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Tracer diffusion in shear flow

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The Boltzmann-Lorentz equation for Maxwell molecules is used to study tracer diffusion in uniform shear flow. It is shown that some values of the mass ratio may prevent the establishment of a hydrodynamic regime. In the region where a hydrodynamic solution exists, a diffusion tensor has been derived by considering terms up to first order in the tracer concentration gradient. This tensor is a highly nonlinear function of both the shear rate and the mass ratio. A comparison with earlier results has been performed.

The study of transport properties and fluctuations in nonequilibrium systems has been a subject of interest for many years. In particular, the case of uniform shear flow (USF) has provided an appropriate framework to discuss such properties for tagged particles in dilute nonequilibrium gases. This problem has been addressed for mechanically identical particles by Marchetti and Dufty [1], who were interested in the study of fluctuations, and more recently by Garzó, Santos, and Brey [2] who provided an explicit expression for the nonlinear shear-rate-dependent self-diffusion tensor. On the other hand, for unequal masses in the Fokker-Planck limit, Rodríguez, Salinas-Rodríguez and Dufty [3] also obtained a shear-rate-dependent diffusion tensor using a generalized Green-Kubo formalism [4]. It must be pointed out that all of these results refer to Maxwell molecules for which an exact solution of the Boltzmann equation is known [5]. Further, other than for these two limits, namely self-diffusion and Fokker-Planck, to our knowledge there has not been a detailed study of diffusion in shear flow for any mass ratio in the context of the Boltzmann equation.

The main aim of this report is to extend the aforementioned results to the case of binary mixtures in which the masses of the components are arbitrary. Due to the technical difficulties embodied in the formulation of this general problem, we have chosen to study a case which shares the simplicity of the tagged particle problem and yet introduces a new ingredient into the dynamics (the mass ratio) that yields not only a generalization but also a richer perspective to previously known results. This case is that of a dilute gas mixture composed of Maxwell molecules in which one of the components, say component 1, is present in tracer concentration, namely $n_1 \ll n_2$, where the n_i $(i=1,2)$ is the number density of species i. We also assume for simplicity that the tracer particles and the particles of the excess component interact via the same force law as holds between particles of the excess component, namely the intermolecular potentials are $V(r)=k/r^4$. Our choice has been motivated by the many interesting results that have been derived for mixtures with one tracer component in linear transport theory, in which the assumption of the tracer limit has played a crucial role in simplifying the calculations [6].

In the tracer limit it is reasonable to expect that the excess component is not appreciably disturbed by the presence of the tracer particles. Also in this limit collisions between tracer particles can be neglected. Therefore the kinetic equations for describing USF in this system reduce to a Boltzmann-Lorentz equation for the velocity distribution of the tracer particles $f_1(\mathbf{r},\mathbf{v}_1,t)$ of the form

$$\frac{\partial f_1}{\partial t}+\mathbf{v}_1\cdot\nabla f_1=J[f_1,f_2] , \tag{1}$$

where $\mathbf{v}_1$ is the molecular velocity of species 1 and J is the usual Boltzmann-Lorentz collision operator. Furthermore, the velocity distribution function of the excess component f_2 satisfies the nonlinear Boltzmann equation corresponding to USF, which is the other kinetic equation required to completely specify the problem. The USF is a macroscopic state characterized by a uniform density and temperature and a velocity field given by $\mathbf{u}_2=\mathbf{a}\cdot\mathbf{r}$, where the matrix $\mathbf{a}$ is defined through $a_{ij}=a\delta_{ix}\delta_{jy}$, where a is the (constant) shear rate. This state is nonstationary since the temperature increases in time at a rate determined by the xy component of the irreversible pressure tensor

$$\frac{dT_2}{dt}+\frac{2}{3n_2k_B}aP_{2,xy}=0 , \tag{2}$$

where in the long time limit (hydrodynamic regime) $P_{2,xy}$ is given by [1,5]

$$\begin{aligned}P_{2,xy}=P_{2,yx}&=\int d\mathbf{v}_2 m_2 V_{2x}V_{2y}f_2\\ &=-p_2\frac{3}{2}\frac{\lambda}{a^*} ,\end{aligned} \tag{3}$$

where m_2 is the molecular mass of the excess component, $\mathbf{v}_2$ its molecular velocity, and $\mathbf{V}_2=\mathbf{v}_2-\mathbf{a}\cdot\mathbf{r}$ is the peculiar velocity of species 2. Here $p_2=n_2k_BT_2=P_{2,kk}/3$ is the partial pressure of component 2 and the intermediate equality serves to define the "temperature" of species 2. As a matter of fact, $\mathbf{u}_2$ and T_2 in the tracer limit coincide with the velocity and temperature of the mixture seen as a whole denoted simply by $\mathbf{u}$ and T. Further, $\lambda=\frac{4}{3}\sinh^2[\frac{1}{6}\cosh^{-1}(1+9a^{*2})]$, $a^*=a/\nu_0$ is the reduced shear rate, and $\nu_0=1.85\pi n_2(k/m_2)^{1/2}$ is an eigenvalue of the Boltzmann operator. It must be noticed that the knowledge of the moments of the velocity distribution function f_2 allows one to solve the Boltzmann-Lorentz equation (1) when diffusion of the tracer particles in the excess component gas takes place. This simplifying feature of the Maxwell interaction is not present for other intermolecular potentials, thus rendering the formulation of diffusion in shear flow for a general interaction a much more complicated problem even in the tracer limit.

In order to solve the Boltzmann-Lorentz equation (1), it is convenient to use the peculiar velocity to introduce a rest frame of reference in which the velocity distribution function of the excess component f_2 is uniform. Therefore, Eq. (1) may be rewritten as

$$\frac{\partial f_1}{\partial t}+(V_{1i}+a_{ij}r_j)\frac{\partial f_1}{\partial r_i}-a_{ij}V_{1j}\frac{\partial f_1}{\partial V_{1i}}=J[f_1,f_2]\ , \tag{4}$$

where $V_{1i}=v_{1i}-a_{ij}r_j$.

It must be pointed out that the right-hand side of Eq. (4) depends implicitly on the mass ratio $\mu=m_2/m_1$. This fact has been used by Rodríguez, Salinas-Rodríguez, and Dufty [3] to expand the Boltzmann-Lorentz operator in the limit of small μ, resulting in a second-order differential operator of the Fokker-Planck form. As a consequence, they are able to determine the distribution function f_1, and hence also the form of the diffusion tensor as a function of the shear rate in this limit. While this approach is perhaps the most natural for small μ, it cannot be generalized for an arbitrary value of μ. Therefore, since our interest lies in assessing the combined effects of mass ratio and shear rate in tracer diffusion, we will pursue a different route. Following the perturbative scheme presented in Ref. [2], namely a Chapman-Enskog type of expansion around a time-dependent nonequilibrium state (with arbitrary shear rate) to be determined consistently later, we assume that

$$f_1=f_1^{(0)}+\epsilon f_1^{(1)}+\epsilon^2 f_1^{(2)}+\cdots\ , \tag{5}$$

where ϵ is an auxiliary parameter measuring the inhomogeneities of the concentration of the tracer species. It is worth emphasizing that the different approximations $f_1^{(k)}$ are of order k in ϵ, but retain all orders in the shear rate. In this paper we will restrict the calculations to first order in ϵ.

To zeroth order one gets

$$\frac{\partial}{\partial t}f_1^{(0)}-a_{ij}V_{1j}\frac{\partial}{\partial V_{1i}}f_1^{(0)}=J[f_1^{(0)},f_2]\ . \tag{6}$$

No closed-form solution for $f_1^{(0)}$ can be obtained from Eq. (6). However, since the moments of f_2 are known, one can also derive the corresponding moments of $f_1^{(0)}$ for the Maxwell interaction. Therefore, taking moments in Eq. (6) we find that n_1 is constant, that the macroscopic velocity field $\mathbf{u}_1=\mathbf{u}_2$, and that the time dependence of the "temperature" T_1 ($p_1=n_1k_BT_1=P_{1,kk}/3$) is governed by the xy component of the pressure tensor $\overleftrightarrow{\mathbf{P}}_1$. The latter quantity is defined by

$$P_{1,ij}=\int d\mathbf{v}_1 m_1 V_{1i}V_{1j}f_1^{(0)}\ , \tag{7}$$

so that from Eq. (6) it follows that

$$\left[\frac{\partial}{\partial t}+\alpha\right]P_{1,ij}+a_{ik}P_{1,kj}+a_{jk}P_{1,ik}-\beta p_1\delta_{ij}=\frac{n_1}{n_2}\left(\gamma P_{2,ij}+\frac{\beta}{\mu}p_2\delta_{ij}\right)\ , \tag{8}$$

where $\alpha=2(1+\mu)^{-3/2}(\nu_1+\mu\nu_2)$, $\beta=2\mu(1+\mu)^{-3/2}\nu_2$, and $\gamma=2(1+\mu)^{-3/2}(\nu_1-\nu_2)$. Here, we have introduced the constants $\nu_1=0.91\mu\nu_0$ and $\nu_2=0.70\mu\nu_0$ to parallel the notation of Ref. [3]. In the long time limit, the dominant contribution to the general solution to Eq. (8) can be written in the form

$$P_{1,ij}(t)=n_1k_BT(t)(A_{ij}e^{-(\lambda\nu_0-k_1)t}+B_{ij})\ , \tag{9}$$

where

$$A_{ij}=\frac{C}{(k_1-k_2)(k_1-k_3)}\times[(k_1+\alpha)^2\delta_{ij}-(k_1+\alpha)(a_{ij}+a_{ji})+2a_{ik}a_{jk}]\ , \tag{10}$$

$$k_1=\beta-\alpha+\frac{4\beta}{3}\sinh^2\left[\frac{1}{6}\cosh^{-1}\left[1+9\frac{a^2}{\beta^2}\right]\right]\ , \tag{11}$$

$$k_2=-\tfrac{1}{2}(k_1+2\alpha-\beta)-\frac{i}{\sqrt{3}}\beta\sinh^2\left[\frac{1}{6}\cosh^{-1}\left[1+9\frac{a^2}{\beta^2}\right]\right]\ , \tag{12}$$

$k_3=k_2^\dagger$, the dagger denoting complex conjugation, C is a constant related to the chosen initial condition, and the nonzero components of the tensor $\overleftrightarrow{\mathbf{B}}$ are given by

$$B_{xx}=\frac{1}{D(\lambda)}\frac{1}{1+\lambda}\{\gamma\nu_0(\lambda\nu_0+\alpha)^2+3\lambda\nu_0\gamma(2\lambda\nu_0+\alpha+\nu_0)(\lambda\nu_0+\alpha-\tfrac{2}{3}\beta)+\frac{\beta\nu_0}{\mu}(1+\lambda)[(\lambda\nu_0+\alpha)^2+2a^2]+2a^2\gamma\nu_0\}\ , \tag{13}$$

$$B_{yy}=B_{zz}=\frac{1}{D(\lambda)}\frac{1}{1+\lambda}\left[\gamma\nu_0(\lambda\nu_0+\alpha)^2+\lambda\nu_0\beta\gamma(2\lambda\nu_0+\alpha+\nu_0)+\frac{\beta\nu_0}{\mu}(1+\lambda)(\lambda\nu_0+\alpha)^2\right]\ , \tag{14}$$

$$B_{xy}=B_{yx}=-\frac{a^*}{D(\lambda)}\frac{1}{(1+\lambda)^2}\left[\gamma\nu_0(\lambda\nu_0+\alpha-\beta)(\lambda\nu_0+\alpha)+\gamma\nu_0^2(1+\lambda)(\lambda\nu_0+\alpha+\beta)+\frac{\beta\nu_0^2}{\mu}(1+\lambda)^2(\lambda\nu_0+\alpha)\right]\ , \tag{15}$$

with

$$D(\lambda)=\nu_0[(\lambda\nu_0+\alpha)^2(\lambda\nu_0+\alpha-\beta)-\tfrac{2}{3}\beta a^2] .$$

A hydrodynamic expression for $\overleftrightarrow{\mathbf{P}}_1$, independent of the initial conditions, is expected to hold after a transient period. In view of Eq. (9) it is clear that the combined effect of mass ratio and shear rate may prevent this from happening if $k_1 \geq \lambda\nu_0$. This is shown in Fig. 1 where we have determined the region of validity of the hydrodynamic solution (hatched zone). Below $a^* \simeq 8.8$, a hydrodynamic solution always exists for any μ, while for $\mu \leq 1$ this region extends up to arbitrary values of the shear rate. Therefore, for practical purposes, one may conclude that the system attains a normal solution for reasonable values of a^*. Hence, from now onwards the first term on the right-hand side of Eq. (9) will be neglected. Notice finally that in the hydrodynamic stage and in contrast with what occurs in the self-diffusion case [2], for any other mass ratio the temperatures of both species are in general different. This concludes our discussion of the zeroth-order approximation to f_1 where it is clear that no diffusion takes place.

To first order it is found that

$$\lambda\nu_0 T\frac{\partial}{\partial T}f_1^{(1)}+V_{1i}\frac{\partial}{\partial r_i}f_1^{(0)}-a_{ij}V_{1j}\frac{\partial}{\partial V_{1i}}f_1^{(1)} =J[f_1^{(1)},f_2] . \qquad (16)$$

Since our main interest lies in computing the diffusion tensor, we may manipulate Eq. (16) to arrive at

$$\lambda\nu_0 T\frac{\partial}{\partial T}j_{1i}+\frac{k_BT}{m_1}B_{ik}\frac{\partial}{\partial r_k}n_1+a_{ik}j_{1k}=-\nu_3 j_{1i} , \qquad (17)$$

where we have introduced the flux of tracer particles $\mathbf{j}_1=\int d\mathbf{v}_1\mathbf{V}_1 f_1^{(1)}$ and $\nu_3=(1+\mu)^{-1/2}\nu_1$. The hydrodynamic solution (long time limit) to Eq. (17) yields a generalized Fick's law of the form

$$j_{1i}=-\frac{k_BT}{m_1\nu_3}D_{ik}\frac{\partial}{\partial r_k}n_1 , \qquad (18)$$

with the nondimensional diffusion tensor given by

$$D_{ik}=\frac{\nu_3}{\lambda\nu_0+\nu_3}\left[\delta_{il}-\frac{a_{il}}{\lambda\nu_0+\nu_3}\right]B_{lk} . \qquad (19)$$

For $a=0$, $D_{ik}=\delta_{ik}$, thus recovering the usual Navier-Stokes results [6]. In Fig. 2, we present the behavior of the trace $D_{kk}/3$ as a function of the reduced shear rate for different values of μ. We find that for $\mu \geq 1$, the value of this tracer coefficient decreases relative to its Navier-Stokes value for all shear rates. On the other hand, for $\mu < 1$ there is a small region of shear rates for which the opposite happens, and this becomes less and less noticeable as μ approaches one. Finally, the decay rate of the value of the coefficient becomes slower with increasing mass ratio.

Equations (18) and (19) have been derived keeping all the orders in the shear rate, and at this stage no expansion in the mass ratio has been carried out. As can be seen from Eq. (19), the shear flow induces cross effects in

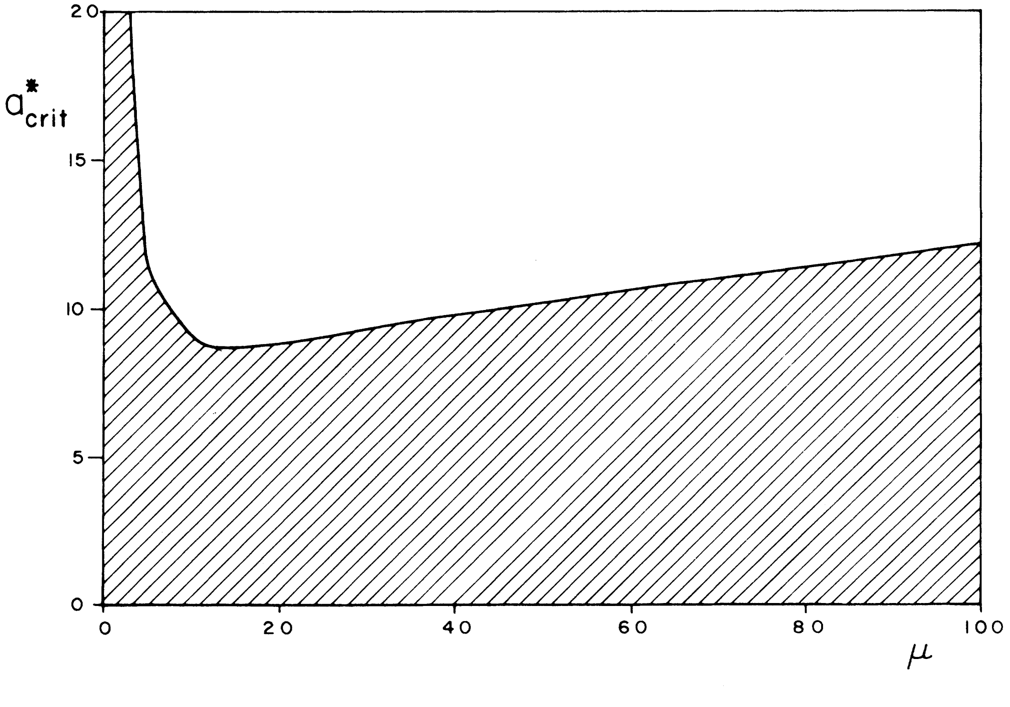

FIG. 1. Plane $a^*_{\rm crit}$-μ showing the region of validity of the hydrodynamic solution to Eq. (9). $a^*_{\rm crit}$ denotes the value of the reduced shear rate for which, given a particular μ, $\lambda\nu_0=k_1$. The hatched region corresponds to the hydrodynamic regime.

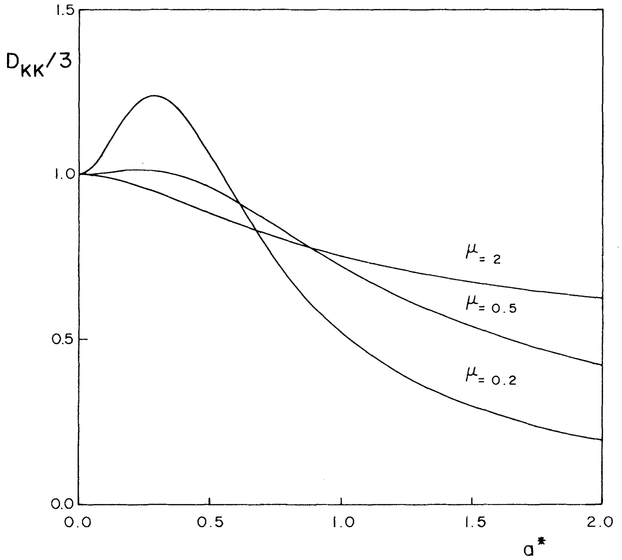

FIG. 2. Shear-rate dependence of the trace $D_{kk}/3$ for $\mu=0.2;0.5;2$.

the diffusion of tracer particles. It must be pointed out that previous results arise from Eqs. (18) and (19) by considering the appropriate limits. In particular, for $\mu=1$ we recover the self-diffusion results [2]. On the other hand, in our approach the Fokker-Planck limit corresponds to setting $\alpha=2\nu_1$, $\beta=0$ (but $\beta/\mu=2\nu_2$), $\gamma=2(\nu_1-\nu_2)$, and $\nu_3=\nu_1$ in Eqs. (13)–(15) and (19), which are the proper values for the small-mass ratio. Once this is done, the results given by Rodríguez, Salinas-Rodríguez, and Dufty [3] easily follow. In the same way we are able to consider the large-mass ratio limit (for which there are no results to our knowledge) by setting $\alpha=\beta=2\mu^{-1/2}\nu_2$, $\gamma=2\mu^{-3/2}(\nu_1-\nu_2)$, and $\nu_3=\mu^{-1/2}\nu_1$, but its explicit form is not very illuminating and hence will be omitted.

In summary, we have considered tracer diffusion in shear flow for an arbitrary ratio of the mass of the tracer to the mass of the excess component in a binary mixture of Maxwell molecules. A perturbative expansion around a nonequilibrium state with arbitrary shear rate was carried out to first order in the gradient of tracer concentration. We found that for some values of the mass ratio the system may not reach a hydrodynamic stage independent of the initial conditions. In the hydrodynamic regime, we derived an explicit expression for the diffusion tensor which is a highly nonlinear function of both the mass ratio and the shear rate. Such an expression generalizes previously known results to which it reduces in the proper limits. This provides a self-consistency test of our calculations.

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