Nonlinear mass and momentum transport in a dilute gas

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(Received 7 February 1992; accepted 24 April 1992)

Far from equilibrium particle and momentum transport in a binary mixture subject to uniform shear flow is analyzed. Particles of each species are labeled by a "color charge." Mutual diffusion is created by the action of an external field that accelerates particles of different species along opposite directions. For a dilute gas of Maxwell molecules, the set of two coupled Boltzmann equations is seen to be solvable by the moment method. The color conductivity tensor and the shear viscosity coefficient are obtained as nonlinear functions of the shear rate and the color field. The usual choice of the external color field [Cummings *et al.*, J. Chem. Phys. **94**, 2149 (1991)] yields a zero-field limit of the color conductivity tensor different from the self-diffusion tensor. In order to avoid the above discrepancy, a different form of the external field is proposed.

I. INTRODUCTION

The study of transport properties in fluids is a subject of great interest from a theoretical perspective, as well as from a practical point of view. For states near equilibrium, the description of transport processes can be considered as well established.[1] Nevertheless, many questions remain still open regarding transport problems in far from equilibrium states.[2] Recently, a great deal of effort has been devoted to the computer simulation of some of these states.[3] However, theoretical advances lag simulation, especially in the case of dense fluids.

In order to capture the essential aspects of nonlinear transport, a monatomic, dilute gas with short-range interactions can be taken as a prototype system. Instead of a fully statistical-mechanical description in terms of the phase-space probability density, it is much more convenient to adopt a kinetic description, according to which the state of the system is characterized by the one-particle velocity distribution function. The evolution equation for this function is the well-known Boltzmann equation.[1,4] However, due to its mathematical complexity, only a few solutions are known for spatially inhomogeneous states far from equilibrium.[5] Perhaps the most physically relevant solutions correspond to planar shear flow at uniform temperature and density (usually referred to as "uniform shear flow")[6] and steady heat flow at constant pressure.[7] Both solutions are restricted to Maxwell molecules and are given in terms of the velocity moments of the distribution function.

The aim of this paper is to analyze particle and momentum transport in a binary mixture subject to uniform shear flow. Particles of each species are labeled by a "color charge," but otherwise they are mechanically equivalent. Mutual diffusion is not created by concentration gradients, but by the action of an external field that accelerates particles of different species along opposite directions. This way of producing particle fluxes is referred to as the color field method and has been proposed in computer simulation works.[8,9] In the problem under consideration, there are two independent parameters measuring the departure from equilibrium: the shear rate and the color vector field. Here we study the problem starting from the Boltzmann equation for Maxwell molecules, i.e., particles interacting via a potential $V(r)=\kappa r^{-4}$. For this particular interaction, the set of two coupled Boltzmann equations can be exactly solved by the moment method. In the case of a general interaction, the problem is much more complicated. The most important transport properties are related to the first few moments, namely, the particle fluxes and the total pressure tensor. From these fluxes one can define generalized transport coefficients, such as the color conductivity and the shear viscosity, which are nonlinear functions of both the shear rate and the color field.

In absence of shear flow, the color field method is an efficient alternative to compute the self-diffusion coefficient as the zero-field limit of the color conductivity coefficient.[8,10] However, this equivalence is not established for arbitrary shear rates.[11] The clarification of this point is one of the main objectives of this paper. In addition, we study the general coupling between mass and momentum transport for arbitrary shear rate and color field.

The plan of this paper is as follows. The physical problem is described in Sec. II. The special case of Maxwell molecules is worked out in Sec. III. The transport coefficients are shown to be expressed in terms of a parameter that obeys a fifth-degree equation. The limit of small shear rate, but finite color field, is considered in Sec. IV. Section V deals with the limit of small color field and finite shear rate. The results show that, with the usual choice of the color field proposed in molecular dynamics simulations,[8,9] the self-diffusion and color conductivity tensors are different. This confirms the analysis of modified Green–Kubo relations for mechanical transport coefficients carried out by Evans *et al.*[11] and shows that the agreement observed by Cummings *et al.*[9] from molecular dynamics results was fortuitous. Section VI is devoted to the analysis of nonlinear transport with finite shear rate and color field. For the sake of clarity, we consider the particular case of a color field parallel to the gradient of the flow velocity. Finally, the results are discussed in Sec. VII.

II. COLOR CONDUCTIVITY UNDER UNIFORM SHEAR FLOW

Let us consider a dilute gas in a steady uniform shear flow state. This nonequilibrium state is characterized by a linear velocity profile and constant density and temperature[3,12]

$$u_i = a_{ij} r_j, \quad a_{ij} = a\delta_{ix}\delta_{jy}, \tag{2.1}$$

$$n = \text{const.}, \tag{2.2}$$

$$T = \text{const.} \tag{2.3}$$

Here a is the constant shear rate. The number density n, the flow velocity $\mathbf{u}$, and the temperature T are defined in terms of moments of the velocity distribution function $f(\mathbf{r},\mathbf{v})$ as

$$n = \int d\mathbf{v}\, f, \tag{2.4}$$

$$n\mathbf{u} = \int d\mathbf{v}\, \mathbf{v} f, \tag{2.5}$$

$$nk_B T = \frac{1}{3}\int d\mathbf{v}\, m(\mathbf{v}-\mathbf{u})^2 f, \tag{2.6}$$

where k_B is the Boltzmann constant and m is the mass of a particle. In order to maintain a steady state, an external drag force must be applied

$$\mathbf{F} = -\alpha \mathbf{V}. \tag{2.7}$$

In this equation, $\mathbf{V} \equiv \mathbf{v} - \mathbf{u}$ is the peculiar velocity and α is a thermostat parameter to be adjusted by consistency. In the uniform shear flow, the distribution function becomes homogeneous under the change of variable $\mathbf{v} \to \mathbf{V}$, i.e., $f(\mathbf{r},\mathbf{v}) \to f(\mathbf{V})$.[12] This state has been extensively studied from the theoretical[13] and the computer simulation[3,14] points of view.

An interesting physical problem is that of diffusion in presence of shear flow. The anisotropy induced by the shear flow makes the diffusion coefficient to become a nonsymmetric tensor that is a nonlinear function of the shear rate. This tensor reduces to the usual scalar diffusion coefficient in the Navier–Stokes limit. Previous theoretical studies have dealt with self-diffusion of tagged particles[15,16] and diffusion in the Fokker–Planck[17] and the tracer limits.[18] Recently, Cummings *et al.*[9] have performed molecular dynamics simulations to compute the self-diffusion tensor through three different routes: Einstein relations, Green–Kubo expressions, and color field method. The first two methods have been subsequently validated by the work of Sarman *et al.*[19] and, consequently, the results from these methods are reliable.

The aim of this paper is to analyze self-diffusion induced by a color field in presence of uniform shear flow, in the framework of the Boltzmann equation. In the color field method, the system is a binary mixture of mechanically equivalent particles that are only distinguished by a "color charge."[8] Particles of color r ($r = 1,2$) are accelerated by the action of a color field

$$\mathscr{F}_r = -k_B T \epsilon_r. \tag{2.8}$$

The macroscopic effect of $\mathscr{F}_r$ is to produce particle fluxes ("color currents") in absence of concentration gradients. Thus the field strengths ϵ_r play the role of chemical potential gradients. The total force acting on each particle of color r is the sum of $\mathbf{F}$, Eq. (2.7), and $\mathscr{F}_r$, Eq. (2.8).

The velocity distribution function $f_r(\mathbf{V})$ of species r satisfies the Boltzmann equation

$$-\frac{\partial}{\partial V_i}\left(a_{ij}V_j - \frac{F_i + \mathscr{F}_{r,i}}{m}\right) f_r = J[f_r, f], \tag{2.9}$$

where $f = f_1 + f_2$ is the total distribution function and J is the Boltzmann collision operator, which in standard notation is[4]

$$J[f_r, f_s] = \int d\mathbf{v}_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \sigma(|\mathbf{v}-\mathbf{v}_1|, \theta) \times [f_r(\mathbf{v}')f_s(\mathbf{v}_1') - f_r(\mathbf{v})f_s(\mathbf{v}_1)]. \tag{2.10}$$

Conservation of total momentum, namely,

$$\int d\mathbf{v}\, \mathbf{v}(J[f_1, f] + J[f_2, f]) = \mathbf{0}, \tag{2.11}$$

leads to the constraint

$$n_1 \boldsymbol{\epsilon}_1 + n_2 \boldsymbol{\epsilon}_2 = \mathbf{0}. \tag{2.12}$$

Here n_r is the number density of species r and is defined by an equation similar to Eq. (2.4). Conservation of total energy,

$$\int d\mathbf{v}\, v^2 (J[f_1, f] + J[f_2, f]) = 0, \tag{2.13}$$

imposes the condition

$$\alpha = -\frac{m}{3}\frac{\mathbf{j}_1 \cdot \boldsymbol{\epsilon}_1}{n_2} - \frac{m}{3} a \frac{P_{xy}}{p}. \tag{2.14}$$

Here

$$\mathbf{j}_r = \int d\mathbf{V}\, \mathbf{V} f_r(\mathbf{V}) \tag{2.15}$$

is the particle flux (or color current) of species r, P_{xy} is the xy element of the total pressure tensor $\mathsf{P} = \mathsf{P}_1 + \mathsf{P}_2$, where

$$\mathsf{P}_r = \int d\mathbf{V}\, m\mathbf{V}\mathbf{V} f_r(\mathbf{V}), \tag{2.16}$$

and $p = p_1 + p_2 = nk_B T$, $p_r = (1/3)\mathrm{Tr}\, \mathsf{P}_r$. Upon writing Eq. (2.14) we have taken into account Eq. (2.12) and the relation $\mathbf{j}_2 = -\mathbf{j}_1$.

In this problem, the most important transport coefficients are the generalized color conductivity tensor σ_{ik} and shear viscosity η. They are defined, respectively, by

$$j_{1,i} = -\sigma_{ik} n_1 \epsilon_{1,k}, \tag{2.17}$$

$$\eta = -\frac{P_{xy}}{a}. \tag{2.18}$$

Making use of Eq. (2.12), one can get from Eq. (2.9) the following set of coupled equations:

$$-\frac{\partial}{\partial V_i}\left(\frac{\alpha}{m} V_i + a_{ij}V_j + \frac{k_B T}{m}\epsilon_{1,i}\right) f_1 = J[f_1, f], \tag{2.19}$$

$$-\frac{\partial}{\partial V_i}\left[\left(\frac{\alpha}{m} V_i + a_{ij}V_j\right) f - \frac{k_B T}{m}\frac{n_1}{n_2}\epsilon_{1,i}\left(f - \frac{n}{n_1} f_1\right)\right] = J[f, f]. \tag{2.20}$$

Equations (2.19) and (2.20) contain all the relevant physical information about the problem. The coupling between momentum and mass (color) transport is represented by the shear rate a and the field strength ϵ_1, which are independent parameters measuring the departure from equilibrium. As a matter of fact, this problem reduces to the homogeneous color conductivity case when $a=0$ (Refs. 8, 10) and to the pure shear flow when $\epsilon_1 = \mathbf{0}$.[3,12-14] According to relation (2.14), it is clear that the nonlinear character of Eqs. (2.19) and (2.20) is not only due to the collision terms. In general, the usual method to solve the Boltzmann equation, Eqs. (2.19) and (2.20) in our case, is the Chapman–Enskog expansion.[4] In this method, the solution is expressed as a perturbation expansion around local equilibrium. In the problem described by Eqs. (2.19) and (2.20) the perturbation parameters are a and ϵ_1. However, the Chapman–Enskog is not expected to be adequate far from equilibrium.

For a general interaction, the exact solution of Eqs. (2.19) and (2.20) does not seem to be feasible. Nevertheless, the hierarchy of moments corresponding to the set of Eqs. (2.19) and (2.20) can be solved recursively if we restrict ourselves to Maxwell molecules. In the next section we will solve the first few equations of the hierarchy in order to obtain the color conductivity and the shear viscosity as functions of both the shear rate and the field strength.

III. TRANSPORT PROPERTIES FOR MAXWELL MOLECULES

The main mathematical advantage of Maxwell molecules is that a moment of order k of the collision operator only involves moments of order less than or equal to k. In particular,[20]

$$\int d\mathbf{V}\,\mathbf{V}J\,[f_r,f_s] = -\lambda(n_s\mathbf{j}_r - n_r\mathbf{j}_s), \tag{3.1}$$

$$\begin{aligned}\int d\mathbf{V}\,m\mathbf{V}\mathbf{V}J\,[f_r,f_s] &= \lambda'[(n_sp_r + n_rp_s + \tfrac{2}{3}m\mathbf{j}_r\cdot\mathbf{j}_s)\mathsf{1} - (n_s\mathsf{P}_r + n_r\mathsf{P}_s)\\ &\quad + m(\mathbf{j}_s\mathbf{j}_r + \mathbf{j}_r\mathbf{j}_s)] - \lambda(n_s\mathsf{P}_r - n_r\mathsf{P}_s),\end{aligned} \tag{3.2}$$

where $\lambda = 1.19\pi(\kappa/m)^{1/2}$, $\lambda' = 0.777\lambda$. The moment equations obtained from Eqs. (2.19) and (2.20) can be solved following a recursive scheme. If all the moments of f and f_1 of order less than k are known, Eq. (2.20) allows one to obtain the moments of f of order k. Once these moments are known, Eq. (2.19) gives the moments of f_1 of order k. As said before, here we will only consider the moments associated to the transport of color and of total momentum. Higher moments, such as the partial pressure tensors and the total energy flux, can also be obtained straightforwardly.

Multiplying both sides of Eq. (2.19) by $\mathbf{V}$ and integrating, one gets

$$\frac{\alpha}{m}j_{1,i} + a_{ik}j_{1,k} + \frac{k_BT}{m}n_1\epsilon_{1,i} = -\lambda n j_{1,i}. \tag{3.3}$$

The solution of this equation can be cast into form (2.17) with $\sigma_{ik} \equiv (k_BT/mn\lambda)\sigma^*_{ik}$, where

$$\sigma^*_{ik} = \frac{1}{1+\gamma\alpha^*}\left(\delta_{ik} - \frac{2\gamma}{1+\gamma\alpha^*}a^*_{ik}\right) \tag{3.4}$$

is the reduced color conductivity tensor. In Eq. (3.4), $\alpha^* \equiv \alpha/(mn\lambda')$, $\gamma \equiv \lambda'/\lambda$, and $a^*_{ij} = a^*\delta_{ix}\delta_{jy}$, with $a^* \equiv a/(2\lambda'n)$. In a similar way, from Eq. (2.20) one gets

$$\begin{aligned}&\frac{1}{2}\frac{p}{n_2}(\epsilon_{1,i}j_{1,k} + j_{1,i}\epsilon_{1,k}) + \frac{\alpha}{m}P_{ik} + \frac{1}{2}[a_{ij}P_{jk} + a_{kj}P_{ji}]\\ &\quad = -\lambda' n(P_{ik} - p\delta_{ik}).\end{aligned} \tag{3.5}$$

Notice that Eq. (2.14) can be reobtained by taking the trace in both sides of Eq. (3.5). Inserting Eqs. (2.17) and (3.4) into Eq. (3.5), one obtains, after some algebra,

$$\begin{aligned}P^*_{ij} = \frac{1}{1+\alpha^*}\Bigg[&\delta_{ij} - \frac{1}{1+\alpha^*}(a^*_{ij} + a^*_{ji})\\ &+ \frac{2}{(1+\alpha^*)^2}a^*_{ik}a^*_{jk} + \frac{3}{2\gamma(1+\gamma\alpha^*)}\epsilon^*_i\epsilon^*_j\\ &- \frac{3}{2\gamma(1+\gamma\alpha^*)}\left(\frac{1}{1+\alpha^*} + \frac{\gamma}{1+\gamma\alpha^*}\right)\\ &\times\left(a^*_{ik}\epsilon^*_k\epsilon^*_j + a^*_{jk}\epsilon^*_k\epsilon^*_i - \frac{2}{1+\alpha^*}a^*_{ik}\epsilon^*_k\epsilon^*_l a^*_{jl}\right)\Bigg].\end{aligned} \tag{3.6}$$

Here $P^*_{ij} \equiv P_{ij}/p$, and

$$\begin{aligned}\epsilon^* &\equiv \left(\frac{2}{3}\frac{k_BT}{mn^2\lambda^2}\frac{n_1}{n_2}\right)^{1/2}\epsilon_1\\ &= -\left(\frac{2}{3}\frac{k_BT}{mn^2\lambda^2}\frac{n_2}{n_1}\right)^{1/2}\epsilon_2.\end{aligned} \tag{3.7}$$

From Eq. (3.6), the generalized shear viscosity defined in Eq. (2.18) turns out to be given as $\eta \equiv (p/2\lambda'n)\eta^*$, with

$$\begin{aligned}\eta^* = \frac{1}{1+\alpha^*}\Bigg[&\frac{1}{1+\alpha^*} - \frac{3}{2\gamma(1+\gamma\alpha^*)a^*}\epsilon^*_x\epsilon^*_y\\ &+ \frac{3}{2\gamma(1+\gamma\alpha^*)}\left(\frac{1}{1+\alpha^*} + \frac{\gamma}{1+\gamma\alpha^*}\right)\epsilon^{*2}_y\Bigg].\end{aligned} \tag{3.8}$$

It is important to point out that Eqs. (3.4) and (3.8) are not sufficient to give the dependence of the reduced conductivity tensor σ^*_{ik} and shear viscosity η^* on the reduced shear rate a^* and field strength ϵ^*. It still remains to determine the parameter α^* as a function of a^* and ϵ^*. In order to close the problem, we impose on Eq. (3.6) the consistency condition $P^*_{xx} + P^*_{yy} + P^*_{zz} = 3$. Thus one gets the following implicit algebraic equation:

$$\begin{aligned}&\alpha^*(1+\alpha^*)^2(1+\gamma\alpha^*)^2\\ &\quad = \frac{2}{3}a^{*2}(1+\gamma\alpha^*)^2 + \frac{\epsilon^{*2}}{2\gamma}(1+\alpha^*)^2(1+\gamma\alpha^*)\\ &\qquad + \frac{1+\gamma(1+2\alpha^*)}{\gamma}a^*[a^*\epsilon^{*2}_y - (1+\alpha^*)\epsilon^*_x\epsilon^*_y].\end{aligned} \tag{3.9}$$

Equations (3.4), (3.8), and (3.9) are the major results of this paper. They have been derived exactly from the Boltzmann equation for a binary mixture of Maxwell molecules. Insertion into Eqs. (3.4) and (3.8) of the physically meaningful solution of Eq. (3.9) yields $\sigma^*_{ik}(a^*,\epsilon^*)$ and $\eta^*(a^*,\epsilon^*)$, respectively. These coefficients describe the coupling between color and momentum transport for arbitrary values of the shear rate and the color field strength.

The asymptotic behavior of α^* in the limit of large shear rate is given by

$$\alpha^* \approx \left(\frac{2}{3}\right)^{1/3} a^{*2/3}. \tag{3.10}$$

On the other hand, in the limit of large color field one has

$$\alpha^* \approx \frac{|\epsilon^*|}{\sqrt{2\gamma}}. \tag{3.11}$$

The particular limits of small shear rate and color field will be analyzed in the next two sections.

IV. SMALL SHEAR RATE LIMIT

For finite field strength but small shear rate, we can write

$$\alpha^*(a^*,\epsilon^*) = \alpha_0(\epsilon^*) + \alpha_1(\epsilon^*)a^* + \mathscr{O}(a^{*2}). \tag{4.1}$$

Substitution into Eq. (3.9) gives

$$\alpha_0(\epsilon^*) = \frac{1}{2\gamma}\left[(1+2\epsilon^{*2})^{1/2} - 1\right], \tag{4.2}$$

$$\alpha_1(\epsilon^*) = -2\,\frac{1+\gamma(1+2\alpha_0)}{(1+2\gamma\alpha_0)\left[\epsilon^{*2}+2\gamma(1+\gamma\alpha_0)\right]}\,\epsilon^*_x\epsilon^*_y, \tag{4.3}$$

where unphysical solutions have been discarded. Inserting Eq. (4.1) into Eqs. (3.4) and (3.6), we get, up to linear order in a^*,

$$\sigma^*_{ik} = \frac{1}{1+\gamma\alpha_0}\left[\left(1 - \frac{\gamma\alpha_1}{1+\gamma\alpha_0}a^*\right)\delta_{ik} - \frac{2\gamma}{1+\gamma\alpha_0}a^*_{ik}\right], \tag{4.4}$$

$$\begin{aligned} P^*_{xy} = \frac{1}{1+\alpha_0}\Biggl\{ & \frac{3}{2\gamma(1+\gamma\alpha_0)}\epsilon^*_x\epsilon^*_y \\ & \times\left[1 - \left(\frac{1}{1+\alpha_0} + \frac{\gamma}{1+\gamma\alpha_0}\right)\alpha_1 a^*\right] \\ & - \frac{3}{2\gamma(1+\gamma\alpha_0)}\left(\frac{1}{1+\alpha_0} + \frac{\gamma}{1+\gamma\alpha_0}\right) \\ & \times a^*\epsilon^{*2}_y - \frac{1}{1+\alpha_0}a^*\Biggr\}. \end{aligned} \tag{4.5}$$

It is worth noticing that, if $\epsilon^*_x \neq 0$ and $\epsilon^*_y \neq 0$, a finite amount of x component of momentum is transferred along the y axis even for very weak shear rates. In absence of shear flow (i.e., $a^*=0$), the color conductivity becomes a scalar and the pressure tensor, Eq. (3.6), can be recast into the form $\mathsf{P}^* = P^*_\perp \mathsf{1} + (P^*_\parallel - P^*_\perp)\,\hat{\epsilon}\hat{\epsilon}$, with $P^*_\parallel = 3 - 2P^*_\perp$ and

$$P^*_\perp = \left(1 + \frac{1}{2\gamma}\epsilon^{*2}\frac{1}{1+\gamma\alpha_0}\right)^{-1}. \tag{4.6}$$

This state of homogeneous color conductivity has been analyzed in detail elsewhere.[10]

V. SMALL COLOR FIELD

If terms of order higher than first in ϵ^* are neglected, Eq. (3.9) reduces to a cubic equation whose real solution is

$$\alpha^* = \tfrac{4}{3}\sinh^2\left[\tfrac{1}{6}\cosh^{-1}(1+9a^{*2})\right]. \tag{5.1}$$

At this order, the pressure tensor $P^*_{ij}(a^*)$ is given by the well-known expressions of the pure uniform shear flow for Maxwell molecules.[6,15] A new result is obtained when Eq. (5.1) is substituted into Eq. (3.4). In this case, the transport coefficient $\sigma^*_{ik}(a^*)$ measures the *linear* response to the external field (2.8) of a system of colored particles under shear flow, being a nonlinear function of the shear rate.

In principle, the color field problem must be distinguished from the familiar self-diffusion problem. In the latter, no external field (such as $\mathscr{F}_r$) is present, but diffusion is created by a gradient of concentration of tagged particles. If the system seen as a whole is subject to uniform shear flow, a generalized self-diffusion tensor $D^*_{ik}(a^*)$ can be defined from a generalized Fick's law. For the case of a dilute Maxwell gas in the context of the Boltzmann equation, this tensor has been explicitly obtained from a generalized Green–Kubo formula[15] and also from a Chapman–Enskog formalism.[16]

Cummings *et al.*[9] have evaluated $\sigma^*_{yy}(a^*)$ (through the color field method) and $D^*_{yy}(a^*)$ (through the Einstein and Green–Kubo methods which have been proved to be correct[19]) by nonequilibrium molecular dynamics of a Lennard-Jones fluid at its triple point. Their results indicate that both quantities agree within the statistical errors. However, the exact results obtained in this paper and in Refs. 15 and 16 show that

$$D^*_{ij}(a^*) = \sigma^*_{ik}(a^*)P^*_{kj}(a^*). \tag{5.2}$$

For nonzero shear rates, the color conductivity and self-diffusion tensors have different qualitative features. For instance, $\sigma^*_{xx} = \sigma^*_{yy} = \sigma^*_{zz}$, while $D^*_{xx} > D^*_{yy} = D^*_{zz}$; $\sigma^*_{xy} < \sigma^*_{yx} = 0$, while $D^*_{xy} < D^*_{yx} < 0$; and $\sigma^*_{xx} < D^*_{xx}$, $\sigma^*_{yy} > D^*_{yy}$, but $\mathrm{Tr}\,\sigma^* < \mathrm{Tr}\,\mathsf{D}^*$. The difference between both tensors is of second order in a^* for the diagonal elements and of first order for the *xy* and *yx* elements. As an illustration, Fig. 1 shows $\Delta_{yy}(a^*)$ and $-\Delta(a^*)$, where

$$\Delta_{yy} \equiv \frac{\sigma^*_{yy} - D^*_{yy}}{D^*_{yy}} = \alpha^*, \tag{5.3}$$

$$\Delta \equiv \frac{\mathrm{Tr}\,\sigma^* - \mathrm{Tr}\,\mathsf{D}^*}{\mathrm{Tr}\,\mathsf{D}^*} = -\frac{\gamma\alpha^*}{1+2\gamma\alpha^*}. \tag{5.4}$$

It can be seen that the relative difference is much more important in the case of the *yy* element than in the case of the trace. The former is about 72% at $a^* = 1$, while the latter is always less than 50%.

Evans *et al.*[11] have recently analyzed the relationship between the self-diffusion tensor (which is a thermal transport coefficient) and the zero-field limit of the color conductivity tensor (which is a mechanical transport coefficient). Their results show the inadequacy of the color method to calculate the self-diffusion tensor in the non-Newtonian regime due to the existence of color current-pressure tensor cross correlations that do not die away at steady state.

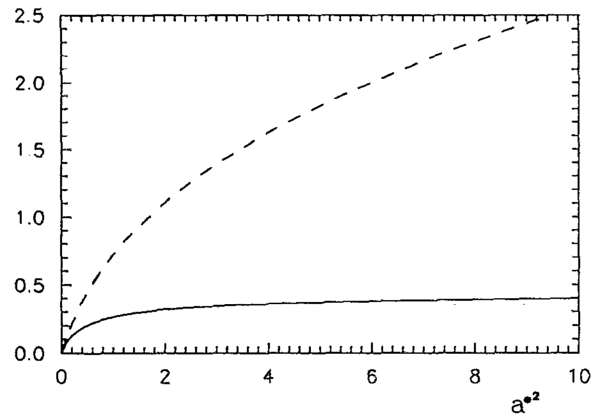

FIG. 1. Plot of the relative difference between the color conductivity and the self-diffusion coefficients vs the shear rate square. The solid line corresponds to the absolute value of the trace ($-\Delta$), and the dashed line corresponds to the yy element (Δ_{yy}).

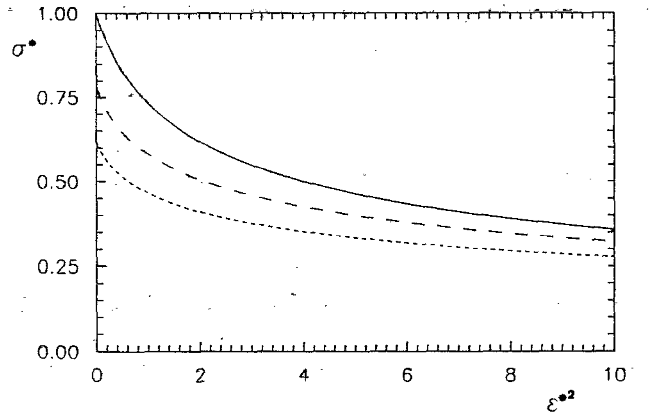

FIG. 2. Plot of the diagonal element of the reduced color conductivity tensor vs the reduced field strength square for several values of the shear rate: $a^*=0$ (—), $a^*=1$ (– – –), $a^*=2$ (---).

VI. NONLINEAR MOMENTUM AND COLOR TRANSPORT

In this section we will study the coupling between momentum and color transport for finite shear rate *and* color field strength. In the special case $\epsilon_y^*=0$, Eq. (3.9) reduces to a quartic equation, which possesses an exact solution. This case has been previously analyzed in Ref. 21. As a complement, here we will deal with the case $\epsilon_x^*=\epsilon_z^*=0$. As a matter of fact, the simulations performed by Cummings *et al.*[9] correspond to this case. For this geometry, Eq. (3.9) becomes

$$\alpha^*(1+\alpha^*)^2(1+\gamma\alpha^*)^2 = \frac{2}{3}a^{*2}(1+\gamma\alpha^*)^2+\frac{\epsilon^{*2}}{2\gamma}(1+\alpha^*)^2(1+\gamma\alpha^*) + \frac{1+\gamma(1+2\alpha^*)}{\gamma}a^{*2}\epsilon^{*2}. \tag{6.1}$$

Since Eq. (6.1) is a fifth-degree equation in α^*, no explicit expression of $\alpha^*(a^*,\epsilon^*)$ is known. However, it can be obtained implicitly from $a^{*2}(\alpha^*,\epsilon^{*2})$ or $\epsilon^{*2}(\alpha^*,a^{*2})$. The color conductivity tensor and the shear viscosity are obtained by substitution of α^* into Eqs. (3.4) and (3.8), respectively. Notice that, according to Eq. (4.5) with $\epsilon_x^*=\epsilon_z^*=0$, P_{xy}^* is of first order in a^* in the limit of small a^*. Thus the shear viscosity is well defined in this limit.

The diagonal element $\sigma_{xx}^*=\sigma_{yy}^*=\sigma_{zz}^*=\sigma^*$ is plotted in Fig. 2 as a function of ϵ^{*2} for several values of a^*. We observe that σ^* decreases as ϵ^* and/or a^* increase. Therefore, the color current increases with the color field more slowly than in a linear law. In addition, the color transport is inhibited by the presence of the shear. Both features contrast with Cummings *et al.*'s results,[9] where the opposite behavior is observed. This qualitative discrepancy may be due to the fact that the Lennard-Jones potential has an attractive tail (which is absent in Maxwell molecules), or that the simulations were carried out for a dense fluid (where the Boltzmann equation is not valid).

In Fig. 3, the shear viscosity is plotted vs a^{*2} for several values of ϵ^*. A generalized shear thinning effect is observed: At a given value of ϵ^*, the viscosity decreases as the shear increases. On the other hand, the viscosity does not behave monotonically with respect to the color field. In particular, at zero shear rate,

$$\lim_{a^*\to 0}\eta^*=\frac{1+(3+4\gamma)\alpha_0+6\gamma\alpha_0^2}{(1+\gamma\alpha_0)(1+\alpha_0)^2}, \tag{6.2}$$

where α_0 is given by Eq. (4.2). This quantity has a maximum equal to 1.694 at $\epsilon^{*2}=1.636$ and is smaller than 1 for $\epsilon^{*2}>23.69$. However, in the case $\epsilon_y^*=0$,[21] the momentum transport is always hindered by the presence of the color field, i.e., η^* decreases as ϵ^* increases.

VII. DISCUSSION

The coupling between mass and momentum transport in a binary mixture of mechanically identical Maxwell molecules described by the Boltzmann equation has been analyzed. The system is in a steady inhomogeneous state (the

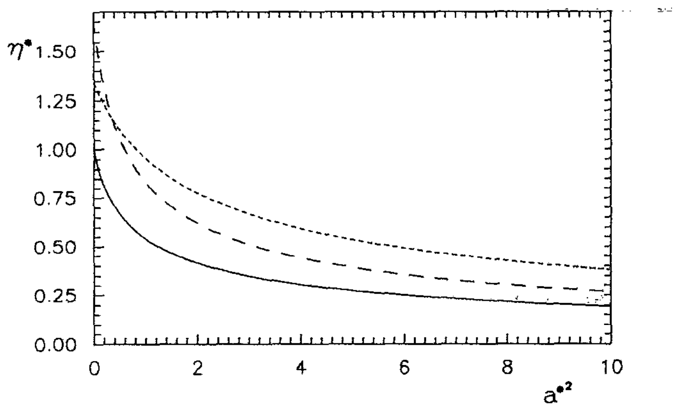

FIG. 3. Plot of the reduced shear viscosity vs the reduced shear rate square for several values of the field strenght: $\epsilon^*=0$ (—), $\epsilon^*=1$ (– – –), $\epsilon^*=3$ (---).

so-called uniform shear flow) macroscopically characterized by a constant total density and pressure, and a mean velocity along the x direction with a constant gradient along the y direction. Further, two different species are distinguished by a label or "color." Mutual diffusion is generated by a constant external force (color field) acting on particles of different colors in opposite directions. A nonconservative drag force is also included to maintain the temperature constant. The system is driven out of equilibrium by the shearing as well as by the color field. This state includes the pure uniform shear flow and the homogeneous color conductivity problem as particular cases. The color field method to produce diffusion in absence of concentration gradients has been previously used in nonequilibrium molecular dynamics simulations.[8,9]

The mathematical properties of the Boltzmann collision operator for Maxwell molecules enable one to solve the hierarchy of moment equations in a recursive way. In this paper, we have focused on the particle fluxes and the total pressure tensor. These quantities are related, respectively, to the transport of mass (or color) and total momentum. The relevant transport coefficients, namely, the color conductivity tensor σ_{ik} and the shear viscosity η, depend in a nonlinear way of both the color field ϵ_1 and the shear rate a. Proceeding further in the recursive scheme, higher order moments can also be obtained.

In the linear limit in a, there exists in general a nonvanishing contribution to the transport of the x component of momentum along the y direction. It comes from the motion of particles induced by the color field. This contribution vanishes if the color field is orthogonal to the x and/or the y axis. In this case, a shear viscosity is well defined in the limit of small shear rate.

In absence of shear ($a = 0$), the color conductivity σ in the limit of small color field reduces to the self-diffusion coefficient D. This coefficient is defined by the familiar Fick's law and can be expressed by means of a Green–Kubo formula. Thus from the molecular dynamics point of view, the color field method represents an efficient alternative to the Green–Kubo formula to compute the self-diffusion coefficient.[8] The interesting question now is whether such an equivalence is still valid when the system as a whole is in a nonequilibrium state (such as the uniform shear flow). The analysis made in Ref. 11 shows that the answer is generally negative. The exact results reported in this paper for a Maxwell dilute gas confirm that D_{ik} and σ_{ik} are clearly different, especially for large shear rates. In fact, this distinction is related to the presence of nonequilibrium normal and shear stresses, as shown by Eq. (5.2).

Let us investigate whether a choice of the color field $\mathcal{F}_r$ different from the one given by Eq. (2.8) could yield consistent results for the self-diffusion and the color conductivity tensors. In the linear order in the color field, the Boltzmann equation for f_1, Eq. (2.9), becomes

$$-\frac{\partial}{\partial V_i}\left[\left(\frac{\alpha}{m}V_i + a_{ij}V_j\right)f_1 - \frac{n_1}{n}\frac{\mathcal{F}_{1,i}}{m}f\right] = J[f_1,f], \tag{7.1}$$

where we have taken into account that in zeroth order in the color field, $f_1 = (n_1/n)f$. Equation (7.1) has a form similar to the one in the self-diffusion problem [see Eq. (4.25) in Ref. 16], except that the term

$$\frac{n_1}{mn}\mathcal{F}_1\cdot\frac{\partial}{\partial \mathbf{V}}f \tag{7.2}$$

should be replaced by

$$\frac{1}{n}\nabla n_1\cdot\mathbf{V}f. \tag{7.3}$$

The color conductivity and the self-diffusion tensors are then identical if Eqs. (7.2) and (7.3) give the same contribution to the particle flux. Equating the first velocity moments of Eqs. (7.2) and (7.3), one gets

$$\mathcal{F}_1 = -\frac{1}{n}\mathsf{P}\cdot\boldsymbol{\epsilon}_1, \tag{7.4}$$

where we have identified the chemical potential gradient $(\nabla n_1)/n_1$ with the field strenght ϵ_1. Notice that Eq. (7.4) reduces to the one originally proposed in the color field method, Eq. (2.8), if the pressure tensor is replaced by that of equilibrium. For finite shear rate, Eq. (7.4) takes into account the anisotropy of the problem, so that the vectors $\mathcal{F}_1$ and ϵ_1 are no longer parallel. We think that Eq. (7.4) gives the adequate external force to obtain the shear rate-dependent self-diffusion tensor from the color field method, even for dense fluids. It would be interesting to perform computer simulations to verify this point.

On the other hand, the analysis of nonlinear transport due to the coupling between the shear flow and the external color field given by Eq. (2.8) is a physically interesting problem in itself. Here we have restricted to a color field parallel to the flow velocity gradient.[22] This is the same geometry as in Ref. 9. For any value of the color field, the shear viscosity exhibits shear thinning. At a given value of the shear rate, the momentum transport is enhanced by color fields smaller than a certain threshold value, and is inhibited by greater color fields. This contrasts with the case $\epsilon_{1,y} = 0$,[21] where inhibition is always the effect of the presence of color field. Concerning the behavior of the color conductivity tensor, its diagonal elements are a monotonically decreasing function of both a and $\epsilon_{1,y}$. The opposite behavior has been observed in computer simulations.[9] The discrepancy is probably due to the potential contribution to transport, which is quite important for dense fluids.[23] It must be noticed that in Ref. 9 the thermostat force is applied only to the motion in the x and z direction, rather than isotropically as in Eq. (2.7). We have verified that this other choice does not affect the main qualitative conclusions reported in this paper.

The analysis carried out in this work stimulates further work along several directions. First, we expect to study the coexistence between the shear flow and the color field given by Eq. (7.4). Moreover, the problem can be extended to the case of arbitrary mass ratio in the so-called tracer limit.[18] Finally, in order to get explicit expressions for the distribution functions, it would be interesting to study the problem by using kinetic models.[24]

ACKNOWLEDGMENT

Partial support from the Dirección General de Investigación Científica y Técnica (Spain) through Grant No. PS 89-0183 is gratefully acknowledged.

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