Journal of Statistical Physics, Vol. 44, Nos. 1/2, 1986

Shear Flow in the Two-Body Boltzmann Gas. II. Small and Large γ Expansion of the Shear Viscosity

Gary P. Morriss,[1] Dennis J. Isbister,[2] and Barry D. Hughes[3]

Received October 30, 1985; final February 25, 1986

In two and three dimensions, the relaxation time Boltzmann equation can be solved analytically for the distribution function for a system of two hard particles subject to isothermal shear. The previous solutions of Morriss, and Ladd and Hoover are shown to be formally equivalent. The integral representation for the average of each of the elements of the pressure tensor in the steady state is obtained for both sllod and dolls tensor equations of motion. Rigorous equations are derived which relate the viscosity and the normal stress differences in these two methods. We obtain asymptotic expansions for each element of the pressure tensor for both small and large γ. For high shear rates, the viscosity is found to vanish as $\gamma^{-2} \log \gamma$ in both two and three dimensions.

KEY WORDS: Boltzmann equation; nonequilibrium; viscosity; molecular dynamics.

1. INTRODUCTION

There are two general approaches to the calculation of transport coefficients. A transport coefficient **L**, such as the shear viscosity is defined by a linear constitutive relation of the form **J** = **LX** where **J** is the thermodynamic flux and **X** is the thermodynamic force. In the shear viscosity example, **J** is the shear stress $-P_{xy}$ and **X** is the strain rate γ. The first

[1] Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia.

[2] Department of Chemistry, University of New South Wales, RMC, Duntroon, Canberra, A.C.T. 2600, Australia.

[3] Department of Mathematics, University of New South Wales, RMC, Duntroon, Canberra, A.C.T. 2600, Australia.

0022-4715/86/0700-0107$05.00/0 © 1986 Plenum Publishing Corporation

approach to calculating **L** is to construct (either physically, or theoretically or computationally) a nonequilibrium steady state by applying a fixed strain rate γ and then measuring or calculating the response P_{xy}.[1] The shear viscosity is given by $-P_{xy}/\gamma$, in the limit as $\gamma \to 0$.

The second approach to calculating the shear viscosity is to observe the autocorrelation function of the thermodynamic flux **J**, that is $\langle \mathbf{J}(0)\,\mathbf{J}(t) \rangle$, in an equilibrium system. The Green–Kubo formulas state that the shear viscosity is related to the infinite time integral of this autocorrelation function.[2] Both of these methods are valid, except in the special cases (such as the Green–Kubo in two dimensions[3]), and the arguments for and against the two approaches are generally based on computational and statistical considerations.

It is clear, however, that the only approach to the study of truly nonequilibrium systems is to observe directly a system under an applied external field. With this approach it is possible to consider an ensemble of equilibrium systems, then apply the same external field to each, and watch the approach of the ensemble to a steady state. In this way we can define a *time*-dependent ensemble average that is equal to the equilibrium average at $t < 0$ and becomes the steady state ensemble average as $t \to \infty$. For all $t > 0$ this ensemble average is well defined, and describes the approach of macroscopic variables to their steady state values.

The initial problem with the study of steady states is that the work done on the system by the applied field is converted into heat, which must be extracted by some thermostatting mechanism. The theoretical understanding of various thermostatting mechanisms, such as the Gaussian isokinetic equations of motion[4,5] is well advanced.[6] However, the thermostatting "force" is in general a many-body force and is not easily incorporated in the usual kinetic theory approaches.[7] For this reason recent investigations[8–11] have considered the dynamics of very small systems whose equations of motion contain both applied field terms and thermostatting terms. Such studies have proved very useful as the results of two particle shearing systems[8–9] for example, display large system effects such as shear thinning and normal stress differences. More importantly, it is possible to obtain analytic results for such systems using the relaxation time approximation to the Boltzmann equation.

There are three current methods of simulating shear flow in molecular dynamics simulations; boundary driven,[12] dolls tensor,[13] and the sllod algorithm.[14,15] The boundary driven method uses Newtonian equations of motion and contains no explicit applied field terms. Both dolls tensor and the sllod algorithm contain explicit applied fields terms and can be thermostatted using Gaussian isokinetic equations. The equations of motion for the two methods are as follows:

dolls tensor

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{p}_i/m + \mathbf{n}_x \gamma y_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{n}_y \gamma p_{xi} - \alpha \mathbf{p}_i \end{aligned} \tag{1}$$

sllod algorithm

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{p}_i/m + \mathbf{n}_x \gamma y_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{n}_x \gamma p_{yi} - \alpha \mathbf{p}_i \end{aligned} \tag{2}$$

In both cases the Gaussian multiplier α, given by

$$\alpha = \left(\sum_{i=1}^{N} \mathbf{F}_i \cdot \mathbf{p}_i - \gamma p_{xi} p_{yi} \right) \Big/ \sum_{i=1}^{N} p_i^2 \tag{3}$$

is chosen so that the temperature T, defined by

$$k_B T d(N-1)/2 = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 \tag{4}$$

is a constant of the motion. Here d is the dimensionality of the system, N is the number of particles, and k_B is Boltzman's constant. The factor of $N-1$ is used rather than N, to remove the irrelevant contribution to the temperature from the supposed motion of the center of mass of the system. The quantity of interest is the pressure tensor $\mathbf{P}$, defined by

$$\mathbf{P} V = \sum_i (\mathbf{p}_i \mathbf{p}_i/m + \mathbf{r}_i \mathbf{F}_i) \tag{5}$$

In what follows we will restrict ourselves to the kinetic contributions to $\mathbf{P}$, namely, $\mathbf{P}^k$ which we define to be

$$\mathbf{P}^k V = \sum_i \mathbf{p}_i \mathbf{p}_i/m \tag{6}$$

The boundary driven method is simply the incorporation of the linear velocity profile in the periodic boundary conditions and is clearly exact. It has been shown[14] that the sllod algorithm is also exact to all orders in the strain rate γ, and that dolls tensor to second order in γ gives the correct values of $Tr(\mathbf{P})$, P_{xy}, and P_{zz}, but incorrect values of P_{xx} and P_{yy}. In this work we show that for the relaxation time approximation to the Boltzmann equation, the kinetic contribution to the shear stress P_{xy}^k in the dolls tensor method is identical to P_{xy}^k in the sllod. Dolls tensor reverses

P^k_{xx} and P^k_{yy} so that the kinetic contribution to the normal stress difference $\psi^k_1 = \langle P^k_{yy} - P^k_{xx} \rangle / \gamma^2$ changes sign to all orders in the strain rate.

Several recent investigations have considered the dynamics of a very small system of two hard particles subjected to a shearing force under isothermal conditions. Ladd and Hoover[8] supplemented a simulation study of the steady state for a Lorentz gas in two dimensions with a numerical solution of the Boltzmann equation. The form of the Boltzmann equation used in this study, they termed the *relaxation-time Boltzmann equation*, as the usual collision term was replaced by $(f_0 - f)/\tau$ where f_0 is the local equilibrium distribution function and τ is a relaxation time. This form of the Boltzmann equation is closely related to the Krook–Bhatnager–Gross equation.[17] The derivation of this equation[18] suggests that its validity will be restricted to systems near equilibrium. However, an equally valid approach is merely to state this kinetic equation and note that for a constant τ, it is consistent with the conservation equations of hydrodynamics. This is the approach that we shall adopt here, and the validity of the approximation will be assessed by direct comparison with computer simulations. The inherent weakness of this phenomenological equation is that the results depend on the value of τ. Near equilibrium, at low density, it is possible to estimate τ from the average collision time, but far from equilibrium this is no longer the case.

A subsequent study by Morriss[9] obtained an analytic solution of the Boltzmann equation for both the time dependent and steady state cases in two dimensions. From the steady state solution in two dimensions the large shear rate behavior of the pressure tensor was calculated. In particular, the steady state shear stress was shown to approach zero in a nonexponential decay for large shear rates, in contrast to earlier expectations.[8] The similarity of the form of the solutions in two- and three-dimensions suggests that the same nonexponential decay may be found in the three-dimensional case as well. Hoover[10] has considered a two particle system under isokinetic and isoenergetic color diffusion. Hoover and Kratky[11] have also considered three particle heat conduction problems. The present paper examines the time dependent and steady state solutions of the Boltzmann equation within the relaxation time approximation for both two and three dimensions for the sllod algorithm and dolls tensor. From the analytic solutions for the distribution function which are presented, we obtain an integral representation for each of the elements of the pressure tensor. Using Mellin transform techniques we obtain the behavior of the pressure tensor in both the small $\gamma\tau$ and large $\gamma\tau$ limits. It is found that the viscosity decays nonexponentially toward zero for large strain rates.

2. THE TWO-BODY BOLTZMANN GAS IN TWO-DIMENSIONS

2.1. Sllod algorithm

Consider a system of two hard disks in periodic boundary conditions whose equations of motion are given by the two-dimensional analog of the sllod equations (that is equation (2)). Define $\mathbf{p} = \mathbf{p}_1 = -\mathbf{p}_2 = p(\cos\theta, \sin\theta)$. The isokinetic constraint ensures that p is a constant of the motion, and it can be shown that the equation of motion for θ between collisions is

$$\dot{\theta}(t) = \gamma \sin^2 \theta(t) \tag{7}$$

thus the trajectory for θ between collisions is given by

$$\cot \theta(t) = -\gamma(t - t_0) + \cot \theta(t_0) \tag{8}$$

The two-dimensional relaxation time Boltzmann equation for the distribution function is

$$\begin{aligned} \frac{\partial f}{\partial t} + \frac{\partial}{\partial \theta}(\dot{\theta} f) &= \left(\frac{\partial f}{\partial t}\right)_{\text{collisions}} \\ &\cong -(f - f_0)/\tau \end{aligned} \tag{9}$$

where f_0 is the equilibrium distribution function, $f_0 = (2\pi)^{-1}$. This equation can be solved[9] to obtain both the steady state distribution function

$$f_{ss}(\theta) = \frac{f_0 \operatorname{cosec}^2 \theta}{\gamma\tau} \int_0^\theta d\psi \exp\left(\frac{\cot\theta - \cot\psi}{\gamma\tau}\right) \tag{10}$$

and the time dependent distribution function

$$\begin{aligned} f(\theta, t) = f_0 \Bigg[&\left(\frac{1 + \cot^2\theta}{1 + (\gamma t + \cot\theta)^2}\right) e^{-t/\tau} \\ &+ \int_0^t \frac{ds}{\tau} \left(\frac{1 + \cot^2\theta}{1 + (\gamma_s + \cot\theta)^2}\right) e^{-s/\tau} \Bigg] \end{aligned} \tag{11}$$

where θ in the time dependent solution is θ at time t.

The phase variable corresponding to the pressure tensor is

$$\beta V \mathbf{P}^k(\theta) = 2 \begin{pmatrix} \cos^2\theta & \cos\theta \sin\theta \\ \cos\theta \sin\theta & \sin^2\theta \end{pmatrix} \tag{12}$$

so the average value of the pressure tensor at an arbitrary time is given by

$$\langle \mathbf{P}^k(t) \rangle = \int_0^{2\pi} d\theta\, f(\theta, t)\, \mathbf{P}^k(\theta) \tag{13}$$

In Reference 9 the analytic integral representations for each of the elements of the pressure tensor in the steady state ($t \to \infty$) were obtained. The expansion of the shear stress for small $\gamma\tau$ is

$$-\beta V \langle P_{xy}^k \rangle_{ss} = -\sum_{n=0}^{\infty} (-)^n (\gamma\tau/2)^{2n+1} (2n+1)! \tag{14}$$

which leads to the following small $\gamma\tau$ expansion for the viscosity

$$\begin{aligned} \eta/\eta_0 &= \sum_{n=0}^{\infty} (-)^n (\gamma\tau/2)^{2n} (2n+1)! \\ &= 1 - \frac{3}{2}(\gamma\tau)^2 + \frac{15}{2}(\gamma\tau)^4 - \frac{315}{4}(\gamma\tau)^6 + \cdots \end{aligned} \tag{15}$$

It is easily seen that as the first coefficient is negative, the fluid is shear thinning. Clearly this expansion is asymptotic, however, it is interesting to compare the coefficient of the term of order $(\gamma\tau)^2$ with the same coefficient in eq. (10) of Ladd and Hoover.[8] In two dimensions the collision operator is anisotropic, so Ladd and Hoover use a first-order perturbation term rather than the relaxation time approximation. This gives the coefficient of $(\gamma\tau)^2$ to be -1 rather than $-3/2$. It might seem from this comparison that the relaxation time approximation is grossly in error at small values of $\gamma\tau$, but this does not appear to be the case. In the Table below we compare the values of η/η_0 obtained from the integral representation (Eq. (16) of Ref. 9) with those of Ladd and Hoover (Table III of Ref. 8).

$\gamma\tau$	$\eta/\eta_0{}^{(8)}$	$\eta/\eta_0{}^{(9)}$
0.017	0.9996	0.9996
0.177	0.9630	0.9587
0.354	0.8837	0.8716
0.884	0.6450	0.6023
1.77	0.4069	0.3820
3.54	0.2096	0.1931

We find that the two different collisional approximations agree remarkably over a wide range of values of $\gamma\tau$.

The small $\gamma\tau$ expansion of the normal stress difference in the steady state $\psi_1^k = \langle P_{yy}^k - P_{xx}^k \rangle / \gamma^2$, can also be obtained by expanding the integral representation (Eq. (18) in Ref. 9). This gives

$$\beta V \psi_1^k = \tau^2/2 \sum_{n=0}^{\infty} (-)^{n+1} (\gamma\tau/2)^{2n} (2n+2)! \tag{16}$$

The $(\gamma\tau) \to \infty$ form for both η/η_0 and $\beta V \psi_1^k$ have been obtained[9] and the results are

$$\begin{aligned} \eta/\eta_0 &= 4/(\gamma\tau)^2 (\ln(\gamma\tau) - C - \ln 2) \\ \beta V \psi_1^k &= -2/\gamma^2 (1 - \pi/(\gamma\tau) + (2/(\gamma\tau))^2 \ln(\gamma\tau)) \end{aligned} \tag{17}$$

2.2. Dolls Tensor

Consider the same two disk system used previously, with in this case the dolls tensor equations of motion. If we define $\mathbf{p} = \mathbf{p}_1 = -\mathbf{p}_2 = p(\sin\theta, \cos\theta)$ then the equation of motion for θ is

$$\dot{\theta}(t) = \gamma \sin^2 \theta(t) \tag{18}$$

This is exactly the same equation of motion for θ as that obtained for the sllod algorithm and leads to precisely the same Boltzmann equation. Clearly both the steady state and the time dependent distribution functions are the same as those obtained for sllod. However, as the definition of θ is different in this case, the phase variable associated with the pressure tensor changes, so that

$$\beta V \mathbf{P}^k(\theta)^{\text{dolls}} = 2 \begin{pmatrix} \sin^2\theta & \cos\theta \sin\theta \\ \cos\theta \sin\theta & \cos^2\theta \end{pmatrix} \tag{19}$$

From Eqs. (12) and (19), we see immediately that this implies the following relations between components of the pressure tensor obtained using the two methods

$$\langle P_{xy}^k \rangle^{\text{dolls}} = \langle P_{xy}^k \rangle^{\text{sllod}} \tag{20}$$

$$\langle P_{xx}^k \rangle^{\text{dolls}} = \langle P_{yy}^k \rangle^{\text{sllod}} \tag{21}$$

$$\langle P_{yy}^k \rangle^{\text{dolls}} = \langle P_{xx}^k \rangle^{\text{sllod}} \tag{22}$$

The shear viscosity obtained with either sllod or dolls is the same to all orders in the strain rate and the normal stress difference ψ_1^k changes sign. The magnitude of ψ_1^k is the same from each method. In this section we have seen that the shear viscosity and the normal stress difference, for the relaxation time approximation in two dimensions, are analytic functions of the field.

3. THE SLLOD ALGORITHM IN THREE-DIMENSIONS

In this section we consider the same two particle system as that in Section 2, in three dimensions. We introduce the nonstandard spherical coordinates (p, θ, ϕ) defined by

$$\begin{aligned} p_x &= p \cos\theta \\ p_y &= p \sin\theta \cos\phi \\ p_z &= p \sin\theta \sin\phi \end{aligned} \tag{23}$$

(note that the roles of θ and ϕ are reversed in Ref. 8). This gives

$$\alpha = -\gamma \cos\theta \sin\theta \cos\phi \tag{24}$$

Furthermore, this particular choice of the spherical coordinates has p and ϕ as constants of the motion, so that we need only consider the equation of motion for θ

$$\dot{\theta}(t) = \gamma \cos\phi(t) \sin^2\theta(t) \tag{25}$$

Integrating this equation, the trajectory for θ between collisions is

$$\cot\theta(t) = -\gamma(t - t_0)\cos\phi + \cot\theta(t_0) \tag{26}$$

The relaxation-time Boltzmann equation in three dimensions is

$$\frac{\partial f}{\partial t} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\dot{\theta}\sin\theta f) + \frac{\partial}{\partial\phi}(\dot{\phi} f) + \frac{\partial}{\partial p}(\dot{p} f) \cong -(f - f_0)/\tau \tag{27}$$

where $f_0 = (4\pi)^{-1}$. From Eq. (25) for $\dot{\theta}$, Eq. (27) becomes

$$\frac{\partial f}{\partial t} + \gamma \sin^2\theta \cos\phi \frac{\partial f}{\partial\theta} + 3\gamma \sin\theta \cos\theta \cos\phi f = (f_0 - f)/\tau \tag{28}$$

3.1. Steady State Solution

In the steady state f has no explicit time dependence, so Eq. (28) becomes

$$\frac{df(\theta)}{d\theta} + \left(3\cot\theta + \frac{\operatorname{cosec}^2\theta}{\gamma\tau\cos\phi}\right) f(\theta) = \frac{\operatorname{cosec}^2\theta}{\gamma\tau\cos\phi} f_0 \tag{29}$$

After careful but straightforward analysis the steady state solution is found to be

$$f_{ss}(\theta,\phi)=\frac{\operatorname{cosec}^3\theta}{4\pi\gamma\tau\cos\phi}\int_0^\theta d\psi\,\sin\psi\,\exp\left(\frac{\cot\theta-\cot\psi}{\gamma\tau\cos\phi}\right)\quad\text{if }\frac{-\pi}{2}<\phi<\frac{\pi}{2}$$
$$=\frac{-\operatorname{cosec}^3\theta}{4\pi\gamma\tau\cos\phi}\int_\theta^\pi d\psi\,\sin\psi\,\exp\left(\frac{\cot\theta-\cot\psi}{\gamma\tau\cos\phi}\right)\quad\text{if }\frac{\pi}{2}<\phi<\frac{3\pi}{2}\tag{30}$$

In Eq. (30), the two domains of definition for ϕ values are precisely those over which $\cos\phi$ is positive and negative, respectively. Ladd and Hoover[8] have also obtained a steady state solution using operational techniques. In Appendix A we show that the two solutions are equivalent.

3.2. The Time-Dependent Solution

To understand the approach to the steady state detailed above, we require the time-dependent solution of Eq. (28). A simple replacement of $\partial f/\partial t$ by the total derivative df/dt using

$$\frac{df}{dt}=\frac{\partial f}{\partial t}+\dot\theta\frac{\partial f}{\partial\theta}+\dot\phi\frac{\partial f}{\partial\phi}\tag{31}$$

allows Eq. (28) to be transformed into a first-order ordinary differential equation. Inserting the equation of motion (25) for $\dot\theta$, Eq. (28) becomes

$$\frac{df}{dt}+(3\gamma\cos\phi\sin\theta\cos\theta+\tau^{-1})f=\tau^{-1}f_0\tag{32}$$

which can be solved to give the time-dependent distribution function

$$f(\theta,\phi,t)=f_0\left[\left(\frac{1+\cot^2\theta}{1+(\gamma t\cos\phi+\cot\theta)^2}\right)^{3/2}e^{-t/\tau}\right.$$
$$\left.+\int_0^t\frac{ds}{\tau}\left(\frac{1+\cot^2\theta}{1+(\gamma s\cos\phi+\cot\theta)^2}\right)^{3/2}e^{-s/\tau}\right]\tag{33}$$

where it should be stressed that the θ appearing on the right-hand side of Eq. (33) is $\theta=\theta(t)$. It can be shown that $f(\theta,\phi,t)$ is normalized to unity at all times t, and reduces to the steady state expression given by Eq. (30) when the limiting form of Eq. (33) is considered as $t\to\infty$. If we consider a fixed large time T, then Eq. (33) can be written as

$$f_{ss}(\theta,\phi)=\lim_{T\to\infty}\frac{f_0\operatorname{cosec}^3\theta}{\gamma\tau\cos\phi}\int_{\cot^{-1}(\cot\theta+\gamma T\cos\phi)}^{\theta}d\psi\,\sin\psi\,\exp\left(\frac{\cot\theta-\cot\psi}{\gamma\tau\cos\phi}\right)\tag{34}$$

In the limit as $T \to \infty$, it is clear that the lower limit of the integral is either 0 or π, depending upon whether $\gamma \cos \phi$ is positive or negative, and we obtain the previous result (Eq. (30)). The similarity in the functional form of the time dependent and steady state distribution functions in two and three dimensions leads to similarities in the physical properties. In particular, the fractional exponents in the three-dimensional distribution function do not lead to nonanalyticities in the shear viscosity, as we shall see in the next section.

We now calculate the average of the kinetic part of the pressure tensor in the steady state. The small and large γ expansions of the kinetic contributions to the shear stress and normal stress differences are then obtained.

4. THE PRESSURE TENSOR UNDER SLLOD DYNAMICS

From the definition of our polar coordinates, Eq. (23), the phase variable for the kinetic part of the pressure is

$$\beta \mathbf{P}^k V = 2 \begin{bmatrix} \cos^2 \theta & \cos \theta \sin \theta \cos \phi & \cos \theta \sin \theta \sin \phi \\ \cos \theta \sin \theta \cos \phi & \sin^2 \theta \cos^2 \phi & \sin^2 \theta \cos \phi \sin \phi \\ \cos \theta \sin \theta \sin \phi & \sin^2 \theta \cos \phi \sin \phi & \sin^2 \theta \sin^2 \phi \end{bmatrix} \tag{35}$$

where we note that the definition of the temperature implies that $\beta p^2/m = 1$. The steady state average of $\langle \mathbf{P}^k \rangle$ is given by

$$\langle \mathbf{P}^k \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta \, f(\theta, \phi) \, \mathbf{P}^k(\theta, \phi) \tag{36}$$

For planar Couette flow the xy component of $\mathbf{P}^k$ determines the viscosity η and it can be shown from Eqs. (30), (35), and (36) that

$$\beta V \langle P^k_{xy} \rangle = -\frac{2}{\gamma \tau} \int_0^{\infty} dz e^{-z} K_1(z)[1 - (1 + \gamma^2 \tau^2 z^2)^{-1/2}] \tag{37}$$

After tedious but straightforward algebra, it can be shown that the integral representations for the diagonal elements of the pressure tensor are

$$\beta V \langle P^k_{xx} \rangle = 2 - 2 \int_0^{\infty} dz \, z e^{-z} K_1(z)[(1 + \gamma^2 \tau^2 z^2)^{-1/2}] \tag{38}$$

$$\beta V \langle P^k_{yy} \rangle = \frac{2}{(\gamma \tau)^2} \int_0^{\infty} dz \, z^{-1} e^{-z} K_1(z)[1 - (1 + \gamma^2 \tau^2 z^2)^{-1/2}] \tag{39}$$

$$\beta V \langle P^k_{zz} \rangle = -\frac{2}{(\gamma \tau)^2} \int_0^{\infty} dz \, z^{-1} e^{-z} K_1(z)[1 - (1 + \gamma^2 \tau^2 z^2)^{1/2}] \tag{40}$$

It is easy to see that there is no response in either $\langle P^k_{xz}\rangle$ or $\langle P^k_{yz}\rangle$. Using the method outlined in Appendix B for $\langle P^k_{xy}\rangle$ we obtain the following asymptotic expansions for the diagonal elements of the pressure tensor: (i) for $\gamma\tau \to 0$

$$\begin{aligned}
\beta V\langle P^k_{xx}\rangle &= \frac{2}{3} + \frac{16}{35}(\gamma\tau)^2 - \frac{96}{77}(\gamma\tau)^4 + \frac{1280}{143}(\gamma\tau)^6 \\
\beta V\langle P^k_{xy}\rangle &= -\frac{2}{5}(\gamma\tau) + \frac{4}{7}(\gamma\tau)^3 - \frac{400}{143}(\gamma\tau)^5 + \frac{70560}{2431}(\gamma\tau)^7 \\
\beta V\langle P^k_{yy}\rangle &= \frac{2}{3} - \frac{12}{35}(\gamma\tau)^2 + \frac{80}{77}(\gamma\tau)^4 - \frac{1120}{143}(\gamma\tau)^6 \\
\beta V\langle P^k_{zz}\rangle &= \frac{2}{3} - \frac{4}{35}(\gamma\tau)^2 + \frac{16}{77}(\gamma\tau)^4 - \frac{160}{143}(\gamma\tau)^6
\end{aligned} \tag{41}$$

and, (ii) for $\gamma\tau \to \infty$

$$\begin{aligned}
\beta V\langle P^k_{xx}\rangle &= 2 - \frac{2}{\gamma\tau}[\ln(\gamma\tau) + 2\ln 2 - C - 1] \\
\beta V\langle P^k_{xy}\rangle &= -\frac{2}{\gamma\tau}[\ln(\gamma\tau) - C - 1] \\
\beta V\langle P^k_{yy}\rangle &= \frac{2}{(\gamma\tau)} \\
\beta V\langle P^k_{zz}\rangle &= \frac{2}{\gamma\tau}[\ln(\gamma\tau) + 2\ln 2 - C - 2]
\end{aligned} \tag{42}$$

where C is Euler's constant.

The only nondiagonal element of the pressure tensor which responds in this shearing geometry is $\langle P^k_{xy}\rangle$. From $\eta = -\langle P^k_{xy}\rangle/\gamma$ and Eq. (b.6) of Appendix B it follows that the shear viscosity is

$$\eta/\eta_0 = 1 - \frac{10}{7}(\gamma\tau)^2 + \frac{1000}{143}(\gamma\tau)^4 - \frac{176400}{2431}(\gamma\tau)^6 + \cdots \tag{43}$$

in agreement with Ladd and Hoover's analysis. For large $\gamma\tau$, it can be shown that

$$\eta/\eta_0 = \frac{5\ln(\gamma\tau)}{(\gamma\tau)^2} - \frac{5(1+C)}{(\gamma\tau)^2} + 0\left(\frac{\ln(\gamma\tau)}{(\gamma\tau)^3}\right) \tag{44}$$

It is appropriate to point out that the high shear rate behavior of the shear stress is functionally independent of dimension, with the only difference being in the coefficient of the $(\gamma\tau)^{-1}$ term. Furthermore, the two-dimensional equivalent of (44) shows that the viscosity vanishes as $\ln(\gamma\tau)/(\gamma\tau)^2$ which is consistent with the earlier conjecture that the viscosity (in two dimensions) vanishes at least as strongly as $(\gamma\tau)^{-3/2}$.

5. THE DOLLS TENSOR METHOD IN THREE-DIMENSIONS

The dolls tensor equations of motion differ from the sllod equations in the strain rate dependent term in the $\dot{\mathbf{p}}_i$ equation. The essential ingredient in obtaining a solution in the three-dimensional sllod example, was to obtain equations of motion for θ and ϕ such that one of these variables was a constant of the motion. In order to do the same for dolls tensor equations of motion, we choose the following definitions of θ and ϕ

$$\begin{aligned} p_x &= p \sin\theta \cos\phi \\ p_y &= p \cos\theta \\ p_z &= p \sin\theta \sin\phi \end{aligned} \tag{45}$$

This choice leads to $\alpha = -\gamma \sin\theta \cos\theta \cos\phi$ as before, Eq. (24) and

$$\dot{\theta} = \gamma \sin^2\theta \cos\phi \tag{46}$$

Substituting into the relaxation-time Boltzmann equation, we obtain the same partial differential equation as we did for sllod dynamics. Therefore the time dependent and steady state distribution functions are the same as those for sllod. Again the change in the definition of θ and ϕ means that the definitions of the elements of the pressure tensor change, and

$$\beta V \mathbf{P}^{k\,\text{dolls}} = 2 \begin{bmatrix} \sin^2\theta\cos^2\phi & \cos\theta\sin\theta\cos\phi & \sin^2\theta\cos\phi\sin\phi \\ \cos\theta\sin\theta\cos\phi & \cos^2\theta & \cos\theta\sin\theta\sin\phi \\ \sin^2\theta\cos\phi\sin\phi & \cos\theta\sin\theta\sin\phi & \sin^2\theta\sin^2\phi \end{bmatrix} \tag{47}$$

Comparing with the definitions for sllod dynamics we find that

$$\begin{aligned} \langle P^k_{xx}\rangle^{\text{dolls}} &= \langle P^k_{yy}\rangle^{\text{sllod}} \\ \langle P^k_{yy}\rangle^{\text{dolls}} &= \langle P^k_{xx}\rangle^{\text{sllod}} \\ \langle P^k_{xz}\rangle^{\text{dolls}} &= \langle P^k_{yz}\rangle^{\text{sllod}} \\ \langle P^k_{yz}\rangle^{\text{dolls}} &= \langle P^k_{xz}\rangle^{\text{sllod}} \end{aligned} \tag{48}$$

For all the other elements of the pressure tensor, sllod and dolls give identical results. In particular the shear stress, and hence the shear viscosity, is the same to all orders in the strain rate.

In three-dimensions there are two independent normal stress differences and these can be defined as

$$\psi_1 = \langle P_{yy} - P_{xx} \rangle / \gamma^2 \tag{49}$$

and

$$\psi_2 = \langle P_{zz} - P_{yy} \rangle / \gamma^2 \tag{50}$$

Using the results above, it is straightforward to show that

$$\psi_1^{k\ \mathrm{dolls}} = -\psi_1^{k\ \mathrm{sllod}} \tag{51}$$

which is the same as the two-dimensional result. The relation between the ψ_2's for the two methods is

$$\psi_2^{k\ \mathrm{dolls}} = \psi_2^{k\ \mathrm{sllod}} + \psi_1^{k\ \mathrm{sllod}} \tag{52}$$

There are only a few simulation calculations in which the kinetic contributions to the pressure tensor have been reported. One particular calculation (Ref. 8, Table 1a) reported the kinetic contribution to the normal stress differences ψ_1^k and ψ_2^k, for a system of 32 soft spheres at a density $\rho^* = N\sigma^3/\sqrt{2}\,V = 0.4$, a temperature $T^* = k_B T/\varepsilon = 1$ and a shear rate $\gamma = 1$. Before performing actual numerical comparisons, it is worthwhile pointing out that the two body Boltzmann equation for hard core particles need not give the same values of ψ_1^k and ψ_2^k as those from a 32 particle soft sphere simulation. However, we would expect to see similar qualitative trends.

This simulation calculation reports the values of ψ_1^k and ψ_2^k obtained from both dolls tensor and the sllod algorithm. The results are, for the sllod algorithm

$$\begin{aligned} \psi_1^{k\ \mathrm{sllod}} &= -0.03 \\ \psi_2^{k\ \mathrm{sllod}} &= -0.01 \end{aligned} \tag{53}$$

Using the relations obtained above, we can use these computer simulation sllod results to predict the dolls tensor results for the same system. This gives

$$\begin{aligned} \psi_1^{k\ \mathrm{dolls}} &= 0.03 \\ \psi_2^{k\ \mathrm{dolls}} &= -0.04 \end{aligned} \tag{54}$$

which are precisely the results obtained in Reference 8 by direct simulation using dolls tensor.

6. COMPARISON WITH SIMULATIONS

In the preceding sections of this paper we have introduced a kinetic equation and discussed its solution in detail. The remarks in the introduction suggested that this relaxation-time approximation to the Boltzmann equation may only be useful near equilibrium. In order to test the validity of this equation away from equilibrium we carried out several simulations of 896 soft disks at a shear rate of $\gamma = 1$ and a temperature of $T^* = 1$. Two densities were considered, $\rho = N\sigma^2/V = 0.5$ and $\rho = 0.9238$. The second of these state points is the most studied soft disk state[3] near the freezing density. The other density is much lower and closer to the region where a kinetic theory approach may be valid. As the comparison of the relaxation-time approach and simulation is dependent upon the choice of τ we decided to select τ so that the shear stresses agreed, and then base the interpretation on a direct comparison of the distribution functions for θ. In dimensionless units it is straightforward to show that

$$\langle P_{xy}^k \rangle = \rho \int_0^\infty d(p^2) \int_0^{2\pi} d\theta\, F(p^2, \theta)\, p^2 \cos\theta \sin\theta \tag{55}$$

where $F(p^2, \theta)$ is the normalized probability distribution function for p^2 and θ. In the two-body Boltzmann approach p^2 is a constant of the motion because the temperature is constant, but in a computer simulation $\sum_i p_i^2$ is constant so that the individual p_i^2 are unconstrained. The average shear stress is

$$\langle P_{xy}^k \rangle = \rho \int_0^{2\pi} d\theta\, f(\theta)\, p^2(\theta) \cos\theta \sin\theta \tag{56}$$

where

$$p^2(\theta) = \frac{\int_0^\infty dp^2\, F(p^2, \theta)\, p^2}{\int_0^\infty dp^2\, F(p^2, \theta)} \tag{57}$$

is the θ dependent expectation value of p^2. In the two-body Boltzmann approach $p^2(\theta)$ is fixed and independent of θ, so it factors out of the integral in Eq. (56).

In the simulations we have calculated $\langle P_{xy}^k \rangle$ directly, as well as $p^2(\theta)$ and the distribution function $f(\theta)$. The first conclusion of this study is that there is a strong correlation between p^2 and θ at both densities considered, $\rho = 0.5$ and $\rho = 0.9238$ (see Figs. 2 and 4). This means that in the simulation there are two distinct contributions to the shear stress. The first is that due to $f(\theta)$ alone, while the second is due to the correlation between p^2 and θ. As the two-body Boltzmann approach ignores the correlation

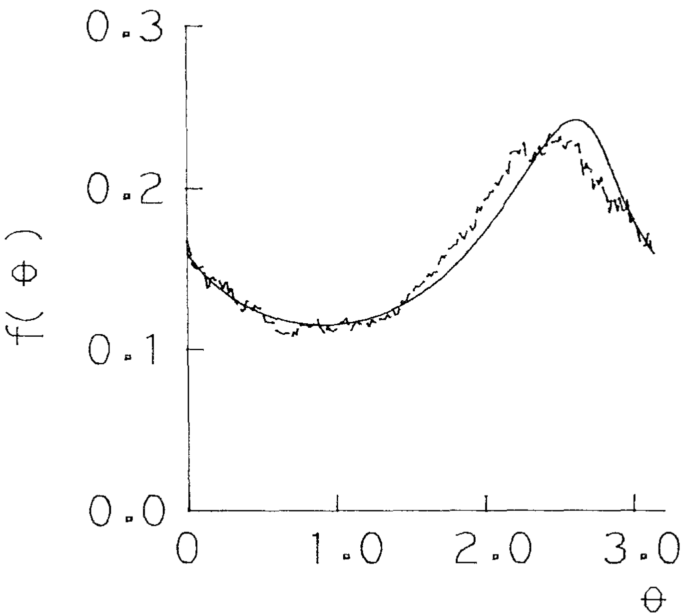

Fig. 1. The distribution function $f(\theta)$ at a density of $\rho = 0.5$, $T^* = 1$ and $\gamma = 1$. The solid line is from the two-body Boltzmann equation and the dashed line is from the 896 particle soft disk simulation.

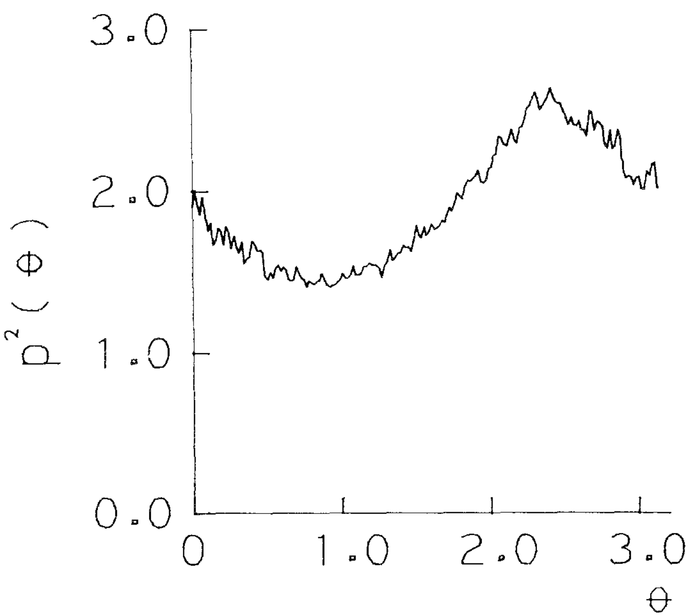

Fig. 2. The dependence of $p^2(\theta)$ on the angle θ, for a density of $\rho = 0.5$ from the simulation.

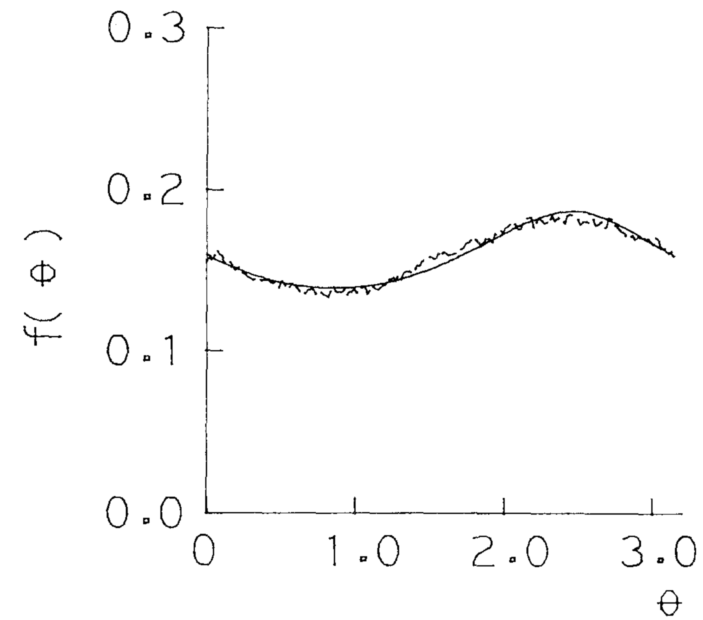

Fig. 3. The distribution function $f(\theta)$ at a density of $\rho = 0.9238$. The solid line is the two-body Boltzmann equation and the dashed line is the simulation.

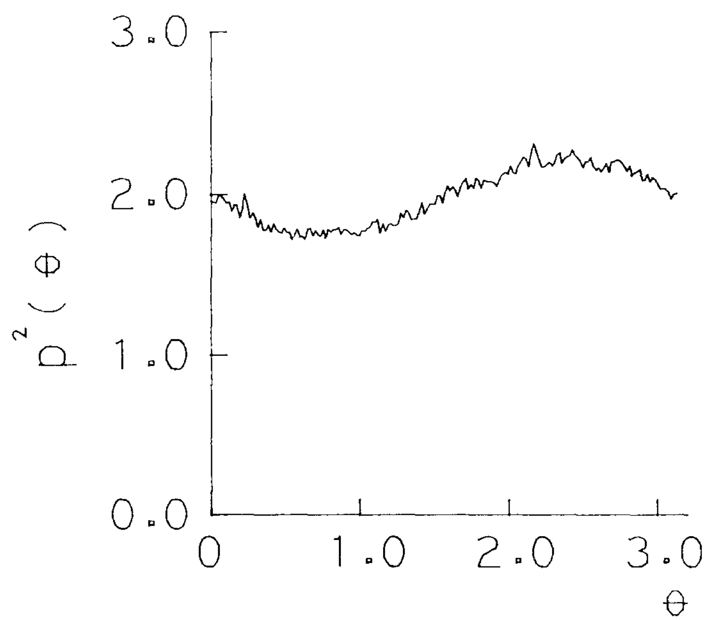

Fig. 4. The dependence of $p^2(\theta)$ on the angle θ, at a density of $\rho = 0.9238$ from the simulation.

between p^2 and θ, we fitted the relaxation time τ by requiring that the shear stress obtained, be equal to that obtained from Eq. (56) with $p^2(\theta)$ replaced by its average value. That is, the two-body Boltzmann solution was required to give only the first contribution to $\langle P^k_{xy} \rangle$ and *not* the second.

The shear stress obtained directly at $\rho = 0.5$ was -0.147, which agrees exactly with that obtained using Eq. (56) and the simulated values of $p^2(\theta)$ and $f(\theta)$. The shear stress obtained by ignoring the correlation between p^2 and θ was -0.084, and choosing $\tau = 0.3955$ the two-body Boltzmann equation gives precisely this value. In Fig. 1 we compare the theoretical distribution function for $\tau = 0.3955$ with that obtained in the simulation. The agreement is good for $0 < \theta < \pi/2$, but for $\pi/2 < \theta < \pi$ systematic differences appear. It is clear that nearly half of the observed shear stress is due to the correlation between p^2 and θ and that this contribution will not appear in an iso-kinetic two-body approach.

At the higher density of $\rho = 0.9238$, the simulated and theoretical distribution functions ($\tau = 0.15$) agree even better than they do at $\rho = 0.5$ (see Fig. 3). Here again, the contribution to the shear stress from the θ dependence of p^2 is large. Ignoring this θ dependence gives -0.0726 for the kinetic shear stress, which is approximately half that obtained from the direct calculation ($\langle P^k_{xy} \rangle = -0.1309$). In Fig. 4 we present this θ dependence of the magnitude of p^2.

The surprisingly good agreement between the distribution functions at such a density suggests that the relaxation-time Boltzmann equation is a good approximation to strongly nonequilibrium systems over a wide range of fluid states.

7. CONCLUSIONS

The behavior of the kinetic contributions to the pressure tensor have been obtained for two and three-dimensional fluids undergoing planar Couette flow using the relaxation-time approximation to the two-body Boltzmann equation. Two methods of driving this flow have been considered; the sllod algorithm and the dolls tensor hamiltonian. The sllod algorithm has previously been proved to be exact to all orders in the strain rate. Here we obtain the shear stress and the normal stress differences for both methods in two and three dimensions. Although the dolls tensor method gives incorrect normal stress differences, we find these are simply related to those for the sllod algorithm, and these relations are useful in understanding the results of larger systems of soft disks. Both the methods considered give the same shear stress, and hence viscosity, to all orders in the strain rate.

It is well known that the dependence of the shear viscosity on the strain rate is nonanalytic at $\gamma = 0$ in both two and three dimensions.[19] The relaxation-time Boltzmann equation predicts that the shear viscosity is analytic at $\gamma = 0$. This is clearly a weakness associated with the implicit lack of correlated collisions in the relaxation time approximation. The solution does display many of the features of real systems in that normal stress differences and shear thinning are observed. In fact it is straightforward to show that the derivative of the viscosity with respect to the strain rate is always negative, and hence the fluid never exhibits shear thickening.

The strong dependence of p^2 on θ observed in the computer simulations is similar to the orientational dependence of the radial distribution function in a shearing system which has already been reported.[20] If the nonequilibrium entropy is defined to be $S(t) = -k \int d\Gamma\, f(t) \ln f(t) - S(0)$, then the biasing of both the spatial and velocity distributions will lead to an decrease in the entropy.[21] We note that the entropy calculated in Fig. 1 of Ref. 9 is incorrect. The correct value of $S(t)$ for $\gamma = 0.1$ and $\tau = 16.2$ is negative for $t > 0$ and approaches the value -0.288 as $t \to \infty$.

Finally it is apparent that the relaxation-time Boltzmann equation is a good approximation for investigating nonequilibrium states over a wide range of fluid states. The major difficulty with its use is that there is as yet no easy and *a priori* method to determine the parameter τ for systems far from equilibrium. In fact it is probable that for such systems the parameter τ may not be constant and may depend on θ and p^2.

ACKNOWLEDGMENTS

GPM wishes to thank Professor W. G. Hoover for stimulating his interest in this subject. DI wishes to thank Professor R. J. Bearman for his support and encouragement.

APPENDIX A. EQUIVALENCE OF THE LADD–HOOVER SOLUTION

The same differential equation for the steady state case has been solved by Ladd and Hoover[8] using operational methods. Such operational techniques may be replaced with their equivalent operations in Fourier space over cot θ by the following steps: Eq. (29) may be rewritten in real space as

$$\left[1 - \gamma\tau \cos\phi \frac{\partial}{\partial \cot\theta}\right] F(\theta) = \frac{\sin^3\theta}{4\pi} \qquad \text{(a.1)}$$

where

$$F(\theta) = f(\theta)\sin^3\theta$$
$$= (2\pi)^{-1}\int_{-\infty}^{\infty} dq\, e^{iq\cot\theta}\tilde{F}(q) \qquad \text{(a.2)}$$

and $\tilde{F}(q)$ is the one-dimensional Fourier transform of $F(\theta) = G(\cot\theta)$ over $x = \cot\theta$ space. The substitution of F from (a.2) and subsequent solution for $\tilde{F}(q)$ by multiplying the resulting equation by $\int_{-\infty}^{\infty} dx e^{-iqx}$ leads to

$$\tilde{G}(q) = \frac{1}{4\pi(1 - iq\gamma\tau\cos\phi)}\int_{-\infty}^{\infty} dx e^{-iqx}(1+x^2)^{-3/2} \qquad \text{(a.3)}$$

Equation (a.3) can be inverted to obtain

$$f(x) = \frac{(1+x^2)^{3/2}}{8\pi^2}\int_{-\infty}^{\infty}\frac{dq e^{iqx}}{(1 - iq\gamma\tau\cos\phi)}\int_{-\infty}^{\infty} dx' e^{-iqx'}(1+x'^2)^{-3/2} \qquad \text{(a.4)}$$

$$= \frac{(1+x^2)^{3/2}}{4\pi^2}\int_{-\infty}^{\infty}\frac{dq e^{iqx}}{(1 - iq\gamma\tau\cos\phi)}\, qK_1(q) \qquad \text{(a.5)}$$

where the definition for the modified Bessel function of the first order $K_1(q)$ has been used in (a.4). In Reference 8 two forms for the steady state distribution function are obtained, Eqs. (16) and (17). However, both of these equations involve an infinite sum which does not converge. In particular the second of these equations requires that $q\gamma\tau\cos\theta < 1$ for convergence, but then q is integrated from $-\infty$ to ∞. The approach used in this work bypasses these convergence problems.

In this appendix we show that Eqs. (30) of the present paper and Eq. (17) of Ref. 8 are equivalent. The Ladd–Hoover solution can be written via a slight rearrangement of equation (a.4) of this paper as

$$f_{\mathrm{LH}} = \frac{(1+x^2)^{3/2}}{8\pi^2}\frac{i}{\alpha\cos\phi}\int_{-\infty}^{\infty} dx'(1+x'^2)^{-3/2}$$
$$\times\int_{-\infty}^{\infty} dq e^{iq(x-x')}[q + i/\alpha\cos\phi]^{-1} \qquad \text{(a.6)}$$

where $x = \cot\theta$, and $\alpha = \gamma\tau = \dot{\varepsilon}\tau$.

For $\alpha\cos\phi > 0$ the integral over q can be evaluated through its associated contour integral in the q plane[16]

$$\frac{i}{\alpha\cos\phi}\int_{-\infty}^{\infty}\frac{dq e^{iq(x-x')}}{q + \dfrac{i}{\alpha\cos\phi}} = \frac{2\pi}{\alpha\cos\phi}e^{(x-x')/\alpha\cos\phi} \qquad \text{if} \quad x < x'$$
$$= 0 \qquad \text{if} \quad x > x' \qquad \text{(a.7)}$$

A similar treatment of the contour integral for $\alpha \cos \phi < 0$ leads to

$$\frac{i}{\alpha \cos \phi} \int_{-\infty}^{\infty} \frac{dq e^{iq(x-x')}}{q + \frac{i}{\alpha \cos \phi}} = 0 \qquad \text{if} \quad x < x'$$

$$= \frac{-2\pi}{\alpha \cos \phi} e^{(x-x')/\alpha \cos \phi} \qquad \text{if} \quad x > x' \qquad \text{(a.8)}$$

The substitution of (a.7) into (a.6) leads to

$$f_{\text{LH}} = \frac{(1+x^2)^{3/2}}{4\pi\alpha \cos \phi} \int_{x=\cot \theta}^{\infty} dx' (1+x'^2)^{-3/2} e^{(x-x')/\alpha \cos \phi} \qquad \text{(a.9)}$$

from which it follows in the change of variables $x = \cot \theta$, $x' = \cot \theta'$, and use of $1 + \cot^2 \theta = \operatorname{cosec}^2 \theta$ that

$$f_{\text{LH}} = \frac{\operatorname{cosec}^3 \theta}{4\pi\alpha \cos \phi} \int_0^{\theta} d\theta' \sin \theta' e^{(\cot \theta - \cot \theta')/\alpha \cos \phi} \qquad \text{(a.10)}$$

provided $\cos \phi > 0$.

For $\cos \phi < 0$ a similar analysis of Eqs. (a.6) and (a.8) leads to

$$f_{\text{LH}} = \frac{\operatorname{cosec}^3 \theta}{4\pi\alpha \cos \phi} \int_{\pi}^{\theta} d\theta' \sin \theta' e^{(\cot \theta - \cot \theta')/\alpha \cos \phi} \qquad \text{(a.11)}$$

Equations (a.10) and (a.11) combine to give Eq. (30) in the present paper with $\alpha = \gamma\tau$.

APPENDIX B. ASYMPTOTIC EXPANSIONS

From Eq. (42) we define the integral $I_{xy}(\alpha)$ as

$$I_{xy}(\alpha) = \int_0^{\infty} dq K_1(q)\, e^{-q} [1 - (1 + \alpha^2 q^2)^{-1/2}] \qquad \text{(b.1)}$$

The initial step in the evaluation of (b.1) for large and small α is the replacement of the $[1 - (1 + \alpha^2 q^2)^{-1/2}]$ term by its inverse Mellin transform.[16] Thus, using

$$(1+x)^{-1/2} - 1 = \frac{1}{2\pi i} \int_{\substack{C - i\infty \\ -1 < C < 0}}^{C + i\infty} ds x^{-s} \Gamma(s)\, \Gamma\left(\frac{1}{2} - s\right) \Big/ \Gamma\left(\frac{1}{2}\right) \qquad \text{(b.2)}$$

with $x=\alpha^2 q^2$, we can write (b.1) as

$$I_{xy}(\alpha) = -\frac{1}{2\pi i \Gamma(1/2)} \int_{\substack{C-i\infty \\ -1<C<0}}^{C+i\infty} ds \alpha^{-2s} \Gamma(s)\, \Gamma\left(\frac{1}{2}-s\right) \int_0^\infty dq\, e^{-q} q^{-2s} K_1(q) \tag{b.3}$$

The integral over q in (b.3) is a Mellin transform (Ref. 16, p. 331, eq. 28) and can be evaluated

$$\int_0^\infty dq e^{-q} K_1(q)\, q^{-2s} = \frac{\Gamma(1/2)\, \Gamma(2-2s)\, \Gamma(-2s)}{2^{1-2s}\Gamma(3/2-2s)} \tag{b.4}$$

provided $\mathrm{Re}(s)<0$.

The combination of Eqs. (b.3) and (b.4) along with the analytic continuation of the Γ function into the region $\mathrm{Re}(s)<0$ in the s plane allows (b.1) to be written as

$$I_{xy}(\alpha) = -\frac{1}{2\pi i} \int_{\substack{C-i\infty \\ -1<C<0}}^{C+i\infty} ds \frac{(\alpha/2)^{-2s}\Gamma(s)\, \Gamma(1/2-s)\, \Gamma(2-2s)\, \Gamma(-2s)}{2\Gamma(3/2-2s)} \tag{b.5}$$

Small Strain Rate Expansion

Closing the contour in the left half plane ($\mathrm{Re}(s)<0$) leads to a power series representation for $I_{xy}(\alpha)$ for small α. Elementary analysis of the residues of the simple poles of $\Gamma(s)$ at $s=-1, -2, -3, -4, \ldots$ leads to

$$I_{xy}(\alpha) = \frac{\alpha^2}{5} - \frac{2}{7}\alpha^4 + \frac{200}{143}\alpha^6 - \frac{35{,}280}{2431}\alpha^8 + \cdots \tag{b.6}$$

From the definition $\beta V\langle P_{xy}^k\rangle = -(2/\alpha)\, I_{xy}(\alpha)$ and (b.6) it can be seen that Eq. (47) follows immediately.

Large Strain Rate Expansion

For large α, we evaluate the contribution to $I_{xy}(\alpha)$ from the double pole at the origin. It is simplest in this case to obtain the residue directly from the Laurent expansion of the integrand about $s=0$. To this end we write

$$\begin{aligned}(\alpha/2)^{-2s} &= \exp[-2s\ln(\alpha/2)] \\ &= 1 - 2s\ln(\alpha/2) + 0(s^2)\end{aligned}$$

and the Taylor series expansion of $\Gamma(z)$ for $z = 1/2 - s,\ 2 - 2s,\ 3/2 - 2s$ as

$$\Gamma(z) = \Gamma(a)[1 + (z - a)\,\psi(a)] + 0(z - a)^2$$

where ψ is the digamma function. The integrand can then be expanded as

$$-\frac{1}{2s^2} + \frac{1}{s}\left[\psi(2) - \psi\left(\frac{3}{2}\right) + \frac{1}{2}\left(\psi(1) + \psi\left(\frac{1}{2}\right)\right) + \ln\left(\frac{\alpha}{2}\right)\right] + 0(1)$$

from which the residue can be identified. Then, $I_{xy}(\alpha)$ is seen to be

$$I_{xy}(\alpha) = \ln \alpha - 1 - C \tag{b.7}$$

with C being Euler's constant. Equation (53) follows from (b.7) and (42).

REFERENCES

1. D. J. Evans, H. J. M. Hanley, and S. Hess, *Phys. Today*, **37**:26 (1984); W. G. Hoover, *Ann. Rev. Phys. Chem.*, **34**:103 (1983); D. J. Evans and W. G. Hoover, *Ann. Rev. Fluid Mech.*, **18**:243 (1986).
2. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, (Academic Press, New York, 1976); B. J. Berne, "Projection Operator Techniques in the Theory of Fluctuations," in *Statistical Mechanics B*, B. J. Berne, ed. (Plenum, New York, 1977).
3. D. J. Evans and G. P. Morriss, *Phys. Rev. Lett.*, **51**:1776 (1983).
4. D. J. Evans, *J. Chem. Phys.*, **78**:3297 (1983).
5. W. G. Hoover, A. J. C. Ladd, and B. Moran, *Phys. Rev. Lett.*, **48**:1818 (1982).
6. G. P. Morriss and D. J. Evans, *Mol. Phys.*, **54**:629 (1985).
7. J. Dufty, proceedings of *International School of Physics, Enrico Fermi, XCVII Course*, (to be published).
8. A. J. C. Ladd and W. G. Hoover, *J. Stat. Phys.*, **38**:973 (1985).
9. G. P. Morriss, *Phys. Lett. A.*, **113A**:269 (1985).
10. W. G. Hoover, *J. Stat. Phys.* **42**:587 (1986).
11. W. G. Hoover and K. W. Kratky, *J. Stat. Phys.* **42**:1103 (1986).
12. A. W. Lees and S. F. Edwards, *J. Phys.* **C5**:1921 (1972).
13. W. G. Hoover, D. J. Evans, R. D. Hickman, A. J. C. Ladd, W. T. Ashurst, and B. Moran, *Phys. Rev.*, **A22**:1690 (1980).
14. D. J. Evans and G. P. Morriss, *Phys. Rev.*, **A30**:1528 (1984).
15. A. J. C. Ladd, *Mol. Phys.* **53**:459 (1984).
16. Erdelyi, Magnus, Oberhettinger and Tricomi, *Tables of Integral Transforms*, Vol. 1. p. 310, Eq. (19) (McGraw-Hill, New York, 1954).
17. E. Gross, D. Bhatnager, and M. Krook, *Phys. Rev.*, **94**:511 (1954).
18. R. L. Liboff, *Introduction to the Theory of Kinetic Equations* (Wiley, New York, 1969).
19. J. R. Dorfman and H. van Beijeren, *The Kinetic Theory of Gases*, in Statistical Mechanics B, B. J. Berne, ed. (Plenum, New York, 1977).
20. D. J. Evans, *Phys. Rev.*, **A23**:1988 (1981).
21. B. L. Holian, *Phys. Rev.*, **A33**:1152 (1986).