Molecular simulation and continuum mechanics study of simple fluids in non-isothermal planar couette flows

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The behavior of simple fluids under shear is investigated using molecular dynamics simulations. The simulated system consists of a fluid confined between two atomistic walls which are moved in opposite directions. Two approaches for shear flow simulations are compared: in one case, the sheared fluid is not thermostatted and only the confining walls are maintained at a constant temperature, while in the other, a thermostat is employed to keep the entire mass of the sheared fluid at a constant temperature. In the first case the sheared fluid undergoes significant viscous heating at the shear rates investigated, consistent with experimental observations and with theoretical predictions. Most simulations to date, however, have used the second approach which is akin to studying a fluid with infinite thermal conductivity. It is shown here that results for transport coefficients are significantly affected by the thermostat; in fact, the transport properties of the fluid determined using the two methods exhibit a qualitatively different shear rate dependence. It is also shown that the temperature profiles observed in our simulations can be described by continuum mechanics, provided the temperature dependence of the viscosity and thermal conductivity is taken into account. © *1997 American Institute of Physics*. [S0021-9606(97)52831-5]

I. INTRODUCTION

Confined fluids display interesting physical behavior and are of practical importance. The equilibrium properties of thin films have been extensively studied via computer simulation[1–4] and our understanding of the static structure is quite advanced. In contrast, the study of fluids far from equilibrium is hampered by the lack of established, well-proven methods for theoretical analysis and simulations, and there are several puzzling experimental phenomena that are not understood. For example, recent surface forces apparatus measurements on confined, molecularly thin films[5,6] indicate that the viscosity of thin films can be as much as three orders of magnitude higher than the bulk value, and no explanation for this phenomenon is available. In this work we focus on the development of simulation algorithms and analysis techniques appropriate to simple confined fluids in shear flows.

In addition to fundamental issues concerning molecularly thin liquid films, engineering applications such as polymer processing and tribology also provide ample motivation for developing techniques for molecular-level investigation of the behavior of fluids undergoing shear. Such processes are generally modeled using macroscopic conservation equations, the solution of which requires specification of appropriate boundary conditions and numerical values for transport coefficients.[7] An ability to predict these boundary conditions, transport coefficients, and stress-strain relationships from molecular-level information would be helpful, particularly for polymer solutions and melts at high shear rates, where measurements are difficult. In this regard, it is interesting to note that the commonly employed no-slip (or stick) boundary condition has been called into question by recent theoretical and experimental studies.[8–10] Molecular simulations provide an ideal tool for investigating these issues, and for investigating the relevant structure-property relationships.

A number of molecular simulations of shear flow have appeared in the literature over the last few years.[11–20] These can be classified into two broad categories: homogeneous shear methods and boundary driven shear methods. Homogeneous shear methods[11] impart shear on a fluid by modifying the equations of motion and employing ''sliding brick'' periodic boundary conditions. These techniques are intended to simulate a small region in the bulk of a sheared fluid. Periodic boundary conditions are used in all three directions to model an infinite system. The results of homogeneous shear simulations are generally extrapolated to low shear to estimate zero shear rheological properties (e.g., shear viscosity). Most of the extrapolation schemes used for this purpose are based on phenomenological arguments and, unless the Newtonian plateau region of viscosity is captured within the shear rate range investigated in simulations, determination of zero shear viscosity from homogeneous shear simulations is questionable. Boundary driven shear methods impart shear on a fluid by the actual motion of confining walls, as is the case in rheometric experiments. Since a solid boundary is modeled explicitly, such methods are of more relevance for our studies of boundary conditions. On the other hand, the boundaries do impart structure in the sheared fluid and estimating bulk properties from such simulations can be delicate.

For both homogeneous shear methods and boundary driven shear methods, most simulations of shear flow reported in literature to date have been carried out by thermostatting the sheared fluid to maintain its entire mass at a constant temperature. These simulations therefore correspond to a fluid with infinite thermal conductivity. This unphysical aspect of these simulations has been pointed out previously in the literature, most recently by Liem *et al.*[21] and by Padilla and Toxvaerd.[22] These authors showed that[22] at a shear rate of $\dot{\gamma}=0.5$ (in standard Lennard-Jones reduced units), which falls well within the shear rate range commonly investigated in simulations, the rate of heat removal by the thermostat is larger than the rate of heat conduction across the fluid. In this paper we quantify the viscous heating effects and we show that they can be important for shear rates as low as $\dot{\gamma}=0.2$, causing a measurable temperature rise in the sheared fluid. We also take the additional step of correlating these effects using continuum mechanics. We show that a continuum mechanics analysis can be used to extract the relevant transport coefficients (e.g., viscosity and thermal conductivity) even from these non-isothermal simulations. Further, the analysis presented here can also be used to find an upper limit to the shear rates that can be investigated by more traditional, thermostatted simulations. It must be pointed out that the main reason for observing viscous heating effects in simulations is the use of very high shear rates, necessary to obtain a high signal to noise ratio. It thus might be argued that these viscous heating effects observed in simulations are unphysical. Indeed, although viscous heating effects are not observed in experiments on simple fluids, they are routinely observed in both rheometric experiments and industrial processing operations for polymeric systems. A vast amount of literature exists[7,23,24] dealing with viscous heating effects in polymer processing operations and the continuum mechanics analysis used in this work is based on those ideas. Furthermore, although the enormously high shear rates used in simulations are inaccessible to experiments as yet, they are comparable to the actual shear rates encountered in high performance lubrication applications such as rocket engines and computer disk drives.

It is thus apparent that two important issues about nonequilibrium simulations must be addressed at the outset. The first issue is that of developing suitable algorithms and techniques applicable to real systems. The second issue is that of developing a methodology for bridging the gap between molecular simulations and continuum mechanics. We present an analysis which combines both the ''molecular'' and ''macroscopic'' approaches by directly simulating a system that closely resembles an experimental device for shearing confined fluids, and by providing a quantitative continuum mechanics analysis of our results. For simplicity, in this initial study, we have chosen to work with simple monomeric fluids interacting via purely repulsive Lennard-Jones interactions.

For boundary driven shear methods, a number of different models for the moving walls have been used in the literature. In one of the first molecular simulation investigations of shear flow, Ashurst and Hoover[12] devised artificial fluid walls to impart shear on the fluid. As a result, surface effects such as inhomogeneous density profiles were absent from their work. For systems as small as 108 particles, their results showed that a linear velocity profile is developed in Couette flow simulations. For soft-sphere and Lennard-Jones systems they observed non-Newtonian (shear thinning) fluid behavior. Similar walls were also used by Bitsanis *et al.*[14,15] in their simulations of Lennard-Jones fluids. They showed that for fluid films six molecular diameters thick, the flow properties could be explained by continuum mechanics if the viscosity was allowed to vary locally in the context of their local average density model (LADM) for transport coefficients.[14] However, for fluid films thinner than four molecular diameters, LADM was unable to capture the dramatic increase in viscosity observed in experiments. Their results demonstrated the importance of fluid layering normal to the walls on the flow behavior of confined fluids.

Trozzi and Ciccotti[13] used stochastic, structureless walls to simulate Couette flow. In their simulations, when a fluid particle reached the stochastic wall, it was reintroduced into the system at the same location but with a different velocity. The new velocity components of the particle in directions parallel to the wall were sampled from a Maxwellian distribution at the wall temperature, in a manner that ensured that the mean flow direction velocity was the same as the wall velocity and the mean velocity in the other direction parallel to the wall was zero. They observed significant slip and temperature drop at the walls, at conditions corresponding to the triple point of a Lennard-Jones fluid. For a system consisting of a fluid confined between stochastic walls separated by 12 molecular diameters, they showed that the velocity profile across the sheared fluid was linear and the temperature profile was parabolic, as predicted by continuum mechanics.

Atomistic walls are more realistic than the surfaces described above. Koplik *et al.*[16] found that the velocity profiles in molecular dynamics simulations of Poiseuille and Couette flow of Lennard-Jones fluids were similar to those predicted by continuum mechanics, even when the walls were atomistic (their wall atoms did not move during the simulation). Later, working with pseudo-crystalline solid walls, Thompson and Robbins[17] showed that for Lennard-Jones fluids, the wall-induced structure in the direction parallel to the walls did play an important role in determining the flow boundary conditions. In addition to the boundary conditions, Thompson *et al.*[18,19] also studied the shear response of confined fluids with simulations in which the component of the stress tensor normal to the walls was held fixed. Most of their results were for simple fluids, polymer chains composed of six beads, and for film thicknesses smaller than three sphere diameters. They found that, for these small film thicknesses, spherical molecules crystallize and short chain molecules enter a glassy state. Using pseudo-crystalline walls similar to those mentioned above,[17] Manias *et al.*[20] also simulated hexamers in a Couette flow in channels of about six atomic diameters. By varying the strength of wall-fluid interactions, they observed a variety of boundary conditions that ranged from no-slip, to slip at the wall-fluid interface, and to slip within the fluid. A strong correlation between velocity and density profiles was observed and slip was found to occur in low density areas and interfacial regions.

In the boundary driven shear simulations of Thompson, *et al.*,[19] Manias *et al.*,[20] as well as in all homogeneous shear simulations,[11] a thermostatting mechanism was used to impose a constant temperature across the entire fluid film; the heat generated in the fluid by ''viscous heating'' was thus removed instantaneously. Such a feat cannot be realized experimentally, and it is therefore of interest to examine to what extent the results of isothermal simulations would deviate from reality. (As a caveat, note that simulations are generally performed at shear rates higher than those accessible by conventional experiments.) These viscous heating effects have been pointed out previously in the literature;[21,22] here we take the additional step of quantifying them in terms of continuum mechanics in order to assess their effect on the simulated values of transport coefficients.

In this work, we report simulations of confined simple fluids under shear. We compare shear flow simulations carried out without thermostatting the sheared fluid with those that employ a thermostat to maintain the sheared fluid at a constant temperature. We find that imposing a constant fluid temperature across the film can lead to rather different results for the transport properties than those obtained when only the walls are maintained at a constant temperature. We use continuum mechanics to analyze our simulation data and show that it is possible to obtain quantitative estimates for the transport coefficients required by continuum models.

The rest of this paper is organized as follows: In section II we describe our simulation approach. In section III we present results for density, velocity and temperature profiles for simple fluids, we compare the shear rate dependence of viscosity obtained by using the two different approaches for shear flow simulations regarding the use of thermostat. We conduct a series of calculations at conditions of constant normal load, and we analyze the flow behavior using continuum mechanics. In section IV we present a summary of our results and several concluding remarks.

II. SIMULATION METHOD

There are two types of atoms in the simulations: those comprising the walls and those comprising the fluid. All atoms have the same mass, m, and interact with each other via a spherically symmetric, pairwise additive, purely repulsive potential, ϕ, given by

$$\phi(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}+\frac{1}{4}\right]\theta(r_c-r), \tag{1}$$

where $r_c=2^{1/6}\sigma$. The potential parameters σ and ϵ are taken as units of length and energy. We employ reduced units for time and temperature given by $\tau=(m\sigma^2/\epsilon)^{1/2}$ and ϵ/k_B, respectively, where k_B is Boltzmann's constant.

The simulation cell consists of the fluid confined between two atomistic walls at a separation H and parallel to the xy plane in Cartesian coordinates. Periodic boundary conditions are employed in the directions parallel to the walls. The walls consist of a single layer of atoms attached to FCC lattice sites by stiff harmonic springs.[25] The walls are characterized by two parameters: the spacing between atoms and the force constant of the springs. A value of 1.3 is used for the former; the nearest neighbor distance between wall atoms is 0.92. A value of 500 in dimensionless units is used for the latter; this ensures that the mean square displacement of wall atoms is below the Lindemann criterion for melting at the temperature of our simulations.[17] No fluid atoms ever leak through the walls during the course of a simulation. Shear is imparted by moving the lattice sites to which the wall atoms are attached at constant speed and in opposite directions.

Different methods are used to calculate the trajectories of the atoms depending on whether the atoms are coupled to a heat bath or not. If the atoms are not coupled to a heat bath, the trajectories are calculated using a velocity Verlet algorithm. If the atoms are coupled to a heat bath, the trajectories are calculated using a Verlet-type algorithm for Brownian dynamics.[26] The following equations are then used to calculate the particle trajectories:

$$\mathbf{r}(t+\delta t)=\mathbf{r}(t)+c_1\delta t\mathbf{v}(t)+c_2\delta t^2\mathbf{a}(t)+\delta\mathbf{r}^G, \tag{2}$$

$$\mathbf{v}(t+\delta t)=c_0\mathbf{v}(t)+(c_1-c_2)\delta t\mathbf{a}(t)+c_2\delta t\mathbf{a}(t+\delta t)+\delta\mathbf{v}^G. \tag{3}$$

The numerical coefficients c_0, c_1, c_2, and the correlated random components $\delta\mathbf{r}^G$ and $\delta\mathbf{v}^G$ are evaluated using the prescription given by Allen and Tildesley.[26] In most of our simulations, the sheared fluid is not thermostatted and only the confining walls are maintained at a specified temperature by coupling the motion of their atoms to a heat bath.[18] In order to investigate the effects of thermostatting on the viscosity of the fluid, a set of simulations was also performed by using a thermostatting scheme reported in literature[17,19] where, in addition to the walls, the fluid is also kept at a constant temperature by coupling the y component of the equation of motion of its atoms to a heat bath maintained at the desired temperature. (Note that we do not advocate the use of this particular type of thermostat; we only use it to compare our results to those published in the literature.) This is achieved by adding Langevin noise and frictional terms to the equation of motion in the y direction:

$$m\ddot{y}=-\frac{\delta}{\delta y}(U)-m\Gamma\dot{y}+W, \tag{4}$$

where Γ is the friction coefficient and W is the Gaussian random force. The variance of W is related to Γ by the fluctuation dissipation theorem:

$$\langle W(t)W(t')\rangle=2mk_BT\Gamma\delta(t-t'). \tag{5}$$

The equation of motion in the y direction is then integrated using the Verlet-type algorithm described above for the wall atoms. All trajectories are calculated with a time step of 0.002 τ. A value of 4.0 in reduced units was used for the friction coefficient in all cases.

Simulations are started from an ordered fluid structure. Initial velocities of fluid atoms are sampled from a uniform distribution corresponding to the wall temperature. Most simulation runs consist of an equilibration stage of at least 300 000 time steps followed by a production run of 700 000 time steps. The initial ordered structure disappears during the equilibration period, and the properties of the system are confirmed to be time independent before the production run is initiated. All the profiles reported are calculated by block averaging over blocks of 50 000 time steps each, with averages within each block determined by sampling every 20 time steps. Quantities in the z-direction are determined by averaging over bins of size = 0.5 σ.

Calculation of the temperature requires knowledge of the local streaming velocity. The latter quantity is determined by two methods: an average over the previous 20 time steps, and an average over a block of the first 50 000 steps immediately following equilibration. The temperature profiles obtained using the two averaging procedures are indistinguishable. The viscosity is determined by measuring the wall shear stress and dividing it by the imposed shear rate. An alternate approach would be to determine the off-diagonal components of the stress tensor τ_{zx}, but large statistical uncertainties make this impractical. (It is perfectly acceptable to measure the stress at the walls since, in the absence of secondary flows, the condition of mechanical equilibrium requires that the shear stress be constant at all z locations.)

The systems investigated in this work consist of 1552 fluid atoms and 256 wall atoms. Unless specified otherwise, results are presented for the following simulation conditions: H = 18 σ, $T_{\text{wall}} = 2.0$ and $\rho = 0.844$, where H is the distance between the two walls and ρ is the number density. All quantities are given in Lennard-Jones reduced units.

For completeness, viscosity and thermal conductivity are also determined for bulk fluids from equilibrium simulations. These simulations are carried out in the microcanonical (NVE) ensemble. The simulated cell is a cube of edge length 10 σ, with the number of atoms adjusted so that the average density is the same as in the corresponding non-equilibrium simulations. Periodic boundary conditions are employed in all three directions. Each simulation consists of an equilibration stage of 150 000 time steps, followed by a production stage of at least 250 000 steps. For the first 125 000 steps of the equilibration period, the velocities of all the particles are re-scaled every twentieth time step to maintain the desired temperature. The temperature during production run remains constant at the desired value (within the statistical uncertainty of the simulations). Values of stress and energy fluxes are recorded every fifth time step during production runs. The viscosity, μ, is then calculated according to:[27]

$$\mu = \frac{V}{10 k_B T} \int_0^\infty \langle \mathbf{P}(t) \mathbf{:} \mathbf{P}(0) \rangle dt, \tag{6}$$

where $\mathbf{P}(t)$ is the traceless symmetric part of the pressure tensor at time t, V is the volume, and T is the temperature. The thermal conductivity, k, is obtained from[28]

$$k = \frac{1}{V k_B T^2} \int_0^\infty \langle \mathbf{J}^z(t) \mathbf{J}^z(0) \rangle dt, \tag{7}$$

where $\mathbf{J}^z$ is the z component of the energy flux. A simple arithmetic average of autocorrelation functions for the energy fluxes in the three directions is used for the calculation of thermal conductivity. It is well known that due to problems such as long time tails in the autocorrelation functions, the values of transport coefficients calculated using the Green-Kubo methods exhibit a notoriously high degree of uncertainty. In this work, such calculations are performed only as an independent check for the values extracted by continuum mechanics; we did not use any sophisticated techniques for accurate determination of these coefficients from Green-Kubo methods. Five independent equilibrium runs were performed at each temperature. For each run, it was confirmed that the autocorrelation functions show a rapid initial decay and assume a value of zero for the first time around 0.6τ, after which their value fluctuates around zero. The transport coefficient calculated by numerical integration of the autocorrelation function will depend on the upper limit chosen for the time integral; we calculated an average value for each run by choosing 31 upper time limits spaced equally between reduced times of 3τ and 6τ. Finally, an average transport coefficient for the given temperature was evaluated by averaging over the values for the five independent runs.

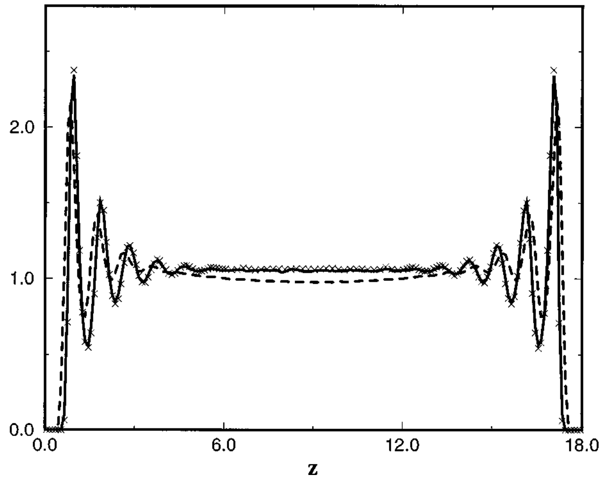

FIG. 1. Density profiles for H = 18.0 σ, $T_{\text{wall}} = 2.0$, $\rho = 0.844$ and $\dot{\gamma} = 0.0$ (crosses), $\dot{\gamma} = 0.2$ (line), and $\dot{\gamma} = 1.0$ (dashed line).

III. RESULTS AND DISCUSSION

A. Density, velocity and temperature profiles

Figure 1 shows the density profile in the direction normal to the walls divided by the average density in the simulation cell. The density profiles exhibit two distinct regions: an interfacial region near the walls and a bulk-like region of uniform density in the central region. In the interfacial re-

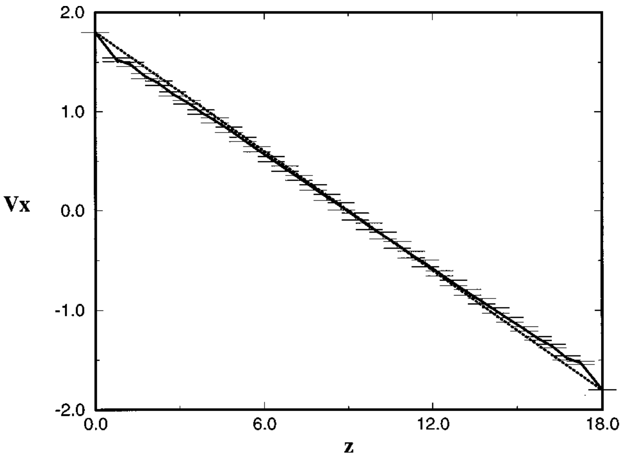

FIG. 2. Velocity profile for H = 18 σ, $T_{\text{wall}} = 2.0$, $\rho = 0.844$, and $\dot{\gamma} = 0.2$. The profile shown by dotted lines is continuum mechanics prediction obtained by assuming no-slip boundary condition. Horizontal lines are error bars.

gion, the fluid exhibits strong layering against the walls; at least four well defined layers are observed. The oscillations in the density profile die out at a distance of about 4-5 σ from either wall. Figure 1 shows that the density profile at a shear rate of 0.2 is virtually identical to that observed at equilibrium (no flow). However, the density profile at a shear rate of 1.0 exhibits a depletion of fluid particles in the central region of the channel. As discussed below, we attribute this behavior to a significant increase in the temperature of the sheared fluid in such a region.

For an isothermal system, continuum mechanics predicts a linear velocity profile throughout the cell when there is no slip at the wall. Figure 2 compares the actual velocity profile of the fluid at a shear rate of $\dot{\gamma} = 0.2$ with the continuum mechanics prediction. The actual velocity profile in the system is almost linear and very similar to that predicted by continuum mechanics. There is a slight discontinuity at either wall, which indicates a slight tendency for slip in these systems. Such slip is, however, negligible compared to what is observed in polymer melts at comparable shear rates.[29] It is also important to note that even in the absence of attractive interactions a no-slip behavior persists up to shear rates that are significantly higher than those typically measured in experiments.

At the shear rates generally employed in molecular simulations, a sheared fluid undergoes significant viscous heating. Figures 3a and 3b show the temperature profiles of the sheared fluid at various shear rates ranging from $\dot{\gamma} = 0.1$ to 1.0. Figure 3a shows that a substantial temperature increase is already seen at shear rates of $\dot{\gamma} = 0.1$ and 0.2; these shear rates are in the middle of the spectrum of shear rates used in simulations. At higher shear rates, e.g. $\dot{\gamma} = 0.7$ and 1.0, there is a pronounced increase in the temperature of the sheared fluid (Figure 3b). The shapes of the temperature profiles observed in simulations are approximately parabolic; they are not completely parabolic because of the temperature dependence of viscosity and thermal conductivity. Such departures from a parabolic profile have been observed previously by Liem *et al.*[21] In the following sections, we show that it is possible to quantitatively predict flow behavior in molecularly thin films using continuum mechanics, provided the temperature dependence of viscosity and thermal conductivity is taken into account.

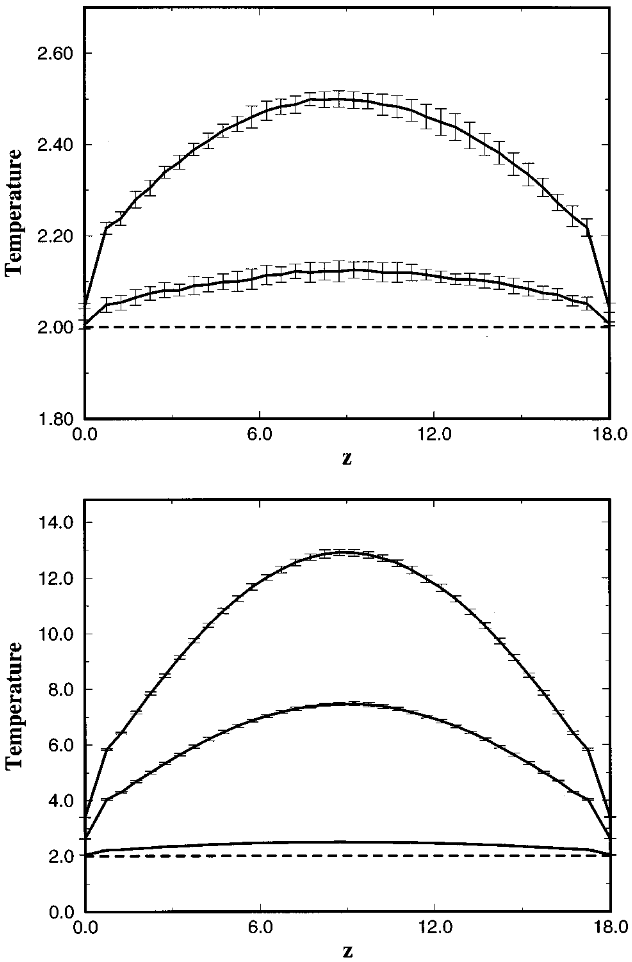

FIG. 3. Temperature profiles for H = 18.0 σ, $T_{\text{wall}} = 2.0$, $\rho = 0.844$ and (a) from top to bottom: $\dot{\gamma} = 0.2$, $\dot{\gamma} = 0.1$; (b) from top to bottom: $\dot{\gamma} = 1.0$, $\dot{\gamma} = 0.7$, $\dot{\gamma} = 0.2$. Dotted line shows the wall temperature in both figures.

B. Shear rate dependence of viscosity

Shearing the fluid imparts considerable energy to the system. In an actual laboratory experiment, the viscous heat generated in the system is conducted to confining walls which are in contact with the surroundings. This process is closely mimicked by our simulation approach, where only the walls are maintained at a constant temperature and the sheared fluid is not thermostatted. Previous simulation studies reported in the literature have often constrained the entire mass of the sheared fluid to remain at a constant temperature. This has been achieved either by using a Gaussian thermostat,[11] or by coupling one of the components of the equations of motion (the component perpendicular to the shear plane) to a heat bath,[17,19] or by re-scaling the velocities of fluid atoms.[20,30] To quantify the effects of using

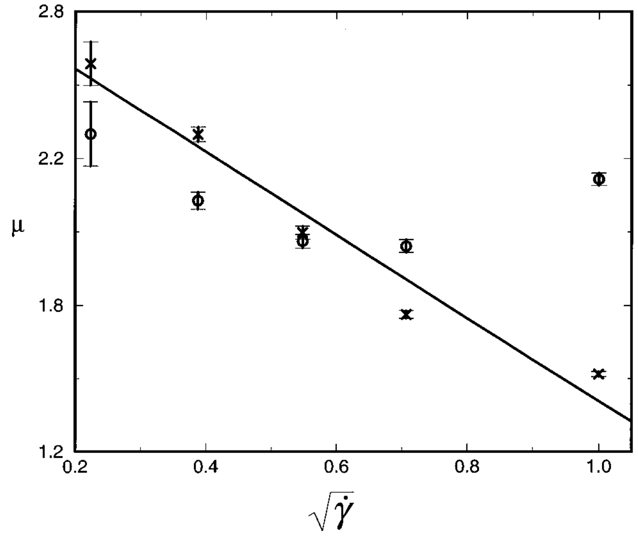

FIG. 4. Viscosity as a function of square root of shear rate for $\rho=0.844$. The crosses show results obtained with the fluid temperature maintained at $T_{\rm fluid}=0.722$, a linear fit to these results is also shown. The circles denote results obtained with only the walls maintained at $T_{\rm wall}=0.722$.

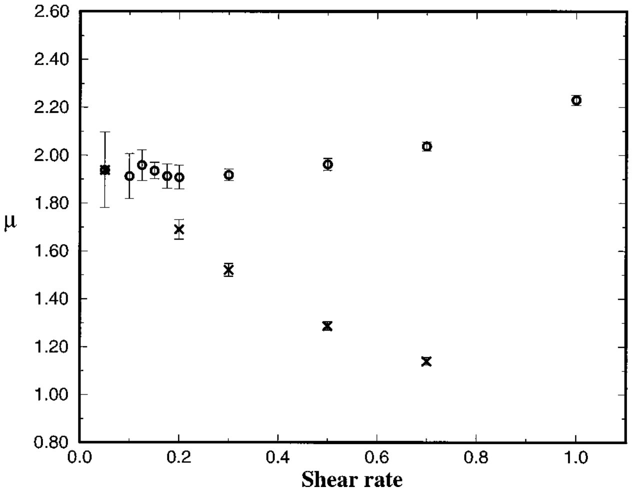

FIG. 5. Shear rate dependence of viscosity with only the walls maintained at $T_{\rm wall}$ = 2.0 for H = 18.0 σ. Circles are for $\rho=0.844$ and crosses are for $P_{zz}=13.0(\pm 0.05)$.

a thermostat on the flow behavior, we compare the viscosity of the fluid obtained using simulations that thermostat the sheared fluid with those that do not employ a thermostat. For this purpose, following Thompson *et al.*,[17,19] we carried out a set of simulations in which the fluid was thermostatted by coupling its y component of the equation of motion to a heat bath maintained at a specified temperature. As mentioned earlier, we do not advocate the use of this procedure, but we merely use it to compare the results obtained by different temperature control schemes. The simulation conditions are: $\rho=0.844$ and $T_{\rm wall}=0.722$ for the case where thermostat is not used, and $\rho=0.844$ and $T_{\rm fluid}=0.722$ for the case in which the fluid is thermostatted. These conditions are identical to those used by Evans *et al.*[11] in their homogeneous shear simulations, in which they showed that viscosity is proportional to the square root of the shear rate.

Figure 4 depicts results for viscosity as a function of the square root of shear rate for these two simulation techniques. For the case where the entire fluid is maintained at a constant temperature (y-rescaling), viscosity values are within 15% of those reported by Evans *et al.*[11] This agreement is encouraging, considering that Evans *et al.*[11] used a different thermostat (Gaussian) and that the viscosity values measured in our work exhibit a weak dependence on the characteristics of the wall. Figure 4 also shows that at low shear rates the viscosity values obtained by constant wall temperature simulations are within 10% of those obtained from constant fluid temperature studies. At high shear rates, however, viscous heating becomes significant and these two approaches lead to a markedly different behavior. The non-isothermal shear rate dependence of viscosity is actually opposite to that observed in isothermal calculations.

Figure 5 shows the shear rate dependence of viscosity obtained using our simulation approach, where a thermostat is not used and only the walls are maintained at a constant temperature ($T_{\rm wall}=2$). At low shear rates ($\dot{\gamma}$ less than 0.3), the fluid is Newtonian and its viscosity remains constant. At higher shear rates, viscosity increases with shear rate. We attribute the observed shear thickening behavior to the isochoric increase in temperature and hence pressure in the system.

In order to characterize the separate effects of temperature and pressure on the viscosity, we carry out a series of shear flow simulations where the average of the component of the stress tensor normal to the walls, $\langle P_{zz}\rangle$, is held constant. This is achieved by adjusting the number density until $\langle P_{zz}\rangle$ is equal to the desired value at the given temperature; for these simulations $\langle P_{zz}\rangle = 13.0(\pm 0.05)$, which is the value measured in simulations at $\dot{\gamma} = 0.05$ and $\rho = 0.844$. (For these constant normal load simulations, we choose to adjust the number of atoms rather than the distance between the walls because the temperature profile is a strong function of wall separation.) The viscosities obtained from these simulations are also shown in Figure 5. Our results indicate that if the normal load on the walls is kept constant, the fluid exhibits shear thinning behavior, whereas if the average density is kept constant, the fluid exhibits shear thickening behavior. These observations are consistent with results of homogeneous shear non-equilibrium molecular dynamics (NEMD) methods.

The results of Figures 4 and 5 demonstrate that the shear rate dependence of viscosity determined by molecular simulations is highly sensitive to the simulation technique used. As opposed to equilibrium systems, where only pressure, density and temperature are sufficient to specify the state of the system, a number of additional variables are necessary to characterize the non-equilibrium shear flow behavior of confined fluids: shear rate, temperature of the confining walls, thickness of the fluid film (which affects the temperature profile in the sheared fluid), and the various components of the pressure tensor. Of the different approaches compared in this work, we believe that simulations where the walls were held at a constant temperature (and in some cases where a constant normal load is applied) resemble more closely a real experimental situation than calculations where the entire mass of sheared fluid is maintained at a constant temperature.

C. Connection with continuum mechanics

In the previous section we observed that the fluid velocity profiles are roughly linear and that the temperature profiles are roughly parabolic. This is similar to continuum mechanics predictions for planar Couette flow under the assumption of constant viscosity and thermal conductivity. In fact, Holian *et al.*[31] have previously shown that the structure of a strong shockwave (density, stress, energy and temperature profiles) in a Lennard-Jones fluid obtained by molecular simulations can be described by continuum mechanics to within 30%, provided the state dependence of transport coefficients is taken into account. We follow a similar approach and show that, provided the temperature dependence of viscosity and thermal conductivity is accounted for, it is possible to use continuum mechanics to arrive at a quantitative description of the flow behavior for a non-isothermal planar Couette flow.

We use perturbation theory to incorporate the temperature dependence of transport coefficients into a continuum mechanics description of the fluid.[7] An expression can be derived for the temperature profile of the sheared fluid in terms of three parameters: the ratio of viscosity and thermal conductivity μ_0/k_0 (evaluated at the wall temperature), and two parameters α_1 and β_1 defined by:

$$k/k_0 = 1 + \alpha_1 \theta, \tag{8}$$

$$\mu_0/\mu = 1 + \beta_1 \theta, \tag{9}$$

where θ is a dimensionless temperature difference given by $\theta = (T - T_{\mathrm{wall}})/T_{\mathrm{wall}}$. For a fluid film of thickness H, simultaneous solution of the momentum and energy balance equations yields the following expression for the temperature profile:

$$\theta = \frac{B}{2}(\zeta - \zeta^2) - \frac{B^2 \alpha_1}{8}(\zeta^2 - 2\zeta^3 + \zeta^4) - \frac{B^2 \beta_1}{24}(\zeta - 2\zeta^2 + 2\zeta^3 - \zeta^4), \tag{10}$$

where the reduced position is defined by $\zeta = z/H$, and B is a dimensionless constant given by: $B = 4\mu_0 U_{\mathrm{wall}}^2 / k_0 T_{\mathrm{wall}}$. Three adjustable parameters arise naturally in this problem; these are μ_0/k_0, α_1 and β_1.

The validity of this continuum mechanics solution at atomic length scales is determined by fitting simulated temperature profiles at five different shear rates: $\dot{\gamma}$ = 0.1, 0.125, 0.15, 0.175 and 0.2 to the above expression. Figure 6 shows the results of the fit and demonstrates that a single set of parameter values can fit the simulated profiles for these five different shear rates. The parameters derived from the fitting procedure have values: $\mu_0/k_0 = 0.3083$, $\alpha_1 = 2.936$ and $\beta_1 = -2.009$.

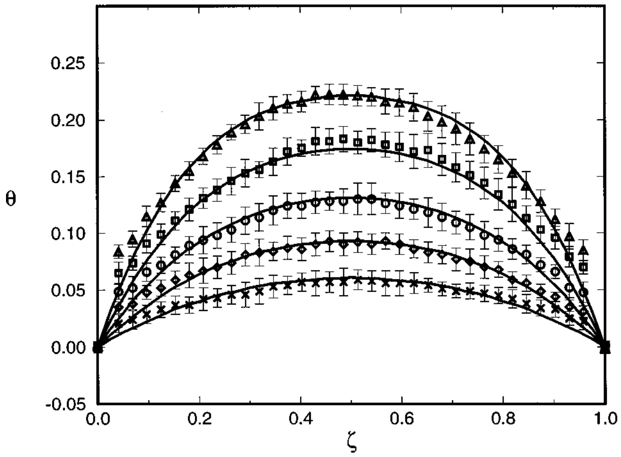

FIG. 6. Temperature profiles for H = 18.0 σ, $T_{\mathrm{wall}} = 2.0$ and ρ = 0.844. Profiles obtained by simulation are shown by points for $\dot{\gamma}$ = 0.1 (crosses), 0.125 (diamonds), 0.15 (circles), 0.175 (squares) and 0.2 (triangles). Continuum mechanics solution fit is shown by a line for each value of shear rate. Reduced temperature θ is defined by $\theta = (T - T_{\mathrm{wall}})/T_{\mathrm{wall}}$ and reduced distance ζ is defined by $\zeta = z/H$.

As an independent test of the above numbers, we use Green-Kubo formulas to determine viscosity and thermal conductivity from equilibrium simulations at three temperatures: T = 1.7, 2.0 and 2.15 (these temperatures bracket $T_{\mathrm{wall}} = 2.0$). These calculations provide a completely independent route for measuring the transport coefficients at zero shear. Results from these equilibrium calculations of zero-shear viscosity and thermal conductivity are shown in Table I. It is seen that the value of the ratio μ/k obtained from the equilibrium simulations via the Green-Kubo formulae is within 20% of the value of μ_0/k_0 obtained from the fit to the continuum mechanics solution. The agreement is particularly encouraging when one considers that the relative error bars on the numbers obtained from the equilibrium simulations are also of the order of 10–15%. Unfortunately, these error bars preclude a meaningful extraction of the parameters α_1 and β_1 from equilibrium simulations. There are two additional complications in a comparison between the transport properties obtained from equilibrium and non-equilibrium simulations. The first complication is that the former provides values of transport coefficients at zero shear, whereas the latter provides the values at non-zero shear rates. Some extrapolation scheme is required to estimate the limiting zero-shear values from non-equilibrium simulations. The second complication is that non-equilibrium simulations are

TABLE I. Viscosity and thermal conductivity from equilibrium simulations via the Green Kubo formulae. Error bars are the standard deviation about the mean of five independent simulations.

Temperature ($k_B T/\epsilon$)	Viscosity (μ)	Thermal conductivity (k)	μ/k
1.70	2.02±0.18	8.16±0.56	0.25±0.04
2.00	2.10±0.13	8.56±0.61	0.25±0.03
2.15	2.28±0.22	8.16±1.07	0.28±0.06

necessarily non-isoenergetic and non-isothermal (because of viscous heating) whereas equilibrium simulations are isoenergetic. As a result, the pressure of a sheared fluid is somewhat higher than that observed in equilibrium simulations at the same density and at a bulk temperature equal to T_{wall} for the sheared systems. These effects are small at the range of shear rate values (0.1–0.2) studied here, but some ambiguities are unavoidable.

IV. CONCLUSIONS

A molecular level approach has been presented for simulation of an experimental set-up for rheological measurements of thin films under shear. It has been shown that the density profiles in sheared fluids are in general the same as those observed at equilibrium. Only at very high shear rates do the shear profiles deviate from those at equilibrium, and this effect could be entirely due to a non-homogeneous temperature across the system. As predicted by continuum mechanics, at steady state the simulated velocity profiles are linear throughout the system. Compared to polymer chains, monomers exhibit hardly any tendency for slip at the fluid-wall interface.

It is shown that for the shear rates typically used in simulations, viscous heating effects are significant. As a result, simulated transport coefficients (e.g., viscosity and thermal conductivity) are sensitive to the use of thermostat in the simulations. We favor a simulation approach that does not thermostat the fluid but maintains only the confining walls of the system at a constant temperature thus allowing a flux of heat across the sheared fluid. This approach is consistent with experimental situations. Isothermal shear flow simulations that thermostat the sheared fluid could arguably be regarded as unphysical in the sense that the simulated fluid is implicitly assumed to have infinite thermal conductivity and therefore exhibits artificial dynamics.

In fact, actual experiments are carried out under the conditions of constant wall temperature, and sometimes constant normal load on the walls. Realistic simulations of experimental conditions could also allow the wall-to-wall distance to fluctuate during the course of a calculation. However, the temperature profile developed across the sheared fluid is a strong function of the wall-to-wall separation and would also fluctuate with variations in the fluid film thickness. Since one of the main objectives of this work was to describe these temperature profiles by using continuum mechanics, we have conducted simulations for constant wall-to-wall separation and have analyzed the results using continuum mechanics.

If the temperature dependence of viscosity and thermal conductivity is accounted for explicitly, it is possible to analyze the temperature profiles observed in thin film molecular simulations using continuum mechanics. We find that the continuum mechanics prediction for the ratio of viscosity and thermal conductivity is in quantitative agreement with an independent estimate obtained from equilibrium simulations using Green-Kubo formulas. The formalism presented here provides a means of obtaining meaningful values of transport coefficients from these non-isothermal, high shear rate flow simulations. We are currently using this formalism to investigate tribological properties of thin films of polymeric fluids as well as wall slip effects during polymer processing.

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