Approximate Solution of the Enskog Equation Far from Equilibrium

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A moment method is used to solve the Enskog equation for the steady-state distribution under conditions of uniform shear flow. Comparison to nonequilibrium molecular dynamics demonstrates that the lowest order solution gives a good quantitative description of nonlinear effects such as shear thinning and normal stresses in a moderately dense fluid. The results are used as a basis in the formulation of a simple and quantitatively accurate kinetic model of the Enskog equation. [S0031-9007(96)02012-1]

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The hard-sphere potential has been the most intensively studied interaction model in many areas of statistical mechanics for at least two reasons. The first reason is that hard-spheres exhibit many phenomena observed in real systems, such as the existence of liquid, solid, and metastable phases, and indeed provide a good first approximation for real systems of such properties as liquid structure, transport properties, and both liquid- and solid-phase thermodynamic properties. The second reason is that the hard-sphere interaction is the only one for which a tractable kinetic equation applicable at moderate densities, the Enskog equation [1–3], exists. The Enskog equation was originally proposed on physical grounds as a finite-density generalization of the Boltzmann equation which, although applicable to arbitrary two-body interaction models, is restricted to low densities. The generalization of the Enskog equation by van Beijeren and Ernst [4] is capable of giving a unified description of liquid, solid, and metastable states [5]. However, because of the complexity of the Enskog equation, the only analytic solutions available are perturbative and recently developed numerical techniques [6] have yet to be widely applied so that little is known about its description of systems far from equilibrium.

The standard method of analyzing either the Boltzmann or the Enskog equation is the Chapman-Enskog expansion [2,3] which is a perturbative expansion of the one-body distribution function, and the kinetic equation describing it, in terms of the uniformity of the system. For example, in a fluid undergoing uniform shear flow (USF), in which the local macroscopic flow velocity along the x axis varies linearly with position along the y axis, $\vec{u}(\vec{r}) = ay\hat{x}$, this amounts to an expansion in powers of the shear rate, a. This expansion has only been performed in the general case to third order in the uniformity parameter and the range of validity of such results is presumably limited to near-equilibrium states; the analytic complexity of the Chapman-Enskog procedure has proven prohibitive of the study of higher-order effects. An alternative method of analysis of the Boltzmann equation is the moment method of Grad [2,7,8] according to which the distribution is expressed as an expansion in terms of velocity about local equilibrium. Keeping all terms in the expansion gives an infinite set of coupled equations for the generally space- and time-dependent coefficients which, assuming the validity of the expansion, is equivalent to the Boltzmann equation. Approximations are then introduced to truncate or decouple the equations allowing for an approximate solution. The method has found particular use in the study of small-wavelength hydrodynamics near equilibrium [9] where the close connection between the moment method and kinetic models has been exploited. The purpose of this Letter is to show that the method may be used to obtain good approximate solutions to the Enskog equation for systems far from equilibrium. In the following, attention is focused on USF since sheared fluids may be reliably simulated and the connection between theory and simulation is well understood. Indeed, for these reasons, USF has been the subject of numerous investigations over the last 20 years (see, e.g., Ref. [10]), and is often viewed as a prototypical nonequilibrium state free from complicating features such as boundary effects. In addition, it has been known for some time that the hard-sphere system is unstable at high shear rates [11] and theories of the instability depend on knowledge of the one-body distribution [12,13]. Since only perturbative results, which lack important physical effects such as shear thinning, have been available, these theories remain tentative. One of the motivations for the present work has been to allow for a more detailed study of this problem.

Both the Boltzmann and Enskog equations may be written in the form

$$\frac{\partial}{\partial t} f + \vec{v} \cdot \frac{\partial}{\partial \vec{q}} f + \frac{\partial}{\partial \vec{v}} \cdot \vec{F}_{\text{ext}} f = J[f, f], \qquad (1)$$

where $f(\vec{q}, \vec{v}, t)$ is the one-body reduced distribution function depending in general on position, velocity, and time, respectively. We include in the last term on the left an external force since this is used in most simulations of shear flow in order to counteract the effects of viscous heating to maintain a constant temperature thus establishing a steady (time-independent) state. The explicit form of the collision operator on the right is given in the literature [2,3] and here we note only that it is a bilinear function of the distribution. The most important difference between the Boltzmann and Enskog collisional terms is that the latter is nonlocal. The moment expansion

of these equations is generated by first expanding the distribution in terms of a complete set of polynomials of the velocity

$$f(\vec{q},\vec{v},t) = \rho(\vec{q};t)\phi(\vec{q},\vec{c};t) \times \left\{1 + \sum_{n=1} \frac{1}{n!} A_{[n]}(\vec{q},t) H_{[n]}(\vec{c};t)\right\}, \quad (2)$$

where $\vec{q}$ is position, the excess velocity reduced by the temperature is $\vec{c} = \frac{1}{\sqrt{k_B T(\vec{q},t)}}[\vec{v} - u(\vec{q},t)]$, ρ is the local density, ϕ is the local-equilibrium velocity distribution and $\{H_{[n]}(\vec{p})\}$ is a complete set of polynomials in the components of $\vec{p}$. The equation is written using a short notation for indices whereby $A_{[n]} \equiv A_{i_1 \cdots i_n}$. The coefficients of the expansion can depend explicitly on time whereas the local equilibrium distribution and the reduced velocity can be time dependent only implicitly through the time dependence of the temperature and velocity fields. The nth moment equation for the coefficients is obtained by substituting the expansion into Eq. (1), multiplying by $H_{[n]}$, and integrating over velocity. The equations for the density, temperature, and velocity fields are a subset of the moment equations. The choice of polynomials is arbitrary at this point and particular choices are relevant only in so far as the set of equations is truncated. I will work with the three-dimensional Hermite polynomials used by Grad [8] since it simplifies the calculations somewhat; kinetic models often use a set based on the spherical harmonics [9]. The Hermite polynomials are orthonormal and the first few are $H_{[0]} = 1$, $H_i = p_i$, and $H_{ij} = p_i p_j - \delta_{ij}$. The orthornormality implies that $\langle H_{[n]}(\vec{c})\rangle = A_{[n]}$, where the brackets indicate a velocity average over the nonequilibrium distribution. In particular, we have that $A_{[0]} = \langle 1\rangle = \rho(\vec{q};t)$, $A_i = \langle c_i\rangle = 0$, and $A_{ij} = \langle c_i c_j - \delta_{ij}\rangle = P^K_{ij}(\vec{q};t) - \delta_{ij}$, where P^K_{ij} is the kinetic part of the stress tensor. Note that the definition of the temperature as the average kinetic energy implies that the second-order coefficient be traceless.

To solve this system of equations, it is necessary to introduce some approximation to the collisional term which in general couples all moments into each equation in the hierarchy. The general form of the collisional term in the nth moment equation is

$$B_{[n][l][m]}A_{[l]}A_{[m]} \equiv \int d\vec{v}\, H_{[n]} J[\phi H_{[l]}, \phi H_{[m]}]A_{[l]}A_{[m]}, \quad (3)$$

where a summation over l, m is implied. For the Boltzmann equation, Grad proposed that a reasonable approximation is to include only collisional terms for which $l + m = n$. This is based on the fact that for atoms interacting via an inverse fourth power potential (Maxwell molecules) all other contributions are exactly zero [8]. In fact, for this reason, the Boltzmann equation can be exactly solved for Maxwell molecules undergoing USF [14]. One reason for expecting this to be a good approximation for other potentials is that a similar truncation in the case of the Chapman-Enskog expansion (the truncation of the Sonine expansion) is known to be quite accurate [3] and is also exact for Maxwell molecules. Although this latter point remains true for the Enskog equation, it is not possible to adopt Grad's approximation unchanged. The reason is that some of the couplings for which $l + m < n$ are unique to the Enskog equation, arising from the nonlocal nature of the collision operator. Thus, for example, the terms $l = m = 0$ are identically zero for the Boltzmann equation because the local-equilibrium distribution is a null eigenvector of the operator whereas for the Enskog operator, this is not true and these terms give an important contribution to the transport coefficients. The simplest way to take this into account then is to write $J[f,f] = J[\phi,\phi] + J'[f,f]$ with $J'[f,f] = J[f,f] - J[\phi,\phi]$ and to apply Grad's approximation to the operator J'.

To apply this method to steady-state shear flow, it is necessary to take account of the external force, or thermostat, used in computer simulations. Many choices for this force are possible but we will work with the simplest $\vec{F}_{\rm ext} = \gamma\vec{c}$, which corresponds to the velocity-rescaling thermostat commonly used. The first nontrivial moment equation then becomes

$$2a(\delta_{x(i}\delta_{j)y} + \delta_{x(i}A_{j)y}) + 2\gamma(\delta_{ij} + A_{ij}) = \rho\chi \int d\vec{v}\, H_{ij}(\vec{c}) J[\phi,\phi] + C_{ij,lm}A_{lm}, \quad (4)$$

where the braced indices indicate symmetrization with, e.g., $\delta_{x(i}\delta_{j)y} = \frac{1}{2}(\delta_{xi}\delta_{jy} + \delta_{xj}\delta_{iy})$ and $C_{[n][m]} \equiv B_{[n][m][0]} + B_{[n][0][m]}$ and χ is the pair distribution function at contact (for which I use the Percus-Yevick approximation to the virial equation of state [15]). The thermostat constant is fixed by taking the trace of this equation and using the tracelessness of the second-order coefficient. This induces a nonlinearity in the equations which must be solved numerically. In the present case, all numerical integrals were performed to a relative accuracy of one part in 10^4 and solution of the moment equations by iteration to one part in 10^3.

To test this approximation, I have performed molecular dynamics simulations of a sheared system of 108 hard spheres using Lees-Edwards [16] boundary conditions and the velocity-rescaling thermostat [17]. The density was chosen to be high enough, $\rho\sigma^3 = 0.5$, that the finite density effects are significant but not so high as to invalidate the Enskog approximation. Figure 1 shows the kinetic contributions to the two viscoelastic functions $a^2\psi_1 = (P_{xx} - P_{yy})$ and $a^2\psi_2 = (P_{yy} - P_{xx})$ as a function of shear rate and compared to the results of the second-moment calculations. The agreement is reasonable over the entire range of shear rates. In

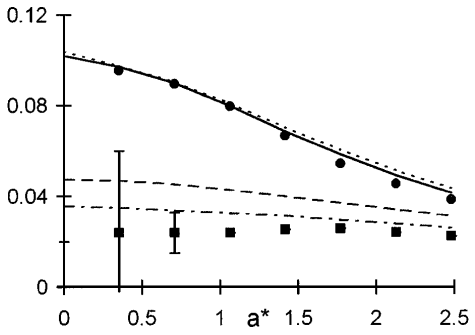

FIG. 1. The kinetic part of ψ_1 (ψ_2) as a function of reduced shear rate. The circles (squares) are the simulation results, the full (dashed) line is the result of the moment solution, and the dotted (dot-dashed) line is the result of the kinetic model, Eq. (6).

particular, while ψ_1 is relatively independent of the shear rate, ψ_2 shows strongly nonlinear behavior which is accurately modeled. Figure 2 shows the kinetic part of the shear viscosity, η, defined by $a\eta = P_{xy}$. This again shows strongly nonlinear behavior and is again well modeled by the calculations. These results verify the accuracy of the second moments since, as indicated above, the measured functions constitute a direct measurement of these coefficients. The collisional contributions to the pressure tensor are not as accurately modeled as are the kinetic contributions due to the fact that they depend in general on all moments of the distribution. They are nevertheless quite reasonable, the deviations from the simulation values being on the order of 20% at the highest shear rates. A detailed comparison of these quantities will be presented at a later date.

In general, it is analytically difficult to calculate the couplings in the moment equations for the higher-order moments even in the case of the Boltzmann equation. An obvious approximation is to replace these by a simple approximation of the form $B_{[n][l][m]} \sim -\nu(\delta_{l0}\delta_{[n][m]} + \delta_{m0}\delta_{[n][l]})$ for $n > n_c$, where n_c is some cutoff. This is known as the Jackson-Gross extension of the BGK model (see, e.g., Ref. [9]); the BGK model itself consists of taking $n_c = 0$ so that the approximation becomes $J[f,f] \sim -\nu(f - \rho\phi)$. Because the BGK model preserves many of the most important properties of the Boltzmann equation, there has been considerable interest in its analysis and a BGK-type model of the Enskog equation, which we refer to as the DSB model, has recently been proposed [18]. The difficulty of formulating such a model lies in capturing the effects of the nonlocality of the collision operator. Most importantly, the local equilibrium distribution is not a null eigenvector of the Enskog operator as it is of the Boltzmann operator so the simple BGK approximation is obviously inappropriate. The idea behind the DSB model is, in our language, to first separate the Enskog collision operator into two parts as $J[f,f] = J^{(B)}[f,f] + (J[f,f] - J^{(B)}[f,f])$, where $J^{(B)}[f,f]$ is the Boltzmann operator, and to approximate the first term as in the BGK model and the second term by its projection onto the conserved variables as

$$(J[f,f] - J^{(B)}[f,f]) \sim H_i(\vec{c})B_{i[l][m]}A_{[l]}A_{[m]} + \tfrac{1}{3}H_{rr}(\vec{c})B_{ss[l][m]}A_{[l]}A_{[m]}. \quad (5)$$

The motivation for this approximation is to keep only those projections of the collision operator that contribute to the pressure tensor and heat-flux vector in the hydrodynamic equations thus including the collisional contributions to those quantities [note that $H_i(\vec{c})$ is just the velocity while $H_{rr}(\vec{c})$ is proportional to the energy]. Note that the coefficients $B_{[n][l][m]}$ occurring in this equation are the same as defined in Eq. (3) since the projection of the Boltzmann operator onto the conserved densities is identically zero. It has been shown to give a good qualitative description of shear-thinning and viscoelastic effects in USF. However, despite its qualitative success, the model does not give the collisional contributions to the distribution function so that, e.g., the kinetic parts of the transport coefficients do not contain any collisional contributions. Furthermore, because of the coupling of the velocity and energy to the full, infinite, set of moments, the model cannot, unlike the BGK model, be explicitly solved even in the case of USF. The first problem is due to the fact that the local equilibrium collisional contributions are being treated too crudely and is easily remedied by separating out the term $J[\phi,\phi]$ explicitly. As to the complexity of the model, our results indicate that it is sufficient to retain only the lowest order contributions in the projection of the collision operator. This leads us to the approximation

$$J[f,f] \sim J[\phi,\phi] - \nu(f - \phi) + H_i(\vec{c})C'_{i,lm}A_{lm} + \tfrac{1}{3}H_{rr}(\vec{c})\,(C'_{ss,lm}A_{lm} + C'_{ss,lm}A_{lmr}), \quad (6)$$

with $C'_{[l][m]} \equiv C_{[l][m]} - C_{[l][0]}$. We have chosen, for simplicity, to include only those terms that give the lowest-order contributions to the pressure and heat flux. The leading, local-equilibrium, term gives rise to the collisional contributions to the kinetic parts of the transport

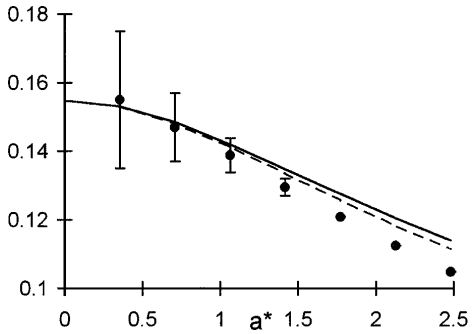

FIG. 2. The kinetic part of the shear viscosity as a function of reduced shear rate. The circles are the simulation results, the full line is the result of the moment solution, and the dashed line is the result of the kinetic model, Eq. (6).

coefficients. It could also be replaced by a projection onto a finite number of moments although this would mean losing all explicit collisional contributions to the higher-order moments. Finally, we note that only the coefficient A_{lrr} contributes directly to the heat flux so that the last term might be further simplified.

In the BGK model of the Boltzmann equation, the choice $\nu = \frac{16\sqrt{\pi}\rho}{5}$ results in the model giving a very good quantitative approximation to the viscosity (within 2% of the exact result from the Boltzmann equation). The equivalent choice for the Enskog equation, $\nu = \frac{16\sqrt{\pi}\rho\chi}{5}$, where χ is the pair-distribution function at contact, gives an equivalently accurate approximation to the Enskog viscosity. Furthermore, the model is, like the BGK model, exactly solvable for USF. The results for the kinetic parts of the normal stresses and the shear viscosity, with the suggested choice of ν, are also shown in Figs. 1 and 2 where it is seen that they are in excellent agreement with the moment solution as well as with the simulations. This serves to justify the fundamental ideas behind the DSB approach to modeling the Enskog equation. However, the utility of such models obviously lies in the analysis of more complex problems for which good approximate solutions to the Enskog equation, as presented here for USF, do not exist.

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