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Effect of mass-ratio dependence of the force law for tracer diffusion in shear flow

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The Boltzmann–Lorentz equation for Maxwell molecules is used to analyze the effect of mass dependence of the force law for tracer diffusion in uniform shear flow. An observed mass dependence of intermolecular forces suitable for disparate mass binary mixtures is explicitly considered. A comparison with earlier results is carried out.

The diffusion of tracer particles in uniform shear flow for arbitrary mass ratio of the tracer to the excess component in a binary mixture has been recently analyzed. The results were derived using independently the Boltzmann–Lorentz equation[1] and well-known kinetic models[2] and the derivation was carried out for Maxwell molecules (repelling each other with intermolecular forces κ_{ij}/r^5, $i,j\equiv 1,2$). For simplicity, it was assumed that the force constants κ_{ij} were identical for all possible interactions, i.e., independent of the subscripts i and j, and hence also independent of the mass ratio. Solutions were constructed by means of a perturbation expansion around a nonequilibrium state with arbitrary shear rate. Up to first order in the tracer concentration gradient, an explicit expression for the diffusion tensor was derived. This tensor turns out to be a nonlinear function of both the shear rate and the mass ratio.

However, it has been pointed out that the assumption of the mass ratio independence of the Maxwell force constants κ_{ij} is physically unrealistic. For instance, in the case of disparate mass binary mixtures, for which the system UF_6-He is an example, Johnson[3] has suggested that the mass dependence of the intermolecular Maxwell force constants can be modeled by the law $\kappa_{ij}\propto(m_i m_j)^{1/2}$. Obviously, for other kinds of mixtures this dependence on the mass ratio may be different and further molecular parameters such as the sizes of the molecules may also be involved. The question arises then as to whether, and if so to what extent, the conclusions drawn from our previous results may be altered when a more realistic behavior for κ_{ij} is supposed. In this Brief Communication, we address this question by considering as a point of departure the kinetic description of the system at the Boltzmann level.

Let us consider a dilute gas mixture of Maxwell molecules in which one of the components, say 1, is present in tracer concentration, i.e., $n_1/n_2 \ll 1$, where n_i is the number density of species $i(i=1,2)$. In this limit, the kinetic equations for describing uniform shear flow reduce to the Boltzmann–Lorentz equation for the velocity distribution function of the tracer particles $f_1(\mathbf{r},\mathbf{V};t)$:

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

where a is the constant shear rate, $V_i=v_i-a_{ij}r_j$ is the peculiar velocity, and J is the usual Boltzmann–Lorentz collision operator. Further, the velocity distribution function of the excess component $f_2(\mathbf{V};t)$ satisfies the nonlinear Boltzmann equation in the uniform shear flow. Following the procedure presented in Ref. 1, to which we refer for all mathematical details, we solve Eq. (1) by using a perturbation method similar to the Chapman–Enskog spirit. The main characteristic of this method is that the successive approximations to the distribution function keep all the hydrodynamic orders in the shear rate a. Thus our description aims at fully taking into account the combined effects of mass ratio and shear rate in the tracer diffusion problem.

To zeroth order, one finds that the temperature of the tracer component T_1 satisfies the differential equation

$$\left(\frac{\partial}{\partial t}+\alpha-\beta\right)T_1+\frac{2}{3}aB_{xy}T=\left(\gamma+\frac{\beta}{\mu}\right)T, \tag{2}$$

where $\mu=m_2/m_1$ is the mass ratio, $\alpha=2(1+\mu)^{-3/2}(\nu_1+\mu\nu_2)$, $\beta=2\mu(1+\mu)^{-3/2}\nu_2$, and $\gamma=2(1+\mu)^{-3/2}(\nu_1-\nu_2)$. Further, the temperature of the excess component $T\propto e^{\lambda\nu_0 t}$, with $\lambda=(4/3)\sinh^2[(1/6)\cosh^{-1}(1+9a^{*2})]$, $a^*=a/\nu_0$, and the xy component of the tensor B is given by[4]

$$B_{xy}=-\frac{a^*}{D(\lambda)}\frac{1}{(1+\lambda)^2}\bigg(\gamma\nu_0(\lambda\nu_0+\alpha-\beta)(\lambda\nu_0+\alpha)+\gamma\nu_0^2(1+\lambda)(\lambda\nu_0+\alpha+\beta\lambda)+\frac{\beta\nu_0^2}{\mu}(1+\lambda)^2(\lambda\nu_0+\alpha)\bigg), \tag{3}$$

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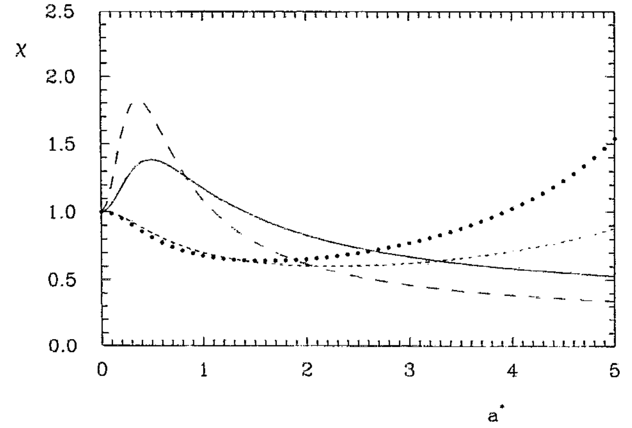

FIG. 1. Shear-rate dependence of the function $\chi(\mu,a^*)$ for several values of the dimensionless function g and the mass ratio μ: $g=\mu^{-1/4}$, $\mu=0.1$ (——); $g=1$, $\mu=0.1$ (– – –); $g=\mu^{-1/4}$, $\mu=10$ (· · ·); $g=1$, $\mu=10$ (- - -).

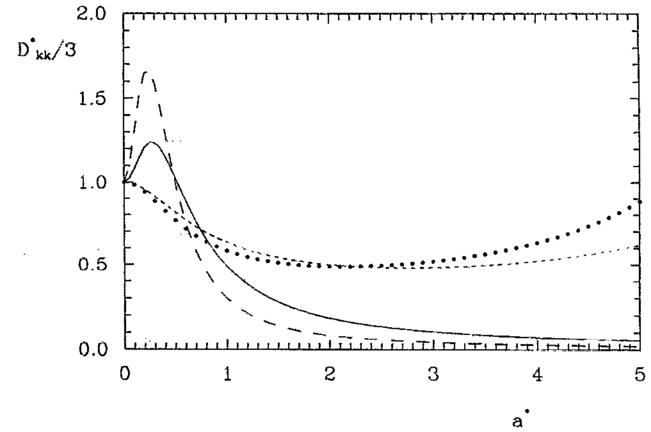

FIG. 2. Shear-rate dependence of the trace $D^*_{kk}/3$ of the dimensionless tracer diffusion tensor for the same cases as in Fig. 1.

where $D(\lambda)=\nu_0[(\lambda\nu_0+\alpha)^2(\lambda\nu_0+\alpha-\beta)-(2/3)\beta a^2]$. Here, the corresponding eigenvalues of the Boltzmann collision operator are given by

$$\nu_0=1.85\pi n_2(\kappa_{22}/m_2)^{1/2}, \tag{4}$$

$$\nu_1=0.91\mu g\nu_0, \tag{5}$$

$$\nu_2=(1/\sqrt{2})\mu g\nu_0, \tag{6}$$

where we have introduced the dimensionless function $g\equiv(\kappa_{12}/\kappa_{22})^{1/2}$.

The function g may be reasonably determined from the experimental values observed for the collision cross section. The simplest choice corresponds to assuming 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, i.e., $g=1$. This case has been considered previously.[1,2] A more realistic choice is that of supposing a mass-ratio dependence of the force law. In the case of disparate mass binary mixtures, it has been suggested[3] that g may be modeled by the law $g(\mu)=\mu^{-1/4}$. It is clear that, for other kinds of mixtures, this behavior can be modeled in a different form and include further parameters, but we will not address this feature here concentrating only on the mass-ratio dependence.

When the combined effect of mass ratio and shear rate allows that the system reaches a hydrodynamic regime (independent of the initial conditions), a normal expression for T_1 can be obtained. Under these conditions from Eq. (2), one finds that $T_1(t)=\chi(\mu,a^*)T(t)$, χ being a nonlinear function of the mass ratio and the shear rate given by

$$\chi(\mu,a^*)=\frac{\gamma+\beta/\mu-\frac{2}{3}a^*\nu_0B_{xy}}{\lambda\nu_0+\alpha-\beta}. \tag{7}$$

The shape of this function is plotted in Fig. 1 for different values of the mass ratio. Moreover, in order to illustrate the effect of μ dependence of the force law on χ, we consider independently the models for which $g=1$ and $g(\mu)=\mu^{-1/4}$. Figure 1 shows that, for a given value of μ, the general shear-rate dependence of χ is quite similar for both models of g. For $\mu=0.1$, and for small shear rates, χ increases as a^* increases, while in the region of large shear rates it decreases as a^* increases. For $\mu=10$, the opposite situation happens. However, there exist appreciable numerical differences between the values predicted by both models. Thus, for $\mu=0.1$ and $a^*<0.4$, the discrepancy comes to be around 25% whereas for $a^*>0.4$ it is around 30%. In the case of large μ ($\mu=10$), noticeable differences appear in the region of large shear rates since the discrepancy reaches the value of 42% for $a^*=5$. Further, the shape of χ for large μ suggests that these numerical differences increase as a^*. On the other hand, it must be pointed out that there are particular combinations of μ and a^* for both models for which $\chi\simeq1$. In this region, a standard Chapman–Enskog description (with only one temperature) can be adequate for describing the transport even for the disparate mass binary mixtures. From Eq. (7), it is easy to show that this will happen when

$$\tfrac{3}{2}\lambda+a^*B_{xy}=0, \tag{8}$$

which is, of course, valid for any mass-ratio dependence assumed for g. Notice that, in particular, for $\mu=1$, $\chi=1$ for any value of a^* and so one recovers the self-diffusion results.[5]

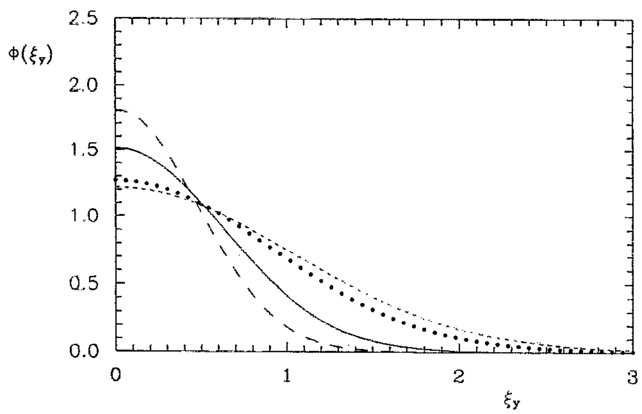

FIG. 3. Plot of the information theory distribution $\phi(\xi_y)$ for the same cases as in Fig. 1 and for a value of the shear rate $a^*=1$.

The next question we address is the effect of this extra-mass-ratio dependence on the shear-rate diffusion tensor. Proceeding in a similar way to the calculations performed in Ref. 1, an explicit expression for the dimensionless diffusion tensor D_{ij}^* is found. Its form happens to be identical to that given by Eq. (19) of Ref. 1 from which it may be obtained by replacing in the latter ν_0, ν_1, and ν_2 by its counterparts equations (4), (5), and (6), respectively. In Fig. 2, we present the behavior of the trace $D_{kk}^*/3$ as a function of the shear rate for the same values of μ and g as in Fig. 1. It is shown again that the influence of $g(\mu)$ on the diffusion of tracer particles becomes very important. In the case of small mass ratio and for $a^* < 0.25$, at a given shear rate the μ dependence of the force law inhibits the tracer diffusion, while the opposite occurs for large shear rates since the mass transport of the tracer component is enhanced because of the mass dependence of g. For large μ, opposite conclusions may be drawn out. Furthermore, the numerical values obtained from both models are again very different. For instance, for $\mu = 0.1$ the highest value for the numerical discrepancy is about 60% whereas for $\mu = 10$ it is around 30%.

Now we turn to the behavior of the distribution function. In contrast with the results derived from kinetic models,[2] here we have not been able to find explicit expressions for the velocity distribution functions. However, in an attempt to construct an approximate velocity distribution function for the tracer component, we use information theory.[6] Since we are interested in the reference state (zeroth-order approximation), we propose a distribution function $f_1^{(0)}$ that maximizes the entropy

$$S_1 = -k_B \int d\mathbf{V}\, f_1^{(0)}(\mathbf{V}) \ln f_1^{(0)}(\mathbf{V}), \tag{9}$$

subject to the constraints that the density, the velocity, and the pressure tensor components are given exactly by this distribution function.[6] One finds that $f_1^{(0)} = n_1(m_1/2k_BT)^{3/2}\psi(\xi,\mu,a^*)$, where $\xi \equiv (m_1/2k_BT)^{1/2}\mathbf{V}$,

$$\psi(\xi,\mu,a^*) = \pi^{-3/2}(\det \bar{\bar{\Gamma}})^{1/2} e^{-\bar{\bar{\Gamma}}:\xi\xi}, \tag{10}$$

and $\bar{\bar{\Gamma}} = (\mathsf{B})^{-1}$. In order to gain some insight into the features of the information theory distribution function, it is convenient to introduce the dimensionless function

$$\phi(\xi_y) = \frac{\int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_z\, \psi(\xi,\mu,a^*)}{\pi^{-3/2} \int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_z\, e^{-\xi^2}}. \tag{11}$$

For a fixed value of $a^* = 1$, we present the behavior of $\phi(\xi_y)$ as a function of ξ_y for the cases previously considered. We observe again that the velocity distribution is appreciably affected by the mass dependence of the Maxwell force constants, especially for small velocities.

In summary, we have analyzed the effect of the mass dependence of the intermolecular potentials for tracer diffusion in shear flow. The results have been obtained from the Boltzmann–Lorentz equation by using a Chapman–Enskog-like perturbation expansion. Expressions for the temperature of the tracer species and the diffusion tensor have been derived by considering terms up to first order in the tracer concentration gradient and all orders in the shear rate. We find that, in general, a two-temperature description is required but certain combinations of values of the shear rate and the mass ratio [cf. Eq. (8)] allow for a standard Chapman–Enskog description even in the case of disparate-mass mixtures. For the sake of illustration, an observed mass dependence of the force law suitable for disparate masses has been explicitly considered. It has been shown that the transport properties of the system are noticeably affected by the assumption of mass dependence for the Maxwell force constants.

Finally, it must be pointed out that the results presented in this paper are not restricted to the explicit form assumed for g. Therefore, in order to perform comparisons with computer simulations or experimental data, it would be very interesting to consider other models for g perhaps including also the sizes of the molecules. Work along this line is in progress.

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