INFLUENCE OF NONCONSERVATIVE EXTERNAL FORCES ON SELF-DIFFUSION IN DILUTE GASES

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The influence of a nonconservative force proportional to the velocity acting on a system described by the Boltzmann equation is analyzed. When this force is the only external action on the system, an *H*-theorem is proved, showing that the distribution function tends towards a Maxwellian with a time-dependent temperature. Self-diffusion in such a state is analyzed in the case of Maxwell molecules. It is shown that the external force can even prevent the system to reach a hydrodynamic stage. Next, self-diffusion in a system under uniform shear flow is considered. For Maxwell molecules, the conditions under which a hydrodynamic regime is reached are discussed. In the hydrodynamic regime, a self-diffusion tensor is obtained to first order in the concentration gradient. This tensor is a highly nonlinear function of both the shear rate and the strength of the external force. Comparison with previous work is carried out.

1. Introduction

A usual way of controlling the temperature of a system in molecular dynamics simulations and also in kinetic theory is to introduce a velocity-dependent external force [1–3]. The simplest choice seems to be a homogeneous force proportional to the (peculiar) velocity of the particle. This is equivalent to a continuous scaling of the velocities [4]. From a practical point of view, the possibility of controlling the temperature is very important. It allows, for instance, to compensate for dissipative heating effects and to maintain the system in a nonequilibrium stationary state. Nevertheless, little is known about the influence of this kind of nonconservative external forces on the properties of the system. In general, there is no reason to expect a simple relationship between the behaviors of the system with and without nonconservative forces. They can even affect the possibility of a hydrodynamic description and the existence of "normal" solutions of a given kinetic equation.

In the particular case of the Boltzmann equation for a system of Maxwell molecules under uniform shear flow, there is a close relationship between the

distribution functions with and without a thermostatic force [4]. However, such a relationship does not exist when other interaction potentials are considered. For instance, the dimensionless generalized shear viscosity is different beyond Navier–Stokes order when the viscous heating is controlled. This has been explicitly shown using the BGK model of the Boltzmann equation [4]. For dense fluids the situation is much more complicated, even for Maxwell molecules [3].

In this paper, we study the influence of a nonconservative force on the self-diffusion transport coefficient in a gas described by the Boltzmann equation. Two different physical situations will be considered. First, the system as a whole is assumed to be at equilibrium. The effect of the external force is just to change the temperature in time, but otherwise the distribution function is always Maxwellian. However, we shall see that the self-diffusion coefficient, computed from the Chapman–Enskog expansion and for the particular case of Maxwell molecules, is strongly modified. In fact, when the system is cooled fast enough, the distribution of tagged particles does not reach a normal or hydrodynamic form.

The second case corresponds to a system under uniform shear flow. We shall restrict ourselves to Maxwell molecules, for which an exact solution to the Boltzmann equation describing that state is known [5, 6]. In order to compute the self-diffusion coefficient, a Chapman–Enskog-like expansion around the above solution is carried out. In this way, we get a shear-rate-dependent transport coefficient tensor. In the case of no external forces, this quantity has been obtained by Dufty [7] using a generalized Green–Kubo formalism. Our results reduce to those of ref. [7] in the proper limit. The analysis shows that, again, a hydrodynamic regime is not reached if the cooling rate is large.

The plan of the paper is as follows. In section 2 the nonconservative force to be considered is defined. It is shown that if that is the only external action on the system, an H-theorem holds. As a consequence, the system reaches in time an equilibrium-like state, but with a time-dependent temperature. Self-diffusion in the above system is considered in section 3. An equation for the first Chapman–Enskog order of the distribution function of tagged particles is derived. Taking moments in this equation, we are able to obtain an expression for the particle flux. The conditions under which a hydrodynamic regime is reached are established. A similar analysis, but using the distribution function itself, is carried out in the appendix. Next, in section 4, self-diffusion in a system under uniform shear flow is considered. The situation is now much more complicated, since the system as a whole is far from equilibrium. Nevertheless, the knowledge of a solution to the Boltzmann equation for Maxwell molecules allows us to carry out explicit calculations. Using again a Chapman–Enskog-like expansion, a generalized Fick law is obtained if certain

conditions are satisfied. Due to the anisotropy of the system, a self-diffusion tensor, rather than a scalar, appears. Finally, the results are discussed and connected with previous work in section 5.

2. Nonconservative forces

We consider a dilute gas whose one-particle distribution function $f(r, v; t)$ obeys the Boltzmann equation

$$\frac{\partial f}{\partial t} + v \cdot \nabla f + \frac{\partial}{\partial v} \cdot \left(\frac{F}{m} f \right) = J[f, f] , \tag{2.1}$$

where $F(r, v; t)$ is an external force, m is the mass of a particle, and J is the Boltzmann collision operator, which in standard notation reads [8]

$$J[f, g] = \int dv_1 \int d\Omega \, |v - v_1| \sigma(|v - v_1|, \theta)[f(v')g(v_1') - f(v)g(v_1)] . \tag{2.2}$$

We are interested in using the external force F as a way of controlling the temperature of the system. The simplest possibility seems to be a homogeneous nonconservative force proportional to the velocity of the particle, i.e.,

$$F(v, t) = \zeta(t)mv . \tag{2.3}$$

It is easily verified that with this choice, eq. (2.1) admits the solution

$$f_0(v, t) = n \left[\frac{m}{2\pi k_B T(t)} \right]^{3/2} \exp \left[-\frac{mv^2}{2k_B T(t)} \right] \tag{2.4}$$

with $T(t)$ being the solution of

$$\frac{dT}{dt} = 2\zeta T . \tag{2.5}$$

Therefore, the system is in a time-dependent "equilibrium" state. By choosing $\zeta(t)$ in an appropriate way one can get any desired temperature evolution. In particular, the choice $\zeta = $ const. leads to an exponential behavior.

The natural question now is whether the form given by eq. (2.4) is reached starting from any initial condition. We are going to prove this in the form of an H-theorem. Let us define the function

$$H(t) = \int \mathrm{d}r \int \mathrm{d}v\, f \ln(f/f_\mathrm{R})\,, \tag{2.6}$$

where

$$f_\mathrm{R}(v, t) = \bar{n}\left[\frac{m}{2\pi k_\mathrm{B}\Theta(t)}\right]^{3/2} \exp\left[-\frac{mv^2}{2k_\mathrm{B}\Theta(t)}\right]. \tag{2.7}$$

Here, $\bar{n}$ is the average number density and $\Theta(t)$ is defined by

$$\frac{3}{2}\,\bar{n}k_\mathrm{B}\Theta(t) = \frac{1}{V}\int \mathrm{d}r \int \mathrm{d}v\, \frac{m}{2}\, v^2 f(r, v; t)\,, \tag{2.8}$$

V being the volume of the system. Notice that $\Theta(t)$ coincides with the temperature of the system $T(t)$ when a homogeneous state is considered. In general, $\Theta(t)$ is proportional to the mean kinetic energy density. From eqs. (2.1) and (2.3) it follows that Θ obeys the equation

$$\frac{\mathrm{d}\Theta}{\mathrm{d}t} = 2\zeta\Theta\,. \tag{2.9}$$

Taking the time derivative of eq. (2.6), one gets

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \int \mathrm{d}r \int \mathrm{d}v\, \frac{\partial f}{\partial t} \ln(f/f_\mathrm{R}) + \int \mathrm{d}r \int \mathrm{d}v\, f\, \frac{\partial}{\partial t} \ln(f/f_\mathrm{R})\,. \tag{2.10}$$

The second term on the right-hand side vanishes, as

$$\int \mathrm{d}r \int \mathrm{d}v\, f\, \frac{\partial}{\partial t} \ln f_\mathrm{R} = \int \mathrm{d}r \int \mathrm{d}v\, f_\mathrm{R}\, \frac{\partial}{\partial t} \ln f_\mathrm{R}$$

$$= \int \mathrm{d}r \int \mathrm{d}v\, \frac{\partial}{\partial t}\, f_\mathrm{R}$$

$$= \int \mathrm{d}r \int \mathrm{d}v\, \frac{\partial}{\partial t}\, f = 0\,. \tag{2.11}$$

Taking into account that

$$\int \mathrm{d}r \int \mathrm{d}v\, (v \cdot \nabla f) \ln(f/f_\mathrm{R}) = -\int \mathrm{d}r \int \mathrm{d}v\, f v \cdot \nabla \ln f$$

$$= 0 \tag{2.12}$$

and

$$\int d\boldsymbol{r} \int d\boldsymbol{v} \left[\frac{\partial}{\partial \boldsymbol{v}} \cdot (\boldsymbol{v} f) \right] \ln(f/f_R) = -\int d\boldsymbol{r} \int d\boldsymbol{v}\, \boldsymbol{v} \cdot \left[\frac{\partial f}{\partial \boldsymbol{v}} - f\, \frac{\partial}{\partial \boldsymbol{v}} \ln f_R \right]$$

$$= \int d\boldsymbol{r} \int d\boldsymbol{v}\, f \left(3 - \frac{mv^2}{k_B \Theta} \right) = 0 \,, \qquad (2.13)$$

eq. (2.10) reduces to

$$\frac{dH}{dt} = \int d\boldsymbol{r} \int d\boldsymbol{v}\, \ln(f/f_R) J[f, f] \leq 0 \,, \qquad (2.14)$$

where the last inequality follows from the general properties of the Boltzmann collision operator [8]. Consequently, $H(t)$ monotonically decreases until it vanishes, which correponds to $f = f_R$, i.e., $f = f_0$.

For homogeneous situations and for interaction potentials of the form $V \sim r^{-\mu}$, there is a close relationship between the solutions to the Boltzmann equation with and without the external force (2.3). When the external force is considered, we have

$$\frac{\partial f}{\partial t} + \zeta\, \frac{\partial}{\partial \boldsymbol{v}} \cdot \boldsymbol{v} f = J[f, f] \,. \qquad (2.15)$$

Let us introduce the new variables

$$\tilde{\boldsymbol{v}} = \left[\frac{T(t)}{T_0} \right]^{-1/2} \boldsymbol{v} \,, \qquad (2.16)$$

$$\tilde{t} = \int_0^t dt' \left[\frac{T(t')}{T_0} \right]^{\frac{1}{2}(1 - 4/\mu)} \,, \qquad (2.17)$$

and the new distribution function

$$\tilde{f}(\tilde{\boldsymbol{v}}, \tilde{t}) = \left[\frac{T(t)}{T_0} \right]^{3/2} f(\boldsymbol{v}, t) \,. \qquad (2.18)$$

In the above expressions T_0 is an arbitrary reference temperature, while $T(t)$ is the actual temperature at time t and verifies eq. (2.5). For a $r^{-\mu}$-potential, the differential cross section σ depends on the relative velocity v as $v^{-4/\mu}$ [9] and one obtains

$$J[f, f] = \left(\frac{T}{T_0} \right)^{-(1 + 2/\mu)} J[\tilde{f}, \tilde{f}] \,. \qquad (2.19)$$

Then, one easily gets eq. (2.15) in the new variables,

$$\frac{\partial}{\partial \tilde{t}} \tilde{f} = J[\tilde{f}, \tilde{f}],$$
(2.20)

which formally coincides with the Boltzmann equation in absence of external forces. The consequence is that the effect of the external force (2.3) for homogeneous systems of particles interacting via $r^{-\mu}$-potentials is just to scale the velocities and to introduce a new time scale. The latter is such that the average number of collisions per unit time, as given by the effective collision frequency, remains constant in time.

3. Self-diffusion at equilibrium

Suppose now that some particles of the system described by eq. (2.1) are tagged, but otherwise all the particles are mechanically equilvalent. Let $h(r, v; t)$ be the distribution function of tagged particles. Its time evolution is given by

$$\frac{\partial h}{\partial t} + v \cdot \nabla h + \frac{\partial}{\partial v} \cdot \left(\frac{F}{m} h \right) = J[h, f].$$
(3.1)

Once the function f is obtained from eq. (2.1), eq. (3.1) becomes a linear equation in h. In particular, if there is no external force and f is the equilibrium Maxwell–Boltzmann distribution, eq. (3.1) reduces to the Boltzmann–Lorentz equation [9]. Notice that the kinetic equation (3.1) holds for any relative number of tagged particles.

In this section, we consider self-diffusion in presence of the external force (2.3), with $\zeta = \text{const}$. We assume that the system has been aged enough to be described by the distribution function (2.4), i.e., we take $f = f_0$ in eq. (3.1). Our aim is to determine the self-diffusion coefficient. We shall carry out a Chapman–Enskog method [8]. As usual, we look for normal solutions to eq. (3.1) by expanding

$$h = h^{(0)} + \varepsilon h^{(1)} + \varepsilon^2 h^{(2)} + \cdots,$$
(3.2)

$$\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \varepsilon \frac{\partial_1}{\partial t} + \varepsilon^2 \frac{\partial_2}{\partial t} + \cdots,$$
(3.3)

where ε is an auxiliary parameter measuring the nonuniformity of the concentration of tagged particles. The term $v \cdot \nabla h$ in eq. (3.1) is assumed to be affected by a factor of ε. The definition of $\partial_k / \partial t$ is taken from the kth order approximation to the hydrodynamic balance equations,

$$\frac{\partial_0}{\partial t} n_1 = 0 \,, \tag{3.4a}$$

$$\frac{\partial_k}{\partial t} n_1 = -\boldsymbol{\nabla} \cdot \boldsymbol{j}^{(k-1)} \,, \qquad k \geqslant 1 \,, \tag{3.4b}$$

$$\frac{\partial_0 T}{\partial t} = 2\zeta T \,, \tag{3.5a}$$

$$\frac{\partial_k T}{\partial t} = 0 \,, \qquad k \geqslant 1 \,. \tag{3.5b}$$

Here, n_1 is the number density of tagged particles and $\boldsymbol{J}$ is the flux of tagged particles. They are given by

$$n_1 = \int \mathrm{d}\boldsymbol{v}\, h = \int \mathrm{d}\boldsymbol{v}\, h^{(0)} \,, \tag{3.6}$$

$$\boldsymbol{j}^{(k)} = \int \mathrm{d}\boldsymbol{v}\, \boldsymbol{v} h^{(k)} \,, \tag{3.7}$$

respectively. Upon writing eqs. (3.4), (3.5) we have taken into account that the system as a whole is at equilibrium with a temperature $T(t)$. It is assumed that all the time and position dependence of the distribution function occurs through the hydrodynamic fields (normal solution), and, therefore,

$$\frac{\partial_k}{\partial t} h^{(l)} = \frac{\partial_k}{\partial t} n_1 \frac{\partial}{\partial n_1} h^{(l)} + \frac{\partial_k}{\partial t} T \frac{\partial}{\partial T} h^{(l)} \,. \tag{3.8}$$

By introducing (3.2) and (3.3) into eq. (3.1), and equating terms of the same order in ε, we get a set of equations. The first two equations are

$$\frac{\partial_0}{\partial t} h^{(0)} + \zeta \frac{\partial}{\partial \boldsymbol{v}} \cdot (\boldsymbol{v} h^{(0)}) = J[h^{(0)}, f_0] \,, \tag{3.9}$$

$$\frac{\partial_0}{\partial t} h^{(1)} + \frac{\partial_1}{\partial t} h^{(0)} + \boldsymbol{v} \cdot \boldsymbol{\nabla} h^{(0)} + \zeta \frac{\partial}{\partial \boldsymbol{v}} \cdot (\boldsymbol{v} h^{(1)}) = J[h^{(1)}, f_0] \,. \tag{3.10}$$

The solution to eq. (3.9) is easily seen to be

$$h^{(0)}(\boldsymbol{r}, \boldsymbol{v}; t) = \frac{n_1(\boldsymbol{r}, t)}{n} f_0(\boldsymbol{v}, t) \,. \tag{3.11}$$

Insertion of this expression into eq. (3.10) yields

$$f_0 \boldsymbol{v} \cdot \boldsymbol{\nabla} \frac{n_1}{n} + 2\zeta T \frac{\partial}{\partial T} h^{(1)} + \zeta \frac{\partial}{\partial \boldsymbol{v}} \cdot (\boldsymbol{v} h^{(1)}) = J[h^{(1)}, f_0] \,, \tag{3.12}$$

where use has been made of eq. (3.8). The external force manifests itself in the two terms proportional to ζ, which explicitly contain the unknown function $h^{(1)}$. Therefore, we are faced with a linear integro-differential equation. This in contrast with the usual Chapman–Enskog expansion [8] for conservative external forces. In that case, a factor of ε in front of the external force term is assumed. As a consequence, the first order equation is an integral equation containing $h^{(1)}$ just through the collision term.

Due to the mathematical complexity of eq. (3.12), we are going to restrict ourselves from now on to Maxwell molecules, namely we consider the interaction potential $V(r) = \kappa/r^4$. In this case, the Boltzmann collision operator has the property [6]

$$\int d\boldsymbol{v}\, \boldsymbol{v} J[f, g] = -\alpha \int d\boldsymbol{v} \int d\boldsymbol{v}_1\, (\boldsymbol{v}_1 - \boldsymbol{v}) f(\boldsymbol{v}_1) g(\boldsymbol{v}) , \qquad (3.13)$$

for arbitrary f and g. Here, α is the constant

$$\alpha = 1.19\pi(\kappa/m)^{1/2}$$

$$= \pi \int_0^\pi d\theta \sin\theta\, v\sigma(v, \theta)(1 - \cos\theta) . \qquad (3.14)$$

Thus, by multiplying eq. (3.12) by $\boldsymbol{v}$ and integrating, the following is obtained:

$$\frac{k_B T}{m} \boldsymbol{\nabla} n_1 + 2\zeta T \frac{\partial}{\partial T} \boldsymbol{j}^{(1)} - \zeta \boldsymbol{j}^{(1)} = -\alpha n \boldsymbol{j}^{(1)} . \qquad (3.15)$$

In absence of an external force ($\zeta = 0$), one recovers the usual Fick equation with a self-diffusion coefficient $D_0 = k_B T/mn\alpha$. For $\zeta \neq 0$, the general solution of the differential equation (3.15) is

$$\boldsymbol{j}^{(1)} = -\frac{k_B T}{m(\alpha n + \zeta)} [\boldsymbol{\nabla} n_1 + \boldsymbol{C} T^{-(\alpha n + \zeta)/2\zeta}] , \qquad (3.16)$$

where $\boldsymbol{C}$ is a constant vector to be determined from the initial conditions. A hydrodynamic expression for the flux, independent of the initial conditions, is expected to hold after a transient period. To analyze whether this is the situation here, let us consider the time dependence of the last term in eq. (3.16). Using eq. (2.5) for $\zeta = $ const., we have

$$T^{-(\zeta + \alpha n)/2\zeta} \propto e^{(\zeta + \alpha n)t} . \qquad (3.17)$$

We see that this term decays to zero in the long-time limit only for $\zeta + \alpha n > 0$. Therefore, the system does not reach a hydrodynamic regime when $\zeta + \alpha n \leqslant 0$. This case corresponds to cooling the system with a rate larger than or equal to the characteristic collision frequency αn. For smaller cooling rates or for arbitrary heating rates, we reobtain Fick's law with an effective self-diffusion coefficient given by

$$D = \frac{k_B T}{m(\alpha n + \zeta)} \ .$$

(3.18)

Therefore, at a given temperature, a system that is being heated has a smaller self-diffusion coefficient than a system kept at constant temperature. The opposite happens if the system is cooled with a rate smaller than αn. Notice that eq. (3.18) becomes unphysical in the non-hydrodynamic region $\zeta \leqslant -\alpha n$, since D becomes divergent or negative.

In any case, it must be noticed that when the system is being cooled with $\alpha n/3 < |\zeta| < \alpha n$ or heated with $\zeta > \alpha n$, the characteristic time of change of the temperature is smaller than the one associated to the decay of the initial condition. Therefore, in practice, it can be hard to reach a hydrodynamic regime in those cases. We could consider a "true" hydrodynamic region to be reached only for $-\alpha n/3 < \zeta < \alpha n$.

The above discussion has been restricted to the behavior of the flux of tagged particles. In the appendix we consider the more general question of analyzing the conditions under which the first Chapman–Enskog approximation $h^{(1)}$ can indeed describe a hydrodynamic regime. There, it is shown that the condition for a hydrodynamic $h^{(1)}$ is just the same as for a hydrodynamic flux.

4. Self-diffusion under uniform shear flow

In the following, we will consider a system under uniform shear flow (USF). The macroscopic state of the fluid is defined by the hydrodynamic fields,

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

(4.1)

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

(4.2)

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

(4.3)

where n is the number density, T is the temperature, u_i is the ith component of the local velocity, and a is a constant shear rate. This state has been extensively

studied theoretically [3–5] and also by means of molecular dynamics simulations [1]. In absence of external forces, the USF state is not stationary, since the temperature increases in time due to viscous heating. This fact has been used to measure a generalized shear viscosity far from equilibrium [11]. On the other hand, some authors have introduced a fictitious nonconservative force to compensate for the viscous heating, looking for a stationary state [1]. It must be pointed out that the relationship between the transport coefficients measured with and without nonconservative forces is not clear beyond the Navier–Stokes order [3, 4].

Our aim here is to study the self-diffusion coefficient in a system under USF and how it is affected by the introduction of a nonconservative external force. This will be done in the context of the Boltzmann equation for Maxwell molecules.

It is convenient to introduce rest-frame velocities defined by

$$V_i = v_i - a_{ij} r_j \,. \tag{4.4}$$

The Boltzmann equation (2.1) then becomes

$$\frac{\partial f}{\partial t} + (V_i + a_{ij} r_j) \frac{\partial}{\partial r_i} f - a_{ij} V_j \frac{\partial}{\partial V_i} f + \frac{\partial}{\partial V_i} \left(\frac{F_i}{m} f \right) = J[f, f] \,. \tag{4.5}$$

In this new frame, the USF state is spatially homogeneous. Therefore, if we assume a homogeneous external force $F(V, t)$, the distribution function of the system obeys the equation

$$\frac{\partial f}{\partial t} - \frac{\partial}{\partial V_i} (a_{ij} V_j - \zeta V_i) f = J[f, f] \,. \tag{4.6}$$

where the simplest generalization of eq. (2.3) has been assumed for the external force, namely $F = \zeta(t) m V$. Taking moments in eq. (4.6), one gets the following evolution equation for the temperature:

$$\frac{dT}{dt} - 2\zeta T + \frac{2}{3nk_B} a P_{xy} = 0 \,, \tag{4.7}$$

where P_{xy} is a component of the pressure tensor

$$P_{ij} = m \int dV \, V_i V_j f \,. \tag{4.8}$$

For Maxwell molecules the solution to eq. (4.6) with arbitrary ζ can be easily

obtained from the solution for $\zeta = 0$. In fact, if we make the change of variables [4]

$$\tilde{V} = R(t)V ,$$ (4.9)

$$\tilde{f}(\tilde{V}, t) = R^{-3}(t)f(V, t) ,$$ (4.10)

with $R(t)$ given by

$$\zeta(t) = \frac{\mathrm{d}}{\mathrm{d}t} \ln R(t) ,$$ (4.11)

eq. (4.6) reduces to

$$\frac{\partial}{\partial t} \tilde{f} - \frac{\partial}{\partial \tilde{V}_i} (a_{ij}\tilde{V}_j\tilde{f}) = J[\tilde{f}, \tilde{f}] .$$ (4.12)

Therefore, the change of variables is formally equivalent to make $\zeta = 0$ in eq. (4.6). Taking moments in this equation one gets a set of equations that can be solved recursively [5]. In particular, the nonzero components of the pressure tensor in the long time limit (hydrodynamic regime) are given by [6]

$$P_{xx} = p \, \frac{1 + 3\lambda(a^*)}{1 + \lambda(a^*)} ,$$ (4.13)

$$P_{yy} = P_{zz} = p \, \frac{1}{1 + \lambda(a^*)} ,$$ (4.14)

$$P_{xy} = P_{yx} = -p \, \frac{3}{2} \frac{\lambda(a^*)}{a^*} ,$$ (4.15)

where $p = nk_\mathrm{B}T$ is the pressure,

$$\lambda(a^*) = \tfrac{4}{3} \sinh^2[\tfrac{1}{6} \cosh^{-1}(1 + 9a^{*2})] ,$$ (4.16)

and a^* is the reduced shear rate,

$$a^* = \frac{a}{\nu_0} .$$ (4.17)

Here, ν_0 is an eigenvalue of the Boltzmann operator,

$$\nu_0 = \tfrac{3}{2} \pi n \int_0^\pi \mathrm{d}\theta \sin \theta \, v\sigma(v, \theta) \sin^2\theta$$

$$= 1.85\pi n(\kappa/m)^{1/2} .$$ (4.18)

Using the relations (4.9) and (4.10), it is easily seen that eqs. (4.13)–(4.15) also hold for the long time limit solution of eq. (4.6).

We consider a system described by eq. (4.6) in the hydrodynamic regime. For the sake of simplicity, we will assume in the following that ζ is a constant. This includes, in particular, the case of a thermostatic force keeping the temperature constant. From eqs. (4.7) and (4.15) it follows that a constant temperature is achieved if

$$\zeta = \zeta_0(a^*) = -\tfrac{1}{2} \nu_0 \lambda(a^*) . \tag{4.19}$$

Now, a concentration of tagged particles is assumed as in section 3. Their distribution function $h(r, V; t)$ obeys the kinetic equation

$$\frac{\partial h}{\partial t} + (V_i + a_{ij} r_j) \frac{\partial}{\partial r_i} h - \frac{\partial}{\partial V_i} (a_{ij} V_j - \zeta V_i) h = J[h, f] , \tag{4.20}$$

where f is given by the hydrodynamic solution of eq. (4.6). To solve eq. (4.20) we will use again a Chapman–Enskog expansion. Nevertheless, now the expansion will be around a time-dependent nonequilibrium state, namely a USF state with arbitrary shear rate a^*. By introducing the expansions (3.2) and (3.3) into eq. (4.20), one gets

$$\frac{\partial_0}{\partial t} h^{(0)} - \frac{\partial}{\partial V_i} (a_{ij} V_j - \zeta V_i) h^{(0)} = J[h^{(0)}, f] , \tag{4.21}$$

$$\frac{\partial_0 h^{(1)}}{\partial t} + \frac{\partial_1}{\partial t} h^{(0)} + (V_i + a_{ij} r_j) \frac{\partial}{\partial r_i} h^{(0)} - \frac{\partial}{\partial V_i} (a_{ij} V_j - \zeta V_i) h^{(1)} = J[h^{(1)}, f] , \tag{4.22}$$

where

$$\frac{\partial_0}{\partial t} n_1 + a_{ij} r_j \frac{\partial}{\partial r_i} n_1 = 0 , \tag{4.23a}$$

$$\frac{\partial_k}{\partial t} n_1 = -\nabla \cdot j^{(k-1)} , \qquad k \geqslant 1 , \tag{4.23b}$$

$$\frac{\partial_0 T}{\partial t} = (2\zeta + \lambda \nu_0) T , \tag{4.23c}$$

$$\frac{\partial_k T}{\partial t} = 0 , \qquad k \geqslant 1 . \tag{4.23d}$$

In these expressions, n_1 and $J^{(k)}$ are given by eqs. (3.6) and (3.7). The solution to eq. (4.21) is

$$h^{(0)}(r, V, t) = \frac{n_1(r, t)}{n} f(V, t) . \tag{4.24}$$

By substituting this expression into eq. (4.22) and using eqs. (4.23), it is found that

$$f V \cdot \nabla \frac{n_1}{n} + (2\zeta + \lambda \nu_0) T \frac{\partial}{\partial T} h^{(1)} - \frac{\partial}{\partial V_i} (a_{ij} V_j - \zeta V_i) h^{(1)} = J[h^{(1)}, f] . \tag{4.25}$$

From this equation, one obtains

$$\frac{P_{ik}}{m} \frac{\partial}{\partial r_k} \frac{n_1}{n} + (2\zeta + \lambda \nu_0) T \frac{\partial}{\partial T} j_i^{(1)} + a_{ik} j_k^{(1)} - \zeta j_i^{(1)} = -\alpha n j_i^{(1)} , \tag{4.26}$$

where eq. (3.13) has been used. Of course, eq. (4.26) reduces to eq. (3.15) in the limit $a^* \to 0$. Notice that the above equation becomes an algebraic equation if the thermostatic expression for the external force, eq. (4.19), is considered. On the other hand, no significant simplification occurs in the absence of external forces ($\zeta = 0$). The general solution to eq. (4.26) is

$$j_i^{(1)} = -\frac{k_B T}{m} \frac{1}{\alpha n + \zeta + \lambda \nu_0} \left[\left(\delta_{ik} - \frac{a_{ik}}{\alpha n + \zeta + \lambda \nu_0} \right) P_{kl}^* \frac{\partial}{\partial r_l} n_1 \right.$$
$$\left. + \left(\delta_{ik} - \frac{a_{ik}}{2\zeta + \lambda \nu_0} \ln T \right) C_k T^{-(\alpha n + \zeta + \lambda \nu_0)/(2\zeta + \lambda \nu_0)} \right] , \tag{4.27}$$

where $P_{ij}^* \equiv P_{ij}/p$ and C is a constant vector. The above expression becomes independent of the initial condition when the last term on the right-hand side can be neglected. To analyze whether this is the case, we use eq. (4.23c) to write

$$T^{-(\alpha n + \zeta + \lambda \nu_0)/(2\zeta + \lambda \nu_0)} \propto e^{-(\alpha n + \zeta + \lambda \nu_0)t} . \tag{4.28}$$

Therefore, a necessary condition for the system to reach a hydrodynamic regime is that $\zeta > -(\alpha n + \lambda \nu_0)$. Nevertheless, if we impose a more restricted condition, namely that the rate of decay of the initial condition must be larger than the rate of change of the temperature, we get $-(\alpha n + 2\lambda \nu_0)/3 < \zeta < \alpha n$. It is seen that both $\zeta = 0$ and $\zeta = \zeta_0$ lie inside the "true" hydrodynamic region.

When the initial condition term can be neglected, a generalized Fick law is found,

$$j_i^{(1)} = -D_{ik} \frac{\partial}{\partial r_k} n_1 , \tag{4.29}$$

with the self-diffusion tensor given by

$$D_{ik} = \frac{k_B T}{m} \frac{1}{\alpha n + \zeta + \lambda \nu_0} \left(\delta_{il} - \frac{a_{il}}{\alpha n + \zeta + \lambda \nu_0} \right) P_{lk}^* .$$ (4.30)

Eqs. (4.29) and (4.30) have been derived keeping the first order in the gradient of the concentration of tagged particles, but all the others in the shear rate are included. Also, no expansion in the strength of the external force has been carried out. The shear flow induces cross effects in the self-diffusion of particles. In particular, a gradient of the concentration along the direction of the flow of the system (x-axis) creates a transport of tagged particles parallel to the gradient of the flow velocity (y-axis). For $a = 0$, $D_{ij} = D\delta_{ij}$, with D given by eq. (3.18).

In fig. 1, we have plotted $D_{xx}^* - D_{yy}^*$ and $D_{ii}^*/3$ versus a^* in absence of an external force ($\zeta = 0$) and also for a thermostatic force ($\zeta = \zeta_0$). Here, $D_{ij}^* = (man/k_B T)D_{ij}$. The figure shows that the anisotropy of the system, as measured by the difference $D_{xx}^* - D_{yy}^*$, is quite important and grows very fast for small values of a^*. In fig. 2 the nondiagonal elements D_{xy}^* and D_{yx}^* are shown. Although they are different, their shape is quite similar. In all the cases, the presence of the thermostatic force strongly affects the self-diffusion tensor and there is not a simple relationship between the results with and without thermostatic. This is in contrast with the distribution function of the
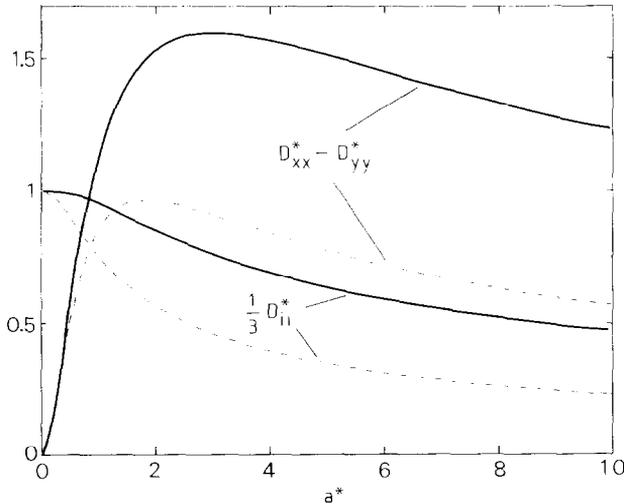

Fig. 1. Shear-rate dependence of the diagonal elements of the reduced self-diffusion tensor D_{ii}^*. The solid line corresponds to the case of a thermostatic force ($\zeta = \zeta_0$), while the dashed line corresponds to the case of no external force ($\zeta = 0$).
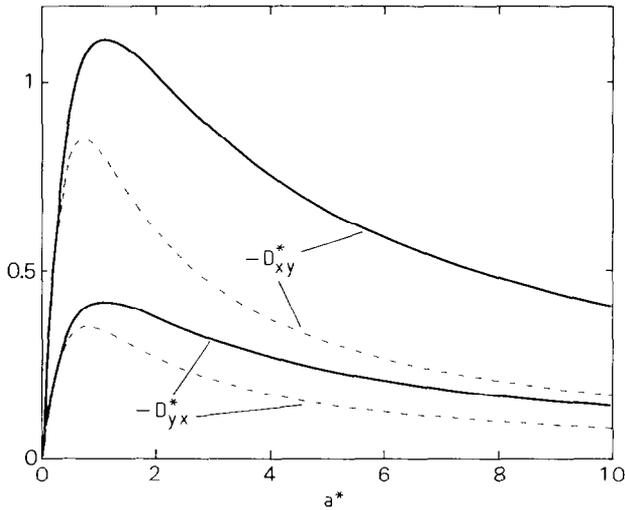
Fig. 2. The same as fig. 1, but for nondiagonal elements of D_{ij}^{*}.

whole system, for which the influence of the thermostatic force reduces to the simple time-dependent scaling defined by eqs. (4.9) and (4.10).

5. Discussion

In this paper we have studied the effect on self-diffusion in a dilute gas of a nonconservative external force proportional to the velocity. The problem involves two parts. First, the influence of the force on the distribution function of the whole system has to be determined. Then, the kinetic equation for the distribution function of tagged particles must be solved.

Two different physical situations have been addressed. In the first one, the nonconservative force was the only one acting on the system. It has been shown by means of an H-theorem that in this case the distribution function of the whole system reaches in the long time limit a Maxwellian form with a time-dependent temperature. Even more, for interaction potentials of the form $V(r) \sim r^{-\mu}$, there is a close relationship between the solutions of the Boltzmann equation with and without force. The self-diffusion coefficient has been obtained by using a Chapman–Enskog-like expansion. In order to carry out explicit calculations, we have restricted ourselves to Maxwell molecules. A hydrodynamic regime, independent of initial conditions, is reached when $\zeta > -\alpha n$, where ζ is a parameter characterizing the strength of the external force, eq. (2.3), and αn is a characteristic frequency of the collision operator,

eq. (3.14). In this regime a self-diffusion coefficient can be identified. The effect of a heating (cooling) external force is to decrease (increase) the self-diffusion coefficient of the system as compared with the equilibrium situation at the same temperature.

The other situation studied corresponds to a system under uniform shear flow. For the particular case of Maxwell molecules, the Boltzmann equation is known to have a solution, indpendent of the initial condition, describing the above state. Besides, the effect of an external force of the kind we are dealing with reduces to a time-dependent scaling of the velocities. Therefore, the distribution function of the whole system is well characterized, although it must be noticed that its explicit form is not known. Using again a Chapman–Enskog-like expansion around the uniform shear flow state, the flux of tagged particles to first order has been calculated. Now, the expression tends towards a hydrodynamic form for $\zeta > -(\alpha n + \lambda \nu_0)$, where ν_0 is a collision frequency given by eq. (4.18), and λ is a function of the reduced shear rate, eq. (4.16). The anisotropy of the system due to the shear flow gives rise to a self-diffusion tensor D_{ij}, which is a highly nonlinear function of the shear rate. We have analyzed the shear-rate dependence of D_{ij} for two choices of ζ, namely $\zeta = 0$, i.e., no external force, and $\zeta = \zeta_0(a^*)$, corresponding to a thermostatic force.

Marchetti and Dufty [6] have computed the velocity autocorrelation function in a system under uniform shear flow without external forces by using a Boltzmann description. They obtain, in our notation,

$$\langle V_i(t)V_j(\tau)\rangle = e^{-\alpha n(t-\tau)}[\delta_{ik} - a_{ik}(t-\tau)]\frac{P_{kj}(\tau)}{mn} \tag{5.1}$$

for $t > \tau$. This expression can be related to the self-diffusion tensor derived in this paper through [7] a generalized Green–Kubo formula,

$$D_{ij}(t) = \int_0^t d\tau\, \langle V_i(t)V_j(\tau)\rangle . \tag{5.2}$$

Substitution of eq. (5.1) into eq. (5.2) yields

$$D_{ij}(t) = -\frac{k_B T(t)}{m}\,\frac{1}{\alpha n + \lambda \nu_0}$$
$$\times \left\{\left(\delta_{ik} - \frac{a_{ik}}{\alpha n + \lambda \nu_0}\right)[1 - e^{-(\alpha n + \lambda \nu_0)t}] + a_{ik}t\, e^{-(\alpha n + \lambda \nu_0)t}\right\}P_{kj}^* . \tag{5.3}$$

Comparison of eqs. (5.3) and (4.30) shows that they agree for long times. Of course, one has to make $\zeta = 0$ in eq. (4.30) since no external forces are

considered in ref. [6]. On the other hand, their calculations can be easily extended for $\zeta = 0$, and one gets

$$\langle V_i(t)V_j(\tau) \rangle = e^{-(\alpha n - \zeta)(t-\tau)}[\delta_{ik} - a_{ik}(t-\tau)]\frac{P_{kj}(\tau)}{mn}\ . \tag{5.4}$$

When this expression is introduced into eq. (5.2) one recovers eq. (4.30). Taking into account that $P_{kj}(\tau) \sim e^{(2\zeta + \lambda \nu_0)\tau}$, it is easily seen that

$$\langle V_i(t)V_j(\tau) \rangle \sim e^{-(\alpha n + \zeta + \lambda \nu_0)(t-\tau)}\langle V_i(t)V_j(t) \rangle\ . \tag{5.5}$$

Therefore, the velocity autocorrelation as a function of the time difference $t - \tau$ only decays to zero when $\alpha n + \zeta + \lambda \nu_0 > 0$. This is precisely the condition we have found for the system to rech a hydrodynamic regime in the discussion of the Chapman–Enskog expansion. This provides a self-consistency test of our calculations.

Acknowledgement

Appendix

In this appendix we study the general solution to eq. (3.12) for Maxwell molecules. The point we are interested in is whether the solution reaches in time an asymptotic form that is independent of the initial conditions. This would be the hydrodynamic solution whose existence is assumed in the Chapman–Enskog procedure.

By using eq. (2.5), eq. (3.12) can be rewritten as

$$\frac{\partial h^{(1)}}{\partial t} + f_0 \boldsymbol{v} \cdot \boldsymbol{\nabla} \frac{n_1}{n} + \zeta \frac{\partial}{\partial \boldsymbol{v}} \cdot (\boldsymbol{v} h^{(1)}) = J[h^{(1)}, f_0]\ . \tag{A.1}$$

It is convenient to introduce the dimensionless velocity $\boldsymbol{\xi}$ by

$$\boldsymbol{\xi} \equiv (2k_B T/m)^{-1/2} \boldsymbol{v}\ , \tag{A.2}$$

and the reduced distribution $\phi(\boldsymbol{\xi}, t)$ by

$$h^{(1)}(\boldsymbol{v}, t) = \frac{m}{2k_B T(t)} \, \hat{f}_0(\boldsymbol{\xi}) |\boldsymbol{\nabla} n_1| \phi(\boldsymbol{\xi}, t) \,, \tag{A.3}$$

where

$$\hat{f}_0(\boldsymbol{\xi}) = \pi^{-3/2} e^{-\xi^2} \,. \tag{A.4}$$

From these equations, one easily gets

$$\frac{\partial}{\partial t} h^{(1)}(\boldsymbol{v}, t) = \frac{m}{2k_B T} |\boldsymbol{\nabla} n_1| \left\{ -2\zeta \hat{f}_0(\boldsymbol{\xi}) \phi(\boldsymbol{\xi}, t) - \zeta \boldsymbol{\xi} \cdot \frac{\partial}{\partial \boldsymbol{\xi}} [\hat{f}_0(\boldsymbol{\xi}) \phi(\boldsymbol{\xi}, t)] \right.$$
$$\left. + \hat{f}_0(\boldsymbol{\xi}) \frac{\partial}{\partial t} \phi(\boldsymbol{\xi}, t) \right\} \tag{A.5}$$

and

$$\frac{\partial}{\partial \boldsymbol{v}} h^{(1)}(\boldsymbol{v}, t) = \left(\frac{m}{2k_B T} \right)^{3/2} |\boldsymbol{\nabla} n_1| \frac{\partial}{\partial \boldsymbol{\xi}} [\hat{f}_0(\boldsymbol{\xi}) \phi(\boldsymbol{\xi}, t)] \,. \tag{A.6}$$

Also

$$J[h^{(1)}, f_0] = \frac{m}{2k_B T} |\boldsymbol{\nabla} n_1| n \hat{f}_0(\boldsymbol{\xi}) \left(\frac{8\kappa}{m} \right)^{1/2} I[\phi] \,, \tag{A.7}$$

where I is the linear operator [10]

$$I[\phi] = \int d\boldsymbol{\xi}_1 \int d\Omega \, F(\theta) \hat{f}_0(\boldsymbol{\xi}_1) [\phi(\boldsymbol{\xi}', t) - \phi(\boldsymbol{\xi}, t)] \,, \tag{A.8}$$

with

$$F(\theta) = \left(\frac{8\kappa}{m} \right)^{-1/2} g \sigma(g, \theta) \,. \tag{A.9}$$

Inserting eqs. (A.5)–(A.7) into eq. (A.1) one gets

$$\frac{\partial \phi}{\partial t} + \zeta \phi + \xi_z = \left(\frac{8\kappa}{m} \right)^{1/2} n I[\phi] \,. \tag{A.10}$$

Here, we have taken the z-axis along $\boldsymbol{\nabla} n_1$.

The general solution of this equation can be expressed in terms of the eigenfunctions of the operator I, i.e., the solutions to

$$I[\psi_{klm}] = -\lambda_{kl} \psi_{klm} \,. \tag{A.11}$$

They are given by [10]

$$\psi_{klm}(\boldsymbol{\xi}) = N_{kl}\xi^l L_k^{l+1/2}(\xi^2) Y_l^m(\boldsymbol{\xi}/|\boldsymbol{\xi}|) ,\qquad(A.12)$$

$$\lambda_{kl} = 2\pi \int\limits_0^\pi d\theta \sin\theta \ F(\theta)[1 - \cos^{2k+l}(\theta/2) P_l(\cos(\theta/2))] .\qquad(A.13)$$

In these expressions, N_{kl} is a normalization constant, $L_k^{l+1/2}$ is an associated Laguerre polynomial, $Y_l^m(\boldsymbol{\xi}/|\boldsymbol{\xi}|)$ is a spherical harmonic in the direction of $\boldsymbol{\xi}$, and P_l is a Legendre polynomial. Now we write

$$\phi(\boldsymbol{\xi}, t) = \sum_{k,l,m} C_{klm}(t)\psi_{klm}(\boldsymbol{\xi}) .\qquad(A.14)$$

Taking into account the orthonormalization property of the functions ψ_{klm}, eq. (A.14) leads to

$$C_{klm}(t) = \int d\boldsymbol{\xi} \ \hat{f}_0(\boldsymbol{\xi})\psi_{klm}^*(\boldsymbol{\xi})\phi(\boldsymbol{\xi}, t) .\qquad(A.15)$$

The coefficient C_{000} vanishes due to eq. (3.6). Substitution of the expansion (A.14) into eq. (A.10) yields

$$\frac{d}{dt} C_{klm} + \zeta C_{klm} + \frac{1}{\sqrt{2}} \delta_{k,0}\delta_{l,1}\delta_{m,0} = -\left(\frac{8\kappa}{m}\right)^{1/2} n\lambda_{kl}C_{klm} ,\qquad(A.16)$$

where use has been made of the fact that $\psi_{010}(\boldsymbol{\xi}) = \sqrt{2} \ \xi_z$. The solution to eq. (A.16) is

$$C_{klm}(t) = C_{klm}(0) \exp\left[-\left(\zeta + \sqrt{\frac{8\kappa}{m}} \ n\lambda_{kl}\right)t\right] ,\qquad(A.17)$$

for $(k, l, m) \neq (0, 1, 0)$, and

$$C_{010}(t) = C_{010}(0) \exp\left[-\left(\zeta + \sqrt{\frac{8\kappa}{m}} \ n\lambda_{01}\right)t\right]$$
$$- \frac{1}{\sqrt{2}} \frac{1}{\zeta + \sqrt{\dfrac{8\kappa}{m}} \ n\lambda_{01}} \left\{1 - \exp\left[-\left(\zeta + \sqrt{\frac{8\kappa}{m}} \ n\lambda_{01}\right)t\right]\right\} .\qquad(A.18)$$

It follows then that $\phi(\boldsymbol{\xi}, t)$ tends towards to an expression that is independent of the arbitrary initial conditions if

$$\zeta + \sqrt{\frac{8\kappa}{m}}\, n\lambda_{kl} > 0 \, , \tag{A.19}$$

for all $(k, l) \neq (0, 0)$. Taking into account the properties of the Legendre polynomials, it is easy to prove that all the eigenvalues λ_{kl} are positive [10] (except $\lambda_{00} = 0$). Also, the following inequalities hold:

$$\lambda_{k0} \leqslant \lambda_{k1} \leqslant \lambda_{kl} \, , \qquad l \geqslant 2 \, , \tag{A.20}$$

$$\lambda_{kl} \leqslant \lambda_{k+1,l} \, , \qquad\qquad l \leqslant 1 \, . \tag{A.21}$$

It must be noticed that these properties follow from eq. (A.13) with independence of the explicit expression of $F(\Theta)$. As a consequence, the smallest eigenvalues are

$$\lambda_{01} = \lambda_{10} = \sqrt{\frac{m}{8\kappa}}\, \alpha \, , \tag{A.22}$$

where α has been defined in eq. (3.14). Therefore, the condition for the existence of a hydrodynamic solution to eq. (A.10), or, equivalently, to eq. (A.1), is

$$\zeta + \alpha n > 0 \, . \tag{A.23}$$

This condition coincides with the one obtained in section 3 from the analysis of the flux of particles. Under this condition, the hydrodynamic first order distribution function for the tagged particles is

$$h^{(1)}(\boldsymbol{v}, t) = -f_0(\boldsymbol{v}, t)\, \frac{1}{\alpha n + \zeta}\, \boldsymbol{v} \cdot \boldsymbol{\nabla}\, \frac{n_1}{n} \, . \tag{A.24}$$

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