

Tracer limit in a gas mixture under shear flow with repulsive interactions

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A dilute binary mixture under uniform shear flow is considered in the tracer limit. The analysis is made from an exact solution of a generalized Gross-Krook model for $r^{-\gamma}$ repulsive forces. The results show that 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 mass ratio, force constant ratios, and the interaction potential considered. This phenomenon can be interpreted as a nonequilibrium phase transition in velocity space. For non-Maxwell molecules ($\gamma \neq 5$), the corresponding order parameter is discontinuous at the critical point (first order transition); on the other hand, the transition becomes continuous at a_c in the special case of Maxwell molecules ($\gamma = 5$). [S1063-651X(97)16008-1]

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A problem of practical and physical interest is the study of nonequilibrium properties of binary mixtures in which the concentration of one of the components (tracer species) is much smaller than that of the other component (excess species). Since the molar fraction of the tracer species is negligible, one expects that the total properties of the mixture are not affected by the presence of the tracer particles. This assumption has been widely used in different physical situations. Quite surprisingly, this is not always true and recently we have presented an example of a violation of the above expectation [1–3] in the case of a dilute binary mixture of Maxwell molecules under uniform shear flow. The results derived from exact solutions to the Boltzmann equation [1,2], as well as to the Gross-Krook (GK) kinetic model [3] show a transition to a new state in which the tracer species contributes significantly to the total properties of the mixture when the system is sufficiently far from equilibrium. That happens for shear rates larger than a *critical* value, which depends on the mass and force constant ratios. Since the above studies have been restricted to the Maxwell interaction, a natural question is whether this transition can be extended to other more realistic interaction potentials or is merely an artifact of Maxwell molecules. Unfortunately, this question cannot be answered analytically from the Boltzmann equation, since no exact solution of this equation beyond the Maxwell interaction is known [4]. For this reason, here we analyze with detail the same problem by starting from a generalized GK model [5]. In this case, the Boltzmann collision integrals $J_{ij}[f_i, f_j]$ are replaced by simple relaxation terms:

$$J_{ij}^{\text{GK}} = -\nu_{ij}(f_i - f_{ij}), \quad (1)$$

where

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

is an effective collision frequency for molecules interacting through repulsive forces of the form $\kappa_{ij} r^{-\gamma}$ ($\gamma = 5, \dots, \infty$).

Here, $\beta \equiv (\gamma - 5)/(\gamma - 1)$ and $C(\beta)$ is a constant for a given potential. The reference distribution function f_{ij} is

$$f_{ij} = n_i (m_i/2\pi k_B T_{ij})^{3/2} \exp[-(m_i/2k_B T_{ij})(\mathbf{v} - \mathbf{u}_{ij})^2], \quad (3)$$

with $\mathbf{u}_{ij} = (m_i \mathbf{u}_i + m_j \mathbf{u}_j)/(m_i + m_j)$ and $T_{ij} = T_i + 2M[(T_j - T_i) + (m_j/6k_B)(\mathbf{u}_i - \mathbf{u}_j)^2]$. In these equations, $M \equiv m_1 m_2 / (m_1 + m_2)^2$ and n_i , \mathbf{u}_i and T_i are the number density, flow velocity, and “temperature” of species i , respectively. According to Eq. (2), the model incorporates a temperature dependence of the collision frequencies ν_{ij} that allows the consideration of general repulsive potentials. The reliability of this kinetic model has been assessed in several nonequilibrium problems [6] by comparison with Monte Carlo simulations of the Boltzmann equation [7].

In the uniform shear flow state, the only nonzero hydrodynamic gradient is $\partial u_x / \partial y = a$, where $\mathbf{u} = \mathbf{u}_1 = \mathbf{u}_2$ is the flow velocity of the mixture and a is the constant shear rate. There is no mutual diffusion and the shear rate is the relevant nonequilibrium parameter of the problem. In addition, an external “thermostat” force is introduced in the system to control viscous heating and achieve a steady state [8]. In the case of Maxwell molecules, the presence of the thermostat does not play any role in the results [3,4], while a certain influence may exist for other repulsive interactions. Very recently, an exact solution of the GK model for this state has been found [3]. In general, the main transport properties of the mixture are given in terms of the thermostat parameter α and the temperature ratio $\chi \equiv T_1/T_2$. Both quantities are determined by solving the following set of nonlinear algebraic equations [3]:

$$(3 - A_1)(3 - A_2) - B_1 B_2 = 0, \quad (4)$$

$$\chi = \frac{3 - A_2}{B_2} = \frac{B_1}{3 - A_1}, \quad (5)$$

where

$$A_1 = \frac{\nu_{11} + \nu_{12}(1 - 2M)}{\nu_1 + 2\alpha} \left[3 + \frac{2a^2}{(\nu_1 + 2\alpha)^2} \right], \quad (6)$$

$$B_1 = \frac{2M\nu_{12}}{\nu_1 + 2\alpha} \left[3 + \frac{2a^2}{(\nu_1 + 2\alpha)^2} \right], \quad (7)$$

and $\nu_1 = \nu_{11} + \nu_{12}$. The remaining coefficients A_2 and B_2 can be obtained from Eqs. (6) and (7) by the adequate changes. The solution of Eqs. (4) and (5) gives α and χ as nonlinear functions of the shear rate a and the parameters of the mixture, namely, the mass ratio $\mu \equiv m_1/m_2$, the concentration ratio $\delta \equiv n_1/n_2$, the force constant ratios $w_{11} \equiv \kappa_{11}/\kappa_{12}$ and $w_{22} \equiv \kappa_{22}/\kappa_{12}$, and the interaction parameter β . In the case of Maxwell molecules ($\beta=0$), the collision frequencies ν_{ij} are independent of the temperature ratio and Eq. (4) reduces to a sixth-degree closed equation in α . For non-Maxwell molecules ($\beta \neq 0$), however, no explicit closed equation in α can be obtained, so that α and χ are nonlinearly coupled. This fact shows the intricacy of the problem beyond the Maxwell interaction. It must be remarked that the *physical* solution of Eqs. (4) and (5) is the one corresponding to the *largest* value of α [3,4].

Thus far, the results apply for an arbitrary concentration δ . The aim of this work is to analyze in detail what happens in the tracer limit ($\delta \rightarrow 0$). For the sake of convenience, we take ν_{12}^{-1} as unit of time. This means that we measure time in units of the mean free time of a particle of the tracer species between collisions with particles of the excess species. Therefore, we will use the reduced quantities $a^* = a/\nu_{12}$, $\alpha^* = \alpha/\nu_{12}$, $\nu_{11}^* = \nu_{11}/\nu_{12} = \zeta_{11}\delta[1 + (\mu/\chi)]^{-\beta/2}$, $\nu_{22}^* = \nu_{22}/\nu_{12} = \zeta_{22}[1 + (\chi/\mu)]^{-\beta/2}$, and $\nu_{21}^* = \nu_{21}/\nu_{12} = \delta$. Here, $\zeta_{11} = \sqrt{2}[w_{11}/(1 + \mu)]^{(1-\beta)/2}$ and $\zeta_{22} = \sqrt{2}[w_{22}\mu/(1 + \mu)]^{(1-\beta)/2}$. Henceforth, we will omit the asterisks. We assume first that χ is finite, so that Eq. (4) factorizes in the limit $\delta \rightarrow 0$ into two equations

$$a^2(1 - 2M) = 3(\alpha + M)(1 + 2\alpha)^2, \quad (8)$$

$$a^2\zeta_{22}\mu^{\beta/2}(\mu + \chi)^{\beta/2} = 3\alpha[2\alpha(\mu + \chi)^{\beta/2} + \zeta_{22}\mu^{\beta/2}]^2. \quad (9)$$

Equation (8) is a closed cubic equation, but Eq. (9) is coupled to

$$\chi = \frac{M[2a^2 + 3(1 + 2\alpha)^2]}{3(\alpha + M)(1 + 2\alpha)^2 - a^2(1 - 2M)}, \quad (10)$$

which comes from the second equality in Eq. (5). Notice that Eq. (8) is independent of the interaction parameter β . As said before, the thermostat parameter is $\alpha = \max(\alpha_0, \alpha'_0)$, where α'_0 is the real root of Eq. (8), while α_0 is the largest real root obtained numerically from Eqs. (9) and (10). In Fig. 1 we plot the shear rate dependence of α_0 and α'_0 for $\mu = 0.15$, $w_{11} = w_{22} = 1$, and several values of β : $\beta = 0$ (Maxwell molecules), $\beta = \frac{1}{2}$, and $\beta = 1$ (hard spheres). There exists a critical shear rate $a_c(\mu, \beta)$, beyond which there is no solution to Eqs. (9) and (10) with a positive real value of χ . Therefore, $\alpha = \alpha'_0$ if $a > a_c$, while $\alpha = \alpha_0$ if $a < a_c$. It is important to remark that α is discontinuous at $a = a_c$, since $\alpha_0(a_c) \neq \alpha'_0(a_c)$. This discontinuity decreases as the interaction becomes softer and eventually disappears for Maxwell molecules ($\beta = 0$). Since the denominator in the right-hand side of Eq. (10) vanishes if $\alpha = \alpha'_0$, we have $\chi \rightarrow \infty$ if $a > a_c$. The

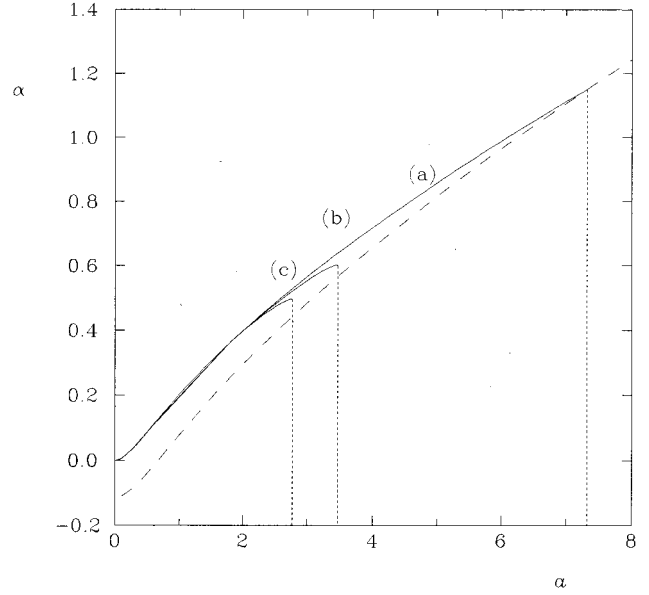


FIG. 1. Plot of α_0 (solid line) and α'_0 (dashed line) vs a for $\mu = 0.15$, $w_{11} = w_{22} = 1$, and several values of β : (a) $\beta = 0$ (Maxwell molecules), (b) $\beta = \frac{1}{2}$, and (c) $\beta = 1$ (hard spheres). The vertical dotted lines indicate the location of a_c in each case.

μ dependence of a_c is shown in Fig. 2 for $\beta = 0, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$, and 1. As happens in the Maxwell case [2], the results suggest the existence of a threshold mass ratio $\mu_0(\beta)$ for each interaction model, such that $a_c(\beta) \rightarrow \infty$ as $\mu \rightarrow \mu_0(\beta)$. The threshold mass ratio is smaller than 1 in the cases of Fig. 2, but it can be larger than 1 if one considers other choices for the force constants. The value of μ_0 can be obtained analytically only for Maxwell molecules. In general, at a given value of μ , the corresponding critical value $a_c(\beta)$ decreases as the interaction parameter increases.

The main physical consequence of the existence of

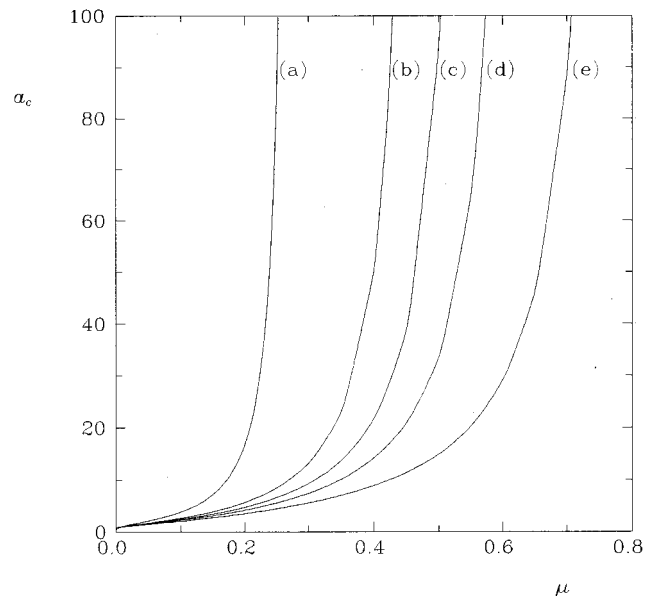


FIG. 2. Plot of a_c as a function of μ for $w_{11} = w_{22} = 1$ and five values of β : 0, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, and 1.

$a_c(\mu, \beta)$ is that in the region $a > a_c$ there is a *finite* relative contribution of the tracer species to the total properties of the mixture. Let us consider the energy ratio $E_1/E = \delta\chi/(1 + \delta\chi)$. To get this quantity for $a > a_c$ one needs to evaluate $\delta\chi$ first and then take the limit $\delta \rightarrow 0$. This function is evaluated from the first equality of Eq. (5). After a careful asymptotic analysis, one gets that

$$\frac{E_1}{E} = \frac{F_0(a)}{1 + F_0(a)} \left[1 + \frac{F_1(a)}{1 + F_0(a)} \delta^{\beta/2} + O(\delta^\beta) \right], \quad (11)$$

if $\mu < \mu_0(\beta)$ and $a > a_c(\mu, \beta)$, being $E_1/E \sim \delta$ otherwise, where

$$F_0(a) = \frac{6\alpha_0'^3}{M(a^2 + 6\alpha_0'^2)}, \quad (12)$$

$$F_1(a) = \mu^{\beta/2} F_0(a)^{-\beta/2} \zeta_{22} \left[\frac{12\alpha_0'^2 - a^2}{12\alpha_0'^3} - \frac{6\alpha_0'\zeta_{22}}{M(a^2 + 6\alpha_0'^2)} \right]. \quad (13)$$

It is interesting to notice that the leading term in Eq. (11) is independent of β . On the other hand, the subleading term depends on β and is of order $\delta^{\beta/2}$, so that it is negligible only for very small values of δ , especially if β is much smaller than 1. The asymptotic analysis leading to Eq. (11) does not apply in the particular case of Maxwell molecules ($\beta=0$) since an infinite number of terms in the series become of the same order. The corresponding exact result is

$$\frac{E_1}{E} = \frac{3\alpha_0'(2\alpha_0' + \zeta_{22})^2 - a^2\zeta_{22}}{a^2(2M - \zeta_{22}) + 3(\alpha_0' + M)(2\alpha_0' + \zeta_{22})^2} + O(\delta), \quad (14)$$

if $\mu < \mu_0$ and $a > a_c$. This means that the limits $\beta \rightarrow 0$ and $\delta \rightarrow 0$ do not commute.

The fact that $\lim_{\delta \rightarrow 0} E_1/E \neq 0$ if $a > a_c$ shows the qualitatively different behavior of the mixture in the tracer limit depending on whether the shear rate a is larger or not than the corresponding critical value a_c . By borrowing the usual terminology of equilibrium phase transitions [9], one can identify a as the ‘‘control’’ parameter and E_1/E as an ‘‘order’’ parameter. In Fig. 3, we plot the order parameter versus a/a_c for $\mu=0.1$ in the case $w_{11}=w_{22}=1$ for $\delta=10^{-2}, 10^{-3}$ and 0. We have considered Maxwell molecules and hard spheres. The curves corresponding to $\delta \neq 0$ have been obtained by solving numerically Eqs. (4) and (5), while the exact tracer limit ($\delta=0$) is given by the dominant terms in Eqs. (11) and (14). We observe that the numerical results tend to the asymptotic behavior as δ goes to zero, this trend being slower in the case of hard spheres. At a given value of $a/a_c > 1$, the energy ratio for non-Maxwell molecules is larger than that of the Maxwell potential. Furthermore, as the order parameter is discontinuous at the critical point, the transition for non-Maxwell molecules is of first order. In the case of Maxwell molecules, the fact that $E_1/E \rightarrow 0$, when $a - a_c \rightarrow 0^+$, indicates that the transition is of second order.

In summary, we have analyzed the tracer limit of an exact solution [3] of the Gross-Krook kinetic equation for a binary

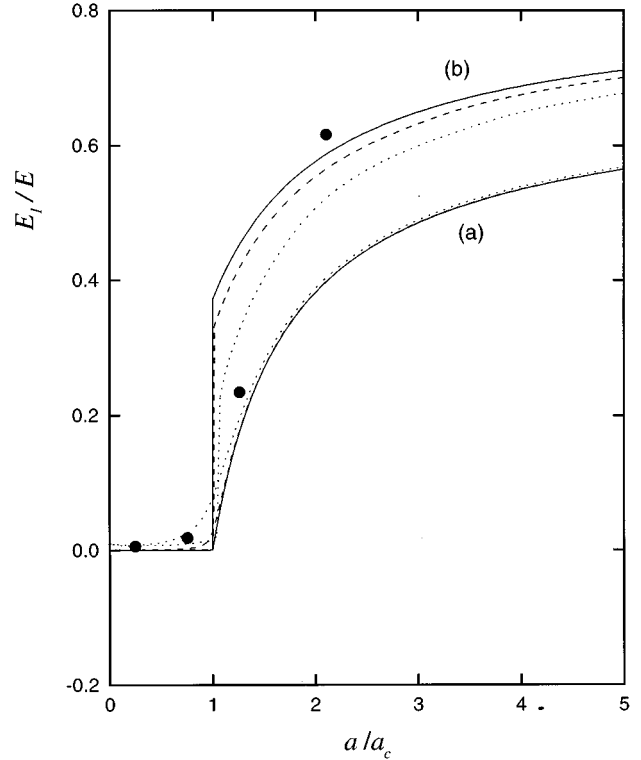


FIG. 3. Plot of the energy ratio E_1/E for $\delta=10^{-2}$ (dotted lines), $\delta=10^{-3}$ (dashed lines), and the exact tracer limit $\delta=0$ (solid lines) for (a) Maxwell molecules and (b) hard spheres. The force constant ratios are $w_{11}=w_{22}=1$ and the mass ratio is $\mu=0.1$. The circles represent simulation data in the case of Maxwell molecules for $\delta=10^{-2}$.

mixture with general repulsive interactions and under uniform shear flow. This work extends previous studies made from the Boltzmann equation in the special case of Maxwell molecules [2]. In the model, the details of the interaction potential are incorporated in the temperature dependence of the collision frequencies. The solution holds for arbitrary values of the shear rate a and the parameters of the mixture (i.e., the mass ratio μ , the concentration ratio δ , the force constant ratios w_{11} and w_{22} , and a parameter β characterizing the interaction law) and is given in terms of the thermostat parameter α and the temperature ratio χ , which are nonlinearly coupled (except in the case of Maxwell molecules, $\beta=0$). In the tracer limit ($\delta \rightarrow 0$), we find that the contribution of the tracer species to the total properties of the mixture does not tend to zero when the system is sufficiently far from equilibrium. That happens for shear rates larger than a critical value a_c , which depends on the mass ratio, force constant ratios, and the interaction parameter. The results indicate that a_c increases as the intermolecular repulsion becomes harder. For $a > a_c$, the temperature ratio χ goes to infinity but the energy ratio E_1/E reaches a finite value. Obviously, identical conclusions can be drawn if one considers other quantities of the system, such as the shear viscosity and the viscometric functions. The fact that E_1/E is zero or not, depending on the value of the control parameter a , can be interpreted as a nonequilibrium phase transition in velocity space. In the case of non-Maxwell molecules, this transition is of first order (E_1/E is discontinuous at a_c), while it is

of second order in the case of Maxwell molecules (E_1/E is continuous at a_c).

One of the objectives of kinetic theory is to offer a description as independent of the specific interaction law considered as possible. To this end, one conveniently scales the physical quantities of the problem. In our study, it has been essential to reduce the shear rate with the collision frequency ν_{12} to identify the phase transition. In this sense, we have extended previous conclusions obtained only for Maxwell molecules. While the choice of the unit of time may be irrelevant in the case of Maxwell molecules (since ν_{ij} is constant), this is not the case for non-Maxwell molecules, where ν_{ij} is a function of the temperature ratio. As a matter of fact, the critical shear rate becomes infinite when one takes ν_{22} as a unit of time, although numerical results indicate that E_1/E can be significant for very large shear rates, even for very small concentration ratios [3]. Since the treatment in this work has been mainly algebraic, involving a delicate limit, it might be possible that the predicted phase transition was an artifact of the algebra. This point can be elucidated by

computer simulations. Preliminary simulations of the Boltzmann equation by using the direct simulation Monte Carlo method [7] support the theoretical predictions. Simulation data for Maxwell molecules with a concentration ratio $\delta=10^{-2}$, a mass ratio $\mu=0.1$, and reduced shear rates $a/a_c=0.25, 0.76, 1.27$, and 2.11 are included in Fig. 3; they have been obtained by using 2×10^5 simulated particles. While at $a/a_c=0.76$ the tracer species stores less than 2% of the total energy, that fraction becomes more than 60% at $a/a_c=2.11$. The quantitative difference between the simulation and the theoretical results is due to the approximate character of the GK model. More extensive simulation results will be published elsewhere.

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