \partial_s x_1 - \frac{\tilde{a}}{1+\mu} \tilde{F}_0 j_{1,y}^{(1)} \\
 &\quad + 2 \frac{p_{12}^{(0)}}{m_1} \tilde{a} \tilde{F}_2 \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \\
 &\quad - \frac{2}{3} \frac{p_{12}^{(0)}}{m_1} \frac{\delta\mu}{1+\mu\chi} \tilde{a} \left(\chi + \frac{2M}{1-2M} \right) (\tilde{F}_2 - \tilde{F}_1) \partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right],
 \end{aligned} \tag{A.5}$$

where in the last term use has been made of the identity

$$\left(\frac{T_1^{(1)}}{T_2} - \chi\right) = \left(\chi + \frac{2M}{1 - 2M}\right) \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1\right). \tag{A.6}$$

The new contributions to the y component of the mass flux can be obtained by following similar mathematical steps as those made for $j_{1,x}^{(1)}$. Thus, one has

$$\begin{aligned} & - \sum_{k=0}^{\infty} \int d\mathbf{v} V_y^{k+1} (-\partial_s)^k \left(\frac{T_1^{(1)}}{T_2} - \chi\right) (f_1^{(0)} - f_{12}^{(0)}) \\ &= \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \right] \sum_{k=0}^{\infty} (k+1)(2k+1)(2k+1)!! \partial_s^{2k} n_2 (k_B T_{12}^{(0)} / m_1)^{k+1} \\ & \quad - \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \right] \sum_{k=0}^{\infty} (2k+1)(2k+1)!! \partial_s^{2k} n_2 (k_B T_{12}^{(0)} / m_1)^{k+1} \\ &= \frac{p_{12}^{(0)}}{m_1} \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \right] (\tilde{F}_1 - \tilde{F}_0), \end{aligned} \tag{A.7}$$

Consequently, the complete expression of $j_{1,y}^{(1)}$ is

$$\begin{aligned} j_{1,y}^{(1)} &= -\frac{p_{12}^{(0)}}{m_1} \tilde{F}_0 \partial_s x_1 + \frac{j_{1,y}^{(1)}}{1 + \mu} [1 - 2\tilde{\gamma}(\tilde{F}_1 + 2\tilde{F}_2)] - \frac{p_{12}^{(0)}}{m_1} \tilde{F}_1 \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \right] \\ & \quad + \frac{p_{12}^{(0)}}{2m_1} \frac{\delta\mu}{1 + \mu\chi} \left(\chi + \frac{2M}{1 - 2M}\right) (\tilde{F}_1 - \tilde{F}_0) \partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1\right) \right]. \end{aligned} \tag{A.8}$$

Since $\partial_s j_{1,y}^{(1)} = 0$, Eqs. (A.5) and (A.8) imply that $\partial_s j_{1,x}^{(1)} = 0$ and $\partial_s^2 x_1 (T_{12}^{(1)} / T_{12}^{(0)}) = 0$, as previously assumed.

Let us consider the new contribution to the partial pressure. It is proportional to the integral

$$- \sum_{k=0}^{\infty} \int d\mathbf{v} V^2 V_y^k (-\partial_s)^k \left(\frac{T_1^{(1)}}{T_2} - \chi\right) (f_1^{(0)} - f_{12}^{(0)}). \tag{A.9}$$

The first piece of Eq. (A.9) is given by

$$\begin{aligned} & \sum_{k=0}^{\infty} \int d\mathbf{v} V^2 (-\partial_s)^k V_y^k x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \sum_{l=0}^{\infty} (-\partial_s)^l V_y^l \varphi_{12}^{(0)} \\ &= x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \sum_{k=0}^{\infty} (k+1) \int d\mathbf{v} V^2 V_y^k (-\partial_s)^k \varphi_{12}^{(0)} \\ & \quad - \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi\right) \right] \sum_{k=0}^{\infty} \frac{(k+1)(k+2)}{2} \int d\mathbf{v} V^2 V_y^{k+1} (-\partial_s)^k \varphi_{12}^{(0)}. \end{aligned} \tag{A.10}$$

Since V^2 is a quadratic function of the variable s , one has the following operator identity:

$$\partial_s^k V^2 = V^2 \partial_s^k - 2\tilde{a}k\partial_s^{k-1} - \tilde{a}^2 k(k-1)\partial_s^{k-2}. \quad (\text{A.11})$$

By using this identity and taking into account the symmetry of the integrals over \mathbf{v} , Eq. (A.10) can be rewritten as

$$\begin{aligned} & x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \left[\sum_{k=0}^{\infty} (k+1)(-\partial_s)^k \int d\mathbf{v} V^2 V_y^k \varphi_{12}^{(0)} \right. \\ & + \tilde{a}^2 \sum_{k=0}^{\infty} (k+1)(k+2)(k+3)(-\partial_s)^k \int d\mathbf{v} V_y^{k+2} \varphi_{12}^{(0)} \left. - \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \right] \\ & \times \left[\sum_{k=0}^{\infty} \frac{(k+1)(k+2)}{2} (-\partial_s)^k \int d\mathbf{v} V^2 V_y^{k+1} \varphi_{12}^{(0)} \right. \\ & + \tilde{a}^2 \sum_{k=0}^{\infty} \frac{(k+1)(k+2)(k+3)(k+4)}{2} (-\partial_s)^k \int d\mathbf{v} V_y^{k+3} \varphi_{12}^{(0)} \left. \right] \\ & = x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \frac{P_{12}^{(0)}}{m_1} \left[\sum_{k=0}^{\infty} (2k)!(2k+3)!(-\tilde{\gamma})^k \right. \\ & \left. + 2\tilde{a}^2 \sum_{k=0}^{\infty} (2k+3)(k+1)(2k+1)!(2k+1)!(-\tilde{\gamma})^k \right] \\ & + \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \frac{k_B P_{12}^{(0)}}{2m_1^2} \partial_s T_{12}^{(0)} \left[\sum_{k=0}^{\infty} (k+1)(2k+2)!(2k+5)!(-\tilde{\gamma})^k \right. \\ & \left. + 2\tilde{a}^2 \sum_{k=0}^{\infty} (k+1)(k+2)(2k+3)(2k+5)(2k+2)!(2k+3)!(-\tilde{\gamma})^k \right] \\ & = x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \frac{P_{12}^{(0)}}{m_1} [3 - 2\tilde{\gamma}(4\tilde{F}_3 + 8\tilde{F}_2 + 3\tilde{F}_1) + 2\tilde{a}^2(2\tilde{F}_2 + \tilde{F}_1)] \\ & + \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \frac{k_B P_{12}^{(0)}}{2m_1^2} \partial_s T_{12}^{(0)} [4\tilde{F}_4 + 8\tilde{F}_3 + 3\tilde{F}_2 \\ & + 2\tilde{a}^2(8\tilde{F}_6 + 28\tilde{F}_5 + 34\tilde{F}_4 + 17\tilde{F}_3 + 3\tilde{F}_2)]. \quad (\text{A.12}) \end{aligned}$$

The second piece of (A.9) can be evaluated in a similar way. It is given by

$$\begin{aligned} & \sum_{k=0}^{\infty} \int d\mathbf{v} V^2 (-\partial_s)^k V_y^k x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \varphi_{12}^{(0)} \\ & = x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \sum_{k=0}^{\infty} \int d\mathbf{v} V^2 (-\partial_s)^k V_y^k \varphi_{12}^{(0)} \end{aligned}$$

$$\begin{aligned}
 & -\partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \sum_{k=0}^{\infty} (k+1) \int d\mathbf{v} V^2 (-\partial_s)^k V_y^{k+1} \varphi_{12}^{(0)} \\
 & = x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \frac{p_{12}^{(0)}}{m_1} \left[\sum_{k=0}^{\infty} \frac{(2k)!(2k+3)!!}{(2k+1)} (-\tilde{\gamma})^k \right. \\
 & \quad \left. + 2\tilde{a}^2 \sum_{k=0}^{\infty} (k+1)(2k+1)(2k+1)!! (-\tilde{\gamma})^k \right] \\
 & \quad + \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \frac{k_B p_{12}^{(0)}}{m_1^2} \partial_s T_{12}^{(0)} \left[\sum_{k=0}^{\infty} \frac{(k+1)(2k+2)(2k+5)!!}{(2k+3)} (-\tilde{\gamma})^k \right. \\
 & \quad \left. + 2\tilde{a}^2 \sum_{k=0}^{\infty} (k+1)(k+2)(2k+3)(2k+3)!! (-\tilde{\gamma})^k \right] \\
 & = x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \frac{p_{12}^{(0)}}{m_1} [3 - 4\tilde{\gamma}(\tilde{F}_2 + \frac{3}{2}\tilde{F}_1) + 2\tilde{a}^2(\tilde{F}_1)] \\
 & \quad + \partial_s \left[x_1 \left(\frac{T_1^{(1)}}{T_2} - \chi \right) \right] \frac{2p_{12}^{(0)}k_B}{m_1^2} \partial_s T_{12}^{(0)} \\
 & \quad \times [2\tilde{F}_3 + 3\tilde{F}_2 + 2\tilde{a}^2(4\tilde{F}_5 + 8\tilde{F}_4 + 5\tilde{F}_3 + \tilde{F}_2)]. \tag{A.13}
 \end{aligned}$$

We are now ready to write the expression of the partial pressure. Taking into account again the results derived in Ref. [1] and using the relation (A.6), one finally arrives at

$$\begin{aligned}
 & \frac{1}{1-2M} x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \\
 & = \frac{k_B}{m_1} (\partial_s T_{12}^{(0)}) (\partial_s x_1) C_1 - \frac{2k_B}{p_{12}^{(0)}} \frac{1}{1+\mu} (\partial_s T_{12}^{(0)}) j_{1,y}^{(1)} C_2 + 2x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) C_3 \\
 & \quad + \frac{2k_B}{m_1} (\partial_s T_{12}^{(0)}) \partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right] C_4 + \frac{2k_B}{p_{12}^{(0)}} \frac{1}{1+\mu} (\partial_s T_{12}^{(0)}) \frac{j_{1,x}^{(1)}}{\tilde{a}} C_5 \\
 & \quad + 2\delta \frac{\mu}{1+\mu\chi} \left(\chi + \frac{2M}{1-2M} \right) x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) C_6 \\
 & \quad + \frac{k_B}{m_1} \delta \frac{\mu}{1+\mu\chi} \left(\chi + \frac{2M}{1-2M} \right) \partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right] (\partial_s T_{12}^{(0)}) C_7, \tag{A.14}
 \end{aligned}$$

where the coefficients C_i are given by

$$C_1 = \frac{1}{6\tilde{F}_1\tilde{\gamma}} [2\tilde{\gamma}(5\tilde{F}_1^2 - 4\tilde{F}_2^2) - \tilde{F}_1(\tilde{F}_0 - 1)] - \frac{2}{\tilde{F}_1\tilde{\gamma}} (\tilde{F}_1 - \tilde{F}_2)\beta, \tag{A.15}$$

$$C_2 = \frac{\tilde{F}_0}{6\tilde{F}_1} (3\tilde{F}_1 + 2\tilde{F}_2) - \frac{2}{\tilde{F}_1\tilde{\gamma}} (\tilde{F}_0 - \tilde{F}_1)\beta, \tag{A.16}$$

$$C_3 = \frac{1}{12}(\tilde{F}_0 + 5) - \frac{\tilde{\gamma}}{6\tilde{F}_1}[6\tilde{F}_0\tilde{F}_1 - (\tilde{F}_1^2 + 4\tilde{F}_2^2)] - \frac{\tilde{F}_2}{\tilde{F}_1}\beta, \quad (\text{A.17})$$

$$C_4 = \frac{1}{12\tilde{\gamma}\tilde{F}_1}[8\tilde{\gamma}\tilde{F}_2(3\tilde{F}_1 + 2\tilde{F}_2) + \tilde{F}_0(\tilde{F}_1 + \tilde{F}_2) - \tilde{F}_1^2 - \tilde{F}_2^2] - \frac{1}{8\tilde{\gamma}^2\tilde{F}_1}(\tilde{F}_0 + 2\tilde{F}_1\tilde{\gamma} + 16\tilde{F}_2\tilde{\gamma} - 1)\beta, \quad (\text{A.18})$$

$$C_5 = \frac{2\tilde{F}_2}{3\tilde{F}_1}\tilde{\gamma}(2\tilde{F}_2 + 3\tilde{F}_1) - 2\frac{\tilde{F}_2}{\tilde{F}_1}\beta, \quad (\text{A.19})$$

$$C_6 = 2\tilde{\gamma}\frac{\tilde{F}_1\tilde{F}_3 - \tilde{F}_2^2}{\tilde{F}_1} + 3\frac{\tilde{F}_2}{\tilde{F}_1}\beta, \quad (\text{A.20})$$

$$C_7 = 2\frac{\tilde{\gamma}}{\tilde{F}_1}[(\tilde{F}_2 + 7\tilde{F}_3 + 18\tilde{F}_4 + 20\tilde{F}_5 + 8\tilde{F}_6)(3\tilde{F}_1 + 2\tilde{F}_2) + \frac{\tilde{F}_1}{\tilde{\gamma}}(2\tilde{F}_3 + 2\tilde{F}_4 - \frac{3}{2}\tilde{F}_2)] - \frac{6}{\tilde{F}_1}(\tilde{F}_2 + 7\tilde{F}_3 + 18\tilde{F}_4 + 20\tilde{F}_5 + 8\tilde{F}_6)\beta. \quad (\text{A.21})$$

The coefficients C_1 – C_5 have been previously obtained in Ref. [1]. Eqs. (A.5), (A.8), and (A.14) are coupled. Derivation of both sides of Eq. (A.14) with respect to s leads to

$$\begin{aligned} & \frac{1}{1-2M}\partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right] \\ &= -2\tilde{\gamma}C_1\partial_s x_1 + \frac{m_1}{p_{12}^{(0)}}\frac{4}{1+\mu}\tilde{\gamma}C_2j_{1,y}^{(1)} + 2C_3\partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right] \\ & \quad - 4\tilde{\gamma}C_4\partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right] - \frac{m_1}{p_{12}^{(0)}}\frac{4}{1+\mu}\tilde{\gamma}C_5\frac{j_{1,x}^{(1)}}{\tilde{a}} \\ & \quad + 2\delta\frac{\mu}{1+\mu\chi} \left(\chi + \frac{2M}{1-2M} \right) (C_6 - \tilde{\gamma}C_7)\partial_s \left[x_1 \left(\frac{T_{12}^{(1)}}{T_{12}^{(0)}} - 1 \right) \right]. \end{aligned} \quad (\text{A.22})$$

From Eqs. (A.5), (A.8), and (A.22), the explicit expression of the mass flux can be obtained. This flux can be written in the form of a generalized Fick law, Eq. (40), where the relevant elements of the tracer diffusion tensor are given by

$$D_{yy} = [\chi + 2M(1-\chi)] \left(\frac{1+\mu}{1+\mu\chi} \right)^{\delta/2} \mu \frac{R_1}{R_2}, \quad (\text{A.23})$$

$$D_{xy} = [\chi + 2M(1-\chi)] \{ R_4 D_{yy} + 2[\chi + 2M(1-\chi)]\mu R_5 \} \frac{\tilde{a}}{R_3}, \quad (\text{A.24})$$

where we have introduced the functions

$$\begin{aligned}
 R_1 = & 24C_5\tilde{\gamma}\lambda(\tilde{F}_0\tilde{F}_2 - \tilde{F}_1^2) - 3(2\tilde{F}_1\tilde{\gamma} + \mu)[2C_1\tilde{F}_1\tilde{\gamma}\lambda + \tilde{F}_0(2C_3\lambda - 4C_4\tilde{\gamma}\lambda + 1)] \\
 & + \frac{\delta\alpha\mu}{1 + \mu\chi}\tilde{\gamma}\{3(2\tilde{F}_1\tilde{\gamma} + \mu)[C_1(\tilde{F}_0 - \tilde{F}_1) + 2\tilde{F}_0(C_6 - \tilde{\gamma}C_7)] \\
 & + 4C_5[\tilde{F}_0(2\tilde{F}_1 + \tilde{F}_2) - 3\tilde{F}_1^2]\}, \tag{A.25}
 \end{aligned}$$

$$\begin{aligned}
 R_2 = & 3(2\tilde{F}_1\tilde{\gamma} + \mu)[4C_2\tilde{F}_1\tilde{\gamma}\lambda - (2\tilde{F}_1\tilde{\gamma} + 4\tilde{F}_2\tilde{\gamma} + \mu)(2C_3\lambda - 4C_4\tilde{\gamma}\lambda + 1)] \\
 & + 12C_5\tilde{\gamma}\lambda[\tilde{F}_0\tilde{F}_1 + 2\tilde{F}_2(2\tilde{F}_1\tilde{\gamma} + 4\tilde{F}_2\tilde{\gamma} + \mu)] \\
 & - 2\frac{\delta\alpha\mu}{1 + \mu\chi}\{3C_2(2\tilde{F}_1\tilde{\gamma} + \mu)(\tilde{F}_0 - \tilde{F}_1)\tilde{\gamma} + C_5\tilde{\gamma}[3\tilde{F}_0^2 - 3\tilde{F}_0\tilde{F}_1 \\
 & + 2(2\tilde{F}_1\tilde{\gamma} + 4\tilde{F}_2\tilde{\gamma} + \mu)(\tilde{F}_1 - \tilde{F}_2)] \\
 & - 3[4\tilde{F}_1^2\tilde{\gamma}^2 + 4\tilde{F}_1\tilde{\gamma}(2\tilde{F}_2\tilde{\gamma} + \mu) + \mu(4\tilde{F}_2\tilde{\gamma} + \mu)](C_6 - \tilde{\gamma}C_7)\}, \tag{A.26}
 \end{aligned}$$

$$\begin{aligned}
 R_3 = & 24C_5\tilde{F}_2\tilde{\gamma}\lambda - 3(2\tilde{F}_1\tilde{\gamma} + \mu)(2C_3\lambda - 4C_4\tilde{\gamma}\lambda + 1) \\
 & - 2\frac{\delta\alpha\mu}{1 + \mu\chi}[4C_5\tilde{\gamma}(\tilde{F}_1 - \tilde{F}_2) - 3(2\tilde{F}_1\tilde{\gamma} + \mu)(C_6 - \tilde{\gamma}C_7)], \tag{A.27}
 \end{aligned}$$

$$\begin{aligned}
 R_4 = & 12\tilde{\gamma}\lambda(2C_2\tilde{F}_2 - C_4\tilde{F}_0) + \tilde{F}_0(2C_3\lambda + 1) \\
 & - 2\frac{\delta\alpha\mu}{1 + \mu\chi}[4C_2\tilde{\gamma}(\tilde{F}_1 - \tilde{F}_2) + 3\tilde{F}_0(C_6 - \tilde{\gamma}C_7)], \tag{A.28}
 \end{aligned}$$

$$\begin{aligned}
 R_5 = & 3\tilde{F}_1 + 6C_3\tilde{F}_1\lambda - 6\lambda\tilde{\gamma}(2C_4\tilde{F}_1 - C_1\tilde{F}_2) \\
 & - \frac{\delta\alpha\mu}{1 + \mu\chi}[2C_1\tilde{\gamma}(\tilde{F}_1 - \tilde{F}_2) + 6\tilde{F}_1(C_6 - \tilde{\gamma}C_7)]. \tag{A.29}
 \end{aligned}$$

In these expressions, $\lambda \equiv 2M - 1 = -(1 + \mu)^2/(1 + \mu)^2$. In the particular case of Maxwell molecules ($\delta = 0$), previous results are recovered [1].

From the knowledge of the mass flux, the partial pressure can be also obtained. It can be written in the form (41), where Ω is

$$\begin{aligned}
 \Omega = & \frac{6}{5} \frac{\mu}{(1 + \mu)^2(1 + 2\mu)} [\chi + 2M(1 - \chi)] \frac{1}{R_6} \\
 & \times \left\{ \left(\frac{1 + \mu}{1 + \mu\chi} \right)^{\delta/2} [\chi + 2M(1 - \chi)]\mu C_1 + 2 \left(C_2 D_{yy} - C_5 \frac{D_{xy}}{\tilde{a}} \right) \right\}, \tag{A.30}
 \end{aligned}$$

where

$$R_6 = 1 + 2\lambda(C_3 - 2\tilde{\gamma}) + 2\frac{\delta\mu}{1 + \mu\chi}[\chi + 2M(1 - \chi)](C_6 - \tilde{\gamma}C_7). \tag{A.31}$$

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