Molecular simulation and continuum mechanics investigation of viscoelastic properties of fluids confined to molecularly thin films

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A combination of molecular dynamics simulations of oscillatory shear flow and continuum mechanics is used to investigate viscoelastic properties of materials confined to molecularly thin films. The atoms of the simple liquid interact via a repulsive Lennard-Jones potential. The chain molecules are modeled as strings of similar spheres connected via finite extensible nonlinear elastic springs. The fluid is confined between two surfaces composed of identical spheres that are moved to simulate oscillatory flow. In order to mimic experiments, the temperature is controlled by coupling the wall atoms to a heat bath, and the viscoelastic properties are obtained via an analysis using continuum mechanics. Both simple and polymeric fluids exhibit linear viscoelastic behavior under typical simulation conditions, although inertial effects play an important role in determining the flow behavior. Simple fluids display a smooth transition from liquidlike to solidlike behavior when confined to molecularly thin films, whereas linear chain polymers and gels display predominantly elastic shear response at all frequencies investigated. These results are in qualitative agreement with the surface forces apparatus experiments on similar systems. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1361077]

I. INTRODUCTION

The rheology of fluids confined to molecularly thin films is important in many practical applications such as lubrication. Advances in experimental techniques, such as the use of the surface forces apparatus to study nonequilibrium behavior, has considerably increased the amount of experimental information on the rheology of fluids confined to thin films. These experiments are both sophisticated and difficult, and studies in different groups often yield contradictory results. For example, although there is a general agreement that the rheological properties of thin fluid films change from liquidlike to solidlike with increasing confinement, there is no consensus on whether this transition is continuous or abrupt. We are interested in studying these phenomena using molecular simulation in an effort to resolve some questions on simple model systems without some of the nagging problems (e.g., dirty samples) of experiments. With this motivation, we present a method for determination of viscoelastic properties of fluids confined to molecularly thin films. This study is a natural extension of our earlier work on planar shear systems where we used molecular dynamics simulations and continuum mechanics to obtain the steady shear properties of confined fluids.[1]

The experiments we are interested in mimicking are those performed using the surface forces apparatus. In these experiments two crossed cylinders, with the fluid contained between them, are placed at a separation of the order of nanometers and moved relative to each other to simulate either planar or oscillatory shear flow. The shear stress is thus measured as a function of the imposed nominal shear strain. In this work we will focus on experiments on octamethylcyclotetrasiloxane (OMCTS) and linear alkanes. OMCTS is a globular, nonpolar molecule and is expected to provide a good representation for typical Lennard-Jones fluids, while alkanes provide the smallest step towards investigating polymer melts.

The viscoelastic properties of OMCTS films confined between mica surfaces were investigated by Demirel and Granick.[2] In their experiments, shear displacement amplitude was restricted to less than 20% of the fluid film thickness (ensuring linear viscoelastic behavior), and the viscoelastic properties of the confined fluid were determined by monitoring the elastic and dissipative shear force. The elastic and viscous shear moduli, denoted G' and G'', respectively, were then obtained by fitting the measured shear stress to the continuum mechanics expression. (Actually Demirel and Granick did not measure G' and G'' but rather closely related quantities, but this distinction is not important to the present discussion.)

By studying the frequency dependence of G'' and G' as

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a function of film thickness, Demirel and Granick concluded that the change in fluid behavior due to confinement was similar to the glass transition in bulk liquids. They observed that in all cases the fluid response was liquidlike at lower frequencies and changed to more solidlike at higher frequencies. For each thickness, a characteristic relaxation time, τ_1, was defined as the reciprocal of the frequency for which $G'' \approx G'$. This relaxation time τ_1 changed continuously with confinement: It increased by about a factor of 3 when film thickness was reduced from 7σ to 4σ (σ is the diameter of the OMCTS molecule), and by about 2–3 orders of magnitude when the film thickness was reduced from 4σ to 2σ. The effect of confinement on the viscoelastic properties was also determined by measuring the values of the elastic spring constant G_c' at τ_1. Again G_c' was observed to change continuously with confinement: It increased by about a factor of 3 when the film thickness was decreased from 7σ to 4σ, and by about 1–2 orders of magnitude when the film thickness was decreased from 4σ to 2σ. Demirel and Granick reduced their data for G' and G'' at different film thicknesses to a single master curve using time-thickness superposition, in a manner similar to the time-temperature superposition used to analyze bulk liquids near the glass transition. The phenomenological similarity of the viscoelastic behavior of confined fluids to bulk glass transition was further demonstrated by showing that G'' could be calculated quantitatively from G' using the Kramers–Kronig relations. Based on this analysis, the authors concluded that the change in OMCTS from liquidlike to solidlike behavior upon confinement is a continuous process, and similar in spirit to the glass transition in bulk liquids.

Klein and Kumacheva[3,4] studied the same system as Demirel and Granick, i.e., OMCTS confined between mica surfaces, using the same technique, i.e., surface forces apparatus measurements, but arrived at a qualitatively different conclusion. Klein and Kumacheva found that for gap ticknesses down to 7σ, confined OMCTS films displayed liquidlike viscosity. However, when the film thickness was reduced by a single molecular spacing (i.e., to 6σ), OMCTS displayed a sudden, reversible transition to a solid. They obtained an estimate of the effective viscosity of the fluid film by monitoring the relaxation of the film following an applied shear stress, and showed that the effective viscosity increased by at least seven orders of magnitude when the OMCTS film thickness was decreased from 7σ to 6σ. These results are in stark contrast to those of Demirel and Granick and no explanation for the different conclusions from these two different groups is available.[5] This is both interesting and disturbing if we consider that there appear to be no significant differences either in the material samples or in the experimental techniques in these two measurements. In addition to OMCTS, Klein and Kumacheva[4] report similar confinement induced abrupt transition from fluidlike to solidlike behavior for cyclohexane and toluene as well.

Granick and co-workers have also investigated the viscoelastic properties of polymeric fluids.[6–8] The linear viscoelastic properties of atactic polyphenylmethylsiloxane (PPMS) were studied at strongly adsorbing (mica) as well as weakly adsorbing (mica coated with self-assembled mono-

layers of condensed octadecyltriethoxysilane) surfaces. (PPMS has a very low bulk glass transition temperature, $T_g = -20\,°\mathrm{C}$, and the bulk glass transition therefore does not interfere with experiments on confined systems.) For PPMS confined between strongly adsorbing surfaces, the following observations were made.[6,7] For film thicknesses larger than 7 R_g (where R_g is the radius of gyration), the polymer film exhibited behavior similar to bulk viscous flow, e.g., $G''(\omega)$ increased linearly with frequency ω. For film thicknesses smaller than $5–6R_g$, however, $G'(\omega)$ was always higher than $G''(\omega)$ over the entire frequency range. In addition, while $G'(\omega)$ showed a very little change with frequency, $G''(\omega)$ exhibited for various film thicknesses either a maximum, or a minimum, or both, over the frequency range studied in the experiments. Furthermore, the value of G' under these conditions was approximately $10^5 N/m^2$ which is a typical value for rubberlike elasticity. This transition from liquidlike to rubberlike behavior upon confinement is qualitatively very similar to what is observed for high molecular weight polymeric fluids at the transition between terminal and plateau zones, except that the polymer chains investigated in their work were too short to be entangled. Granick and co-workers therefore proposed that confinement enhances or induces entanglements in polymer melts. For films confined between weakly adsorbing surfaces no measurable response was observed until the PPMS film was squeezed to a thickness comparable to R_g. At this point, the shear response observed was qualitatively similar to that observed for PPMS sheared between mica surfaces at film thicknesses smaller than $5–6R_g$.

In our opinion, there are no satisfactory explanations for this behavior. Some information regarding the liquid structure in these confined fluids would be helpful but the films are so thin it is difficult to probe the liquid using, for example, x-ray diffraction. Computer simulation provides a complementary approach that allows a microscopic investigation of these systems, and is therefore of considerable interest. In some ways, this is a perfect problem for molecular simulation because the films are molecularly thin and therefore one has to use relatively small systems.

In this work we use computer simulation to study confined liquids undergoing oscillatory shear flow. The system consists of a fluid confined between atomistic surfaces one of which is moved sinusoidally to simulate oscillatory shear. We investigate three models of the fluid intended to mimic OMCTS, linear alkanes, and gels. In the first model the molecules interact via spherically symmetric repulsive Lennard-Jones potentials, in the second model the molecules are bead-spring chains composed of spheres that interact via the same potential as in the first model, and in the third model the chains are connected to form perfect gels. The wall atoms are connected by springs to rigid lattice points and interact via the same potential as the sites of the fluid. Energy is removed from the system by coupling the wall atoms to a heat bath. We monitor the wall shear stress and the instantaneous velocity profiles in the fluid and use a continuum mechanics analysis to extract the viscoelastic properties of the fluid, namely the loss and storage moduli of the fluid as a function of the frequency of the imposed strain. Although

our goal is to investigate model systems that resemble those studied experimentally, we would like to emphasize that we cannot really ''settle'' the controversy between Demirel and Granick work and Klein and Kumacheva work because our model systems are too simple to quantitatively describe the experiments. With this important caveat to our conclusions, our simulation results are completely consistent with what was seen in the experiments of Granick and co-workers (described above). In particular, in simple liquids we see a continuous change from liquidlike to solidlike behavior and in polymers we see that the fluid response is predominantly elastic at all frequencies.

Our simulation technique differs fundamentally from the previous homogeneous shear simulations of oscillatory shear flow of bulk fluids.[9–15] The methodology employed in these oscillatory shear simulations of bulk fluids assumes an instantaneous velocity profile throughout the entire mass of the sheared fluid which itself has an infinite extent due to the use of periodic boundary conditions. The present work, on the other hand, tries to represent the experimental situation (in surface forces apparatus measurements) more faithfully by explicitly accounting for the confining surfaces. Our work shows that both the inertial effects (shear wave propagation effects) and the shear wave attenuation effects play a significant role in determining the actual velocity profile of the sheared fluid at the conditions investigated. Furthermore we show that, as was the case for simple shear simulations, the simulated flow behavior of fluids undergoing oscillatory shear flow is also consistent with continuum mechanics predictions.

The rest of this paper is organized as follows: In Sec. II we describe our approach for calculation of viscoelastic properties using a combination of molecular dynamics simulations of oscillatory shear flow and continuum mechanics. In Sec. III we present results that illustrate linear viscoelastic response of the sheared fluid, the importance of inertial effects, and frequency and film thickness dependence of loss and storage moduli for simple fluids and chain molecules. In Sec. IV we present a summary of our results and offer several concluding remarks.

II. METHODS

We have previously used continuum mechanics to explain the velocity and temperature profiles, and viscosity of fluids undergoing simple shear flow in thin films. Here, that approach is extended to obtain the viscoelastic properties of fluids confined to molecularly thin films. We perform molecular dynamics simulations of fluids undergoing oscillatory shear flow and analyze the flow behavior using continuum mechanics to yield values for the loss and storage moduli. Our basic simulation model and method has been described in details previously[1,16] and only a brief description will be presented here.

A. Molecular model

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.

All atoms constituting the fluid and the wall 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 $\theta(r)$ is the Heaviside step function, and $r_c = 2^{1/6}\sigma$. 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. All other quantities are reported in reduced units obtained by appropriate combination of these quantities. Both simple fluids and chain molecules are investigated in this work. The polymer chains are modeled as bead spring chains having 10, 20, or 50 beads per chain. The springs are represented by a finitely extendable nonlinear elastic (FENE) potential:

$$\phi^{\text{FENE}}(r) = -\frac{\kappa Q^2}{2} \ln \left[1 - \left(\frac{r}{Q} \right)^2 \right], \tag{2}$$

where κ is the spring constant and Q is the maximum extension of the spring. We use values of $\kappa = 100$ and $Q = 1.5$, and the resulting bond length is approximately $0.9\,\sigma$. The model gel used in this work consisted of a regular network made up of tetravalent nodes connected by strands containing 10 beads each. The chain segments between two network nodes consisted of beads interacting via the same potentials (FENE springs and purely repulsive nonbonded interactions) as the constituent beads of the linear chains.

The walls consist of a single layer of atoms attached to FCC lattice sites by stiff harmonic springs.[17] The walls are characterized by two parameters: the spacing between atoms and the force constant of the springs. A value of 1.3 and 500 (in dimensionless units) are used for these two parameters. This ensures that the mean square displacement of wall atoms is below the Lindemann criterion for melting at the temperature of our simulations[18] and no fluid atoms ever leak through the walls during the course of a simulation.

B. Simulation details

Oscillatory shear flow is simulated by oscillating one wall sinusoidally with an amplitude A and frequency ω, while the other wall is held stationary. Different methods are used to calculate the trajectories of the atoms that constitute the walls (since they are coupled to a heat bath) and the atoms that constitute the fluid. The walls are held at a constant temperature by coupling the wall atoms to a heat bath maintained at the desired temperature. The trajectories of the wall atoms are then calculated using a Verlet-type algorithm for Brownian dynamics.[19] The trajectories of the fluid atoms are calculated using the standard velocity Verlet algorithm for molecular dynamics. At the amplitudes and frequencies employed in this work viscous heating effects are negligible and the temperature of the sheared fluid is the same as the wall temperature within statistical uncertainties.

For simple fluids an ordered structure is used as the initial configuration, while for polymeric fluids, initial configu-

rations are generated using a growth and equilibration algorithm.[20] 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 200 time periods of oscillation followed by a production run of at least 600 periods. Longer production runs (up to 1600 time periods) are used for the lower frequencies investigated. It is also confirmed that runs carried out with production runs of 600 time periods yield the same values of moduli as those with 1600 periods in the production run. All the profiles reported are calculated by block averaging over blocks composed of 40 to 160 time periods each. The frequency at which the properties are sampled within each block varies from 15 to 50 time steps. The time step used in the simulation is also varied with frequency and is in the range $(2\pi/3072)\tau$ to $(2\pi/2048)\tau$ with most of the simulations carried out with a time step of $(2\pi/3072)\tau$. Spatial variation of fluid properties in the z direction is determined by computing profiles that were obtained by averaging over bins of size$=0.5\,\sigma$.

The simulation conditions are the same as those used in earlier simulations of planar flow of simple liquids[1] and polymers.[16] For simple fluids the walls are maintained at a reduced temperature $T_{\text{wall}}=2.0$ and the reduced number density of the fluid is $\rho=0.844$. For polymeric fluids, the walls are maintained at a reduced temperature $T_{\text{wall}}=4.0$ and the reduced bead number density of the fluid is $\rho=0.8$. The effect of confinement on fluid properites is investigated by carrying out the simulations at three different film thicknesses: $H=8\sigma$, $H=7\sigma$, and $H=6\sigma$.

C. Continuum mechanics analysis

We have previously shown that for steady shear flows such as the planar Couette flow, the velocity and temperature profiles obtained in molecular dynamics simulations can be analyzed using the macroscopic momentum and energy balance equations to yield values of viscosity and thermal conductivity. This approach is extended here to obtain the linear viscoelastic constants, namely the loss and storage moduli of the confined fluids undergoing oscillatory shear flow. Our approach is to monitor the wall shear stress τ_{wall} profiles as a function of time in the simulations, and then fit these to the continuum mechanics expression for τ_{wall} in order to obtain values of G' and G''. This procedure is briefly described below.

The linear viscoelastic constants G' (storage modulus) and G'' (loss modulus) are defined implicitly in terms of the shear stress tensor component τ_{zx}, using

$$\tau_{zx} = -G'(\omega)\gamma_0 \sin(\omega t) - G''(\omega)\gamma_0 \cos(\omega t), \tag{3}$$

where $\gamma_0 = A/H$ is the shear strain amplitude. Note that τ_{zx} can also be equivalently expressed as a function of shear rate using

$$\tau_{zx} = -\eta'(\omega)\dot{\gamma}_0 \cos(\omega t) - \eta''(\omega)\dot{\gamma}_0 \sin(\omega t), \tag{4}$$

where $\dot{\gamma}_0 = A\omega/H$ is the shear rate amplitude. The coefficients in the two expressions are related by $G' = \eta''\omega$ and $G'' = \eta'\omega$.

At first glance it appears that a straightforward way to calculate G' and G'' would be to measure the in phase and out of phase components of the wall shear stress over the oscillation time period and then divide these by the strain amplitude to obtain the values of G' and G''.[21] However, such an approach places severe restrictions on the oscillation frequency ranges that can be studied in simulations, and is appropriate only in the limit of very small film thicknesses, i.e., H much smaller than the wavelength λ of the shear wave (see below), when the instantaneous velocity profiles across the fluid are linear and the shear rate is independent of position. For typical simulation conditions this limit is rarely achieved because instantaneous velocity profiles in the fluid are not linear as a result of inertial (or, alternatively, shear wave propogation) effects. The importance of these shear wave propogation effects on the experimental determination of dynamic rheological properties has been pointed out in the literature.[22–25] Using the theory of waves, Schrag and co-workers[23–25] have presented expressions for the velocity and shear rate profiles (as functions of time and position) in the fluid when these inertial effects play an important role. Here we present a brief outline of an alternate derivation of these expressions starting from the equation of motion of the fluid.

In development below we use stick boundary conditions, i.e., the velocity of the fluid at the surface is the same as the velocity of the surface itself. This boundary condition is not expected to be generally valid and merits some discussion. In our studies of simple liquids and polymers in planar shear flow[1,16] we found that the stick boundary condition was very accurate for fluids composed of spherical molecules at all shear rates, and for polymeric fluids at low shear rates. In this work, the simulations demonstrate that stick boundary conditions are very accurate for all the cases investigated. This is because the frequencies of the oscillatory shear are very low.

The mathematical treatment is facilitated by the use of complex notation.[26] The shear strain, γ_{zx}, and the shear rate, $\dot{\gamma}_{zx}$ are then defined by

$$\gamma_{zx}(0,t) = -\gamma_0 \,\mathrm{Re}\{ie^{i\omega t}\}, \tag{5}$$

$$\dot{\gamma}_{zx}(t) = \dot{\gamma}_0 \,\mathrm{Re}\{ie^{i\omega t}\}, \tag{6}$$

where γ_0 and $\dot{\gamma}_0$ are real numbers. If the material exhibits linear viscoelastic behavior, then the shear stress can be expressed as

$$\tau_{zx} = \mathrm{Re}\{\tau_{zx}^0 e^{i\omega t}\}, \tag{7}$$

where τ_{zx}^0 is a complex number given by

$$\tau_{zx}^0 = iG^* \gamma_0 = -\eta^* \dot{\gamma}_0, \tag{8}$$

and the complex modulus, G^*, and the complex viscosity, η^* are defined by

$$G^* = G' + iG'', \tag{9}$$

$$\eta^* = \eta' - i\eta''. \tag{10}$$

We now return to our original task of obtaining expressions for velocity, shear rate, and shear stress as functions of

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time and position. For the problem at hand, the only equation of motion of interest is the momentum balance equation in the x direction, and all quantities show spatial variation only along the z direction. The x direction momentum balance equation thus reduces to

$$\rho \frac{\partial V_x}{\partial t} = \eta^* \frac{\partial^2 V_x}{\partial z^2}, \tag{11}$$

where V_x is the x component of the velocity. The appropriate boundary conditions are

$$V_x = V_0 \cos(\omega t) \quad \text{for } z=0$$
$$= 0 \quad \text{for } z=H, \tag{12}$$

where $V_0 = A\omega$ is the velocity amplitude. With the substitution

$$V_x = \phi(z) e^{i\omega t}, \tag{13}$$

the differential equation may be written as

$$\frac{\partial^2 \phi}{\partial z^2} - \frac{i\omega\rho}{\eta^*} \phi = 0, \tag{14}$$

where

$$\phi = V_0 \quad \text{for } z=0$$
$$= 0 \quad \text{for } z=H. \tag{15}$$

The resulting velocity profile is

$$V_x(z) = V_0 \frac{\sin(\epsilon(H-z))}{\sin(\epsilon H)} e^{i\omega t}, \tag{16}$$

where

$$\epsilon^2 = -\frac{i\omega\rho}{\eta^*}. \tag{17}$$

It is now a straightforward matter to use the defining equations and obtain the relevant expressions for the shear rate and shear stress in terms of time, position, G' and G''. The mathematical treatment is facilitated by expressing the complex propogation factor ϵ as

$$\epsilon = \beta - i\alpha, \tag{18}$$

where the parameter α denotes the attenuation factor and β is the phase factor which is related to the wave propogation velocity and frequency by

$$\beta = \frac{\omega}{v}. \tag{19}$$

The final expression for the physically observable part of the wall shear stress (at the oscillating wall) takes the form

$$\tau_{zx}(\xi,t) = \eta' \frac{V_0 \cos(\omega t)}{CC} \{AA[\beta\cos(\beta\xi)\cosh(\alpha\xi) + \alpha\sin(\beta\xi)\sinh(\alpha\xi)] + BB[\alpha\cosh(\alpha\xi)\cos(\beta\xi)$$
$$- \beta\sinh(\alpha\xi)\sin(\beta\xi)]\} - \eta' \frac{V_0 \sin(\omega t)}{CC} \{BB[\beta\cos(\beta\xi)\cosh(\alpha\xi) + \alpha\sin(\beta\xi)\sinh(\alpha\xi)]$$
$$- AA[\alpha\cosh(\alpha\xi)\cos(\beta\xi) - \beta\sinh(\alpha\xi)\sin(\beta\xi)]\} + \eta'' \frac{V_0 \cos(\omega t)}{CC} \{BB[\beta\cos(\beta\xi)\cosh(\alpha\xi)$$
$$+ \alpha\sin(\beta\xi)\sinh(\alpha\xi)] - AA[\alpha\cosh(\alpha\xi)\cos(\beta\xi) - \beta\sinh(\alpha\xi)\sin(\beta\xi)]\} + \eta'' \frac{V_0 \sin(\omega t)}{CC}$$
$$\times \{AA[\beta\cos(\beta\xi)\cosh(\alpha\xi) + \alpha\sin(\beta\xi)\sinh(\alpha\xi)] + BB[\alpha\cosh(\alpha\xi)\cos(\beta\xi) - \beta\sinh(\alpha\xi)\sin(\beta\xi)]\}, \tag{20}$$

where $\xi \equiv z - H$, and the constants AA, BB, and CC are given by

$$AA = \sin(\beta H)\cosh(\alpha H), \tag{21}$$

$$BB = \sinh(\alpha H)\cos(\beta H), \tag{22}$$

$$CC = \sin^2(\beta H)\cosh^2(\alpha H) + \sinh^2(\alpha H)\cos^2(\beta H). \tag{23}$$

The shear stress at the oscillating wall is measured during the course of the simulation as a function of time within an oscillation period. The above continuum mechanics expression for the wall shear stress is then fit to the measured values of the shear stress to yield values for G' and G''.

III. RESULTS AND DISCUSSION

A. Simple fluids

The continuum mechanics treatment presented above is valid only for a fluid exhibiting linear viscoelastic behavior. Hence we first check to ensure that the fluid exhibits linear viscoelastic response to the applied perturbation (oscillatory shear in this case). This test is carried out by taking a Fourier transform of the fluid response (shear stress). A fluid showing linear viscoelastic behavior will exhibit response only at the applied frequency while for nonlinear viscoelastic behavior, higher harmonics will also be seen in the Fourier transform. (Note that only odd harmonics are seen, i.e., in addition to the primary response peak at frequency ω, peaks will also be seen at frequencies of 3ω, 5ω, etc., in the Fourier transform.) In addition to the Fourier transform test, a
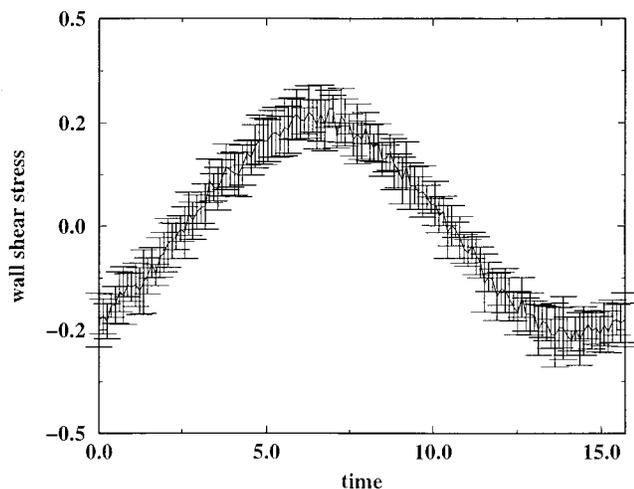
FIG. 1. Average shear stress as a function of time within the oscillation period. Simulation conditions are $N=1$, $\rho=0.844$, $T_{wall}=2.0$, $H=7\sigma$, amplitude $A/H=0.15$ and frequency $\omega=0.4$.
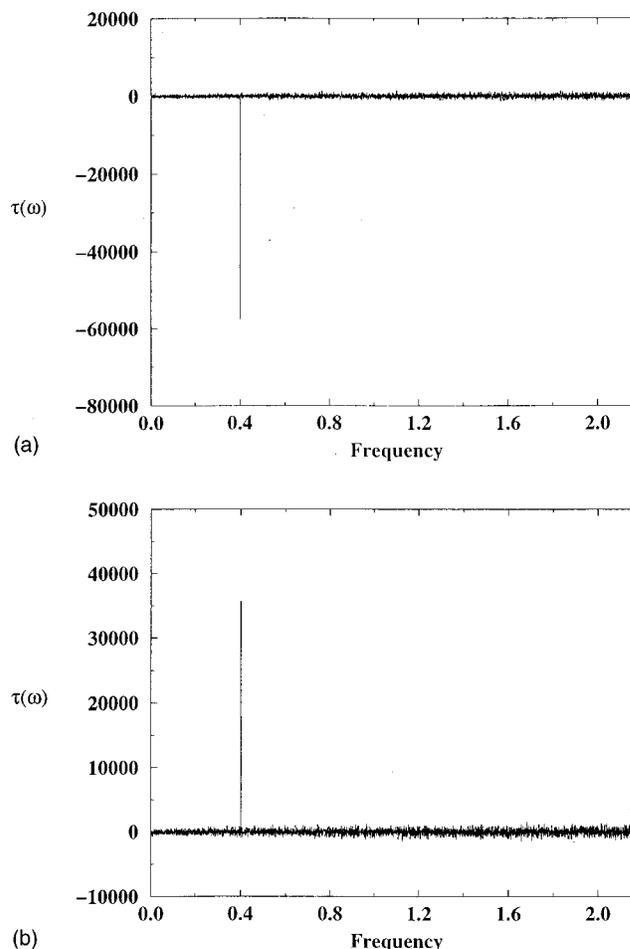

FIG. 2. Real (a) and imaginary (b) parts of the Fourier transform of the wall shear stress (at the oscillating wall) as a function of frequency. Simulation conditions are $N=1$, $\rho=0.844$, $T_{wall}=2.0$, $H=7\sigma$, amplitude $A/H=0.15$, and frequency $\omega=0.4$.

supplementary test is also implemented in some cases: it is ensured that viscoelastic parameters (i.e., G' and G'') determined from simulations are independent of amplitude of oscillation and are functions of frequency only. However this test involves carrying out two simulations (at same frequency but different amplitudes) and is therefore implemented in only a few cases.

The primary quantity measured in an oscillatory shear experiment is the wall shear stress. Figure 1 shows the average shear stress (at the oscillating wall) as a function of time within one period for a fluid film of thickness 7σ and at a frequency of 0.4 in reduced units. The average stress and the uncertainties were obtained by averaging over 10 blocks, each of which contained 160 time periods of oscillation. At first glance, it seems that the shear stress leads, rather than lags, the shear rate in time, which is counterintuitive. However, this observation is a manifestation of the inertial effects in the system discussed in the earlier section. The overall appearance of the shear stress wave form is sinusoidal suggesting linear viscoelastic behavior. It is to be noted that, such a conclusion based on mere visual inspection of the shear stress wave form could be dangerous and a more rigorous test involves taking a Fourier transform of the shear stress as shown in Fig. 2. Values of wall shear stress (at the oscillating wall) are written out at fixed intervals (15 time steps in this case) over the entire length of the production run. Figures 2(a) and 2(b) show the real and imaginary parts of the Fourier transform of this stress trajectory plotted as a function of the frequency. The figures clearly demonstrate that the response shows only one peak (at the frequency of the oscillation) and no higher harmonics are seen indicating that the fluid exhibits linear viscoelastic behavior under given conditions. A similar test is carried out for all the simulation conditions investigated and the viscoelastic properties G' and G'' were calculated only after ensuring that the fluid exhibited linear viscoelastic behavior.

The wall shear stress measured in simulations is fit to the continuum mechanics solution presented in the earlier section where the storage and loss moduli are used as fit param-

eters. As a check of the calculation procedure, the values of G' and G'' obtained from this procedure are used to predict the instantaneous velocity profiles in the sheared fluid. Figure 3 shows a comparison of the predicted and simulated values of instantaneous velocity profiles at six different time instants within an oscillation time period for a film of thickness 7σ. The figure shows that for all the cases, the simulated velocity profiles can be represented by the continuum mechanics prediction. It is to be noted that an even better fit to the velocity profiles is obtained if instead of fitting G' and G'' only to the wall shear stress, they are determined from a simultaneous fit to both shear stress and velocity profiles. However, in keeping with experimental practice, we have chosen to obtain G' and G'' by fitting continuum mechanics solution to just the shear stress.

Surface forces apparatus experiments carried out by Demirel and Granick[2,27] have reported the frequency dependence of G' and G'' and the relaxation times for OMCTS (which provides a good representation of simple fluids used in simulation) at different fluid film thicknesses spanning the range 7σ to 2σ. Figure 4 shows the simulated frequency dependence of the storage and loss moduli at three different film thicknesses for a simple fluid. This particular range of
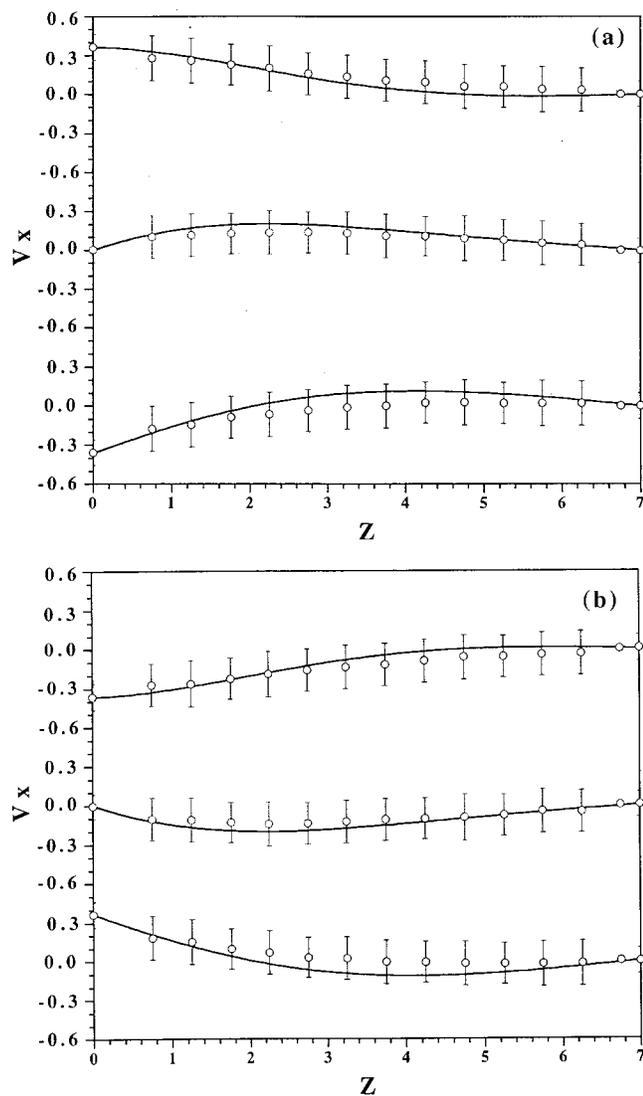
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FIG. 3. Simulated (symbols) and predicted (lines) values of instantaneous velocity profiles for $N=1$, $\rho=0.844$, $T_{wall}=2.0$, $H=7\sigma$, amplitude A/H $=0.15$, and frequency $\omega=0.4$. The figures show profiles at (from top to bottom) (a) 640, 1920, and 3200 time step within a period. (b) 4480, 5760, and 7040 time step within a period. The time period of oscillation consists of 7680 time steps and the velocity amplitude is 0.42.

FIG. 4. Storage (triangles) and loss (circles) moduli as a function of frequency for $N=1$, $\rho=0.844$, $T_{wall}=2.0$. The figures show profiles for film thicknesses of (a) 8σ, (b) 7σ, and (c) 6σ.

frequencies was chosen because at frequencies higher than those studied here, fluid response turns nonlinear, while at frequencies lower than those investigated here, the simulation runs become prohibitively long with current computational resources. Nevertheless the frequency window investigated exhibits a change in the behavior of confined fluid from liquidlike to solidlike response. It can be seen that in all three cases, G'' is higher than G' at low values of frequencies indicating that the fluid response is more liquidlike at these conditions. On the other hand, at higher frequencies, the fluid shows more solidlike repsonse in all cases. As the fluid is confined more, the relaxation time of the fluid increases and as a result, the frequency ω_c at which the fluid response changes from predominantly liquidlike to solidlike, shifts to a lower value. Our results indicate that in going from a film thickness of 8σ to 6σ, the frequency ω_c decreases by a factor of about 3 (and consequently the relax-
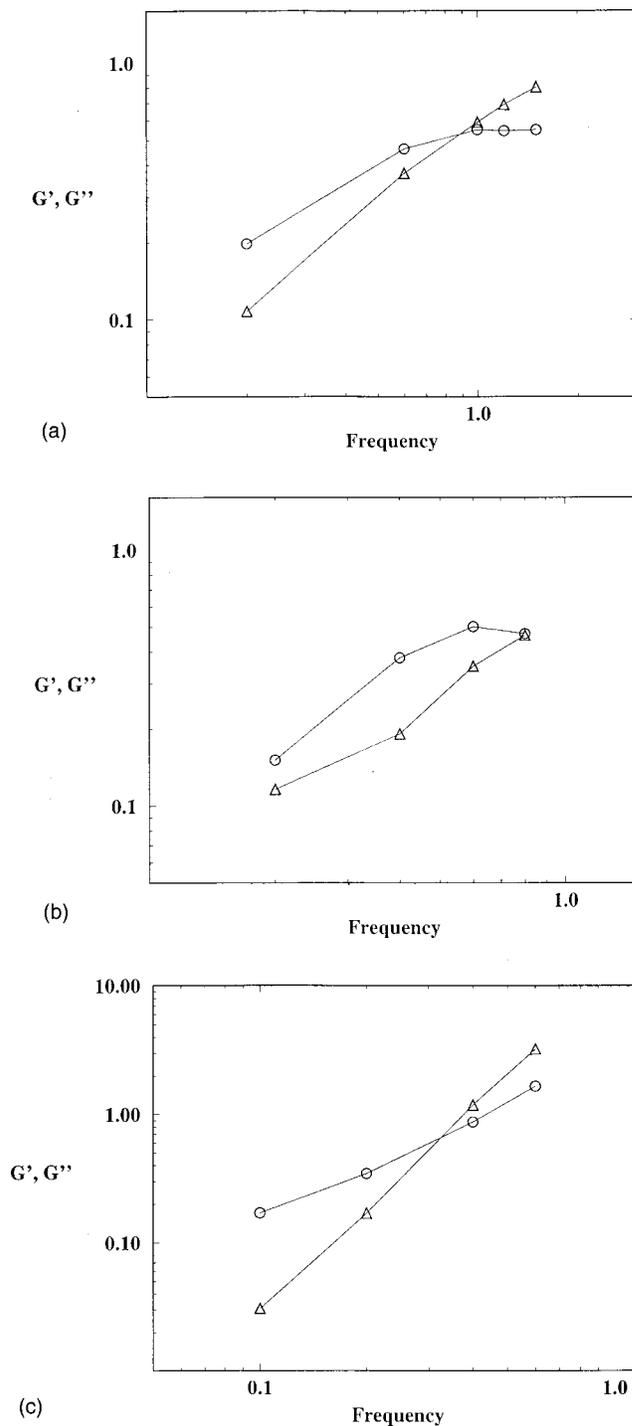
ation time of the fluid increases by a factor of 3). An inspection of the values of G' also indicates that in going from a film of thickness 8σ to 6σ, the value of the storage modulus increases at the most by one or two orders of magnitude and not by six to seven orders of magnitude as the case would be for a sudden, first order phase transition. All these observations are qualitatively consistent with those reported by Demirel and Granick[2,27] in their surface force apparatus investigation of rheology of OMCTS. The surface force appa-

ratus experiments described above were carried out at room temperature which is only slightly higher than the melting point of OMCTS $(17\,°C–19\,°C)$.[27] On the other hand, our simulations are carried out at a reduced temperature of 2.0 which is significantly higher than the freezing point of WCA fluid, thus precluding any possibility of confinement induced crystallization. In spite of these large differences between the state points of the liquids investigated in simulations and experiments, very similar behavior is obtained for both frequency and thickness dependence of the storage and the loss moduli.

B. Chain molecules

The same procedure as implemented for the simple fluids is followed to calculate the values of G' and G'' for chain fluids. Figure 5 shows the frequency dependence of G' and G'' for chain fluids consisting of linear chains having 10, 20, and 50 beads confined to films of thickness 8σ in each case. Compared to the simple fluids, the chain fluids show a qualitatively different viscoelastic response. The value of G' for the chain fluids is higher than that of G'' over the entire frequency range investigated thus suggesting that the chains show predominantly elastic behavior. Furthermore, the G'' curve shows a peak in all cases, suggesting a relaxation process occuring in the system which leads to energy dissipation. Very similar observations were reported by Granick and co-workers for frequency dependence of G' and G'' of polyphenylmethylsiloxane confined between mica surfaces.[6–8]

Figure 6 shows the calculated values of G' and G'' for a gel confined to a film of thickness 8σ and at the same temperature and density as the conditions employed for the linear chains. The gel consists of a regular network containing tetravalent junction points connected by strands containing 10 beads. The viscoelastic behavior of the confined gel is qualitatively similar to that of the linear chains. In particular, the value of G' for the gel appears to be higher than that of G'' over the entire frequency range investigated thus suggesting that the gel shows predominantly elastic behavior. While the storage modulus increases with frequency, the loss modulus exhibits a maximum indicating a relaxation process underlying the energy dissipation. The values of G' for the gel are higher than those for linear chains at the same frequency while the position of the maximum in the G'' is shifted to a slightly higher frequency. It is to be noted that although the gel is at the same density and temperature as the linear chains, the system pressure (component of the stress tensor normal to the confining walls) is lower for the gel.

IV. CONCLUSIONS

A molecular level approach has been presented for the simulation of viscoelastic properties of fluids confined to thin films. The oscillatory shear flow of confined fluids is simulated using the technique of molecular dynamics. The fluid response (wall shear stress) is analyzed using continuum mechanics to yield values of the viscoelastic paramaters, namely the storage and loss moduli (G' and G'') of the confined fluid.
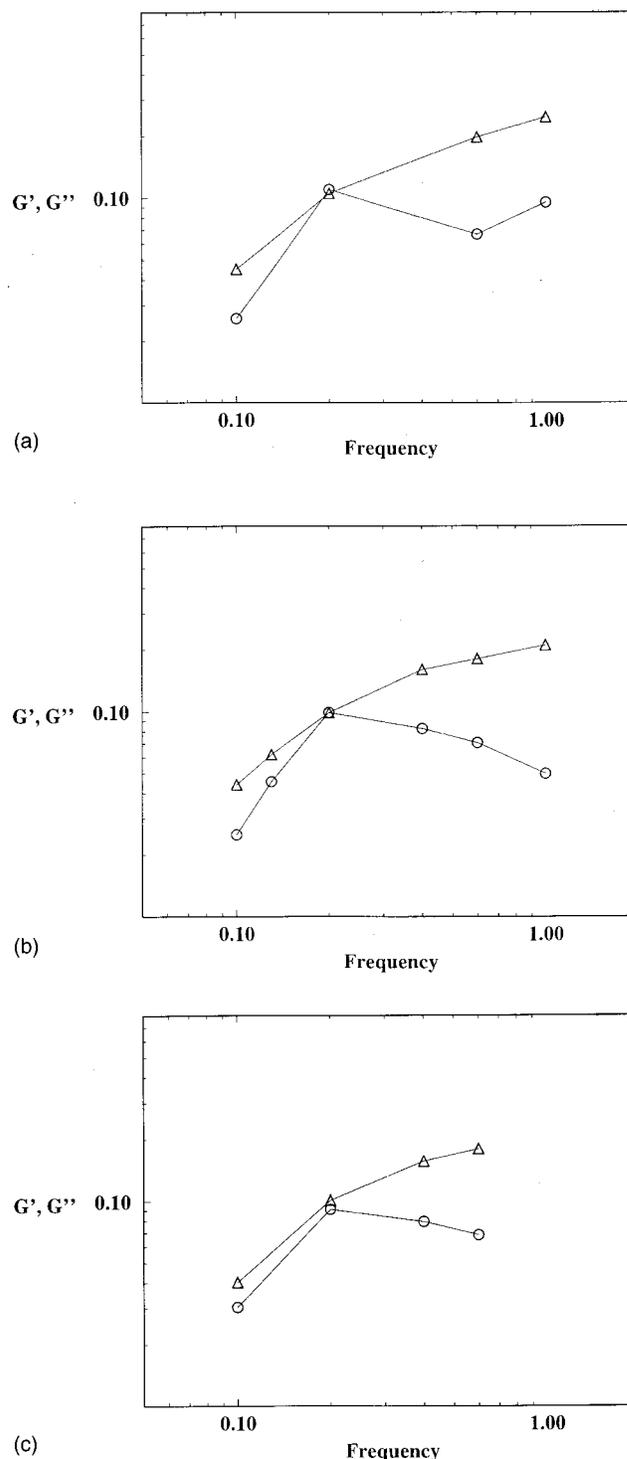

FIG. 5. Storage (triangles) and loss (circles) moduli as a function of frequency for chain molecules at simulation conditions of $H=8\sigma$, $\rho=0.8$, and $T_{wall}=4.0$. The figures show profiles for chain lengths of (a) $N=10$, (b) $N=20$, and (c) $N=50$.

The linear viscoelastic behavior of both simple fluids and chain molecules is investigated using the above approach. An investigation of the frequency dependence of G' and G'' for simple fluid shows that at low values of frequencies, the fluid response is more liquidlike, while at higher values of frequencies, the response is more solidlike. The frequency at which the fluid response changes from predomi-
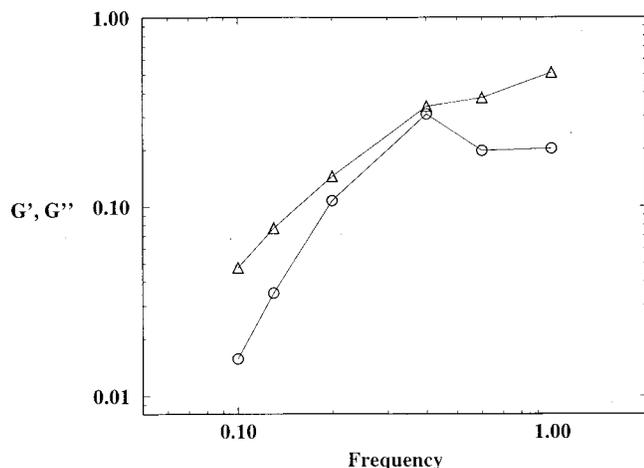
FIG. 6. Storage (triangles) and loss (circles) moduli as a function of frequency for a gel confined to a film of thickness 8σ. The simulation conditions are $\rho = 0.8$ and $T_{wall} = 4.0$.

nantly liquidlike to predominantly solidlike behavior is used as a measure of the characteristic relaxation time of the confined fluid. It is found that on confinement, the relaxation time of the fluid increases as expected. An inspection of the values of G' at various film thicknesses shows that as the fluid is confined to thinner films, the value of G' at a given frequency increases. However the increase is continuous (at the most by one or two orders of magnitude and not by six to seven orders of magnitude), thus suggesting that on confinement, the fluid response changes continuously from liquidlike to solidlike. These observations are consistent with recent surface forces apparatus data on the rheology of liquid OMCTS.[2,27]

Chain molecules show a qualitatively different viscoelastic behavior compared to the simple fluids. The chains exhibit predominantly elastic behavior over the entire frequency range investigated. Furthermore, when plotted as a function of frequency, the G'' of linear chains shows a peak indicating a relaxation process. Again, these observations are consistent with the surface forces apparatus experiments on the rheology of polyphenylmethylsiloxane confined between mica surfaces.[6–8]

The approach followed in this work — investigation of viscoelastic properties by a combination of molecular dynamics simulations and continuum mechanics — is an extension of our previous work dealing with investigation of steady shear properties. As opposed to traditional fluid me-

chanics calculations which by default start by assuming a constitutive model for the rheological behavior of the fluid, by resorting to computer simulations no *a priori* assumptions regarding constitutive relationships and other properties of the fluid are necessary. In fact, along with the values of the transport coefficients, such constitutive relationships can also be predicted using this technique, given the intermolecular potentials in the fluid. The latter can be obtained from first principles (e.g., by quantum mechanical calculations) or by fitting static properties (e.g., phase behavior) of the fluid.

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