

## Nonlinear transport in a dilute binary mixture

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### ABSTRACT

An overview of recent work on nonlinear transport properties in a dilute binary mixture under uniform shear flow is presented. The physical situation is such that the only nonzero hydrodynamic gradient is  $\partial u_x / \partial y = a = \text{const}$ , where  $u$  is the flow velocity. The description applies for arbitrary values of the shear rate  $a$  and is not limited to specific values of particle masses, concentrations, and particle sizes. We explicitly obtain the rheological properties of the mixture (non-Newtonian shear viscosity and viscometric functions) as nonlinear functions of the shear rate and the parameters of the mixture. The results are obtained from three different and complementary routes: (i) from the Boltzmann equation for Maxwell molecules, (ii) from a kinetic model for general repulsive interactions, and (iii) from Monte Carlo simulations. In the tracer limit, a transition to an

alternative state is identified. In this new state, surprisingly the partial contribution of the tracer species to the total properties of the mixture becomes finite if the shear rate is larger than a certain critical value. The relevance of the results presented in the review as well as its relation with more realistic flows is discussed.

### I. INTRODUCTION

The analysis of transport phenomena in fluid systems is certainly more complicated when one deals with a mixture than when one considers the case of a monocomponent system. Not only is the number of transport coefficients higher but also they are functions of parameters such as the molar fractions, the mass ratios and/or the size ratios. In addition, if one attempts to study far from equilibrium situations, namely, those for which the assumptions of linear irreversible thermodynamics break down, the difficulties increase considerably. Due to this complexity, tractable specific situations for which a complete description can be offered are of great value in order

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to gain some insight into the understanding of more general problems.

In order to capture the essential aspects of nonlinear transport phenomena, a dilute binary mixture with short-range interactions can be chosen as a prototype system. Further, we adopt a kinetic level of description according to which the state of the mixture is characterized by the one-particle velocity distribution functions  $f_s(\mathbf{r}, \mathbf{v}; t)$  ( $s \equiv 1, 2$ ) of each species. These functions obey a set of two coupled Boltzmann equations [1]. Nevertheless, it is a very hard task to find explicit solutions of the Boltzmann equations, especially in states far from equilibrium. One of the rare exceptions corresponds to the so-called uniform shear flow (USF). In this state, the only nonzero gradient is  $\partial u_x / \partial y = a = \text{const}$ , where  $u$  is the flow velocity. Due to its simplicity, this flow problem has been one of the most extensively studied states in the past, especially in the case of a monocomponent gas [2–6]. The relevant transport coefficients of USF are the nonlinear shear viscosity  $\eta$  and viscometric functions  $\Psi_{1,2}$  which are related to the total pressure tensor  $\mathbf{P}$ . In the case of a single monocomponent gas of Maxwell molecules (repulsive  $r^{-4}$  potential), Ikenberry and Truesdell [7] obtained explicit expressions of the rheological properties  $\eta$  and  $\Psi_{1,2}$  for arbitrary values of the shear rate  $a$ . Although the Ikenberry-Truesdell solution only holds for Maxwell molecules, it presents a good agreement with computer simulations for other potentials [8,9].

The aim of this review is to analyze the transport properties of a dilute binary mixture under USF. The molar fractions are constant so that no mutual diffusion exists in the mixture and the transport of momentum is the relevant phenomenon. On the other hand, since our description holds for arbitrary values of the masses, concentrations and force constants, the transport coefficients are nonlinear functions of the shear rate as well as of the parameters of the mixture. In the context of the Boltzmann equation, explicit results can only be obtained in the particular case of Maxwell molecules. In this case, the infinite hierarchy for the moments of the velocity distribution functions can be solved exactly, and in particular the pressure tensor  $\mathbf{P}$  (which is related to the second order moments) can be determined. Our results show that, independently of the parameters considered,  $\eta$  and  $\Psi_1(a)$  monotonically decrease as  $a$  increases (shear thinning effect), while  $\Psi_2$  vanishes [10]. Obviously, the solution of Ikenberry and Truesdell is recovered in the limit of mechanically equivalent particles. Unfortunately, the above description cannot be regarded as general since the model of Maxwell molecules is not a very realistic representation of intermolecular interactions, except in some particular conditions. In order to evaluate the effect of the interaction potential on the rheological properties, we formulate the same problem using a convenient kinetic model. The idea is to replace the exact Boltzmann collision integrals by simple relaxation terms which retain their main phys-

ical properties, such as the conservation laws. Our model is a generalization of the well-known Gross-Krook (GK) kinetic model [11] for a dilute binary mixture that incorporates a temperature dependence of the collision frequencies [12]. This allows for the consideration of general repulsive interactions. Apart from obtaining the transport properties, and in contrast to the case of the Boltzmann equation, the use of a kinetic model allows us to derive explicit expressions for the velocity distribution functions [13]. The behavior of these distributions is tested against the results obtained from the well-known Direct Simulation Monte Carlo method [14] for a dilute gas. In general, the comparison of the GK predictions with those given by exact results of the Boltzmann equation as well as from Monte Carlo simulations shows a qualitatively good agreement for not too large shear rates and/or not too large disparity of the parameters of the mixture.

An interesting point is to investigate what happens in the tracer limit, namely, when the molar fraction of one of the components tends to zero. In this limit, the results obtained from the Boltzmann equation for Maxwell molecules [15] and from the kinetic model for general repulsive potentials [16] show that surprisingly the partial contribution of the tracer species to the total properties of the mixture becomes *finite* if the shear rate is larger than a certain critical value  $a_c$ , which is a function of the parameters of the mixture and the interaction model considered. This

phenomenon can be interpreted as a nonequilibrium phase transition in velocity space. While for non-Maxwell molecules, the corresponding order parameter is discontinuous at the critical point (first order transition), the transition becomes continuous at  $a_c$  in the special case of Maxwell molecules. It must be remarked that all these analytical predictions are also supported by Monte Carlo simulations of the Boltzmann equation.

The organization of the review is as follows. In Sec. II we describe the shear flow problem and introduce the starting kinetic equations. Section III is concerned with the evaluation of the steady transport properties from the Boltzmann and GK equations as well as with the derivation of the GK velocity distribution functions. In Sec. IV, we illustrate the shear-rate dependence of the above quantities and compare the predictions made from the Boltzmann equation with those from the GK approximation. The tracer limit is analyzed in Sec. V, and we close the paper with a brief discussion on the results obtained.

## II. DESCRIPTION OF THE PROBLEM

Let us consider a dilute binary mixture. In terms of the velocity distribution function  $f_s(\mathbf{r}, \mathbf{v}, t)$ , the number density  $n_s$ , the mean velocity  $\mathbf{u}_s$ , and temperature  $T_s$  of species  $s$  are defined as

$$\{n_s, n_s \mathbf{u}_s, n_s k_B T_s\} = \int d\mathbf{v} \left\{ 1, \mathbf{v}, \frac{1}{2} m_s (\mathbf{v} - \mathbf{u}_s)^2 \right\} f_s, \quad (1)$$

where  $m_s$  is the mass of a particle of species  $s$ , and  $k_B$  is the Boltzmann constant. From the partial quantities appearing in (1), one can define the total number density  $n = n_1 + n_2$ , the flow velocity  $\mathbf{u} = (\rho_1 \mathbf{u}_1 + \rho_2 \mathbf{u}_2) / (\rho_1 + \rho_2)$ ,  $\rho_s = m_s n_s$  being the mass density of species  $s$ , and the temperature of the mixture  $T$  (which is the relevant one at a hydrodynamic level) as

$$nk_B T = \sum_{s=1}^2 \left( n_s k_B T_s + \frac{1}{3} \rho_s (\mathbf{u}_s - \mathbf{u})^2 \right). \quad (2)$$

The macroscopic state of uniform shear flow (USF) is characterized by constant densities  $n_s$ , uniform temperature  $T$ , and a flow field of the form

$$u_{s,i}(\mathbf{r}) = u_i = a_{ij} r_j, \quad a_{ij} = a \delta_{ix} \delta_{jy}, \quad (3)$$

$a$  being the constant shear rate. Since there is no mutual diffusion in the mixture, the shear rate (which may be arbitrarily large) is the only nonequilibrium parameter of the problem and the pressure tensor  $\mathbf{P}$  is the relevant irreversible flux. It is defined as

$$\begin{aligned} \mathbf{P} &= \sum_{s=1}^2 m_s \int d\mathbf{v} \mathbf{V} \mathbf{V} f_s \\ &= \sum_{s=1}^2 \mathbf{P}_s, \end{aligned} \quad (4)$$

where  $V_i = v_i - a_{ij} r_j$  is the peculiar velocity, and the expression for the partial pressure tensor of species  $s$ ,  $\mathbf{P}_s$ , can be easily identified. From the total pressure tensor, the main transport coefficients of the problem may be defined: the shear viscosity

$$\eta(a) = -\frac{P_{xy}}{a} \quad (5)$$

and the viscometric functions

$$\Psi_1(a) = \frac{P_{yy} - P_{xx}}{a^2}, \quad (6)$$

$$\Psi_2(a) = \frac{P_{zz} - P_{yy}}{a^2}. \quad (7)$$

In the USF problem, the shearing motion produces viscous heating, so that the temperature increases in time. Although the state is not stationary, for sufficiently long times and taking suitable initial conditions, it is possible to get a stationary representation by using appropriate dimensionless variables (e.g., scaling the velocity relative to the thermal velocity). In this sense, Eqs. (5)–(7) must be understood in the long-time limit where the influence of the initial conditions has disappeared.

At a microscopic level, the USF is a state that is spatially homogeneous in the Lagrangian frame moving with the flow velocity  $\mathbf{u}$ . As a consequence, the distribution functions become homogeneous under the above change, namely,  $f_s(\mathbf{r}, \mathbf{v}; t) \equiv f_s(\mathbf{V}; t)$ . This is the main reason for which this state has received great attention in the past, especially in the case of a single gas. Nevertheless, much less is known about it in the case of multicomponent systems. Under the conditions of the USF, the distributions  $f_s$  obey the set of Boltzmann equations:

$$\frac{\partial}{\partial t} f_1 - \frac{\partial}{\partial V_i} a_{ij} V_j f_1 = J_{11}[f_1, f_1] + J_{12}[f_1, f_2] \quad (8)$$

and a similar equation for  $f_2$ . Here,  $J_{rs}[f_r, f_s]$  is the Boltzmann collision operator [1], which in standard

notation reads

$$J_{rs}[f_r, f_s] = \int d\mathbf{V}_1 \int d\Omega |\mathbf{V} - \mathbf{V}_1| \sigma_{rs}(\mathbf{V} - \mathbf{V}_1, \theta) [f_r(\mathbf{V}') f_s(\mathbf{V}_1') - f_r(\mathbf{V}) f_s(\mathbf{V}_1)]. \quad (9)$$

We are interested in evaluating the rheological properties  $\eta$  and  $\Psi_{1,2}$  for arbitrary values of  $a$  and the parameters of the mixture. In the context of the Boltzmann equation, this is only possible in the case of Maxwell molecules, namely, a potential of the form  $\Phi_{rs} = \kappa_{rs} r^{-4}$ . The key point is that the collision rate  $g\sigma_{rs}(g, \theta)$  is independent of the relative velocity  $g$  so that the collisional moments of a given order do not involve moments of higher order [7]. However, for non-Maxwell interactions the above property does not hold and one must resort to simple kinetic models. Here, we will start from a generalization of the conventional Gross-Krook (GK) model [11] to  $r^{-4}$  repulsive potentials. In this case, the exact  $J_{rs}[f_r, f_s]$  is replaced by a relaxation term of the form

$$J_{rs}^{\text{GK}}[f_r, f_s] = -\nu_{rs}(f_r - f_{rs}), \quad (10)$$

where, in the case of the USF problem, the reference distribution  $f_{rs}$  is given by

$$f_{rs} = n_r \left( \frac{m_r}{2\pi k_B T_{rs}} \right)^{3/2} \exp\left(-\frac{m_r}{2k_B T_{rs}} V^2\right), \quad (11)$$

and

$$T_{rs} = T_r + 2 \frac{m_r m_s}{(m_r + m_s)^2} (T_s - T_r). \quad (12)$$

Further, an effective collision frequency  $\nu_{rs}$  is defined as [12]

$$\nu_{rs} = A(\beta) n_s \left( \kappa_{rs} \frac{m_r + m_s}{m_r m_s} \right)^{(1-\beta)/2} \left( \frac{2k_B T_r}{m_r} + \frac{2k_B T_s}{m_s} \right)^{\beta/2} \quad (13)$$

where  $\beta = 1 - 4/\ell$ , and  $A(\beta)$  is a constant for a given potential. The reliability of this kinetic model has been assessed in several nonequilibrium problems [12,17] by comparison with exact analytical results [18] as well as with Monte Carlo simulations of the Boltzmann equation [19].

Before analyzing the shear-rate dependence of the transport coefficients, it is instructive to show that Eq. (8) (and its corresponding GK approximation) admits a nice scaling property in the case of Maxwell molecules. Let us introduce the scaled quantities

$$\bar{\mathbf{V}} = e^{-\alpha t} \mathbf{V}, \quad (14)$$

$$\bar{f}_s(\bar{\mathbf{V}}, t) = e^{3\alpha t} f_s(\mathbf{V}, t), \quad (15)$$

where  $\alpha$  is an arbitrary constant. In terms of these scaled variables, Eq. (8) reduces to

$$\frac{\partial}{\partial t} \bar{f}_1 - \frac{\partial}{\partial \bar{V}_i} (a_{ij} \bar{V}_j + \alpha \bar{V}_i) \bar{f}_1 = J_{11}[\bar{f}_1, \bar{f}_1] + J_{12}[\bar{f}_1, \bar{f}_2]. \quad (16)$$

In deriving Eq. (16), use has been made of a symmetry property of  $J_{rs}[f_r, f_s]$  for Maxwell molecules [21]. Equation (16) can be seen as the Boltzmann equation in USF under the action of a nonconservative drag force  $\mathbf{F}_s = -m_s \alpha \mathbf{V}$ . This shows the equivalence between the description with and without the external forces  $\mathbf{F}_s$  in the case of Maxwell molecules. Most

computer simulations of USF use forces of this kind to enforce constant temperature [20]. In this context,  $\alpha$  is chosen as a function of the shear rate by the condition that the temperature achieves a constant value in the long-time limit. Here, for the sake of simplicity, we will adopt this point of view and will incorporate isothermal constraints. For non-Maxwell molecules, the presence of the thermostat does not play a neutral role in the results and a certain influence may exist in the evaluation of the rheological properties [21].

### III. NONLINEAR TRANSPORT PROPERTIES IN THE STEADY USF STATE

The objective now is to explicitly determine the rheological properties of the mixture in the thermostatted shear flow state. In this case, we will start from Eq. (16) with  $\partial \bar{f}_1 / \partial t = 0$  and will determine  $\alpha$  by consistency. Henceforth, and for the sake of simplicity, we will drop the bars in Eq. (16). The transport coefficients  $\eta$  and  $\Psi_{1,2}$  will be given in terms of the shear rate  $a$ , the mass ratio  $\mu = m_1/m_2$ , the concentration ratio  $\delta = n_1/n_2$ , and the force constant ratios  $w_{11} = \kappa_{11}/\kappa_{12}$  and  $w_{22} = \kappa_{22}/\kappa_{12}$ . The analysis will be made from the exact Boltzmann equations for Maxwell molecules and from the GK model for general repulsive interactions.

#### A. Description based on the Boltzmann equation

As was noted above, the main transport prop-

erties are related to the total momentum flux  $\mathbf{P} = \mathbf{P}_1 + \mathbf{P}_2$ . It is also interesting to analyze partial contributions corresponding to each species, such as the temperature ratios  $T_{1,2}/T$ . These quantities measure how the kinetic energy is distributed between the two species. In order to determine  $\mathbf{P}_1$ , we multiply both sides of Eq. (16) (with  $\partial f_1 / \partial t = 0$ ) by  $m_1 V_i V_j$  and integrate over velocity space. The result is [10]

$$2\alpha P_{1,ij} + a_{ik} P_{1,kj} + a_{jk} P_{1,ki} + B_{11} P_{1,ij} + B_{12} P_{2,ij} = (A_{11} p_1 + A_{12} p_2) \delta_{ij}, \quad (17)$$

where  $p_s = n_s k_B T_s$ , and we have introduced the coefficients

$$A_{11} = \frac{\lambda'_{11}}{m_1} n_1 + \frac{\lambda'_{12}}{m_1 + m_2} \frac{m_2}{m_1} n_2, \quad (18)$$

$$A_{12} = \frac{\lambda'_{12}}{m_1 + m_2} n_1, \quad (19)$$

$$B_{11} = A_{11} + 2 \frac{\lambda_{12}}{m_1 + m_2} n_2, \quad (20)$$

$$B_{12} = A_{12} - 2 \frac{\lambda_{12}}{m_1 + m_2} n_1. \quad (21)$$

In the above equations, the eigenvalues  $\lambda_{r,s}$  and  $\lambda'_{r,s}$  of the Boltzmann collision operator are given by

$$\lambda_{r,s} = 1.69\pi \left( \kappa_{r,s} \frac{m_r m_s}{m_r + m_s} \right)^{1/2}, \quad (22)$$

$$\lambda'_{r,s} = 2.61\pi \left( \kappa_{r,s} \frac{m_r m_s}{m_r + m_s} \right)^{1/2}. \quad (23)$$

The corresponding equation for  $\mathbf{P}_2$  can be easily inferred from Eq. (17) by just making the changes  $1 \leftrightarrow 2$ . The thermostat parameter  $\alpha$  is determined

by the consistency condition  $P_{1,kk} + P_{2,kk} = 3nk_B T$ , which leads in general to a sixth-degree equation that must be solved numerically [10]. When  $\alpha$  is known, Eq. (17) is easily solved and provides a microscopic basis for evaluating such non-Newtonian transport coefficients as functions of  $a$ ,  $\mu$ ,  $\delta$ , and  $w_{rr}$ . Their corresponding expressions are very large and, for the sake of brevity, will be omitted here. They can be found in Ref. [10]. The shear-rate dependence of these quantities will be illustrated and compared later with the predictions of the GK model.

### B. Description based on the Gross-Krook

#### (GK) equation

The results derived in the previous section cannot be seen as general, since a model of Maxwell molecules is somewhat limited. Nevertheless, if one wants to derive explicit expressions of the rheological properties for non-Maxwell molecules, one needs to use a kinetic model. As said before, here we will start from the generalized GK model defined by Eqs. (10)–(12). Since in general the reference distribution  $f_{rs}$  depends on space and time through its dependence on the densities, the flow velocities, and the temperatures (which are moments of the distributions  $f_s$ ), the GK equation is actually *more* nonlinear than the original bilinear Boltzmann equation. This means that the model is not restricted to near equilibrium situations and can be used to evaluate nonlinear transport

properties. The results obtained in the past few years have shown the reliability of this kinetic model in such nonequilibrium problems [12,17,19].

Let us define the reduced velocity moments  $M_{k,\ell,m}^{(s)}$  corresponding to species  $s$ :

$$M_{k,\ell,m}^{(s)} = \frac{1}{n_s} \left( \frac{2k_B T}{m_s} \right)^{-(1/2)(k+\ell+m)} \int d\mathbf{V} V_x^k V_y^\ell V_z^m f_s(\mathbf{V}). \quad (24)$$

In the context of the GK equation, these moments verify the hierarchy

$$akM_{k-1,\ell+1,m}^{(1)} + [\nu_1 + \alpha(k + \ell + m)]M_{k,\ell,m}^{(1)} = N_{k,\ell,m}^{(1)}, \quad (25)$$

and a similar equation for  $M_{k,\ell,m}^{(2)}$ . Here,  $\nu_1 = \nu_{11} + \nu_{12}$ , and

$$N_{k,\ell,m}^{(1)} = \pi^{-3/2} C_k C_\ell C_m [\nu_{11} \chi_1^{(k+\ell+m)/2} + \nu_{12} \chi_{12}^{(k+\ell+m)/2}] \quad (26)$$

where  $C_k = \Gamma((k+1)/2)$  if  $k$  is even, being zero otherwise. Also,  $\chi_1 = T_1/T$ , and  $\chi_{12} = T_{12}/T$ . The solution of Eq. (25) can be written as [13]

$$M_{k,\ell,m}^{(1)} = \sum_{q=0}^k \frac{k!}{(k-q)!} (-a)^q [\nu_1 + \alpha(k + \ell + m)]^{-(1+q)} \times N_{k-q,\ell+q,m}^{(1)}. \quad (27)$$

This equation is still formal since the parameters  $\alpha$ ,  $\chi_1$ , and  $\chi_2$  are unknown. They can be determined from the consistency conditions:

$$\frac{3}{2}\chi_s = M_{2,0,0}^{(s)} + M_{0,2,0}^{(s)} + M_{0,0,2}^{(s)}, \quad (28)$$

$$\chi_2 = 1 + \delta(1 - \chi_1). \quad (29)$$

Except in the particular case of Maxwell molecules ( $\beta = 0$ ), Eqs. (28) and (29) must be solved numerically since the collision frequencies are nonlinear functions of the temperature ratios. Once  $\alpha$  and  $\chi_s$  are known, one can easily evaluate all the relevant transport coefficients of the problem.

The use of a kinetic model allows us to derive the explicit expressions of the velocity distribution functions  $f_s$ . Even for Maxwell molecules, it is not possible to obtain an explicit solution of the Boltzmann equation and the only information about  $f_s$  is given indirectly through its first moments. This is one of the main advantages of using kinetic models. In the steady shear flow state, after some algebra, the distribution  $f_1$  can be written as  $f_1(\mathbf{V}) = n_1(m_1/2k_B T)^{3/2} g_1(\boldsymbol{\xi})$ , where  $\boldsymbol{\xi} \equiv (m_1/2k_B T)^{1/2} \mathbf{V}$  and the reduced distribution  $g_1$  is

$$g_1(\boldsymbol{\xi}) = \pi^{-3/2} \int_0^\infty d\tau e^{-(\nu_1 - 3\alpha)\tau} \left[ \nu_{11} \chi_1^{-3/2} \times \exp(-\chi_1^{-1} e^{2\alpha\tau} \boldsymbol{\xi} \cdot \boldsymbol{\Gamma}_\tau \cdot \boldsymbol{\xi}) + \nu_{12} \chi_{12}^{-3/2} \times \exp(-\chi_{12}^{-1} e^{2\alpha\tau} \boldsymbol{\xi} \cdot \boldsymbol{\Gamma}_\tau \cdot \boldsymbol{\xi}) \right]. \quad (30)$$

Here,  $\boldsymbol{\Gamma}_\tau$  is the matrix defined as  $\Gamma_{ij}(\tau) = \delta_{ij} + a^2 \tau^2 \delta_{iy} \delta_{jy} + a\tau(\delta_{ix} \delta_{jy} + \delta_{iy} \delta_{jx})$ . The highly nonlinear dependence of  $g_1$  on the parameters of the problem is very apparent.

#### **IV. COMPARISON BETWEEN THE BOLTZMANN AND GK RESULTS**

In this section we illustrate the shear-rate depen-

dence of the transport coefficients and the velocity distribution functions for several values of the parameters of the mixture. We also compare the predictions made by the GK model with those obtained from the Boltzmann equation for Maxwell molecules. This comparison can be seen as a stringent test of the kinetic model computation of nonlinear transport properties and distribution functions in a binary mixture. To make such a comparison, we introduce dimensionless quantities and choose

$$\zeta = 1.85 \pi n \kappa_{12}^{(1-\beta)/2} \left( \frac{m_1 + m_2}{m_1 m_2} \right)^{1/2} (2k_B T)^{\beta/2} \quad (31)$$

as an effective collision frequency, and hence define the reduced shear rate  $a^* = a/\zeta$ . The numerical coefficient appearing in the expression for  $\zeta$  has been chosen to give the same results in both the GK and Boltzmann equations in the USF problem for a single monocomponent gas [7].

The temperature ratio  $T_1/T_2$  is a measure of the lack of equal distribution of energy. The shear-rate dependence of this quantity is plotted in Fig. 1 for  $\delta = 3$ , two values of  $\mu$ , and for simplicity, we have assumed that  $\kappa_{12} = \kappa_{22} = \kappa_{12}$ . The curves of the GK model correspond to the cases of Maxwell molecules ( $\beta = 0$ ) and hard spheres ( $\beta = 1$ ). We see that, independently of the interaction considered, the temperature ratio is not monotonic. In particular, the two temperatures coincide at a certain value of the shear rate which depends on the parameters of the mixture. The qualitative trends predicted by the ex-



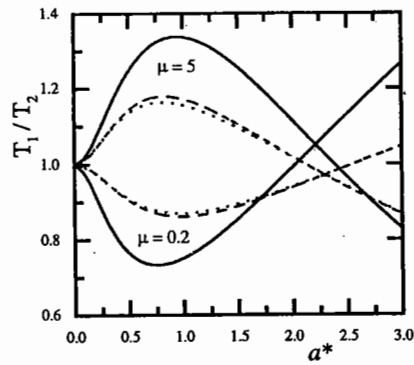


FIG. 1. Plot of the temperature ratio  $T_1/T_2$  versus the reduced shear rate  $a^*$  for  $\kappa_{rs} = \kappa$ ,  $\delta = 3$ , and two values of the mass ratio  $\mu$ . The solid lines refer to the Boltzmann results for Maxwell molecules while the dashed and dotted lines correspond to the GK model results for Maxwell molecules and hard spheres, respectively.

act solution are also given by the GK model while, at a quantitative level, the discrepancies between the two theories are less important when the mass of the excess component is larger than that of the defect component. Concerning the effect of the interaction potential, we observe that  $T_1/T_2$  is practically insensitive to the interaction potential for small shear rates, while this influence becomes more significant as the system moves away from equilibrium.

The most important quantity in a sheared mixture is the nonlinear shear viscosity  $\eta(a^*)$ . In Fig. 2 we plot the reduced shear viscosity  $\eta(a^*)/\eta(0)$  versus the reduced shear rate  $a^*$  for the same cases considered previously. Here,  $\eta(0)$  represents the Navier-Stokes shear viscosity coefficient.

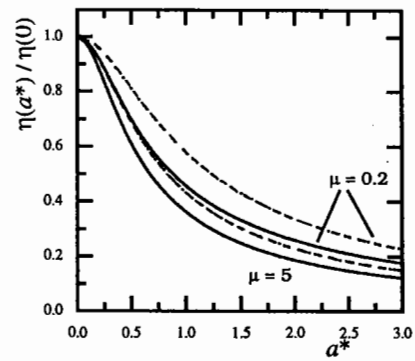
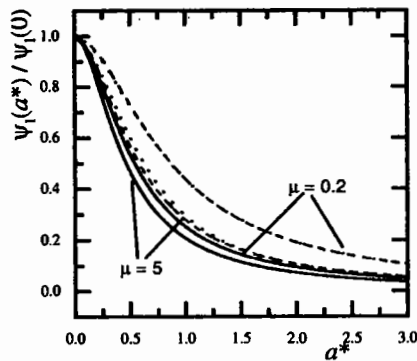


FIG. 2. Plot of the reduced shear viscosity  $\eta(a^*)/\eta(0)$  versus the reduced shear rate  $a^*$  for  $\kappa_{rs} = \kappa$ ,  $\delta = 3$ , and two values of the mass ratio  $\mu$ . The solid lines refer to the Boltzmann results for Maxwell molecules while the dashed and dotted lines correspond to the GK model results for Maxwell molecules and hard spheres, respectively.

In the same way as in the monocomponent case, a shear thinning effect is observed, namely, the shear viscosity decreases as the shear rate increases. The inhibition of momentum transport is more noticeable when the mass of the excess component is larger than that of the defect component. The GK results indicate that the shear viscosity is practically independent of the details of the interaction law considered. This universal character has been also observed in the single gas case [9]. We observe again that the GK predictions are closer to the Boltzmann ones when the excess particles are heavier than the defect particles. Normal stresses are measured by the viscometric functions. The Boltzmann and GK results lead

to  $\Psi_2 = 0$  regardless of the values of the parameters of the mixture considered. This result is exact for Maxwell molecules, although for non-Maxwell molecules one expects that  $\Psi_2 \neq 0$  (but very small) as occurs for a monocomponent gas [8,9]. The shear-rate dependence of  $\Psi_1(a^*)/\Psi_1(0)$  is plotted in Fig. 3. This quantity is also a decreasing function and its dependence on the parameters of the mixtures is similar to that of the shear viscosity. However, and in contrast to  $\eta(a)$ , a more significant influence of the potential interaction on  $\Psi_1(a)$  appears for  $\mu > 1$ .

As said before, the distribution function  $f_s(\mathbf{V})$  provides all the information on the shear flow problem. Unfortunately, since no explicit expression is



\*FIG. 3. Plot of the reduced first viscometric function  $\Psi_1(a^*)/\Psi_1(0)$  versus the reduced shear rate  $a^*$  for  $\kappa_{rs} = \kappa$ ,  $\delta = 3$ , and two values of the mass ratio  $\mu$ . The solid lines refer to the Boltzmann results for Maxwell molecules while the dashed and dotted lines correspond to the GK model results for Maxwell molecules and hard spheres, respectively.

known for this quantity in the context of the Boltzmann equation, one has to resort to computer simulations or start from a kinetic model. With respect to the first possibility, here we will use the DSMC method due to Bird [14], which has been proved to be an efficient tool to study transport properties in dilute mixtures [19]. This is the only way to test the predictions made from the GK model at the level of the distribution (30). Since  $g_1(\xi)$  depends on the three components of  $\xi$ , for practical purposes, it is useful to define some marginal distributions:

$$g_{1,x}(\xi_x; a^*) = \int_0^\infty d\xi_y \int_{-\infty}^\infty d\xi_z g_1(\xi; a^*), \quad (32)$$

$$g_{1,y}(\xi_y; a^*) = \int_0^\infty d\xi_x \int_{-\infty}^\infty d\xi_z g_1(\xi; a^*). \quad (33)$$

For the sake of illustration, in Figs. 4 and 5 we plot the ratios  $\varphi_x(\xi_x) \equiv g_{1,x}(\xi_x; a^*)/g_{1,x}(\xi_x; 0)$  and  $\varphi_y(\xi_y) \equiv g_{1,y}(\xi_y; a^*)/g_{1,y}(\xi_y; 0)$ , respectively, for  $w_{rr} = 1$ ,  $\delta = 3$ ,  $\mu = 5$ , and  $a^* = 2.771$ . We have considered the case of Maxwell molecules. In general, referring to Figs. 4 and 5, a distortion from equilibrium ( $\varphi_{x,y} = 1$ ) is clearly observed. This could be anticipated on the basis of the highly nonlinear dependence of the transport coefficients on the shear rate and the parameters of the mixture. We also see that the GK distributions reproduce fairly well the general behavior of the Boltzmann distributions obtained from the simulation. However, it is evident that there exist significant discrepancies between the simulation data and the GK predictions, especially in

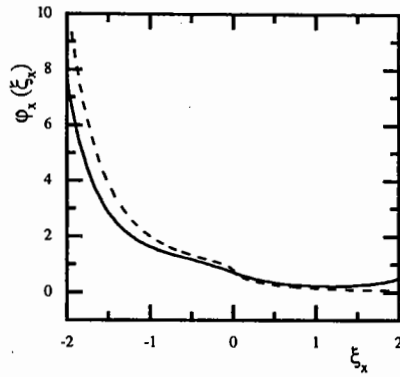


FIG. 4. Reduced distribution function  $\varphi_x(\xi_x)$  versus  $\xi_x$  for  $\kappa_{rs} = \kappa$ ,  $\delta = 3$ ,  $\mu = 5$  and  $a^* = 2.771$  in the case of Maxwell molecules as obtained from Monte Carlo simulations (solid line) and from the GK model (dashed line).

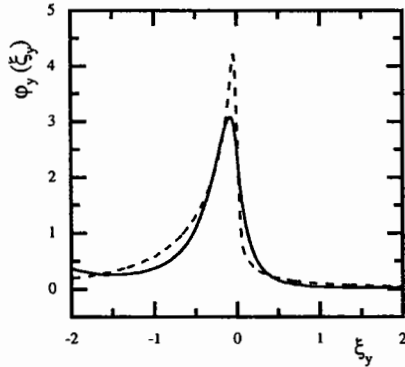


FIG. 5. Reduced distribution function  $\varphi_y(\xi_y)$  versus  $\xi_y$  for  $\kappa_{rs} = \kappa$ ,  $\delta = 3$ ,  $\mu = 5$  and  $a^* = 2.771$  in the case of Maxwell molecules as obtained from Monte Carlo simulations (solid line) and from the GK model (dashed line).

the region of high velocities in the case of  $\varphi_x$  when  $\xi_x < 0$  and near the maximum for  $\varphi_y$ . In this latter

case, the GK distribution predicts well the location of the maximum although not its value.

### V. TRACER LIMIT

So far, all the results apply for arbitrary values of the ratios of mass, concentration and force constants. An interesting limit corresponds to the *tracer* limit, namely, when  $\delta = n_1/n_2 \ll 1$ . In this situation, one usually assumes that the properties of the excess component (bath) are not affected by the tracer particles and, in addition, one neglects collisions among tracer particles themselves in the kinetic equation of the tracer component. As a consequence, one expects that the contribution of the tracer species to the total properties of the mixture will be negligible. Nevertheless, as we will see later, this expectation may be violated in the shear flow problem since, when the mixture is sufficiently far from equilibrium, the relative contribution of the tracer particles to the total properties can be even larger than that of the excess component.

Let us consider first the Boltzmann description in the special case of Maxwell molecules. In the tracer limit ( $\delta \rightarrow 0$ ), the corresponding sixth-degree equation for  $\alpha$  decouples into two cubic algebraic equations, whose real solutions are [15]

$$\alpha_0 = \nu_{22} \varphi \left( \frac{a}{\nu_{22}} \right), \quad (34)$$

$$\alpha'_0 = \frac{2\nu_{12}}{(1+\mu)^2} \left[ \varphi \left( \frac{a(1+\mu)^2}{2\nu_{12}} \right) - 0.648\mu \right], \quad (35)$$

where  $\varphi(x) \equiv \frac{2}{3} \sinh^2[\frac{1}{6} \cosh^{-1}(1+9x^2)]$  and  $\nu_{rs}^{-1}$  is an effective mean free time of a particle of species  $r$  for collisions with particles of species  $s$ . Its definition is similar to the one given for the GK model, Eq. (13). The analysis of the transient regime shows that the suitable thermostat to achieve steady values for  $T_1$  and  $T_2$  is  $\alpha = \max(\alpha_0, \alpha'_0)$ . As long as  $\delta \neq 0$ ,  $\alpha_0 > \alpha'_0$ . Nevertheless, if  $\delta \rightarrow 0$ , and for a given choice of the force constants, one finds that: (i)  $\alpha = \alpha_0$  if  $\mu$  is larger than a certain threshold value  $\mu_{th}$ , which is the solution of  $\nu_{12}(\mu) = (1 + \mu)^2/2$ ; and (ii) if  $\mu < \mu_{th}$ , then  $\alpha = \alpha'_0$  for shear rates larger than a critical value  $a_c(\mu)$ . The behavior of  $a_c(\mu)$  shows that  $a_c \rightarrow \infty$  both when  $\mu \rightarrow 0$  and  $\mu \rightarrow \mu_{th}$ .

What are the main physical consequences of the existence of a critical value  $a_c(\mu)$ ? Let us focus our attention on the relative contribution of the tracer particles to the total energy of the system,  $E_1/E$ . In this case, after a careful asymptotic analysis, one obtains that [15]

$$\lim_{\delta \rightarrow 0} \frac{E_1}{E} = F(a, \mu, w_{11}, w_{22}) \quad (36)$$

if  $\mu < \mu_{th}$  and  $a > a_c(\mu)$ , being  $E_1/E \sim \delta \approx 0$  otherwise. Here,  $F(a, \mu, w_{11}, w_{22})$  is a known function that depends in a nonlinear way on the different parameters of the problem. The above result shows the qualitatively different behavior of the mixture in the tracer limit depending on whether  $a$  is larger than  $a_c$  or not. Although the molar fraction of the tracer particles is negligible, their contribution to the total

energy may be significant if the shear rate is larger than a certain critical value. By borrowing the usual terminology of equilibrium phase transitions [22], one can identify the shear rate  $a$  as the ‘‘control’’ parameter and  $E_1/E$  as an ‘‘order’’ parameter. The fact that the order parameter goes to zero when  $a - a_c \rightarrow 0^+$  indicates that the transition can be interpreted as of second order in velocity space.

An interesting question is if this transition can also be extended beyond the Maxwell interaction. This question can be answered analytically from the GK model. In the context of this model, a detailed analysis [16] of the tracer limit for general repulsive interactions allows us again to identify such a transition in velocity space. The results show again that the transition becomes continuous at  $a_c(\mu)$  in the case of Maxwell molecules (first-order transition) while for non-Maxwell molecules the order parameter is discontinuous at the critical point. In order to illustrate the different behaviors, in Fig. 6 we plot the order parameter  $E_1/E$  versus  $a/a_c$  when  $\delta = 0$  as given from the Boltzmann equation for Maxwell molecules and from the GK model for Maxwell molecules and hard spheres. We have considered the case  $\mu = 0.1$  and  $\kappa_{12} = \kappa_{22}$ . It is evident that, for non-Maxwell molecules,  $E_1/E \rightarrow 0$  when  $a \rightarrow a_c^-$  while  $E_1/E \rightarrow$  finite value when  $a \rightarrow a_c^+$ . Also, regardless of the interaction considered, the tracer contribution to the total energy can be even larger than that of the excess component for sufficiently large values of the

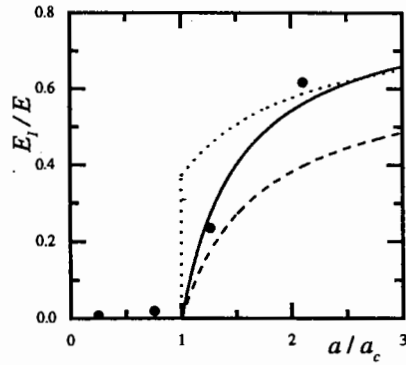


FIG. 6. Plot of the energy ratio  $E_1/E$  versus  $a/a_c$  in the tracer limit ( $\delta \rightarrow 0$ ) for  $\kappa_{rs} = \kappa$ , and  $\mu = 0.1$ . The solid line corresponds to the Boltzmann results for Maxwell molecules while the dashed and dotted lines refer to the GK model results for Maxwell molecules and hard spheres, respectively. The circles represent simulation data in the case of Maxwell molecules for  $\delta = 10^{-2}$ .

shear rate. We also observe that, although the GK model predicts qualitatively well the transition for Maxwell molecules, there exist important discrepancies between the Boltzmann and GK results, especially for very large shear rates.

Since so far all the results presented have been obtained analytically after taking a delicate limit, it might be possible that the above transition was an artifact of the algebra involved. One way to elucidate such a point is to perform Monte Carlo simulations. For this reason, we include in Fig. 6 simulation data for Maxwell molecules with a concentration ratio  $\delta = 10^{-2}$  and reduced shear rates  $a/a_c = 0.25, 0.76, 1.27$ , and  $2.11$ . These points were

obtained by using  $2 \times 10^5$  simulated particles. We see that the simulation data support our previous theoretical predictions. For instance, at  $a/a_c = 0.76$  the tracer particles store less than 2% of the total energy while the relative contribution to the total energy becomes more than 60% at  $a/a_c = 2.11$ . This provides a self-consistency check of our analytical results.

## VI. DISCUSSION

In this paper we have offered a brief overview of a special nonequilibrium state for which the transport properties of a multicomponent system can be *exactly* evaluated from the Boltzmann equation for Maxwell molecules. More specifically, we have considered a binary mixture in a far from equilibrium state characterized by uniform density and temperature and a linear profile of the  $x$  component of the flow velocity along the  $y$  direction. Consequently, the constant shear rate  $a$  is the only nonequilibrium parameter of the problem. The description is not limited to specific values of the mass, concentration, and size of each species. By taking moments in the Boltzmann equations, one obtains a set of coupled equations for the pressure tensor of each species. From its solution, one obtains the relevant transport coefficients of the problem, namely, the shear viscosity  $\eta(a)$  and the viscometric functions  $\Psi_{1,2}(a)$ . The results show that  $\Psi_2 = 0$ , and the non-linear response of the mixture (as measured by the transport coeffi-

cients) is weaker than the one corresponding to the linear regime (Navier-Stokes order). In other words,  $\eta(a)/\eta(0)$  and  $\Psi_1(a)/\Psi_1(0)$  decrease as  $a$  increases whatever the parameters of the mixture considered are. Besides the transport coefficients, we also determine the temperature ratio  $T_1/T_2$  which measures how the kinetic energy is distributed between each species. In contrast to  $\eta$  and  $\Psi_1$ ,  $T_1/T_2$  is not a monotonic function of the shear rate. It must be stressed that the Boltzmann analysis does not provide the corresponding velocity distribution functions of each species.

Apart from the Maxwell interaction, we have not been able to explicitly obtain the transport properties of the shear flow state from the Boltzmann equation. A possible alternative that might overcome this obstacle is to replace the exact Boltzmann collision kernel by an approximate kinetic model that retains its essential features. In this paper, we have considered a generalized Gross-Krook (GK) kinetic model [11] where all the details of the interaction potential are introduced through effective collision frequencies which depend on the temperature of each species. Starting from this model, all the velocity moments are evaluated in terms of the shear rate, the parameters of the mixture, and a parameter characterizing the interaction potential. In the particular case of Maxwell molecules, the shear-rate dependence of the rheological properties agrees qualitatively well with the results derived from the Boltzmann equation showing

again the reliability of this model in computing transport properties. With respect to the influence of the interaction potential, we conclude that the reduced transport coefficients are practically insensitive to the choice of the interaction law when one conveniently scales the physical quantities. This influence becomes more significant in the case of the temperature ratio. In addition, explicit expressions for the distribution functions  $f_s(\mathbf{V})$  were derived. These functions exhibit a highly nonlinear dependence on the parameters of the problem and, as a consequence, their shape is strongly distorted with respect to equilibrium. In order to assess the degree of reliability of the GK distribution, we have solved numerically the Boltzmann equation by means of the Direct Simulation Monte Carlo method in the case of Maxwell molecules. The comparison shows that the GK distribution reproduces quite well the main qualitative features of the distribution function although important differences between the two predictions appear in the high velocity region.

An interesting situation considered in the paper has been the tracer limit, i.e.,  $n_1/n_2 \ll 1$ . In this limit, a natural expectation (which has been widely used in various physical problems) is that the contribution of the tracer species to the total properties of the mixture is negligible. Nevertheless, here we give an example of a violation of such expectation since the Boltzmann and GK equations predict a transition to a new state where the relative contribution of

the tracer species becomes finite if the system is sufficiently far from equilibrium. This phenomenon can be interpreted as a non-equilibrium phase transition in velocity space. Our asymptotic analysis shows that the transition is continuous at the critical point  $a_c$  for Maxwell molecules (second-order transition) while the order parameter becomes discontinuous at  $a_c$  for non-Maxwell molecules. These predictions are also supported by Monte Carlo simulations of the Boltzmann equation for Maxwell molecules, which indicates that the above transition is not merely an artifact of the algebra.

Although the uniform shear flow state is a useful prototype for computing rheological properties under extreme conditions, it is evident that it corresponds to an idealized (non-trivial) state which may be experimentally unrealizable for large shear rates. However, the results derived in this situation allow one to progress in the understanding of complex transport mechanisms taking place in more realistic flows, such as the nonlinear Couette flow. Another reason for which the exact solution of the Boltzmann equation described in this paper is important is that it can be used as a tool to test approximate methods, such as Grad's method, kinetic models and/or Monte Carlo simulations. In this context, the comparison made here between the Boltzmann and GK solutions allows one to infer the degree of reliability of the transport coefficients obtained from the GK model. On the other hand, it must be noted that any extrapola-

tion of the conclusions reported here to dense fluids must be made with caution, as the collisional transfer mechanism (which is the dominant one in a fluid) is absent in the low-density regime. However, a qualitatively good agreement with simulation results could be obtained by introducing appropriate scaled variables [23]. Comparisons carried out in the shear flow problem for a single gas support the above expectation [24,25].

In summary, it appears that many interesting questions regarding nonequilibrium statistical mechanics of multicomponent systems may be addressed accurately by using the Boltzmann and GK kinetic equations. In this context, one expects that new and more complex situations than those reported here will be described in the near future. Such exact solutions can be useful in interpreting a wide class of nonequilibrium computer simulations.

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