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Transport properties in a binary mixture under shear flow

C. Marín, V. Garzó, and A. Santos
Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain
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The Boltzmann equation for a binary mixture of Maxwell molecules under uniform shear flow is exactly solved. The transport coefficients (shear viscosity and viscometric functions) are nonlinear functions of the shear rate and the parameters of the mixture (particle masses, concentrations, and force constants). The results apply for conditions arbitrarily far from equilibrium. In the particular case of mechanically equivalent particles, the Ikenberry-Truesdell solution is recovered. In the tracer limit previous results are reobtained and a transition to an alternative state is identified. In this alternative state, the tracer species has a finite contribution to the properties of the mixture.

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I. INTRODUCTION

One of the most interesting problems in statistical mechanics is the study of transport phenomena in fluids far from equilibrium. Since the general problem is very difficult to attack, it is convenient to consider specific situations which lend themselves to a tractable description. One of the most extensively studied states is the so-called uniform shear flow (USF) [1]. In this state all the hydrodynamic gradients are zero, except one (which is a constant), namely, $\partial u_x/\partial y = a = \text{const}$, where $\mathbf{u}$ is the flow velocity. The relevant transport properties are the nonlinear shear viscosity $\eta(a)$ and viscometric functions $\Psi_{1,2}(a)$. In the case of dense fluids, these quantities have been obtained by molecular dynamics simulations [2].

In the low density regime, the essential information of the system is given by the one-particle velocity distribution function $f(\mathbf{r},\mathbf{v};t)$, which obeys the nonlinear Boltzmann equation [3]. In the USF, the transport coefficients are related to the second order moments, namely, the pressure tensor P. In order to get P as a function of the shear rate a, one needs, in general, to solve the infinite hierarchy of moments. Nevertheless, this hierarchy can be recursively solved only in the special case of Maxwell molecules, i.e., particles interacting via a repulsive r^{-4} potential. For a *single* gas of Maxwell molecules, Ikenberry and Truesdell (IT) [4] obtained the time evolution of P for arbitrary a. The hydrodynamic quantities $\eta(a)$ and $\Psi_{1,2}(a)$ are then obtained from the long-time limit of P. The shear viscosity and the first viscometric function monotonically decrease as the shear rate increases (shear thinning), while the second viscometric function vanishes. Although the IT solution is restricted to Maxwell molecules, it shows a good agreement with computer simulations for other potentials [5]. Recently, the IT solution has been extended to get the time evolution of the fourth order moments [6]. It has been shown that these moments diverge in time for shear rates larger than a certain critical value, although this singularity does not have any influence on the transport properties.

An interesting problem is the description of transport phenomena in mixtures. The aim of this paper is to exactly obtain the transport properties of a binary mixture of Maxwell molecules described by the Boltzmann equation under USF. We assume that the molar fractions are constant, so that no mutual diffusion exists. On the other hand, no restriction on the masses, concentrations, and force constants will be considered. Consequently, the transport coefficients depend on the shear rate as well as on the parameters characterizing the mixture. Obviously, our results reduce to the IT solution in the case of mechanically equivalent particles. Further, when one takes the tracer limit, previous results are recovered [7] and a new phenomenon appears. To the best of our knowledge, this is the first time that the rheological properties of a sheared *mixture* are obtained from an *exact* solution of the Boltzmann equation [8]. A different solution has recently been derived for a nonequilibrium homogeneous problem generated by a color field [9].

The plan of the paper is as follows. The problem is described in Sec. II and some peculiar properties of the Maxwell interaction are presented. In Sec. III, the transient regime is analyzed and it is shown that the pressure tensor reaches a stationary form in the long-time limit. The main results are derived in Sec. IV. Specifically, the transport coefficients, as well as the partial contributions of each species to the pressure tensor, are obtained in terms of the shear rate and the ratios of mass, density, and force constants. Finally, we close the paper in Sec. V with a brief discussion.

II. DESCRIPTION OF THE PROBLEM

Let us consider a *dilute* mixture, $f_s(\mathbf{r},\mathbf{v};t)$ being the one-particle velocity distribution function of species s. In the absence of external forces, the distributions f_s obey a set of coupled Boltzmann equations:

$$\frac{\partial}{\partial t} f_s + \mathbf{v}\cdot\nabla f_s = \sum_r J_{sr}[f_s,f_r] \,. \tag{1}$$

Here, $J_{sr}[f_s,f_r]$ is the Boltzmann collision term, which in standard notation is given by

$$J_{sr}[f_s,f_r] = \int d\mathbf{v}_1 \int d\Omega |\mathbf{v}-\mathbf{v}_1| \sigma_{sr}(\mathbf{v}-\mathbf{v}_1,\theta) \times [f_s(\mathbf{v}')f_r(\mathbf{v}_1') - f_s(\mathbf{v})f_r(\mathbf{v}_1)] \ . \tag{2}$$

In terms of the first few moments of f_s, the number density and mean velocity of species s are defined, respectively, as

$$n_s = \int d\mathbf{v} f_s \ , \tag{3}$$

$$\mathbf{u}_s = \frac{1}{n_s}\int d\mathbf{v}\mathbf{v} f_s \ . \tag{4}$$

These quantities define the total number density $n = \sum_s n_s$ and the flow velocity $\mathbf{u} = \sum_s \rho_s \mathbf{u}_s/\rho$, where $\rho_s \equiv m_s n_s$ is the mass density of species s and $\rho \equiv \sum_s \rho_s$. The hydrodynamic temperature T is defined as

$$nk_B T = \sum_s \frac{m_s}{3}\int d\mathbf{v}\mathbf{V}^2 f_s \ , \tag{5}$$

where k_B is the Boltzmann constant and $\mathbf{V} \equiv \mathbf{v}-\mathbf{u}$ is the peculiar velocity. The quantities n_s, $\mathbf{u}$, and T are associated to the densities of conserved quantities (mass of each species, total momentum, and total energy). Their corresponding balance equations define the dissipative fluxes of mass, $\mathbf{j}_s = \rho_s(\mathbf{u}_s - \mathbf{u})$, momentum (pressure tensor),

$$\mathsf{P} = \sum_s m_s \int d\mathbf{v}\mathbf{V}\mathbf{V} f_s \ , \tag{6}$$

and energy,

$$\mathbf{q} = \sum_s \frac{m_s}{2}\int d\mathbf{v} V^2 \mathbf{V} f_s \ . \tag{7}$$

The uniform shear flow (USF) state is macroscopically characterized by

$$n_s = \text{const} \ , \tag{8}$$

$$\nabla T = \mathbf{0} \ , \tag{9}$$

$$u_i = a_{ij} r_j \ , \ a_{ij} = a\delta_{ix}\delta_{jy} \ , \tag{10}$$

a being the constant shear rate. Equation (8) implies that there is no mutual diffusion in the system, so that the shear rate is the only nonequilibrium parameter and the transport of momentum is the relevant phenomenon. This transport is measured by the pressure tensor, which defines the main transport coefficients of the problem: the shear viscosity

$$\eta(a) = -\frac{P_{xy}}{a} \tag{11}$$

and the viscometric functions

$$\Psi_1(a) = \frac{P_{yy}-P_{xx}}{a^2} \ , \tag{12}$$

$$\Psi_2(a) = \frac{P_{zz}-P_{yy}}{a^2} \ . \tag{13}$$

In the USF problem, the temperature increases in time due to viscous heating, so that the state is not stationary. In this context, Eqs. (11)–(13) must be understood in the long-time limit, where the influence of the initial conditions has disappeared. Usually, a thermostat force is introduced in computer simulations to control the viscous heating and keep the temperature constant [2]. Nevertheless, the presence of the force may not play a neutral role on the transport properties [10].

At a microscopic level, the USF corresponds to a state that is uniform when one refers the velocities of the particles to the Lagrangian frame moving with the flow velocity. This means that the distribution functions become homogeneous under the above transformation, namely, $f_s(\mathbf{r},\mathbf{v};t) = f_s(\mathbf{V},t)$. Henceforth, we will restrict ourselves to a binary mixture. In that case, Eq. (1) becomes

$$\frac{\partial}{\partial t} f_1 - \frac{\partial}{\partial V_i} a_{ij} V_j f_1 = J_{11}[f_1,f_1] + J_{12}[f_1,f_2] \tag{14}$$

and a similar equation for f_2.

We are interested in deriving explicit expressions for $\eta(a)$ and $\Psi_{1,2}(a)$ for arbitrary values of the shear rate and the characteristic parameters of the mixture. This does not seem to be possible for a general interaction potential. However, when one restricts oneself to Maxwell molecules, a complete description can be obtained. The Maxwell potential for interactions between particles of species r with particles of species s is of the form $V_{rs}(r) = \kappa_{rs} r^{-4}$. The key point is that the collision rate $g\sigma_{rs}(g,\theta)$ is independent of the relative velocity g. Consequently, the collisional moments of a given order do not involve moments of higher order. For instance [11]

$$\begin{aligned}\int d\mathbf{v} m_r \mathbf{V}\mathbf{V} J_{rs}[f_r,f_s] &= \frac{\lambda'_{rs}}{(m_r+m_s)m_r}[(\rho_r p_s + \rho_s p_r)\mathbb{1} - \rho_r \mathsf{P}_s - \rho_s \mathsf{P}_r] \\ &\quad - \frac{\lambda_{rs}}{(m_r+m_s)m_r} 2\left(\frac{m_r}{m_s}\rho_s \mathsf{P}_r - \rho_r \mathsf{P}_s\right) \ , \end{aligned}\tag{15}$$

where we have taken into account that $\mathbf{j}_s = \mathbf{0}$. In Eq. (15),

$$\lambda_{rs} = 1.69\pi\left(\kappa_{rs}\frac{m_r m_s}{m_r+m_s}\right)^{1/2} \ , \tag{16}$$

$$\lambda'_{rs} = 2.61\pi\left(\kappa_{rs}\frac{m_r m_s}{m_r+m_s}\right)^{1/2} \ , \tag{17}$$

P_s is the partial pressure tensor of species s,

$$\mathsf{P}_s = m_s \int d\mathbf{v}\mathbf{V}\mathbf{V} f_s, \tag{18}$$

and $p_s = \frac{1}{3}\mathrm{tr}\mathsf{P}_s$ is the partial hydrostatic pressure. From it one can define a "temperature" T_s associated to species s as $p_s = n_s k_B T_s$.

Equation (14) admits a nice scaling property in the special case of Maxwell molecules. Let us introduce the scaled quantities

$$\overline{\mathbf{V}} = e^{-\alpha t}\mathbf{V} , \tag{19}$$

$$\overline{f}_s(\overline{\mathbf{V}},t) = e^{3\alpha t} f_s(\mathbf{V},t) , \tag{20}$$

where α is an arbitrary constant. Then Eq. (14) reduces to

$$\frac{\partial}{\partial t}\overline{f}_1 - \frac{\partial}{\partial \overline{V}_i}(a_{ij}\overline{V}_j + \alpha\overline{V}_i)\overline{f}_1 = J_{11}[\overline{f}_1,\overline{f}_1] + J_{12}[\overline{f}_1,\overline{f}_2] . \tag{21}$$

This equation can be understood as the Boltzmann equation for USF in the presence of a nonconservative external force of the form $\mathbf{F}_s = -m_s\alpha\mathbf{V}$. This shows that in the particular case of Maxwell molecules, the drag force $\mathbf{F}_s$ (with arbitrary α) does not affect the properties of the system. With no loss of generality, we will choose α as a function of the shear rate by the condition that the temperature reaches a constant value in the long-time limit. Therefore, we will start from Eq. (21), and its counterpart for f_2, with the above choice for α and, for the sake of simplicity, we will drop the bars.

III. TRANSIENT REGIME

Although the main transport properties are defined in the long-time limit, it is instructive to analyze the transient regime from an arbitrary (but uniform in the Lagrangian frame) initial condition. Multiplying both sides of Eq. (21) by $m_1\mathbf{VV}$ and integrating over the velocity space, one gets

$$\frac{\partial}{\partial t}P_{1,ij} + 2\alpha P_{1,ij} + a_{ik}P_{1,kj} + a_{jk}P_{1,ki} + B_{11}P_{1,ij} + B_{12}P_{2,ij} = (A_{11}p_1 + A_{12}p_2)\delta_{ij}, \tag{22}$$

where use has been made of Eq. (15). In Eq. (22), we have introduced the coefficients

$$A_{11} = \frac{\lambda'_{11}}{m_1}n_1 + \frac{\lambda'_{12}}{m_1+m_2}\frac{m_2}{m_1}n_2 , \tag{23}$$

$$A_{12} = \frac{\lambda'_{12}}{m_1+m_2}n_1 , \tag{24}$$

$$B_{11} = A_{11} + 2\frac{\lambda_{12}}{m_1+m_2}n_2 , \tag{25}$$

$$B_{12} = A_{12} - 2\frac{\lambda_{12}}{m_1+m_2}n_1 . \tag{26}$$

A similar equation can be obtained for P_2, by just making the changes $1 \leftrightarrow 2$.

It is convenient to choose a time unit. In general there are several characteristic times in a binary mixture, so that the choice of the adequate time unit depends on the case of interest (tracer limit, disparate-mass mixture, ...). Since our description applies for arbitrary mass, concentration, and size ratios, we take, for simplicity, an effective collision frequency ζ given by

$$\zeta = 2n\lambda'_{12}/(m_1+m_2) \tag{27}$$

and define ζ^{-1} as the time unit. This means that we will use the dimensionless quantities $t^* = \zeta t$, $a^* = a/\zeta$, and $\alpha^* = \alpha/\zeta$. Henceforth, we will omit the asterisks. The corresponding expressions of the coefficients A_{rs} and B_{rs} in reduced units are given in the Appendix as functions of the mass ratio $\mu \equiv m_1/m_2$, the concentration ratio $\nu \equiv n_1/n_2$, and the ratios $\gamma_{11} \equiv \lambda'_{11}/\lambda'_{12}$, $\gamma_{22} \equiv \lambda'_{22}/\lambda'_{12}$, and $\gamma_{12} \equiv \lambda_{12}/\lambda'_{12} = 0.648$. The parameters γ_{11} and γ_{22} depend on the force constant ratios κ_{11}/κ_{12} and κ_{22}/κ_{12}, respectively.

Equation (22) along with its counterpart for P_2 constitute a linear homogeneous set of coupled differential equations. In fact, $P_{1,yz}$, $P_{2,yz}$, $P_{1,xz}$, $P_{2,xz}$, $P_{1,yy}-P_{1,zz}$, and $P_{2,yy}-P_{2,zz}$ are uncoupled to the remaining elements. They tend to zero as a linear combination of terms of the form $e^{-\ell t}$, with characteristic times ℓ^{-1} given by the roots of the quadratic equation

$$(2\alpha-\ell)^2 + (B_{11}+B_{22})(2\alpha-\ell) + B_{11}B_{22} - B_{12}B_{21} = 0. \tag{28}$$

The relevant elements are $\mathcal{P} \equiv \{P_{1,xx}, P_{1,yy}, P_{1,xy}, P_{2,xx}, P_{2,yy}, P_{2,xy}\}$. Their evolution equation is

$$\left(\frac{\partial}{\partial t} + \mathcal{L}\right)\mathcal{P} = 0 , \tag{29}$$

where $\mathcal{L}$ is the 6×6 matrix

$$\mathcal{L} = \begin{pmatrix} 2\alpha + B_{11} - \frac{1}{3}A_{11} & -\frac{2}{3}A_{11} & 2a & B_{12} - \frac{1}{3}A_{12} & -\frac{2}{3}A_{12} & 0 \\ -\frac{1}{3}A_{11} & 2\alpha + B_{11} - \frac{2}{3}A_{11} & 0 & -\frac{1}{3}A_{12} & B_{12} - \frac{2}{3}A_{12} & 0 \\ 0 & a & 2\alpha + B_{11} & 0 & 0 & B_{12} \\ B_{21} - \frac{1}{3}A_{21} & -\frac{2}{3}A_{21} & 0 & 2\alpha + B_{22} - \frac{1}{3}A_{22} & -\frac{2}{3}A_{22} & 2a \\ -\frac{1}{3}A_{21} & B_{21} - \frac{2}{3}A_{21} & 0 & -\frac{1}{3}A_{22} & 2\alpha + B_{22} - \frac{2}{3}A_{22} & 0 \\ 0 & 0 & B_{21} & 0 & a & 2\alpha + B_{22} \end{pmatrix} . \tag{30}$$

The solution of Eq. (29) is expressed in terms of the roots ℓ of the corresponding characteristic polynomial, i.e.,

$$\det(\mathcal{L} - \ell \mathbb{1}) = 0 \,. \tag{31}$$

Equation (31) is a sixth-degree equation that, in general, must be solved numerically to get $(2\alpha-\ell)$ as functions of a, μ, ν, γ_{11}, and γ_{22}. Nevertheless, there are some limit cases for which Eq. (31) factorizes into two cubic equations. For instance, in the case of mechanically equivalent particles $(\mu = 1, \gamma_{11} = \gamma_{22} = 1)$, Eq. (31) reduces to

$$\frac{3}{2}(2\alpha - \ell)[1 + (2\alpha - \ell)]^2 = a^2 \,, \tag{32}$$

$$\frac{3}{4}(2\alpha - \ell + \gamma_{12})[1 + 2(2\alpha - \ell) + 2\gamma_{12}]^2 = a^2 \,. \tag{33}$$

Equation (32) coincides with the one obtained in the case of a single gas [4]. Its smallest root gives the dominant behavior of the *total* pressure tensor P and its expression is

$$\ell_{\min} = 2\alpha - F(a) \,, \tag{34}$$

where $F(a) \equiv \frac{4}{3}\sinh^2[\frac{1}{6}\cosh^{-1}(1 + 9a^2)]$. On the other hand, Eq. (33) is related to the time evolution of the *difference* between P_1/n_1 and P_2/n_2. The smallest root is now

$$\ell'_{\min} = 2\alpha + \gamma_{12} - \frac{1}{2}F(2a) \,. \tag{35}$$

It can be easily proved that $\ell'_{\min} > \ell_{\min}$ for any value of the shear rate. This means that the relative temperature difference $(T_1 - T_2)/T$ tends to zero over a time scale shorter than the time scale of variation of $T(t)$.

Another interesting limit corresponds to the so-called tracer limit, i.e., $\nu \to 0$. In this situation, the excess component is not disturbed by the presence of the tracer particles, and the collision among tracer particles can also be neglected. In this limit, Eq. (31) factorizes into

$$\frac{3}{(1+\mu)\gamma_{22}}(2\alpha - \ell)\left[\frac{\gamma_{22}(1+\mu)}{2} + (2\alpha - \ell)\right]^2 = a^2 \,, \tag{36}$$

$$3\mu(2\alpha - \ell + \gamma_{12})\left[\frac{1}{2\mu} + (2\alpha - \ell) + \gamma_{12}\right]^2 = a^2 \,. \tag{37}$$

Equation (36) is associated with the time evolution of the excess component. In fact, Eq. (36) is equivalent to that of a single gas, Eq. (32), with the adequate change of time unit. Its smallest root is

$$\ell_{\min} = 2\alpha - \frac{(1+\mu)\gamma_{22}}{2}F\left(\frac{2}{(1+\mu)\gamma_{22}}a\right) \,. \tag{38}$$

On the other hand, Eq. (37) gives the transient behavior of the tracer component. Its smallest root is

$$\ell'_{\min} = 2\alpha + \gamma_{12} - \frac{1}{2\mu}F(2\mu a) \,. \tag{39}$$

These results were already obtained by Garzó and López de Haro [7] in their study of tracer diffusion under shear flow. For small shear rates, $\ell_{\min} < \ell'_{\min}$ for any value of μ. It can be proved that if μ is larger than a certain value μ_0, $\ell_{\min}$ is smaller than $\ell'_{\min}$ for any value of a. However, if $\mu < \mu_0$, then $\ell'_{\min} < \ell_{\min}$ for a larger than a certain shear rate $a_0(\mu)$. The threshold value μ_0 can be obtained by the condition $\ell_{\min} = \ell'_{\min}$ when $a \to \infty$, which yields

$$\mu_0(1 + \mu_0)\gamma_{22} = 1 \,. \tag{40}$$

For instance, if we assume $\kappa_{22} = \kappa_{12}$, the solution is $\mu_0 \simeq 0.5437$. In addition, $a_0(\mu)$ has a minimum approximately equal to 10.83 at $\mu \simeq 0.145$. It is interesting to understand the physical consequences of the difference between $\ell_{\min}$ and $\ell'_{\min}$. For shear rates not too large, the eigenvalue $\ell_{\min}$ is smaller than the eigenvalue $\ell'_{\min}$, so that the ratio T_1/T tends towards a stationary value with a characteristic time $(\ell'_{\min} - \ell_{\min})^{-1}$. However, if $\mu < \mu_0$ and $a > a_0(\mu)$, then T_1/T grows exponentially in time. As a consequence, it is possible that the contribution of the tracer species to the global properties cannot be neglected. This possibility will be discussed in the next section.

Except in the two limit cases just discussed, Eq. (31) must be solved numerically. Figure 1 shows the real part of the roots $(2\alpha - \ell)$ of Eq. (31) versus a for the case $\mu = 0.2$, $\nu = 0.2$, and $\kappa_{11} = \kappa_{12} = \kappa_{22}$. Obviously, exactly the same curves are obtained in the case $\mu = 5$, $\nu = 5$. At a given value of the shear rate, the difference between the two largest values of $(2\alpha-\ell)$ gives the inverse

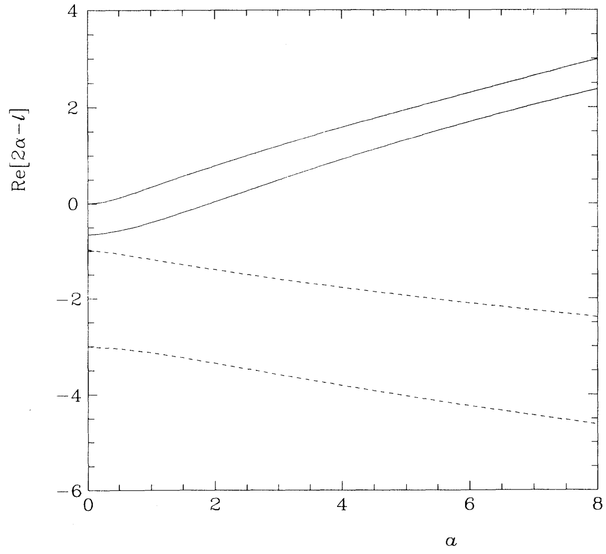

FIG. 1. Shear-rate dependence of the real part of the roots of Eq. (31) for the case $\mu = 0.2$, $\nu = 0.2$, and $\kappa_{11} = \kappa_{12} = \kappa_{22}$. The solid lines refer to the real roots, while the dashed lines refer to the complex roots.

of the relaxation time of the transient regime. It can be proved that this difference does not vanish if $\nu \neq 0$.

As was said at the end of Sec. II, we take $\alpha(a)$ under the condition that $T(t)$ reaches a stationary value in the long-time limit. This is equivalent to choosing α so that $\ell = 0$ is the smallest root of Eq. (31). In other words, $\alpha(a)$ is the largest root of the sixth-degree equation $\det \mathcal{L} = 0$. Thus, the upper curve in Fig. 1 represents $2\alpha(a)$ for the case $\mu = 0.2$, $\nu = 0.2$. In the limit of small shear rates, $\alpha \approx \alpha_0 a^2$, where

$$\alpha_0 = \frac{2}{3(\mu+1)} \frac{\nu^2\mu(2\gamma_{12}+\mu) + \nu\{\gamma_{11}(\mu+1) + \mu[4\gamma_{12} + \gamma_{22}(\mu+1) - 2]\} + 2\gamma_{12}\mu + 1}{\nu^2\gamma_{11}(2\gamma_{12}+\mu) + \nu(\mu+1)(\gamma_{11}\gamma_{22} + 2\gamma_{12}) + \gamma_{22}(2\gamma_{12}\mu + 1)} \,. \tag{41}$$

On the other hand, in the limit of large shear rates, $\alpha \approx \alpha_\infty a^{2/3}$, where

$$\alpha_\infty = \frac{1}{2 \times 3^{1/3}} \left[A_{11} + A_{22} + \sqrt{(A_{11} - A_{22})^2 + 4A_{12}A_{21}} \right]^{1/3} \,. \tag{42}$$

IV. TRANSPORT PROPERTIES

This section concerns the derivation of the main transport properties of the problem for arbitrary values of the shear rate a as well as of the ratios μ, ν, γ_{11}, and γ_{22}. These properties are related to the elements of the pressure tensor P in the long-time limit, i.e., in the stationary regime according to our choice of α. In the USF problem, the relevant transport coefficients are the shear viscosity and the first and second viscometric functions defined by Eqs. (11)–(13). These quantities refer to the properties of the mixture as a whole (total momentum flux). It is also interesting to study the partial contribution corresponding to each species. In particular, we will pay attention to the temperature ratio T_1/T_2. It provides information about how the kinetic energy is distributed between both species.

The stationary forms of P_1 and P_2 are obtained from Eq. (29) by solving the homogeneous equation $\mathcal{L}\mathcal{P} = 0$. This equation has a nontrivial solution since $\det \mathcal{L} = 0$. Such a solution can be written as

$$\mathcal{P}' = \mathcal{L}'^{-1}\mathcal{Q}\,, \tag{43}$$

where

$$\mathcal{P}' = \begin{pmatrix} p_1 \\ P_{1,yy} \\ P_{2,yy} \\ P_{1,xy} \\ P_{2,xy} \end{pmatrix} , \tag{44}$$

$$\mathcal{L}' = \begin{pmatrix} 2\alpha - A_{11} + B_{11} + A_{12} - B_{12} & 0 & 0 & \frac{2}{3}a & 0 \\ A_{12} - A_{11} & 2\alpha + B_{11} & B_{12} & 0 & 0 \\ A_{22} - A_{21} & B_{21} & 2\alpha + B_{22} & 0 & 0 \\ 0 & a & 0 & 2\alpha + B_{11} & B_{12} \\ 0 & 0 & a & B_{21} & 2\alpha + B_{22} \end{pmatrix} , \tag{45}$$

and

$$\mathcal{Q} = \begin{pmatrix} A_{12} - B_{12} \\ A_{12} \\ A_{22} \\ 0 \\ 0 \end{pmatrix} p\,. \tag{46}$$

The explicit expression for p_1/p, $P_{1,yy}/p$, and $P_{1,xy}/p$ can be found in the Appendix. The corresponding expressions for species 2 are easily obtained by adequately changing the indices.

The temperature ratio T_1/T_2 is a measure of the lack of equidistribution of the kinetic energy. The behaviors for small and large shear rates are, respectively,

$$\frac{T_1}{T_2} \approx 1 + \frac{4(\nu+1)(\mu\gamma_{22} - 1 + \mu\nu - \nu\gamma_{11})}{3\gamma_{12}[\nu^2\gamma_{11}(\mu + 2\gamma_{12}) + \nu(\mu+1)(2\gamma_{12} + \gamma_{11}\gamma_{22}) + \gamma_{22}(2\mu\gamma_{12} + 1)]} a^2 \,, \tag{47}$$

$$\frac{T_1}{T_2} \approx \frac{1}{2(\nu+1)(12\alpha_\infty^3 - A_{11})} \,. \tag{48}$$

These equations show that the temperature ratio does not present a monotomic behavior. The ratio T_1/T_2 reaches a maximum (minimum) if $\mu\gamma_{22} - 1 + \mu\nu - \nu\gamma_{11}$ is positive (negative). Consequently, both temperatures coincide at a certain value of the shear rate, which depends on the parameters of the mixture. Obviously, $T_1 = T_2$ for any value of the shear rate in the case of mechanically equivalent particles. For the sake of illustration, we plot in Fig. 2 T_1/T_2 versus a for several values of μ and ν. In this figure, we have assumed that the force constants have a mass dependence of the form $\kappa_{rs} \propto (m_r m_s)^{1/2}$. Such a dependence has been proposed [12] to model the cross section observed in disparate-mass binary mixtures. We observe that, for small shear rates, the kinetic energy per particle of the solute component is larger than that of the solvent component if the former is heavier than the latter. However, the opposite happens for sufficiently large shear rates.

The most important quantity is the shear viscosity η. Its explicit expression can be obtained from Eq. (A7). In the Navier-Stokes limit one recovers the well-known result [13]

$$\eta(0) = 2\frac{(1-\nu\mu)^2 + \nu(\mu+1)(\gamma_{11}+\mu\gamma_{22}) + 2\mu(\nu+1)^2\gamma_{12}}{(1+\mu)[\nu(\mu+1)(\gamma_{11}\gamma_{22}+2\gamma_{12}) + \gamma_{22}(1+2\mu\gamma_{12}) + \nu^2\gamma_{11}(\mu+2\gamma_{12})]}\frac{p}{\zeta} . \tag{49}$$

Figure 3 shows $\eta(a)/\eta(0)$ for $\nu = 0.1$, $\mu = 0.05$, 0.1, 1, 5, 10, and for $\kappa_{rs} \propto (m_r m_s)^{1/2}$. The known shear thinning effect for a single gas extends as well to binary mixtures, i.e., $\eta(a)$ decreases as a increases. Furthermore, at given values of the concentration ratio and the shear rate, the relative viscosity decreases as the mass ratio increases for $\mu < 1$, while the opposite happens for $\mu > 1$.

The viscometric functions provide information about normal stresses in the system. As seen in the preceding section, $P_{zz} - P_{yy}$ tends to zero in the long-time limit. Consequently, the second viscometric function is zero regardless the values of a, μ, ν, γ_{11}, and γ_{22}. This property is peculiar of the Maxwell interaction. The expression for Ψ_1 can be obtained from Eqs. (A5) and (A6) by taking into account that $P_{1,xx} = 3p_1 - 2P_{1,yy}$. In the limit $a \to 0$, one gets

$$\Psi_1(0) = -8\frac{1+\nu}{(1+\mu)^2}\frac{\Lambda}{[\nu(1+\mu)(\gamma_{11}\gamma_{22}+2\gamma_{12}) + \nu^2\gamma_{11}(2\gamma_{12}+\mu) + \gamma_{22}(1+2\mu\gamma_{12})]^2}\frac{p}{\zeta^2} , \tag{50}$$

where

$$\begin{aligned}\Lambda \equiv\ & \nu^3\mu^2(\mu+2\gamma_{12})^2 + \nu^2[\mu^2(1-2\mu) + 4\mu^2\gamma_{12}(3\gamma_{12}+\mu-2) + (1+\mu)^2\gamma_{11}^2 \\ & +2\mu(1+\mu)(2\gamma_{11}\gamma_{12} - \gamma_{11} + \mu^2\gamma_{22} + 2\mu\gamma_{22}\gamma_{12})] + \nu[\mu(\mu-2) + 4\mu\gamma_{12}(3\mu\gamma_{12}+1-2\mu) + \mu^2(1+\mu)^2\gamma_{22}^2 \\ & +2(1+\mu)(\gamma_{11} + 2\mu\gamma_{11}\gamma_{12} - \mu^2\gamma_{22} + 2\mu^2\gamma_{12}\gamma_{22})] + (1+2\mu\gamma_{12})^2 .\end{aligned} \tag{51}$$

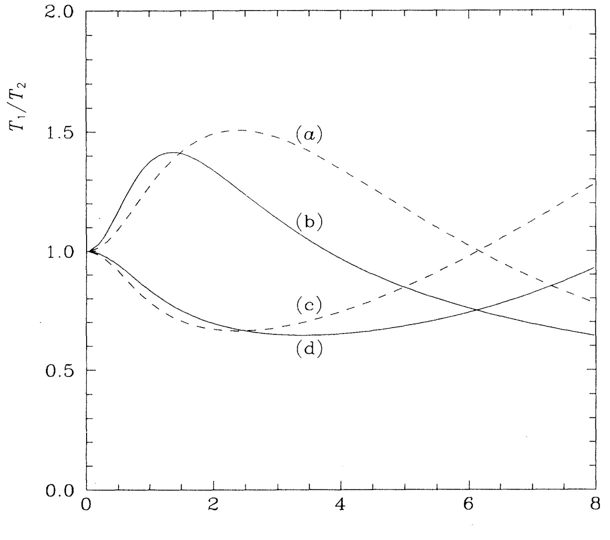

FIG. 2. Shear-rate dependence of the temperature ratio T_1/T_2 for (a) $\nu = 1$, $\mu = 10$, (b) $\nu = 0.1$, $\mu = 10$, (c) $\nu = 1$, $\mu = 0.1$, and (d) $\nu = 0.1$, $\mu = 0.1$. The force constants have been assumed to be of the form $\kappa_{rs} \propto (m_r m_s)^{1/2}$.

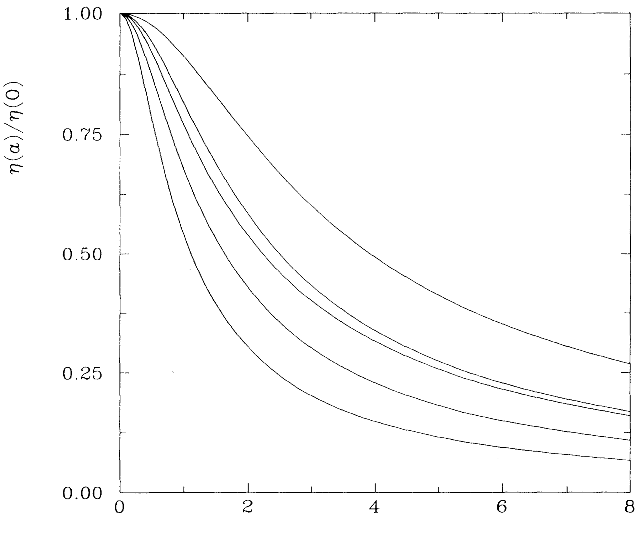

FIG. 3. Shear-rate dependence of the reduced shear viscosity for $\nu = 0.1$, $\kappa_{rs} \propto (m_r m_s)^{1/2}$, and (from top to bottom) $\mu = 0.05$, 0.1, 10, 5, and 1.

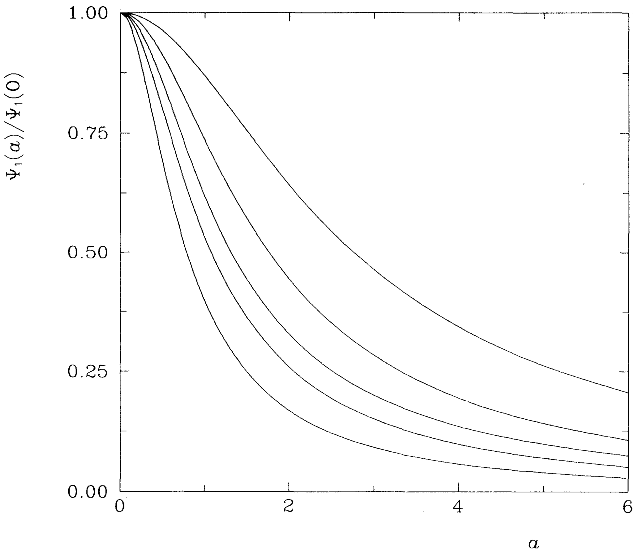

FIG. 4. The same as in Fig. 3, but for the first viscometric function.

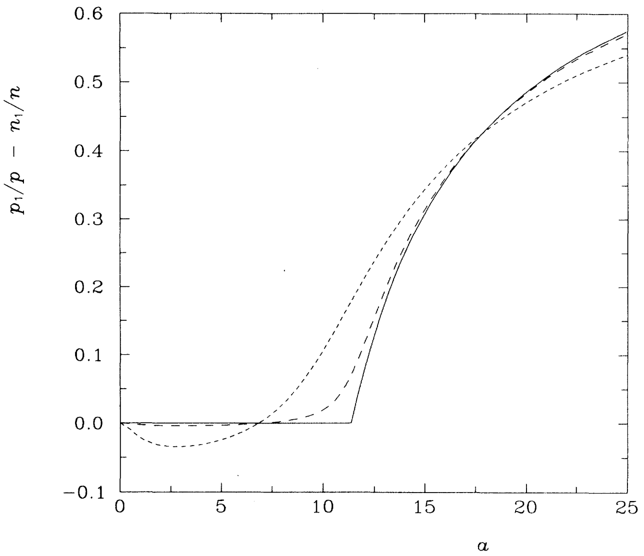

FIG. 5. Shear-rate dependence of $p_1/p - n_1/n$ for $\mu = 0.1$, $\kappa_{11} = \kappa_{12} = \kappa_{22}$, and $\nu = 0.1$ (- - -), 0.01 (– – –), and 0 (—).

Notice that $\Psi_1(0)$ is a Burnett transport coefficient. We are not aware of any previous derivation of this coefficient for a binary mixture. In Fig. 4 we plot $\Psi_1(a)/\Psi_1(0)$ as a function of a for the same cases as in Fig. 3. As happens in a single gas, $\Psi_1(a)$ is a decreasing function. In addition, the dependence of Ψ_1 on the parameters of the mixture is qualitatively similar to that of the shear viscosity.

Before closing this section, let us analyze the properties of the system in the tracer limit ($\nu \to 0$). In this limit, α has a singularity at $a = a_0(\mu)$ if $\mu < \mu_0$, where μ_0 is the solution of Eq. (40). More specifically, α is given by Eq. (38) (with $\ell_{\rm min} = 0$) if $a < a_0$, while α is given by Eq. (39) (with $\ell'_{\rm min} = 0$) if $a > a_0$. Consequently, α is continuous at $a = a_0$, but its first derivative is discontinuous. From a physical point of view, the implications of this singularity are interesting by themselves. Let us consider the ratio p_1/p, i.e., the relative contribution of species 1 to the total kinetic energy. By carefully taking the limit $\nu \to 0$ in Eq. (A5) one finds that $p_1/p \to 0$ if $a < a_0$, while p_1/p tends to a nonzero value if $a > a_0$. This means that, despite the fact that the molar fraction of the tracer particles is negligible, their contribution to the total energy is relevant if the system is sufficiently far from equilibrium. This transition only happens if the tracer particles are sufficiently lighter than the excess particles. To illustrate this phenomenon, Fig. 5 shows $p_1/p - n_1/n$ versus a for $\mu = 0.1$ and $\nu = 10^{-1}$, 10^{-2} and 0, in the case $\kappa_{11} = \kappa_{12} = \kappa_{22}$. We observe that in the tracer limit, $p_1/p \neq 0$ if $a > a_0 \simeq 11.37$. As a matter of fact, the tracer contribution is larger than that of the solvent for $a > 20.7$. Of course, the transition at $a = a_0(\mu)$ also occurs for the tracer contribution to the transport properties of the mixture.

V. DISCUSSION

In this paper we have considered a binary mixture far from equilibrium. The state is characterized by uniform density and temperature and a linear profile of the x component of the flow velocity along the y direction. Consequently, the only nonequilibrium parameter is the constant shear rate a. On the other hand, the transport properties also depend on the parameters of the mixture, namely the mass, concentration, and size of each species. In order to offer a description as detailed as possible, we have restricted ourselves to the low-density regime, in which case all the physical information can be obtained from the set of two coupled Boltzmann equations. In addition, we have specialized to the Maxwell interaction, which lends itself to an exact solution of the problem. Thus, our results are *exact* and valid for arbitrary values of the shear rate and the ratios of mass, concentration, and force constants. In this sense, our solution extends the well-known Ikenberry-Truesdell solution [4] for a single gas of Maxwell molecules. The generalization to mixtures with more than two components is just a matter of a more complex algebra.

By taking moments in the Boltzmann equations for Maxwell molecules, one gets a set of coupled equations for the elements of the pressure tensor of each species. From its solution, the shear viscosity η and the viscometric functions $\Psi_{1,2}$ are obtained. The second viscometric function is identically zero. The expressions for η and Ψ_1 contain a parameter α, which is the largest root of a sixth-degree equation with coefficients depending on the parameters of the problem. The qualitative behaviors of η and Ψ_1 are similar to those of a single gas, i.e., both quantities decay as the shear rate increases. On the other hand, at a given value of the shear rate, η and Ψ_1 are always larger than the one of the single gas. In addition to the transport properties, it is also interesting to study the temperature ratio, which measures the distribution of the kinetic energy between both species. Depending on the parameters of the mixture, its shear-rate dependence presents a maximum or minimum.

It is worthwhile to analyze the limit in which one of the species, say 1, is present in tracer concentration, i.e., $n_1/n_2 \to 0$. This limit was previously studied in Ref. [7] by starting from a closed Boltzmann equation for f_2 and a Boltzmann-Lorentz equation for f_1. It was shown that the temperature ratio T_1/T diverges if the shear rate is larger than a certain threshold value a_0, which depends on the mass ratio. Our general results allow us to particularize to the limit $n_1/n_2 \to 0$. We have found that $p_1/p = n_1T_1/nT$ goes to zero if $a < a_0$, while it tends to a finite value if $a > a_0$. The main physical implication is that, if $a > a_0$, the presence of the tracer particles has a remarkable influence on the properties of the mixture. As a consequence, the effect on the state of the excess component of collisions with the tracer particles cannot be neglected if $a > a_0$. It must be stressed that the threshold shear rate a_0 is rather large in units of an effective collision frequency. In fact, a_0 becomes infinity if the mass ratio m_1/m_2 is larger than a certain value.

The problem studied in this paper is interesting by itself. Furthermore, it can be taken as a starting point to analyze mutual diffusion under shear flow. In the same way as done in the tracer limit [7], the idea is to perform a perturbation expansion in powers of the concentration gradient around the solution obtained here. To first order, one can get a generalized Fick's law with a shear-rate-dependent mutual diffusion tensor. Work is in progress along this line.

ACKNOWLEDGMENTS

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APPENDIX

The coefficients A_{rs} and B_{rs}, expressed in reduced units, are

$$A_{11} = \frac{\gamma_{11}}{2}\frac{\nu}{\nu+1}\frac{\mu+1}{\mu} + \frac{1}{2\mu(\nu+1)}\ , \tag{A1}$$

$$A_{12} = \frac{1}{2}\frac{\nu}{\nu+1}\ , \tag{A2}$$

$$B_{11} = A_{11} + \frac{\gamma_{12}}{\nu+1}\ , \tag{A3}$$

$$B_{12} = A_{12} - \gamma_{12}\frac{\nu}{\nu+1}\ . \tag{A4}$$

The remaining coefficients are obtained by the adequate changes ($\mu \leftrightarrow \mu^{-1}$, $\nu \leftrightarrow \nu^{-1}$, $\gamma_{11} \leftrightarrow \gamma_{22}$).

From Eq. (43) one gets

$$\frac{p_1}{p} = \frac{Ka^2+L}{Ra^2+S}\ , \tag{A5}$$

$$\frac{P_{1,yy}}{p} = \frac{Ma^2+N}{Ra^2+S}\ , \tag{A6}$$

$$\frac{P_{1,xy}}{p} = -\frac{Q}{Ra^2+S}a\ , \tag{A7}$$

where

$$K = 8\,\alpha^2 A_{12} + 8\,\alpha\,(A_{12}B_{22} - A_{22}B_{12}) + 2\,A_{12}\,\left(B_{12}B_{21} + B_{22}{}^2\right) - 2\,A_{22}B_{12}\,(B_{11}+B_{22})\ , \tag{A8}$$

$$L = 3\,(A_{12} - B_{12})\,\left[4\,\alpha^2 + 2\,\alpha\,(B_{11}+B_{22}) + B_{11}B_{22} - B_{12}B_{21}\right]^2\ , \tag{A9}$$

$$M = 2\,B_{12}(A_{12}A_{21} - A_{11}A_{22})\ , \tag{A10}$$

$$\begin{aligned} N = {} & 48\,A_{12}\,\alpha^4 + 24\,\alpha^3\,[2\,A_{12}\,(B_{11}+B_{22}) - B_{12}\,(A_{11}+A_{22})] \\ & +12\,\alpha^2\,[A_{12}\,(B_{11}^2 + B_{22}^2 + 4\,B_{11}B_{22}) - A_{12}B_{12}\,(A_{21}+B_{21}) \\ & +B_{12}A_{11}\,(A_{22} - B_{11} - 2\,B_{22}) - B_{12}A_{22}\,(B_{22} + 2\,B_{11}) + B_{12}^2A_{21}] \\ & +6\,\alpha[B_{11}B_{12}\,(A_{11}A_{22} - A_{12}A_{21} + A_{21}B_{12} - A_{12}B_{21} - 2\,A_{11}B_{22} - 2\,A_{22}B_{22} - A_{22}B_{11}) \\ & +B_{12}^2(A_{11}B_{21} + A_{22}B_{21} + A_{21}B_{22}) + B_{12}B_{22}(A_{11}A_{22} - A_{12}A_{21} - A_{12}B_{21} - A_{11}B_{22}) \\ & +2\,A_{12}B_{11}B_{22}\,(B_{11}+B_{22})] + 3\,(B_{12}B_{21} - B_{11}B_{22})[B_{12}(A_{12}A_{21} - A_{11}A_{22}) \\ & +B_{11}\,(B_{12}A_{22} - A_{12}B_{22}) + B_{12}\,(A_{11}B_{22} - B_{12}A_{21})], \end{aligned} \tag{A11}$$

$$
\begin{aligned}
Q = {} & -24\,A_{12}\,\alpha^3 + 12\,\alpha^2\,[B_{12}\,(A_{11} + 2\,A_{22}) - A_{12}\,(B_{11} + 2\,B_{22})], \\
& +6\,\alpha\,[2\,B_{12}\,(A_{12}\,A_{21} - A_{11}\,A_{22}) + A_{22}\,B_{12}\,(3\,B_{11} + B_{22}) \\
& -A_{12}\,(B_{22}^2 + 2\,B_{11}\,B_{22}) + B_{12}\,(2\,A_{11}\,B_{22} - 2\,A_{21}\,B_{12} - a_{12}\,B_{21})] \\
& +3\,\left[A_{12}\,A_{21}\,B_{12}\,(B_{11} + B_{22}) - A_{22}\,B_{11}\,B_{12}\,(A_{11} - B_{11}) + B_{12}^2\,(A_{11}\,B_{21} - A_{21}\,B_{11})\right. \\
& \left.-A_{12}\,B_{11}\,(B_{12}\,B_{21} + B_{22}^2) + A_{11}\,B_{12}\,B_{22}\,(B_{22} - A_{22}) + B_{12}\,B_{22}\,(A_{22}\,B_{11} - A_{21}\,B_{12})\right],
\end{aligned}
\tag{A12}
$$

$$
\begin{aligned}
R = {} & 8\,\alpha^2\,(A_{12} - A_{11}) + 8\,\alpha\,[B_{12}\,(A_{21} - A_{22}) + B_{22}\,(A_{12} - A_{11})] \\
& +2\,B_{12}\,(A_{21} - A_{22})\,(B_{11} + B_{22}) + 2\,(A_{12} - A_{11})\,\left(B_{12}\,B_{21} + {B_{22}}^2\right),
\end{aligned}
\tag{A13}
$$

$$
S = 3\,(2\,\alpha - A_{11} + A_{12} + B_{11} - B_{12})\,\left[4\,\alpha^2 + 2\,\alpha\,(B_{11} + B_{22}) + B_{11}\,B_{22} - B_{12}\,B_{21}\right]^2, \tag{A14}
$$

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