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Model for nonequilibrium computer simulation methods

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Several methods for nonequilibrium computer simulation of plane Couette flow are analyzed by kinetic theory. The boundary-value problem for the nonlinear Boltzmann equation is related to the stochastic, Lees-Edwards, and "non-Newtonian" dynamics methods. It is found that the kinetic-theory and computer simulation methods can be put into close correspondence, except for one form of the non-Newtonian equations of motion. The effects of homogeneous, nonconservative forces used to maintain constant temperature are also studied. For a special interatomic force law exact scaling relations are obtained to relate isothermal and nonisothermal solutions to the Boltzmann equation. For other force laws this scaling relationship is only approximate.

I. INTRODUCTION

One of the simplest examples of a macroscopic nonequilibrium state is that of plane Couette flow between parallel plates in a relative motion. Because of its simplicity, it has attracted a great deal of attention in recent years as a proving ground for theoretical developments in nonequilibrium statistical mechanics[1] and for new methods developed to simulate nonequilibrium states on the computer.[2] The typical laboratory conditions correspond to a boundary-value problem with forces on the fluid applied only at the surfaces of the two plates. The computer simulation of such physical boundary conditions was first considered by Lees and Edwards,[3] and Ashurst and Hoover.[4] Subsequently, however, it was found that the uniform shear flow field could be produced more efficiently by replacing the boundary conditions with properly chosen homogeneous, nonconservative forces applied everywhere throughout the fluid.[5] Furthermore, additional forces could be used to extract energy uniformly from the gas to exactly compensate for viscous heating, leading to a macroscopic state of isothermal uniform shear flow.[6] Such an idealized state is clearly desirable for practical reasons, and computer simulations in this way have provided extensive data on the shear viscosity and other non-Newtonian properties of the pressure tensor.[2] Recently, attempts have been made to simulate a more realistic flow, similar to the spirit of Ashurst and Hoover,[4] using stochastic boundary conditions.[7] The latter represent a complete accommodation of an incident particle with the thermodynamics and flow of the walls before being reemitted. A stationary state is attained in this case without the need for additional external forces. Implicit in these studies is the assumption that, since the macroscopic flow field is the same in all cases as that obtained by physical boundary conditions, the transport properties agree as well. However, the macroscopic flow field places only a weak constraint on the microscopic state, so the relationship of transport properties determined from computer simulation to those that might be determined experimentally or from the corresponding theoretical boundary-value problem has not yet been determined. The objective here is to clarify this relationship and to interpret the methods of computer simulation, for the simple case of a Boltzmann gas. A brief summary of the main features of these methods is given in Sec. II.

Two different questions regarding the computer simulation are isolated: (1) How is the macroscopic flow field generated?, and (2) what are the effects of isothermal constraints? The first question is addressed in Sec. III where the Boltzmann equation is applied to a gas between two parallel plates in relative motion. A suitable class of boundary conditions is introduced to emphasize that the nonequilibrium flow field is due to momentum transfer at the boundaries. The stochastic boundary conditions are a special case corresponding to local interactions with the walls. It is shown that the Lees-Edwards periodic conditions are also a special case, although by definition they have an unrealistic nonlocalicity. Further analysis of the Lees-Edwards model is possible using a transformation to the local rest frame of the fluid. In this frame the Boltzmann equation admits a spatially homogeneous solution, corresponding to the "homogeneous shear flow" studied by computer simulation.[3,5,6] Alternatively, the inertial force generated by this local Galilean transformation may be viewed as a fictitious force in Newton's second law. The associated "non-Newtonian" equations of motion agree with one of two such prescriptions currently used for molecular dynamics simulations.[8,9] The other ("dolls tensor"[5]) predicts incorrect transport properties. The interpretation given here provides a criterion for choosing between the two, and suggests that the non-Newtonian equations are simply Newton's equations in a special noninertial frame.

A homogeneous "drag" force is introduced in Sec. IV to compensate for the viscous heating generated by the Lees-Edwards or non-Newtonian methods. Solutions to the Boltzmann equation for constant temperature are studied relative to those without the thermostat. For the special case of Maxwell molecules, a scaling relation is obtained for the two classes of solutions. This result leads to similar scaling laws for all transport properties. In particular, the shear viscosity and viscometric functions in appropriate dimensionless form have a shear rate dependence that is invariant with respect to the thermostat forces. This exact result is indeed the desired property implicitly assumed in isothermal computer simulations. However, the analysis here also suggests that the relationship may not be so simple for other interatomic force laws and more complex fluids. These results are discussed critically in Sec. V, and related to some other recent analyses of computer simulation methods.

II. NONEQUILIBRIUM COMPUTER SIMULATION METHODS

The review articles, Ref. 2, provide a discussion of most current methods for simulation of uniform shear flow, and have extensive references. Here, only the basic ideas of the approaches mentioned in the Introduction are recalled to clarify the discussion in the following sections. These are described in order of increasing abstraction from the experimental conditions.

A. Stochastic boundary conditions (Ref. 7)

N particles are placed in a unit cell and their dynamics is generated from Newton's equations subject to periodic boundary conditions in the x and z directions, just as for equilibrium computer simulation. The stochastic boundary conditions are imposed on the surfaces at $y=\pm L$, as follows. A particle incident on the plane at $y=L$ ($y=-L$) is reemitted into the region $y<L$ ($y>-L$) from the same point with a velocity sampled randomly from a Gaussian distribution. The parameters of the Gaussian are chosen to represent a fixed temperature at both walls, but a mean x component of the velocity equal to $\pm U_0$ at $\pm L$, respectively. These boundary conditions represent a physically "rough" wall in the sense that an incident particle is actually trapped long enough to be thermalized to the state of the wall. More realistic conditions of this type (Maxwell conditions), whereby an incident particle is elastically scattered or stochastically reemitted with some prescribed relative probability (accommodation coefficient), could be simulated without additional difficulty. Although the detailed molecular interaction between the system and the wall is not described by such boundary conditions, it may be expected that many properties of the system are only weakly dependent on such details. For such properties this type of computer simulation is therefore quite representative of a laboratory condition to produce shear flow. In practice, it is found that these boundary conditions lead to a stationary state with an approximately linear velocity profile between $y=\pm L$ and an approximately quadratic profile for the temperature, with constant pressure. These are generally the results expected from Navier-Stokes order hydrodynamics, complicated by a boundary layer.

B. Lees-Edwards periodic boundary conditions (Ref. 3)

The N particles in the unit cell again have their dynamics generated from Newton's equations with the usual equilibrium periodic boundary conditions in the x and z directions. However, when a particle leaves the unit cell through the top surface at $y=L$ it is given a new position and velocity on the lower surface. Specifically, it is reentered at $y=-L$ with the same z position and the same y and z components of the velocity, but with a new x position, x_N, and a new x component of the velocity, v_{xN}, given by

$$x_N=x-2U_0t,\quad v_{xN}=v_x-2U_0\ , \tag{2.1}$$

where $\pm U_0$ again denotes the velocities of the surfaces at $y=\pm L$, respectively. The new x position reflects the relative displacement of two points at $y=\pm L$ with the same x coordinate at $t=0$. The new velocity differs from the original velocity by the relative velocities of the two surfaces. A complementary boundary condition is imposed at $y=-L$, such that the particle is reentered through $y=+L$ in a manner similar to (2.1) but with the sign of U_0 changed. Finally, these conditions are periodically extended along the y axis. There are some significant differences between the Lees-Edwards and stochastic boundary conditions. The former are nonlocal and are not intended to represent the interaction of the particles with physical walls. Furthermore, work is done on the system when particles are moved from one surface to the other with a velocity change. As a consequence no stationary state is possible. Instead, a linear velocity profile is attained as desired, and the temperature is spatially constant but increases with time (viscous heating). Additional nonconservative forces must be introduced somewhat artificially to obtain a stationary state with these boundary conditions. It is also interesting that a strictly linear velocity profile is possible in this case, without any boundary layer. This can be a useful feature of the simulation if the primary interest is bulk transport properties. An additional difference is that the Lees-Edwards boundary conditions are restricted to shear flow, whereas the stochastic boundary conditions have been used to describe other types of transport as well.[10]

C. "Non-Newtonian" dynamics (Ref. 5)

The simulation methods in Secs. II A and II B represent a boundary-value problem in the sense that the evolution under Newtonian dynamics is interrupted only at the spatial surfaces. The non-Newtonian dynamics method goes beyond this to change the actual equations of motion throughout the domain, by the addition of homogeneous external forces designed to drive the system to uniform macroscopic shear flow. The first such dynamics proposed is the "dolls tensor" method[5] for which the equations of motion are

$$\dot{q}_{\alpha i}=\tilde{v}_{\alpha i}+a_{ij}q_{\alpha j},\quad m\dot{\tilde{v}}_{\alpha i}=F_{\alpha i}-m\tilde{v}_{\alpha j}a_{ji}\ , \tag{2.2}$$

where $\mathbf{F}_\alpha$ is the force on the αth particle due to all other particles, $\mathbf{v}_\alpha$ is the "peculiar" velocity of the αth particle (interpreted as the actual velocity relative to the local average flow velocity), and a_{ij} is a tensor of the form

$$a_{ij}=a\delta_{ix}\delta_{jy}\ . \tag{2.3}$$

In these simulations, shearing boundary conditions similar to (2.1) are used for the position, but the peculiar velocity is not changed, i.e., $\tilde{\mathbf{v}}_N=\tilde{\mathbf{v}}$. The dynamics (2.2) leads to $\langle\tilde{v}_{\alpha i}\rangle=0$, consistent with a macroscopic flow velocity,

$$U_i(\mathbf{r})=a_{ij}r_j \tag{2.4}$$

and a spatially constant, but temporally increasing, temperature. These results are quite similar to those from the Lees-Edwards boundary conditions, with $a=U_0/L$. Subsequently, a modified version of these equations has been proposed.[8,9] The form is the same as that in (2.2), except with a_{ij} replaced by its transpose in the velocity equations. This change does not affect the resulting macroscopic state of uniform shear flow, and it is possible to show that the linear-response functions (first order in a_{ij}) are the same for the two sets of dynamics. This situation illustrates the microscopic degeneracy with respect to a given macroscopic state and suggests that further considerations are required for a choice between these two methods.

D. Gauss's principle (Refs. 2 and 6)

Except for the stochastic boundary condition approach, the above computer simulation methods do not yield a stationary state for uniform shear flow, due to viscous heating. However, with the introduction of suitably determined homogeneous, nonconservative forces, the heat may be extracted at the same rate as it is produced. The resulting temperature is constant in both space and time, but without additional effects on the velocity field. One method for the choice of such external forces is by means of Gauss's variational principle subject to the macroscopic constraint of constant temperature (both constant kinetic energy and total energy choices have been used). This ensures self-consistency between the resulting dynamics and the macroscopic constraint. It should be stressed, however, that Gauss's principle goes beyond Newton's laws and is only a hypothesis that may not give correct results for a given physical system. The constant temperature condition is satisfied by additional forces on each particle of the form

$$\begin{aligned}(\mathbf{F}_\alpha)_{\text{ext}}&=-m\zeta\tilde{\mathbf{v}}_\alpha\ ,\\ \zeta&=\langle\tilde{v}_i[F_i-ma_{ij}\tilde{v}_j]\rangle/\langle m\tilde{v}^2\rangle\ ,\end{aligned} \tag{2.5}$$

where the brackets denotes an average as a summation over all particles. Typically, computer simulations of the Lees-Edwards or non-Newtonian type are supplemented by such forces for a fictitious thermostat.

III. KINETIC BOUNDARY-VALUE PROBLEM

Consider a gas between two infinite parallel plates located at $y=\pm L$. The plane at L has a velocity of magnitude U_0 along the x axis, while the plane at $-L$ has an opposite velocity of equal magnitude. The Boltzmann equation for $-L<y<L$ is then

$$\left[\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right]f=J[f,f]\ , \tag{3.1}$$

where $f=f(\mathbf{r},\mathbf{v};t)$ is the distribution function for the position $\mathbf{r}$ and velocity $\mathbf{v}$, and $J[f,f]$ denotes the collision operator. The appropriate boundary conditions express the distribution of velocities for particles entering the region $-L<y<L$ in terms of the distribution for particles leaving this region,[11]

$$\Theta(\hat{\mathbf{n}}\cdot\mathbf{v})\left[|\hat{\mathbf{n}}\cdot\mathbf{v}|f(\mathbf{s},\mathbf{v};t)-\int d\mathbf{s}'\int d\mathbf{v}'K(\mathbf{s},\mathbf{v};\mathbf{s}',\mathbf{v}'\,|\,t)\,|\hat{\mathbf{n}}'\cdot\mathbf{v}'|\,\Theta(-\hat{\mathbf{n}}'\cdot\mathbf{v}')f(\mathbf{s}',\mathbf{v}';t)\right]=0\ . \tag{3.2}$$

Here $\mathbf{s}$ and $\mathbf{s}'$ are position vectors on the surface of the confining planes, $\hat{\mathbf{n}}$ is a local unit vector normal to the surface directed toward the interior, and $\Theta(x)$ is the Heaviside unit step function. Equation (3.2) expresses a linear relationship between the distributions of particles leaving the surfaces and those incident on the surfaces. The function $K(\mathbf{s},\mathbf{v};\mathbf{s}',\mathbf{v}'\,|\,t)$ characterizes the detail effect of the wall on the gas. The form (3.2) includes the case of nonlocal and time-dependent boundary conditions, to allow for discussion of the Lees-Edwards method.

Two natural conditions to impose on the kernel, $K(\mathbf{s},\mathbf{v};\mathbf{s}',\mathbf{v}'\,|\,t)$, for the case of interest here are conservation of particle number (normalization of f), and admissibility of a stationary Maxwell-Boltzmann solution when the parameters of all walls are thermally and mechanically the same. A trivial example consistent with these conditions is elastic scattering, whereby only the component of the velocity normal to the wall is changed in direction at the point of contact. A physically opposite extreme, also consistent with these conditions, is complete accommodation,

$$\begin{aligned}K_s(\mathbf{s},\mathbf{v};\mathbf{s}',\mathbf{v}')\equiv{}&\delta(\mathbf{s}-\mathbf{s}')\,|\hat{\mathbf{n}}\cdot\mathbf{v}|\,[m^2\beta^2(\mathbf{s})/2\pi]\\ &\times\exp\{-\beta(\mathbf{s})m[\mathbf{v}-\mathbf{U}(\mathbf{s})]^2/2\}\ ,\end{aligned} \tag{3.3}$$

where $T(\mathbf{s})=[k_B\beta(\mathbf{s})]^{-1}$ is the temperature, and $\mathbf{U}(\mathbf{s})$ is the velocity of the wall at the point, $\mathbf{s}$. The delta function implies that this boundary condition is local. Substitution of (3.3) in (3.2) shows that the distribution function for particles coming off the wall, $\hat{\mathbf{n}}\cdot\mathbf{v}>0$, is a Gaussian centered about $\mathbf{v}=\mathbf{U}(\mathbf{s})$ with a width determined by the temperature of the wall. Clearly this corresponds in spirit and in detail to the computer simulation method using stochastic boundary conditions. For example, the case of uniform shear flow corresponds to $\beta(\mathbf{s})=\text{constant}$ and $\mathbf{U}(s)=\pm U_0\hat{\mathbf{x}}$ at $y=\pm L$. Therefore, a precise connection between the theory and the computer simulation method is established for stochastic boundary conditions. Reasonable models for the Boltzmann equation (e.g., BGK models) have been solved with the boundary condition, (3.3), and the planar geometry assumed here.[11] Many of the qualitative features to be expected in a computer simulation (e.g., boundary layer, temperature profile) can be predicted from such models, although no dense fluid kinetic theory calculations have been formulated for a quantitative comparison.

A less obvious boundary condition for the Boltzmann equation is one corresponding to the Lees-Edwards simulation method. By analogy with conditions (2.1), the Lees-Edwards kernel is defined by

$$K_{\mathrm{LE}}(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}'\mid t)=\delta(v_x\mp 2U_0-v_x')\delta(v_y-v_y')\delta(v_z-v_z')\delta(x\mp 2U_0t-x')\delta(y+y')\delta(z-z') \tag{3.4}$$

for $y=\pm L$. The conditions for particle conservation and equilibrium solution are easily shown to hold for (3.4) [for equilibrium, $U_0=0$ and (3.4) is seen to be the usual periodic boundary conditions for equilibrium simulations]. Again it is clear from substitution into Eq. (3.2) that this represents boundary conditions for the Boltzmann equation that are precisely the same as the Lees-Edwards conditions for computer simulation of shear flow. It is instructive to give (3.4) an equivalent but somewhat different interpretation. The stationary macroscopic flow field for these boundary conditions is expected to have the form of Eq. (2.4). In this case, a simpler description is expected in a frame of reference that is instantaneously at rest with respect to each fluid element. This is obtained from a local pseudo-Galilean transformation,

$$\begin{aligned}&\tilde{\mathbf{r}}\equiv\mathbf{r}-\mathbf{U}(\mathbf{r})t\ ,\\&\tilde{\mathbf{v}}\equiv\mathbf{v}-\mathbf{U}(\mathbf{r})\ ,\\&g(\tilde{\mathbf{r}},\tilde{\mathbf{v}};t)\equiv f(\mathbf{r},\mathbf{v};t)\ .\end{aligned} \tag{3.5}$$

Under this transformation the position is referred to the Lagrangian frame for plane Couette flow. The Lees-Edwards kernel, (3.4), in these variables becomes (for $\tilde{y}=\pm L$)

$$K_{\mathrm{LE}}'(\tilde{\mathbf{r}}',\tilde{\mathbf{v}}';\tilde{\mathbf{r}},\tilde{\mathbf{v}})=\delta(\tilde{\mathbf{v}}'-\tilde{\mathbf{v}})\delta(\tilde{x}'-\tilde{x})\delta(\tilde{y}'+\tilde{y})\delta(\tilde{z}'-\tilde{z})\ . \tag{3.6}$$

Consequently, (3.6) is the usual equilibrium periodic boundary condition [i.e., (3.4) with $U_0=0$], except that it is applied to the new coordinates. Use of (3.6) in (3.2) gives two sets of conditions on the transformed distribution function for $\hat{\mathbf{n}}\cdot\tilde{\mathbf{v}}>0$ at $\tilde{y}=\pm L$. These may be combined to give the single condition

$$[g(\tilde{\mathbf{r}},\tilde{\mathbf{v}};t)]_{\tilde{y}=-L}=[g(\tilde{\mathbf{r}},\tilde{\mathbf{v}};t)]_{\tilde{y}=L}\ . \tag{3.7}$$

The boundary conditions (3.6) imply that the solution to the Boltzmann equation in the local rest-frame variables can be periodically extended. The form of the Boltzmann equation in this frame is easily found to be,

$$\left[\frac{\partial}{\partial t}+\Lambda_{ij}(t)\tilde{v}_j\frac{\partial}{\partial\tilde{r}_i}-a_{ij}\tilde{v}_j\frac{\partial}{\partial\tilde{v}_i}\right]g=J[g,g]\ , \tag{3.8}$$

where $\Lambda_{ij}(t)\equiv\delta_{ij}-a_{ij}t$, and the time derivative is taken at constant $\tilde{\mathbf{r}},\tilde{\mathbf{v}}$. Use has been made of the fact that the collision operator, J, is invariant under the transformation (3.5).

The noninertial frame Boltzmann equation, (3.8), with the simple "equilibrium" periodic boundary conditions, (3.7), is fully equivalent to the inertial frame Boltzmann equation, (3.1), with velocity changes at the boundaries, (3.4). Both forms give the same nonequilibrium state, but the effects of the boundaries in the rest frame have been transferred to explicit inertial terms in the kinetic equation itself. There are further simplifications of Eq. (3.8) for a special class of "homogeneous" solutions. These solutions are suggested by the fact that a possible set of hydrodynamic variables consistent with the boundary conditions are a flow field, (2.4), and spatially constant temperature and density. In the local rest frame, therefore, the system is completely homogeneous, at least with respect to the hydrodynamic variables. It might be expected that this macroscopic state corresponds to homogeneous solutions of (3.8). In this case $g(\tilde{\mathbf{r}},\tilde{\mathbf{v}};t)=g_0(\tilde{\mathbf{v}},t)$ and Eq. (3.8) reduces to the homogeneous form

$$\left[\frac{\partial}{\partial t}-a_{ij}\tilde{v}_j\frac{\partial}{\partial\tilde{v}_i}\right]g_0=J[g_0,g_0]\ . \tag{3.9}$$

The boundary condition, (3.7), is automatically satisfied, and so it is sufficient to choose an initial condition that is homogeneous [although it is expected that for a wider class of initial conditions the solutions to Eq. (3.8) would approach a homogeneous state]. It follows directly that (3.9) yields the expected a hydrodynamic state. For the special case of Maxwell molecules, Eq. (3.9) can be solved exactly for the pressure tensor and associated transport coefficients (shear viscosity, viscometric functions) as a function of the shear rate.[12] The rate of viscous heating is also obtained. Further progress has been made only with the Introduction of approximations to the Boltzmann collision operator.[13] The special solutions, (3.9), correspond to the "homogeneous shear flow" obtained in the Lees-Edwards computer simulations. Such solutions are useful to describe the above transport properties, but other solutions to the more general Eq. (3.8) are required for inherently inhomogeneous properties (e.g., hydrodynamic fluctuations).

Finally, a connection between the non-Newtonian simulation methods and the Boltzmann equation can be made. As described in Sec. II, the variables in the equations of motion are the rest-frame velocities, and the laboratory-frame coordinates. The Boltzmann equation in these variables is

$$\left[\frac{\partial}{\partial t}+(\tilde{v}_i+a_{ij}r_j)\frac{\partial}{\partial r_i}-a_{ij}\tilde{v}_j\frac{\partial}{\partial \tilde{v}_i}\right]g'=J[g',g'] \ , \tag{3.10}$$

where $g'(\mathbf{r},\tilde{\mathbf{v}};t)\equiv f(\mathbf{r},\mathbf{v};t)$ and the time derivative is now taken at constant, $\mathbf{r},\tilde{\mathbf{v}}$. If Eq. (3.10) is formally rewritten as

$$\left[\frac{\partial}{\partial t}+(\dot{r}_i)\frac{\partial}{\partial r_i}+\frac{\partial}{\partial \tilde{v}_i}\frac{\mathcal{F}_i}{m}(\tilde{\mathbf{v}})\right]g'=J[g',g'] \ , \tag{3.11}$$

it is seen that the shear-rate dependence of (3.10) represents a modification of the kinematics corresponding to a change in Newton's laws according to

$$\begin{aligned}
&\dot{r}_{\alpha i}=\tilde{v}_{\alpha i}+a_{ij}r_{\alpha j},\\
&\dot{\tilde{v}}_{\alpha i}=(F_{\alpha i}+\mathcal{F}_{\alpha i})/m \ ,\\
&\mathcal{F}_{\alpha i}\equiv -ma_{ij}\tilde{v}_{\alpha j} \ ,
\end{aligned} \tag{3.12}$$

when $\mathbf{F}_\alpha$ is again the force on the αth particle due to all other particles. In other words, Eq. (3.10) could be interpreted as the Boltzmann equation for a system of particles satisfying Eqs. (3.12). These equations of motion are very similar to the non-Newtonian equations, (2.2), except that the shear-rate tensor is transposed in the second equation of (3.12). It was noted in Sec. II that an alternative form of "dolls tensor" equations has been suggested that differs only by this transposed shear-rate tensor, and hence is given by (3.12). The reason to choose (3.12) is now clear: Since only a change of variables was performed to obtain (3.10), that result and consequently also (3.12) are still equivalent to Newtonian dynamics. The additional shear-rate dependent terms in these equations are simply inertial effects due to the change of variables. In fact Eqs. (3.12) follow immediately from Hamilton's equations for $\{\mathbf{r}_\alpha,\mathbf{v}_\alpha\}$ by the substitution $v_{\alpha i}=\tilde{v}_{\alpha i}+a_{ij}r_{\alpha j}$, so that the non-Newtonian dynamics is just Newtonian dynamics referred to a noninertial frame. No such basis appears to exist for the "dolls tensor" equations, and the shear-rate dependence must be assigned to a true external force whose meaning and consequences are ill-defined.

IV. ISOTHERMAL CONSTRAINTS

The boundary condition (3.4) preserves conservation of total mass and momentum, but not energy. Since work is done on the system the average kinetic energy of the gas, or equivalently the temperature, will increase with time. For practical purposes, it would be desirable to have a corresponding stationary state whose transport properties are essentially the same as those calculated from (3.1) and (3.4), except with constant temperature. The simplest way to control the temperature is to introduce a homogeneous external force on each particle in the gas to extract energy from the particles at the same rate at which it is produced by viscous heating. Since the temperature is uniform for the kinetic model considered here, this external force will also have to be uniform. Many choices are possible but attention will be limited to a drag force proportional to the velocity relative to the local convection field.

$$\mathbf{F}_\zeta(\tilde{\mathbf{v}},t)=-m\zeta(t)\tilde{\mathbf{v}} \ . \tag{4.1}$$

The appearance of $\tilde{\mathbf{v}}$ rather than $\mathbf{v}$ is physically reasonable, but also is required by the macroscopic hydrodynamic equations for consistency with uniform shear flow. The parameter $\zeta(t)$ is adjusted to fit the condition of constant temperature. [A time dependence of $\zeta(t)$ is included to allow for the possibility of nonstationary solutions, even at constant temperature. It is shown below, however, that $\zeta(t)$ approaches a constant after a short initial transient.] It is straightforward to extend the homogeneous Boltzmann equation (3.9) to include the nonconservative force,

$$\left[\frac{\partial}{\partial t}-\frac{\partial}{\partial \tilde{v}_i}[\zeta(t)\tilde{v}_i+a_{ij}\tilde{v}_j]\right]g_0=J[g_0,g_0] \ . \tag{4.2}$$

The rest-frame form has been chosen and the associated boundary condition (3.6) is unchanged. The comments of Sec. III concerning the connection with molecular dynamics methods is also unchanged except for the addition of $\mathbf{F}_\zeta$ to the Newtonian force in both the Lees-Edwards and non-Newtonian equations of motion methods. The average kinetic energy, $\varepsilon(t)$, can be calculated from (15) to give

$$\frac{\partial}{\partial t}\varepsilon(t)+2\zeta(t)\varepsilon(t)+a_{ij}P_{ij}(\zeta(t),a,t)=0 \ , \tag{4.3}$$

where $P_{ij}(\zeta(t),a,t)$ is the pressure tensor,

$$P_{ij}(\zeta(t),a,t)\equiv\int d\tilde{\mathbf{v}}\, m\tilde{v}_i\tilde{v}_j g_0(\zeta(t);\tilde{\mathbf{v}},t) \ , \tag{4.4}$$

and the dependence of P_{ij} on both $\zeta(t)$ and shear rate, a, has been made explicit. For isothermal conditions $\zeta(t)$ is chosen such that $\partial\varepsilon(t)/\partial t=0$.

Equation (4.3) shows that the nonconservative force is a function of the shear rate through $\zeta(t)$. However, this also implies that the pressure tensor with the isothermal constraint is not the same function of shear rate as that obtained without the constraint,

$$P_{ij}(\zeta(t),a,t)\neq P_{ij}(0,a,t) \ . \tag{4.5}$$

In general, it is possible that results obtained with isothermal constraints have little relationship to the corresponding results for laboratory conditions with viscous heating. On the contrary, the application of such constraints for molecular dynamics simulations assumes that the differences occur in a more or less trivial way that can be scaled out, leaving transport properties that are essentially the same in the two cases. The objective of this section is to justify this view from the kinetic model for a particular potential (Maxwell molecules), and to show the precise relationship of all transport properties calculated with and without isothermal constraints. For other potential models these relationships are only approximate.

To relate the solution of Eq. (4.2) to that of (3.9), define a change of variables for the former by

$$\begin{aligned}
&\boldsymbol{\xi}\equiv R(t)\tilde{\mathbf{v}} \ ,\\
&\zeta(t)=\frac{\partial}{\partial t}\ln R(t) \ ,\\
&\bar{g}(\boldsymbol{\xi},t)\equiv R^{-3}(t)g_0(\zeta(t);R^{-1}(t)\boldsymbol{\xi},t) \ ,
\end{aligned} \tag{4.6}$$

which is simply a time-dependent scale transformation on the velocities. Equation (4.2) then transforms to

$$\left[\frac{\partial}{\partial t}-a_{ij}\xi_j\frac{\partial}{\partial \xi_i}\right]\bar g=\bar J[\bar g,\bar g] \tag{4.7}$$

with

$$\bar J[\bar g,\bar g](\xi)\equiv R^{-3}J[R^3\bar g,R^3\bar g](R^{-1}\xi)\ . \tag{4.8}$$

In general the transformation properties of the Boltzmann collision operator under such scale transformations, as indicated by the right-hand side of (4.8), is quite complicated. However, for potentials of the form, $V(r)\sim r^{-n}$, it reduces to[14]

$$\bar J[\bar g,\bar g](\xi)=R^{-(n-4)/n}J[\bar g,\bar g](\xi)\ . \tag{4.9}$$

Interestingly, for $n=4$ (Maxwell molecules) the collision operator is invariant under scale transformations and Eq. (4.7) reduces to

$$\left[\frac{\partial}{\partial t}-a_{ij}\xi_j\frac{\partial}{\partial \xi_i}\right]\bar g=J[\bar g,\bar g]\ , \tag{4.10}$$

which is formally equivalent to Eq. (3.9). It is also verified that the boundary conditions are invariant under this transformation. If, further, initial conditions are chosen such that at $t=t_0$

$$g_0(\zeta(t_0);\tilde{\mathbf v},t_0)=g_0(\zeta=0;\tilde{\mathbf v},t_0)\ , \tag{4.11}$$

and we take $R(t_0)=1$, then it follows that the function g_0 at $\zeta(t)=0$ is identical to $\bar g$, for all times, $t\geqq t_0$,

$$\bar g(\tilde{\mathbf v},t)=g_0(\zeta=0;\tilde{\mathbf v},t) \tag{4.12}$$

or, equivalently,

$$g_0(\zeta(t);\tilde{\mathbf v},t)=R^3(t)g_0(0;R(t)\tilde{\mathbf v},t)\ . \tag{4.13}$$

This is the primary result for the analysis here. For Maxwell molecules, the distribution function including the external force, (4.1), is simply related to the distribution function without it by a time-dependent velocity scaling.

Until now no restriction has been placed on the parameter $\zeta(t)$. An expression for it follows by calculating the average kinetic energy from the left- and right-hand sides of (4.13) and requiring that the temperature on the left-hand side be constant,

$$\varepsilon(\zeta(t),t)=\text{const}=R^{-2}(t)\varepsilon(0,t)\ , \tag{4.14}$$

and with (4.6), $\zeta(t)$ is found to be

$$\zeta(t)=\frac{1}{2}\frac{\partial}{\partial t}\ln\varepsilon(0,t)\ . \tag{4.15}$$

The right-hand side of (4.15) can be evaluated exactly for Maxwell molecules as a function of the shear rate and time. For times large compared to the mean free time it is asymptotically time independent with a value[12,13]

$$\zeta(t)\to\tfrac{2}{3}\nu\sinh^2\{\tfrac{1}{6}\cosh^{-1}[1+(3a/\nu)^2]\}\ , \tag{4.16}$$

where ν is an eigenvalue of the Boltzmann collision operator that is proportional to the density, but otherwise depends only on parameters of the potential. The right-hand side of (4.16) is proportional to a^2 for small shear rates and is a monotonically increasing positive function of a.

Many of the transport properties of interest for shear flow are determined from the pressure tensor. It is common to define a shear viscosity function $\eta(a)$ and the first and second viscometric functions $\psi_1(a)$ and $\psi_2(a)$ as

$$\begin{aligned}\eta(a)&=-P_{xy}/a\ ,\\ \psi_1(a)&=-(P_{xx}-P_{yy})/a^2\ ,\\ \psi_2(a)&=-(P_{yy}-P_{zz})/a^2\ .\end{aligned} \tag{4.17}$$

Since the pressure tensor is given by (4.4) it follows that the isothermal pressure tensor is related to that with viscous heating by

$$P_{ij}(\zeta(t),a,t)=R^{-2}(t)P_{ij}(0,a,t)\ . \tag{4.18}$$

The entire difference in the shear-rate dependence for the isothermal and nonisothermal cases can be eliminated by considering the corresponding dimensionless transport properties.

$$\begin{aligned}&P_{ij}^*\equiv P_{ij}/p,\quad \eta^*\equiv\eta\nu/p\ ,\\ &\psi_1^*\equiv\psi_1\nu^2/p,\quad \psi_2^*\equiv\psi_2\nu^2/p\ ,\end{aligned} \tag{4.19}$$

where $p=\frac{1}{3}P_{ii}$ is the pressure. These quantities are invariant functions of the reduced shear rate, $a^*\equiv a/\nu$, with respect to the thermostat,

$$\begin{aligned}P_{ij}^*(\zeta(t),a^*,t)&=P_{ij}^*(0,a^*,t)\ ,\\ \eta^*(\zeta(t),a^*,t)&=\eta^*(0,a^*,t)\ ,\\ \psi_1^*(\zeta(t),a^*,t)&=\psi_1^*(0,a^*,t)\ ,\\ \psi_2^*(\zeta(t),a^*,t)&=\psi_2^*(0,a^*,t)\ .\end{aligned} \tag{4.20}$$

Other transport properties can be identified from higher moments of the distribution function. The pth order moments are related as in (4.18) except with a factor of $R^{-p}(t)$. The corresponding dimensionless properties are again invariant, as in (4.20). Consequently, all transport properties of the isothermal system have a simple relationship to those of the "real" system with viscous heating. These results are exact and apply at all values of the shear rate for which solutions to the Boltzmann equation exist.

The scaling law, (4.20), does not apply for potentials other than the Maxwell potential. Furthermore, exact solutions are not known for other potentials so it is difficult to determine precisely the difference between solutions with and without a thermostat in these cases. However, a realistic estimate can be obtained using a model of the Boltzmann collision operator, the nonlinear Bhatnagar-Gross-Krook (BGK) model

$$J[f,f]\to-\nu(T(t))[f-f_L]\ . \tag{4.21}$$

Here f_L is the local equilibrium distribution as a function of $T(t)$, and $\nu(T(t))$ is an effective collision frequency. This model preserves the conservation laws associated with $J[f,f]$ and consequently leads to a proper description of hydrodynamics and transport phenomena. The dependence on the potential model is entirely contained in the choice of $\nu(T(t))$. For the r^{-n} potential the effective collision frequency is given by

$$\nu(T(t))=[T(t)]^{(n-4)/2n}\nu' , \tag{4.22}$$

where ν' is a constant independent of the temperature and proportional to the density. Then, the BGK collision operator (4.21) also has the scaling property (4.9). The simplification afforded by Eq. (4.21) allows determination of the pressure tensor from an ordinary differential equation,[13] whose solution provides the shear-rate dependence of the shear viscosity. The corresponding result including the force, (4.1), required for constant temperature is straightforward to calculate. In that case, as ν is a constant, the BGK model is essentially the same for all n and, therefore, the dimensionless pressure tensor coincides with the one for Maxwell molecules ($n=4$). The differences between the shear viscosities with thermostat and without thermostat are illustrated in Fig. 1, for the case of hard spheres. At small shear rates it is possible to show that the transport coefficients of order $(a^*)^2$ (super-Burnett) differ by about 33%, while for asymptotically large shear rate the nonlinear shear viscosities differ by about 14%. These differences suggest that a detailed comparison of computer simulation results obtained using a thermostat with theoretical methods implying viscous heating could be misleading.

V. DISCUSSION

The calculations presented in the last two sections show that several of the assumptions implicit in some methods for nonequilibrium computer simulations can be related to, and studied by, kinetic theory. To put these results in proper context and summarize, several comments are offered.

(1) Although the Lees-Edwards and stochastic boundary conditions lead to the same velocity field in the bulk, they actually represent quite different macroscopic states for the system. It is possible to show from the kinetic theory, and from the computer simulations, that the temperature fields are different in the two cases. This can lead to complications in the comparison of transport properties calculated by the two methods. In the case of the stochastic boundary conditions, the nonlinear shear viscosity cannot be extracted directly from the pressure tensor until effects due to spatial gradients of the temperature are accounted for. In the Lees-Edwards case, the shear-rate dependence of the shear viscosity includes an undesired contribution from viscous heating. Neither of these complications is insurmountable, but both illustrate the need for analysis of computer simulation results beyond tabulation of the pressure tensor as a function of the shear rate.

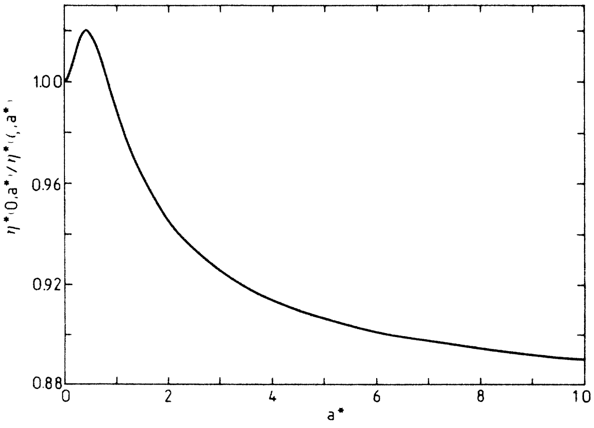

FIG. 1. Reduced shear viscosity without thermostat, $\eta^*(0,a^*)$, relative to the one with thermostat, $\eta^*(\zeta,a^*)$, as a function of the reduced shear rate, a^*, in the case of hard spheres.

(2) A second important difference between the stochastic and Lees-Edwards methods is the absence of a boundary layer for the latter. In practice, the transport properties obtained from stochastic boundary conditions are defined at finite Knudsen number, whereas no such effect is present using the Lees-Edwards method. This difference suggests that the two methods are complementary ways of studying a fluid with plane Couette flow. For example, if the primary interest is in transport coefficients, then the Lees-Edwards method has the advantage of efficiency (speed) and effectively zero Knudsen number (bulk limit). On the other hand, the stochastic boundary conditions simulate realistic wall effects such as boundary layers and transition region where hydrodynamics is inapplicable. A greater emphasis on these latter properties would appear warranted in the future.

(3) The non-Newtonian dynamics methods include a case, Eqs. (3.12), which has been interpreted here as simply Newton's equation in the noninertial Lagrangian frame of the macroscopic fluid, defined by the transformation, (3.5). This is the frame in which the Lees-Edwards conditions are formally the same as the usual periodic boundary conditions for equilibrium simulations. This form of dynamics is therefore identical to the Lees-Edwards method. More specifically, Newton's equations with the boundary conditions, (2.1), in the laboratory frame, are the same as Eqs. (3.12), with simple periodic boundary conditions in the local rest frame. This latter form of Newton's equations was introduced by Yamada and Kawasaki[15] in precisely this same spirit to simplify the statistical mechanics of shear flow, and has been used in virtually all subsequent theoretical treatments of this problem. Evans and Morriss[9] have recently emphasized this equivalence with equations independently suggested for computer simulations.

In contrast, the original "dolls tensor"[5] equations, (2.2), do not seem to have any simple interpretation or origin. Furthermore, it is possible to show that they predict viscometric functions of an opposite sign from those of Eqs. (3.12). Since nonlinear response theory agrees with the latter it must be assumed that the algorithm is inappropriate.[16]

(4) The results at the end of Sec. IV indicate that in general the relationship of transport properties obtained with and without thermostat forces is not simple. For the kinetic theory analysis given here these differences are due to a variation of the collision frequency due to viscous heating. In a dense fluid additional effects associated with a finite force range and correlation length complicate matters further. For example, the Boltzmann collision

operator is invariant under the local Galilean transformation (3.5) whereas more generally a dependence on $a\tau_c$ (τ_c = typical collision time) is expected. At high densities $a\tau_c \sim a/v$ and such effects could further invalidate any simple scaling relationships. However, the exact results obtained here for the low-density gas of Maxwell molecules provide some indication that such a relationship might be a reasonable approximation.

(5) Ladd and Hoover[8] have recently compared the Boltzmann equation for the dynamics (3.12), with the conventional Chapman-Enskog solutions. As expected from the interpretation here the two problems are the same. Evans and Morriss[9] have described a structurally simple formal solution to the Liouville equation using Yamada and Kawasaki's local velocity transformation [the second of Eqs. (3.5)]. However, neither of Refs. 8 and 9 explicitly includes the thermostat forces, (4.1), although both implicitly assume constant temperature. As a consequence Ladd and Hoover obtain a shear viscosity for hard spheres at constant temperature, and not the Zwanzig solution as claimed [compare Eqs. (22) of Ref. 8 with Eq. (43) of Ref. 13]. For similar reasons, the formal solution of Evans and Morriss yields the shear viscosity as a function of $T(0)$, rather than $T(t)$ as in the Chapman-Enskog method. Similar formal expressions for transport coefficients as a function of the initial time thermodynamical variables have been obtained by Visscher.[17] However, it is expected that expansions of such expressions in powers of the gradients have awkward secular terms not present in the Chapman-Enskog—type expansions.[18]

Finally, it is worth emphasizing that conclusions based on the kinetic theory of gases should not be extrapolated to more complex rheological fluids, without caution. As simulation techniques improve, it is expected that models of such fluids (e.g., polymers) will be simulated. The relationship of non-Newtonian properties calculated from both computer simulation and simple kinetic theories to those of real polymers is still quite uncertain.

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[1] See, for example, *Nonlinear Fluid Behavior*, edited by H. Hanley (North-Holland, Amsterdam, 1983); Phys. Today **37**, No. 1 (1983).

[2] Recent reviews with references are W. G. Hoover, Annu. Rev. Phys. Chem. **34**, 103 (1983); D. J. Evans and G. P. Morriss, Comput. Phys. Rep. **1**, 299 (1984).

[3] A. Lees and S. Edwards, J. Phys. C **5**, 1921 (1972).

[4] W. T. Ashurst and W. G. Hoover, Phys. Rev. A **11**, 658 (1975).

[5] W. G. Hoover, D. J. Evans, R. B. Hickman, A. J. C. Ladd, W. T. Ashurst, and B. Moran, Phys. Rev. A **22**, 1690 (1980).

[6] W. G. Hoover, A. J. C. Ladd, and B. Moran, Phys. Rev. Lett. **48**, 1818 (1982).

[7] C. Trozzi and G. Ciccotti, Phys. Rev. A **29**, 916 (1984).

[8] A. J. C. Ladd and W. G. Hoover, J. Stat. Phys. **38**, 973 (1985).

[9] D. J. Evans and G. P. Morriss, Phys. Rev. A **30**, 1528 (1984).

[10] A. Tenenbaum, G. Ciccotti, and R. Gallico, Phys. Rev. A **25**, 2778 (1982).

[11] C. Cercignani, in *Nonequilibrium Phenomena I*, edited by J. Lebowitz and E. Montroll (North-Holland, Amsterdam, 1983).

[12] E. Ikenberry and G. Truesdell, J. Rat. Mech. Anal. **5**, 55 (1956); M. C. Marchetti and J. W. Dufty, J. Stat. Phys. **32**, 255 (1983), Appendix A2.

[13] R. Zwanzig, J. Chem. Phys. **71**, 4416 (1979).

[14] R. Rodriguez, E. Salinas-Rodriguez, and J. W. Dufty, J. Stat. Phys. **32**, 279 (1983), Appendix A.

[15] T. Yamada and K. Kawasaki, Prog. Theor. Phys. **38**, 1031 (1967); see particularly Appendix B [actually, only the velocity transformation in Eq. (3.5) was used].

[16] It is perhaps worth pointing out a flaw in the derivation of the Eqs. (2.2) from a Hamiltonian (Ref. 5),

$$H = H_0 + \sum_{\alpha=1}^{N} m a_{ij} \tilde{v}_{\alpha i} q_{\alpha j} ,$$

where H_0 is the usual Hamiltonian for the fluid except with $\mathbf{v}_\alpha$ replaced by $\tilde{\mathbf{v}}_\alpha$. Application of Hamilton's equations in these variables leads to Eqs. (2.2). However, the interpretation of the velocities as "peculiar" is inconsistent with the application of Hamilton's equations, since there exists no canonical transformation of $\mathbf{v}_\alpha \to \tilde{\mathbf{v}}_\alpha$ without a corresponding nontrivial change of the coordinates as well [see, for example, L. Pokrovsky and M. Sergeev, Physica (Utrecht) **70A**, 62 (1973)]. Consequently, the equations should be understood as a postulated pseudodynamics, without a simple relationship to a Hamiltonian formalism. In particular, it appears inappropriate to discuss Gibbs ensembles based on this Hamiltonian.

[17] W. M. Visscher, Phys. Rev. A **10**, 2461 (1974).

[18] This comment is readily verified using a simple BGK model as described at the end of Sec. IV.