Comparison of shear flow of hexadecane in a confined geometry and in bulk

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We examine the shear flow of hexadecane confined between plates with separation of 1–10 nm using molecular dynamics simulations. We also performed non-equilibrium molecular dynamics (NEMD) simulations of bulk hexadecane to compare with the simulations in the confined geometry. The stiffness of hexadecane and its high melting temperature result in a tendency to crystallize at room temperature or large load. We find that when confined between hydrocarbon walls, shearing hexadecane exhibits a velocity profile with substantial slip at the wall and essentially constant velocity over most of the interior space between the walls. As the strength of the wall-fluid interaction increases the amount of slip decreases, but slip always occurs at the boundary for the range of parameters studied. The results are compared with recent surface force apparatus experiments on hexadecane and with similar simulations of model bead-spring fluids.

I. INTRODUCTION

Over the past few years, our understanding of the properties of fluids in confined geometries has progressed considerably due to the development of new experimental techniques that probe the nanometer scale. Measurements by the surface force apparatus (SFA),1–9 and the quartz crystal resonator10 have revealed much about boundary lubrication phenomena. Simulations of confined fluids11–24 have played an important theoretical role. The dynamic properties of fluids confined to the nanometer scale are found experimentally to be dramatically different from the bulk properties.5,9 Some understanding of the processes involved has come from simulations, which work well for the small, confined systems, though most of this simulation work has concentrated on simplified models of atomic or molecular fluids. In this paper, we present results of molecular dynamics simulations in which the fluid is modeled more realistically. In particular, we simulate hexadecane which is one of the fluids studied experimentally.3,7

In the next two paragraphs we describe results from the SFA. We emphasize that, while these experiments motivated the present simulations, because of the large difference in shear velocity (see Sec. II B), the simulations do not model directly the SFA experiments. The shear velocity in most simulations, including the present ones, are of order 1–100 m/s, which is typical of applications such as the lubrication of disk drives and micromachines. In fact, for most applications, the velocity regime probed by the SFA (∼1 μm/s) is far too low. The same difference in shear velocities also exists for the coarse-grained simulations which, nevertheless, reproduce the SFA measurements. One of the aims of the present work is to discuss how the coarse-grained simulation can model the experiments in spite of the shear velocity difference.

In the SFA experiments5 the effective viscosity η_eff is calculated from experimental measurements of the shear stress σ and the applied shear rate γ_app,25 which is determined using the measured plate separation h and assuming a linear profile between the plates. For plate separations less than about 7 atomic diameters, the confined fluid flow is very different from bulk fluid flow. In the Newtonian regime γ_app ≤10 Hz, the effective viscosity is orders of magnitude larger than the bulk viscosity. For example for hexadecane at room temperature, η_eff=500 P at plate separation h=24 Å and load P_z=0.066 MPa.3,7 In the bulk, at room temperature and normal pressure, the shear viscosity η=0.03 P. At higher shear rates, there is a transition, at a critical shear rate γ_c, to a non-Newtonian regime where the effective viscosity decreases with increasing γ_app. For a number of fluids including dodecane, hexadecane, and the silicone-liquid octamethylcyclotetrasiloxane (OMCTS), a power law behavior of the effective viscosity for γ_app > γ_c has been found. At these higher shear rates, the viscosity decreases with increasing shear rate according to a power law, η_eff ~ γ_app^α. Experiments4,5 on a number of systems find that α=2/3, though the value of α for hexadecane is somewhat less than 1/2 and depends on the the load.26 Simulations on model molecular systems of short flexible chains at constant load
find $\alpha = 2/3$ for a variety of applied loads and plate separations,\textsuperscript{17,18} while under conditions of constant plate separation, $\alpha = 1/2$.\textsuperscript{18} This shear thinning of fluids under confinement has also been studied theoretically.\textsuperscript{27–29}

The experimental dependence of viscosity on other parameters can be summarized as follows. The variation of the plate separation with applied load depends on the architecture of the molecule. For linear or nearly linear hydrocarbon chains, the plate separation is quantized for plate separations less than about 7 atomic diameters, while for branched alkanes, the separation is a continuous function of load.\textsuperscript{1,2,8} For both linear and branched alkanes at these small separations, the density oscillations induced by the walls span the separation. Since the SFA experiments are always carried out in an open system in which the fluid molecules confined by the two surfaces are in contact with a reservoir, the layer spacing is not fixed. As the external load is increased for linear alkanes such as the one considered here, the separation between the plates is maintained until a critical load is reached. At this point fluid is expelled from between the plates and the plates snap to the next integral multiple of the atomic diameter.\textsuperscript{1–3,8} Both simulation and experiment find that as the load is increased at a fixed number of layers, the viscosity increases.

By using realistic molecular potentials, the effect of chain stiffness and architecture on the flow properties of lubricants in confined geometry can be studied. We also examine how the flow depends on the wall-fluid interaction by varying the wall-fluid interaction strength. In this first paper, we present the results for hexadecane, $\text{C}_{16}\text{H}_{34}$, using a united atom model. For our initial investigation, we chose hexadecane for its simplicity and since it has been studied experimentally.\textsuperscript{3,5} It also shows a smaller value of $\alpha$ than seen in other experimental systems. Using the same united atom model, we have also performed non-equilibrium molecular dynamics (NEMD) simulations of bulk hexadecane to compare with the simulations in the confined geometry. This comparison has both methodological and practical interest, and it allows us to directly investigate the effect of confinement on the transition between Newtonian and shear-thinning regime. As discussed in Section IV, this is of crucial importance for an understanding of the SFA experiments.\textsuperscript{3,7} In a future paper, we will investigate the detailed effects of different types of walls and the effect of chain branching.

The rest of the paper is organized as follows. In the next section, we describe the details of the simulation methods. In Section III, we present the results of simulations performed at varying number of fluid layers and wall-fluid interaction parameters and compare the results with bulk measurements and simulations. In Sec. IV, we present a comparison of the present simulations and the earlier bead spring model simulations.\textsuperscript{17,18} In the final section, we summarize our main results.

II. SIMULATION METHOD

We performed both confined and bulk simulations. Simulations in a confined geometry are similar to the earlier work of Thompson et al.\textsuperscript{17,18} Bulk nonequilibrium molecular dynamics simulations were also performed in order to compare the shear rate dependence of the bulk viscosity to that obtained in the confined geometry. We describe the details of both simulation methods below.

A. Potentials

The model used for hexadecane is similar to the earlier treatment of decane.\textsuperscript{30,31} We used a united atom (UA) model in which each carbon atom with its attached hydrogens is grouped to form a single “united” atom. This model is essentially the same as that used by Siepmann et al.\textsuperscript{32} in calculating the liquid-gas coexistence curves of alkanes. The intermolecular interaction and the interaction between atoms separated by three or more atoms in the same molecule is described by a Lennard-Jones potential whose parameters are given in Table I. The LJ potentials were cutoff at 2.5$\sigma$. In addition, the intramolecular interactions include bond angle bending and torsional potentials. We use a harmonic bending potential and the torsional potential is that used by Jorgensen et al.\textsuperscript{33} We performed many of the simulations in confined geometry using a fixed bond length. For the NEMD and some of the confined geometry simulations a stiff harmonic bond-stretching potential was used. The bond spring constant is somewhat different for the two sets of simulations, but we do not expect this will significantly affect any of the results presented here.

B. Confined simulations

In the confined simulations, both constraint dynamics (RATTLE algorithm)\textsuperscript{34,35} and rRESPA multi-timestep dynamics\textsuperscript{36} were used. In the constraint MD the carbon–carbon bond length was fixed at 1.54 Å and the time step was 5 fs. In the rRESPA dynamics, a harmonic bond potential is used (see Table II for spring constant) with the same average

<table>
<thead>
<tr>
<th>Group</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon$ (kcal/mol)</th>
</tr>
</thead>
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<tr>
<td>CH₄</td>
<td>3.93</td>
<td>0.227</td>
</tr>
<tr>
<td>CH₂</td>
<td>3.93</td>
<td>0.093</td>
</tr>
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</table>

\textsuperscript{*}The parameters are taken from Ref. 32.

<table>
<thead>
<tr>
<th>bond length</th>
<th>$1.54$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_s$ (stretching)</td>
<td>646 kcal/(mol Å²)\textsuperscript{*}</td>
</tr>
<tr>
<td>$k_b$ (bending)</td>
<td>900 kcal/(mol Å²)\textsuperscript{*}</td>
</tr>
<tr>
<td>$\theta_b$</td>
<td>114°</td>
</tr>
<tr>
<td>$a_0$ (X–CH₂–CH₂–Y)</td>
<td>2.007 kcal/mol</td>
</tr>
<tr>
<td>$a_1$</td>
<td>4.012</td>
</tr>
<tr>
<td>$a_2$</td>
<td>0.271</td>
</tr>
<tr>
<td>$a_3$</td>
<td>−6.290</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Intramolecular parameters for n-alkanes from Ref. 32. Torsional potentials are taken from Ref. 33.

\textsuperscript{b}Used in confined rRESPA simulations.

\textsuperscript{c}Used in NEMD simulations.
bond length as the constrained MD. Two timesteps were used in the rRESPA MD. For all the intramolecular interactions we used a 1 fs timestep. The LJ interactions were integrated using a 5 fs timestep. The rRESPA method is preferred over the constraint method since, for equal CPU time, the rRESPA method gives better energy conservation in the microcanonical ensemble. Most simulations were performed for 1 ns, although, at the lower shear rates, runs were extended to several ns.

The simulations were performed at constant temperature. Temperature was controlled using a Langevin thermostat\(^\text{27,38}\) with a damping constant of 1 ps\(^{-1}\). For each atom, only the velocity component in the direction perpendicular to the shear direction and parallel to the plates (i.e. the vorticity direction) was coupled to heat bath. In this manner, the velocity profile is not disturbed by the thermostat. Khare et al. (Ref. 24) have performed simulations thermostating the walls thus allowing any possible thermal gradient to form. For the narrow nm separations that we study, they find that the temperature profile is constant across the gap. In other words, thermostating the fluid is equivalent to thermostating the walls for our simulations.

The system size was determined such that the average fluid density between the plates equals the bulk density. The volume of the fluid is determined from the measured density. The walls are then placed outside the fluid volume, at a distance \(\Delta z = a_w / \sqrt{3}\), where \(a_w\) is the wall nearest neighbor spacing and the \(z\)-direction is perpendicular to the wall. There is some uncertainty whether this yields the desired effective volume for the fluid at small wall separations. At large separations, the calculated density in the central region of the simulation volume, where the density profile is flat, is equal to the target fluid density. We are thus comfortable that our procedure gives a consistent value of the density.

To determine the appropriate load at the given density, equilibrium simulations were initially performed at constant volume (plates fixed). The force on the wall calculated in the constant volume simulations was then used to determine the correct load for simulations under shear at constant load. In calculating this pressure, the long range corrections were not included since the system is confined. However, to compare with experimental data, some correction would be necessary since the UA potentials were derived using the long range corrections. These corrections are not small in the bulk, being about \(-50\text{ MPa}\) with our choice of LJ cutoff.

The number of hexadecane molecules in our simulations ranged from about 30 to 200 depending on the number of layers in the system. The plate dimensions are approximately 30 Å by 30 Å and were kept constant as the number of layers was varied. The size of the plates varied by a few Å as the wall lattice constant was varied.

The geometry of the confined simulations is basically the same as in earlier simulations of Thompson et al.\(^\text{15,17,18}\) The fluid is confined between two walls composed of LJ atoms. The wall atoms form a rigid fcc lattice with the surfaces being the (111) surface with nearest neighbor distance \(a_w\). For the shear simulations, the top wall is pulled at a velocity \(v_w\) in the \(x\)-direction with the bottom wall stationary. Simultaneously, a load \(P_{z^*}\) is applied to the top wall in the \(z\)-direction perpendicular to the wall. The wall motion in the \(z\)-direction is determined by the net force due to the fluid particles on the wall particles and the load. The mass of a wall atom is equal to twice the mass of a CH\(_2\) united atom as this corresponds to the simulations of Thompson et al. The stress on the wall can be determined from the force of the fluid on the wall in the \(x\)-direction\(^\text{21}\) and from the usual virial relation applied only to the fluid particles (see Sec. II C). In our simulations, the two stresses are equal within uncertainty. However, the fluctuations (uncertainty) in the virial are considerably larger than in the direct calculation. Furthermore, recent work suggests that the virial formulation requires higher order gradient terms for inhomogeneous systems such as confined fluids.\(^\text{39}\) For these reasons, we favor the direct method of calculation and only report these stresses.

The height of the cell is naturally determined by the number of layers, \(m_r\). For small \(m_r\) the number of layers can be determined directly from the density profile, \(\rho(z)\). In these cases, the oscillations in \(\rho(z)\) span the height of the cell and clearly define the layers as shown in Fig. 1(b).\(^\text{40}\) At large separations \((m_r \geq 14)\), the middle of the density profile is flat (Fig. 1(a)) and the number of layers is determined from the average layer spacing \((\sim 4\text{ Å})\) found at the narrower separations.

The shear velocities, or, equivalently, the shear rates in our simulations are not in the same regime as the SFA experiments. For a timestep of order 1 fs and a fundamental length scale of order 1 Å, shear velocities are on the order of \(1\text{ Å/1 fs} = 10^5\text{ m/s}\), though we can actually simulate much
smaller velocities. For simulations of 1 ns duration and for displacements of the top plate \(\Delta x\) of the order of the length of the simulation cell, about 30 Å, \(v_w \sim 30 \text{ Å/1 ns}=3 \text{ m/s}\). The range we can study is about 1–400 m/s, although, for \(v_w \approx 20 \text{ m/s},\) runs longer than 1 ns are needed. For very high velocities, \(v_w \approx 400 \text{ m/s},\) difficulties thermostatting the system were sometimes encountered.

Experimentally, the shear velocity range for the SFA is \(v_w \sim 1 \text{ nm/s} – 1 \mu \text{m/s}.\) Such small velocities only effect processes with very long relaxation times. In 1 ns, with \(v_w = 1 \mu \text{m/s},\) the plate moves only \(10^{-15} \text{ m/1 Å}\)! The molecules do not even notice the plate motion until about 0.1 ms when the plates have moved 1 Å. Thus, the relevant relaxation time, for the confined fluid must be greater than 0.1 ms.

Three wall parameters define the wall-fluid interaction: the Lennard-Jones potential parameters \(\sigma_w\) and \(\epsilon_w\), which describe the wall particle-fluid interaction, and the wall lattice parameter \(a_w\). In this paper, \(\sigma_w\) is fixed at 2.5 Å, and the value of \(\epsilon_w\) is varied from 0.1 kcal/mol to 0.7 kcal/mol. The minimum value of this range corresponds to the value of \(\epsilon\) for a \(\text{CH}_4\) united atom, the maximum to 3 times the value of \(\epsilon\) for a \(\text{CH}_3\) united atom. This range of values is similar to that of the earlier model fluid simulations. The lower range corresponds to a hydrocarbon fluid interacting with a hydrocarbon surface, such as a self-assembled monolayer of alkanes on mica. For direct interaction with mica, on the other hand, the wall-atom parameter \(\epsilon_w\) should be 0.7 to 1.0 kcal/mol.\(^{41,42}\) Note that, since we use the Lorentz-Berthelot rules for combing LJ parameters, \(\epsilon_{w,\text{CH}_4} = 0.40 \text{ kcal/mol,}\) when \(\epsilon_{w} = 0.7 \text{ kcal/mol.}\) We have also varied the wall lattice parameter \(a_w\). Initially we set \(a_w = 4.97 \text{ Å}\) which is the lattice parameter for alkane self-assembled monolayers.\(^{43}\) We have then increased \(a_w\) up to 7 Å. Larger values of \(a_w\) correspond to larger peaks and valleys in the potential surface of the wall. This makes the wall rougher and therefore increases the effective strength of the wall-fluid interaction.

C. NEMD

The NEMD calculations of bulk shear viscosity were performed on the massively parallel Intel Paragon at ORNL using a replicated data algorithm. The temperature was controlled using the Nosé thermostat applied to each atom and not to the molecular center of mass; Travis et al.\(^{44}\) have shown that the difference between atomic and molecular thermostats is negligible for the strain rates investigated here (i.e., reduced strain rates less than unity). Details of the rRESPA method, also applied to NEMD simulations, can be found in Refs. 30 and 36. The large timestep was 2.35 fs, and the small timestep was 0.235 fs. The NEMD simulations were performed at two state points: density \(\rho = 0.770 \text{ g/cm}^3\), temperature \(T = 300 \text{ K}\); and \(\rho = 0.753 \text{ g/cm}^3, \) \(T = 323 \text{ K}\), with 100 chains in the simulation cell. The system was equilibrated for at least 2 ns before starting the NEMD simulation. The strain-rate-dependent properties of the systems were calculated based on the simulation runs after the system has reached the steady state under the influence of the shear flow. This time required to reach steady state is roughly estimated to be the time for the particle at the top of the simulation cell to traverse the entire box length, about 19 ps at strain rate \(\dot{\gamma} = 425 \text{ GHz}\) and density \(\rho = 0.753 \text{ g/cm}^3\). The configuration from a neighboring higher strain rate was used as the initial configuration for the next smaller strain rate as this allows the system to reach the steady state more quickly than starting from an equilibrium configuration. In practice, we allowed a relatively large time for the system to reach the steady state, ranging between 100 ps for high strain rates to 470 ps for low strain rates.

For comparison, we have also performed a 40 ns equilibrium simulation of 64 hexadecane molecules at the 323 K state point. For this simulation we have used constraint dynamics (fixed bond-length) and the Berendsen-velocity-rescaling temperature control.\(^{45}\) The viscosity was then calculated applying the generalized Green-Kubo relation\(^{46}\) to the time-correlation of the symmetrized stress-tensor, in both the atomic and molecular representations. We extended the relative integrations up to 800 ps.

The NEMD simulations were carried out using the the SLLOD equations with Nosé dynamics.\(^{30}\) For planar Couette flow these equations are

\[
\dot{\mathbf{r}}_{ia} = \frac{\mathbf{p}_{ia}}{m_{ia}} + \gamma z_{ia} \mathbf{\hat{x}},
\]

\[
\dot{\mathbf{p}}_{ia} = \mathbf{F}_{ia} - \gamma \mathbf{z}_{ia} \mathbf{\hat{x}} - \mathbf{\dot{\mathbf{p}}}_{ia},
\]

\[
\ddot{z}_{ia} = \frac{p_{ia}}{Q}.
\]

\[
\dot{p}_{ia} = F_{ia} = \sum_{i,a} \frac{p_{ia}^2}{m_{ia}} - 3Nk_B T,
\]

where \(\mathbf{r}_{ia}, \mathbf{p}_{ia}, \mathbf{F}_{ia}\) are, respectively, the vector coordinates, momentum and forces of atom \(a\) in molecule \(i\), \(z_{ia}\) and \(p_{z,ia}\) are their \(z\) components, \(m_{ia}\) is its mass, \(\mathbf{\hat{x}}\) is a unit vector in \(x\) direction, \(N\) is the total number of atoms, and \(\dot{\gamma}\) and \(p_{\gamma}\) and \(Q\) are the variables of the Nosé thermostat.

In an NEMD calculation, the shear-rate dependent viscosity \(\eta\) is determined from the constitutive relation

\[
\eta = \left\langle P_{z\alpha} \right\rangle + \left\langle P_{z\beta} \right\rangle, \tag{5}
\]

where \(\langle P_{\alpha\beta} \rangle\) are the average of the \(\alpha\beta\) components of the pressure tensor field.

Note that there are potential differences in results depending on whether the atomic or molecular tensor is used in Eq. (5). A number of publications have discussed the subject of the atomic and molecular pressure tensor formalism in molecular simulation.\(^{47–50}\) For a system in an equilibrium state without influence of external force, the equivalence between the two in calculating the transport coefficients has been proven analytically\(^{47,48}\) and verified numerically.\(^{37,49}\) For a system in planar Couette flow, the equivalence between the two has been discussed by Edberg et al.\(^{30}\) In this calculation, since the streaming velocity is applied to the atomic site, the corresponding pressure tensor \(\mathbf{P}\) is calculated using the atomic formalism.

\[
P V = \sum_{i,a} F_{ia}P_{ia} + \frac{1}{2} \sum_{i,a} \sum_{j \neq i,b} (r_{ia} - r_{jb})f_{ia,jb} + \sum_{i,a} \delta r_{ia}f_{ia}^{(\text{intra})},
\]

where the indices \( i \) and \( j \) refers to molecules, indices \( a \) and \( b \) refer to interaction sites in molecules \( i \) and \( j \) respectively, \( f_{ia,jb} \) is the interaction force between site \( a \) on molecule \( i \) and site \( b \) on molecule \( j \), \( \delta r_{ia} \) is the position vector of site \( a \) on molecule \( i \) relative to the center mass of molecule \( i \), \( f_{ia}^{(\text{intra})} \) is the total intramolecular force on site \( a \) on molecule \( i \). Note that since the total intramolecular forces sum to zero for a given molecule, the last term in Eq. (6) does not depend on the choice of origin in the determination of \( \delta r_{ia} \), so this can be conveniently chosen to be the center of mass of the molecule.

III. RESULTS AND DISCUSSION

Initially, we performed simulations at room temperature, \( T = 300 \text{ K} \), which is the temperature of the SFA experiments. However, we found a tendency for the fluid to become ordered in a partially crystalline state for the confined systems. The bulk crystallization temperature of hexadecane, \( T_m = 292 \text{ K} \), is very close to 300 K. In addition, the bulk crystallization pressure \( P = 35.2 \text{ MPa} \) is small, particularly in comparison with the pressure fluctuations in the simulations. All this demands very accurate potential parameters to achieve the correct phase at room temperature. In the bulk NEMD simulations the system remains fluid. Crystallization can occur above \( T_m \) due to confinement. However, such confinement-induced crystallization will depend on the commensurability of our simulation cell and/or the wall structure with the hexadecane crystal structure. Because we are primarily interested in the flow properties, not in crystallization, we decided to avoid this region for the present and concentrate on cases where the confined hexadecane remains liquid. Some discussion of the simulations at 300 K are given later in Sec. III E. We thus performed most simulations at \( T = 323 \text{ K} \), which also has a larger bulk crystallization pressure. Some runs were performed at \( T = 373 \text{ K} \) which has a relatively high bulk crystallization pressure (470 MPa), offering the opportunity to examine the effects of large loads.

The dynamical properties are predominantly determined by the experimental flow profile. Unfortunately, for nanometer scale separations the flow profile cannot be measured directly. In MD simulations, on the other hand, calculation of the flow profile is straightforward. From the flow profile \( v(z) \), the shear rate

\[
\dot{\gamma} = \frac{dv(z)}{dz}
\]

(7)
can be evaluated directly. Using this “actual” shear rate, the “actual” viscosity \( \eta = \sigma/\dot{\gamma} \) can be calculated. If there is a slip or stick boundary condition, then the actual viscosity will differ from the effective viscosity \( \eta_{\text{eff}} \), which is measured experimentally assuming a no slip boundary condition.\(^{3,5,7}\)

\[\eta_{\text{eff}} = \sigma/\dot{\gamma}_{\text{app}} = \sigma h/\nu_w.\]  

(8)

Thus, \( \eta \) and \( \eta_{\text{eff}} \) are equivalent only if there is no slip at the boundary. We calculated the flow profiles by averaging the monomer velocities in layers. The layers are determined from the density profile.

We initially performed a series of simulations at \( T = 323 \text{ K} \) varying the number of layers \( m_r \) along with the strength of the wall-fluid interactions. We found that the actual and applied shear rates differed greatly depending on the nature of the walls. For this reason, we show first the calculated flow profiles and then discuss both the actual and effective viscosities and how they relate to experiments and previous simulations.

A. Flow profiles

The effect on the flow profiles of changing the various wall parameters is shown in Fig. 2. For the weak wall-fluid coupling (Fig. 2(a); \( \epsilon_w = 0.1 \text{ kcal/mol} \) and \( a_w = 4.97 \text{ Å} \), we always find a velocity profile with substantial slip at the wall and essentially constant velocity over most of the interior space between the walls (Fig. 2(a)); we shall call such a velocity profile “plug flow.” This is true up to \( m_r = 19 \), our largest system size, for which we expect to see bulk-like behavior. For these cases the wall-fluid interaction corresponds to a weak hydrocarbon–hydrocarbon interaction. Be-
tween the fluid and the wall is a plane that is not crossed by any carbon–carbon bonds, and because of excluded volume effects, there is a lower site density at this interface than in the bulk fluid. More precisely, the nearest (non-bonded) neighbor distance in the fluid or at the wall-fluid interface is the same, about \(1\sigma = 3.93\) Å. However, the next nearest intermolecular neighbors are much closer in the fluid since the nearest neighbor is bonded to a monomer only 1.54 Å away. The next nearest shell of atoms in the wall must be at least \(a_w \approx 4.97\) Å away which yields a total distance almost beyond the LJ cutoff. The fluid atoms therefore interact with more neighbors within the fluid than at the wall interface and the cohesion in the fluid is correspondingly stronger than the adhesion of the fluid to the wall. Since the wall-fluid interaction is weak, it is easier at these high shear rates for shear to occur almost totally at the wall-fluid interface, rather than within the fluid. This leads to almost complete slip at the boundary and plug flow.

Increasing \(a_w\) makes the walls rougher which should increase the wall-fluid interaction, but also decreases the number of wall monomers that are within the interaction range of the fluid monomers. Not surprisingly, we find that increasing \(a_w\) to 7 Å by itself does not change the velocity profile from plug flow. However, increasing \(\epsilon_w\) to 0.7 kcal/mol \(\approx 3\) eCH\(_3\) dramatically changes the flow profile. A linear velocity profile is now observed with large slip at the interface (Figs. 2(b) and (c)). By increasing the adhesion of the fluid to the wall surface, the velocity gradient can be made to occur in the fluid as well as at the interface. For \(m_w = 6\), or lower, there is still large slip at the walls (Fig. 2(b)), but we do not have plug flow. Increasing \(m_w\) to 12 reduces the amount of slip (Fig. 2(c)). Since the middle of the 12 layer system shows uniform bulk density, one expects for this region a flow profile closer to the bulk no-slip profile. In the absence of plug flow, this leads to less slip at the boundary for \(m_w = 12\) than for \(m_w = 6\).

### B. Actual viscosity

We determine the shear rate from the slope [Eq. (7)] of the least squares linear fit to the flow profile (cf. Fig. 2). For \(v_w \approx 20\) m/s, the velocity profiles are too noisy to determine the slope, but for \(v_w \approx 20\) m/s they are clearly linear and the calculated shear rates (in rescaled variables) are largely independent of \(v_w\). We thus use the higher velocity simulations to find a single ‘actual’ shear rate. Using this shear rate to calculate the viscosities, we plot in Fig. 3 the \(\eta-\dot{\gamma}\) curves for the large \(m_w\) data of Fig. 2(a) (\(\epsilon_w = 0.1\) kcal/mol). Also included in the figure are the NEMD data (\(T = 300\) K and 323 K). Since the slopes of the velocity profiles are large, so is the uncertainty in \(\dot{\gamma}\). For the \(m_w = 19\) system in Fig. 3, we include error bars. The uncertainty in the shear rate was determined from straight lines that bound the flow profiles. The uncertainty for \(m_w = 19\) encompasses the data for the other two separations making them indistinguishable. The experimental value of the shear viscosity is 1.9 cP at \(T = 323\) K and 1 atm.\(^{51}\) Within their large uncertainty the confined simulation data are consistent with the experimental bulk value, whereas the NEMD simulations give a somewhat lower value, 1.24 cP, at low shear rates. The equilibrium simulation also gives a lower viscosity, 1.14 cP. Small systematic effects, due to the differences in methods, may explain the 10% discrepancy between the constraint-dynamics equilibrium and multi-step NEMD results. The observed difference, however, is within the statistical uncertainty of the two results. While one would like to reduce the overall uncertainty, these results suggest that the bulk limit can be obtained in the confined simulations in the limit of large plate separation but only after one has properly accounted for the velocity profiles.

For the simulations with the strong wall-fluid interactions, the well defined Couette flow makes it easier to determine \(\dot{\gamma}\) accurately from the flow profile. In Fig. 4 we show the actual viscosities for a variety of cases with \(a_w = 7\) Å. For these cases of strong wall-fluid interaction, we find shear thinning at shear rates comparable to the NEMD data. There appears to be a Newtonian regime within the examined shear rate values, although the uncertainty is sufficiently large at these low shear rates that we cannot exclude continued shear thinning. From the overall scatter in the data, the actual viscosities for the different \(\epsilon_w\) and \(m_w\) overlap. For \(m_w = 4\) and 6, the Newtonian viscosity appears to be smaller than for the NEMD simulations or the large separation \(m_w = 12\) cases. However, a definitive conclusion cannot be made because of the large uncertainty in the data at low shear rates. On the other hand, the actual viscosities for the confined simulations with strong walls clearly tend to be smaller than the viscosities for the simulations with weak walls (Fig. 4 compared with Fig. 3).

Previous confined simulations of bead-spring chains found \(\alpha\) to be constant at 2/3 for varying \(m_w\) and \(P_w\),\(^{17,18}\) though more recent simulations find a dependence of \(\alpha\) on...
the wall-fluid interaction. The experimental (effective) value of $\alpha$ for hexadecane determined from effective viscosities is about 0.5, though $\alpha$ is smaller for low loads. The solid straight line in Fig. 4 shows that, in all cases considered in the simulation, $\alpha$ is definitely less than 0.50. A least square fit to the NEMD shear-rate viscosity data for $\gamma > 10$ GHz gives an actual value of $\alpha$ = 0.39 and the reference dotted line indicates that the same value gives a reasonable fit for the confined simulation data at strong wall-fluid interactions. As discussed in the next section, the $\alpha$ for the effective viscosity curves is about the same as for the actual viscosity curve at strong wall-fluid coupling. This value for $\alpha$ (0.39) is less than that observed in earlier bulk simulations for hexadecane and bead spring chains, which were both for constant volume. However the hexadecane simulations of Berker et al. are at a much higher temperature, 477.6 K, and high pressure, 690 MPa than considered here. Constant volume and constant load simulations are known to give different results in the non-Newtonian regime in that the plates separate slightly as the shear rate increases in the constant load simulations. We also find that the plates separate for high shear under constant load for hexadecane even for weak wall-fluid coupling.

C. Effective viscosity

In order to compare directly with experiment, we must examine the effective viscosity, calculated using the applied shear-rate. Results for the effective viscosity for the weak wall-fluid coupling $\epsilon_w = 0.1$ kcal/mol and $a_w = 4.97$ Å are shown in Fig. 5 (compare with Fig. 3). Note that the data are rather flat and there is no indication of the crossover to Newtonian behavior. The range of $\alpha$ is from 0.05 to 0.17. In contrast to the results of experiments and earlier simulations, we find the viscosity increases with increasing plate separation. This observed dependence of $\eta_{eff}$ on $m_r$ is a consequence of the plug flow discussed earlier (Sec. III A). Since plug flow is interfacial, there is no dependence of the shear stress $\sigma$ on $h$. From Eq. (8), this implies $\eta_{eff} \propto h$. In other words, $\eta_{eff}$ increases with $m_r$.

Increasing $\epsilon_w$ to 0.7 kcal/mol not only changes $\alpha$, but also the magnitude of the effective viscosity. Figure 5 shows $\eta_{eff}$ for $m_r = 4$ and 12 ($\epsilon_w = 0.7$ kcal/mol and $a_w = 7$ Å), to be compared with Fig. 4. We see an increase in $\eta_{eff}$ of almost one order of magnitude when comparing $m_r = 4$ for $\epsilon_w = 0.7$ kcal/mol and the interpolation of the $m_r = 3$ and $m_r = 5$ results for 0.1 kcal/mol. The increase in $\eta_{eff}$ comes directly from the increased shear stress at the higher $\epsilon_w$, which results from having to shear the fluid instead of just the wall-fluid interface. Furthermore, stronger wall-fluid coupling does reduce the viscosity difference between thin and thick films. Figure 5 shows that the difference in $\eta_{eff}$ between $m_r = 4$ and 12 is appreciably smaller at $\epsilon_w = 0.7$ kcal/mol than the difference between $m_r = 5$ and 14 at $\epsilon_w = 0.1$ kcal/mol. The slopes at high $\gamma$ give $\alpha$ = 0.42 and 0.39 for $m_r = 4$ and 12, respectively, which are equal to the $\alpha$ of the actual viscosity curves. Thus, the magnitude of $\alpha$ from the effective viscosity curves increases substantially as the wall-fluid interaction increases.

D. High temperature

To examine the effect of load we performed simulations at $T = 373$ K at which temperature hexadecane has a high...
bulk crystallization pressure. The confined simulations were performed for two different loads. Figure 6 summarizes the results. Data at $P_\perp = 73$ MPa yield the bulk 1 atm density for $m_\perp = 6$. As at $T = 323$ K, the effective viscosity is much lower than the bulk viscosity. The slope of the log–log curve is also small, yielding $\alpha = 0.18$. Increasing the load to 400 MPa ($\rho = 872$ g/cm$^3$) at $m_\perp = 4$, increases $\alpha$ to 0.39 which is the same as the NEMD value at lower $T$ and 1 atm. The change in load primarily changes only $\alpha$ as the effective viscosity is the same as the lower load at $g_\dot{=}$. Increasing $e_w$ to 0.7 kcal/mol increases the effective viscosity as at $T = 323$ K. At $m_\perp = 4$, the magnitude of $\eta_{\text{eff}}$ increases and $\alpha$ increases to 0.50. Basically, the effects of changing $e_w$ operate at high $T$ and high load as they did at low $T$ and low load. The increase of $\alpha$ with increasing load is consistent with the experimental results of Carson.$^{26}$

Some ordering does occur in the high load simulations for low $v_w$. At $T = 373$ K and $P_\perp = 400$ MPa, the end-to-end distance, $R$, becomes anomalously large for $v_w = 50$ m/s; the average value of $R$ is just outside the fluctuation range for $v_w = 100$ m/s and $v_w = 200$ m/s. We generally find that such an increase in $R$ is an indication of the presence of ordering in the system. Note, however, that the viscosity at $v_w = 50$ m/s fits within the trend of the other shear rates. Figure 7 shows two projections of a configuration taken from the simulation with $v_w = 50$ m/s. On average, the chains line up at an angle to the shear direction, but the ordering is not complete. The easy shear direction of the fcc walls is also at a larger angle to the shear direction. The chains maintain an intermediate orientation between these two directions. The chain orientation can be more clearly seen in Fig. 7 for the two black chains. While the chains remain flexible, the orientation of their longest principal axis can clearly be identified. The top part of the figure indicates that the system is composed of two regions with differing degree of order. If the system is near a two phase regime, then the simulations could easily have difficulty in obtaining the correct phase or concentrations of both phases. In the next section we show that low load simulations at $T = 300$ K exhibit similar phenomena. Problems such as these led us, in the beginning of this work, to perform most simulations at low load and at $T$ greater than room temperature.

E. Room temperature simulations

As noted earlier, we performed some sequences of simulations at $T = 300$ K. We found it rather easy to partially crystallize the confined system. Even with no load $P_\perp = 0$, we find partial crystallization at $T = 300$ K for a 3 layer system at shear velocity $v_w = 20$ m/s. Figure 8 shows a snapshot of the partially crystallized 3 layer system. The system cannot form a single crystal because the simulation cell dimensions are not commensurate with the crystal structure. Furthermore, our system sizes are small in the lateral dimensions and finite size effects for a phase transition may be large. For the same parameters, with $m_\perp = 5$ the system

![Graph showing log-log plot of $\eta_{\text{eff}}$ vs. $\gamma_{\text{app}}$](image-url)

**FIG. 6.** The effective viscosities at $T = 373$ K are shown. The parameters are: (△) $P_\perp = 73$ MPa, $m_\perp = 6$, $e_w = 0.1$ kcal/mol; (□) $P_\perp = 400$ MPa, $m_\perp = 4$, $e_w = 0.1$ kcal/mol; (○) $P_\perp = 400$ MPa, $m_\perp = 4$, $e_w = 0.7$ kcal/mol.

![Two projections are shown for $T = 373$ K at $P_\perp = 400$ MPa at $v = 50$ m/s. The bottom part shows the degree of rotation in the shear plane along which the chains are oriented. Top part is a projection in the direction indicated by the arrow in the bottom part of the figure. Two chains are colored black in order to see examples of individual chains.](image-url)

**FIG. 7.** Two projections are shown for $T = 373$ K at $P_\perp = 400$ MPa at $v = 50$ m/s. The bottom part shows the degree of rotation in the shear plane along which the chains are oriented. Top part is a projection in the direction indicated by the arrow in the bottom part of the figure. Two chains are colored black in order to see examples of individual chains.
remains fluid. The difference between the 3 and 5 layer systems indicates that for \( m_l = 3 \) the walls induce sufficient order on the system that it can partially crystallize below the bulk crystallization pressure, \( P = 35.2 \) MPa. Since this crystallization pressure is small in comparison with the pressure fluctuations in our system, it is not surprising that partial crystallization occurs due to confinement.

That the crystallization is induced by confinement is confirmed by the system remaining fluid in the bulk simulations. Figure 3 shows the NEMD data at 300 K as well as 323 K. While the Newtonian value of the viscosity at 300 K, 1.6 cP, is larger than the value at 323 K, 1.24 cP, as expected, in the shear thinning regime the viscosities for both temperatures are very similar. The curves yield identical \( \alpha = 0.39 \). Thus, the bulk value of \( \alpha \) is in the range of the measured \( \alpha \) for confined hexadecane.

IV. COMPARISON TO BEAD-SPRING SIMULATIONS

Several differences exist between the results of the present simulations and the bead-spring chain simulations of Thompson \textit{et al.}\textsuperscript{17,18} In particular, the viscosity curves of the hexadecane simulations are qualitatively different from the curves of the bead-spring simulations and from experiment. The differences between the hexadecane simulations and experiments are not surprising given that shear rates in our simulations are up to 5 orders of magnitude larger than the experimental values. However, as we see below the usual mapping of the shear rates for the bead-spring system are at most only one to two orders of magnitude less than for the present simulations, even though the bead-spring chains have been successful in reproducing many aspects of the experiments. The main difference between the two simulations turns out to be the state points investigated.

One way to determine the effective shear rates of the bead-spring simulations is to map the model to a linear alkane, neglecting the difference in chain flexibility. Using typical LJ parameters yields time and pressure scales of the same order of magnitude as for the hexadecane simulations. For example, taking \( \epsilon = 0.1 \) kcal/mol, \( m = 14 \) g/mol (the mass of CH\(_2\)), and \( \sigma = 3.93 \) Å, the LJ time unit is \( \tau = (m\sigma^2/\epsilon)^{1/2} = 2.3 \) ps, and the pressure unit \( \epsilon/\sigma^3 = 11.4 \) MPa. This would map applied shear rates in the range \( 10^{-3} - 1 \) \( \tau^{-1} \) to the 1–100 GHz range. Typical loads of one dimensionless unit would map to values larger than 1 atm = 0.1 MPa, but loads of about 10 MPa are common in the experiments. On the other hand, if one considers the single bead simulations (\( n = 1 \)) to correspond to OMCTS, which is a spherical molecule of mass 236 g/mol for which the same scaling of \( \eta_{\text{eff}} \) on \( \dot{\gamma} \) has been observed,\textsuperscript{4} then one finds \( \tau = 21.3 \) ps and \( \epsilon/\sigma^3 = 0.95 \) MPa = 9.5 atm. Thus, the loads in the bead-spring simulations\textsuperscript{15} and the shear rates would be only a factor of 10 lower than found in the first mapping. For example, at \( m_l = 4 \), the minimum velocity of Ref. 17 is \( 4\sigma/\tau = 0.168 \) m/s. The applied shear rates are of order \( 10^{-3} \tau^{-1} = 0.5 \cdot 10^{-3} \) ps\(^{-1} = 0.5 \) GHz.

Because the bead-spring model is very flexible, it is probably more appropriate to map these simulations to polymers using the dimensionless diffusion constants.\textsuperscript{55} The ratio of the center of mass diffusion constant to the Rouse diffusion constant has been used to map \( \tau \) for various polymers.\textsuperscript{55} For polyethylene at 448 K, \( \tau \) is mapped to 6.6 ps which is similar to the values obtained for the mapping above. Even if we use the values for polydimethylsiloxane (PDMS) at 300 K, where \( \tau = 230 \) ps, the lowest shear rates are still about \( 10^8 \) Hz which is well above the 10 to \( 10^5 \) Hz experimental range. Since the shear rates for the bead-spring system are

FIG. 8. A snapshot of a \( m_l = 3 \) run at \( P_L = 0 \) MPa at \( T = 300 \) K and \( v = 20 \) m/s shows a projection normal to the walls (not shown). The shear direction is to the right.
numerically similar to the values used in the hexadecane simulations and far above the experimental regime, there must be another reason why one reproduces the experiment so well and the other does not.

The reason for the difference between the two simulations lies in their state points. Since we do not know the phase diagram for the bead-spring system, we examine the temperature in terms of the LJ coupling parameter. In most of the bead-spring simulations, the temperature \( T \) is 1.1e/k\(_B\), and the LJ coupling strength is \( \epsilon = 0.91k_B T \). For the hexadecane simulations the LJ parameters, in units of temperature (\( T = 323 \) K), are much smaller, \( \epsilon_{CH_2} = 0.15k_B T \) and \( \epsilon_{CH_3} = 0.35k_B T \). To simulate hexadecane at a temperature equivalent to the bead-spring system we would need to go to the 50 to 100 K range. Hexadecane is crystalline in this range. As seen in Fig. 3 and is well known, the viscosity increases as the temperature decreases. The bead-spring system is thus at a more viscous point in the bulk phase diagram, let alone the confined one. Moreover, the bulk viscosity shear-rate curves at various temperatures can be scaled onto a universal curve yielding a time-temperature superposition.\(^\text{36}\) That is, lowering the temperature is equivalent to decreasing the critical shear rate where the transition to non-Newtonian flow occurs. In other words, the temperature shift is equivalent to a shift of the time scales.

The significant contrast between the crystallization/vitrification tendencies of the two systems is also important here. As noted above, hexadecane is crystalline at the temperatures corresponding to the bead-spring simulations. In contrast, the bead-spring system is vitreous at these temperatures.\(^\text{17,18}\) The greater stiffness of hexadecane results in a stronger tendency to order in comparison to the fully flexible bead-spring molecule. This tendency to crystallize plays an especially important role in the confined simulations of hexadecane under a load. At 300 K, confinement can induce crystallization under zero load. At higher \( T \), the hexadecane molecules tend to elongate under large load, and for large enough load the chains become sufficiently rod-like that ordering occurs rather easily. In contrast, the bead-spring chains under shear do not show any tendency to stretch out as the load is increased.\(^\text{17,18}\) In fact, if anything, the chains tend to contract.

Because the system of bead-spring chains does not crystallize, the simulations can be performed at a state point that has a relatively large bulk viscosity, but where the relaxation times are still within reach of the simulations, at least for small \( n \). For the bead-spring simulations to see the confinement-induced increase in viscosity, the value of the critical shear rate \( \dot{\gamma}_c \) must be greater than \( 10^{-3} \). In other words, the relaxation time, \( \tau_r \), cannot be larger than 1000 \( \tau \). In the bulk, \( \tau_r \) for the bead-spring system at \( T = 0.9e/k_B \) is naturally much larger than at 3–57, which corresponds to the temperature range of the hexadecane simulations. Fortunately, magnitude of \( \tau_r \) is within range of simulation. In confinement at \( T = 0.9e/k_B \), \( \tau_r \) is not much larger than in bulk. In the bead-spring simulations the Newtonian viscosity increases only by a factor of 10 compared to the bulk viscosity; consequently, the relaxation time should also increase by only a factor of 10. Using the results of Ref. 55 we obtain a bulk \( \tau = 20\tau \), which yields a confined \( \tau = 200\tau \) and \( \gamma_c = 1/\tau = 5 \cdot 10^{-3} \tau^{-1} \). This is rather close to the value found in the simulations, \( \gamma_c = 10^{-2} \tau^{-1} \).\(^\text{17,18}\) This value of the confined relaxation time is within the range found in other bead-spring simulations.\(^\text{20,23}\) We thus find a time-temperature superposition that effectively puts the bead-spring system into a regime similar to the experimental regime.

On the other hand, there is an apparent inconsistency in similar arguments for the experimental results. The experimental viscosities are up to \( 10^8 \) times larger than bulk.\(^\text{3,7}\) This suggests that the relaxation time for hexadecane has increased by the same factor. However, the relaxation time for alkanes of similar length are all less than 1 ns.\(^\text{35}\) A factor of \( 10^5 \) increase yields relaxation times of about a microsecond, but this gives critical shear rates of \( 10^6 \) Hz which are much larger than that observed in experiment, \( \dot{\gamma}_c \sim 10 \) Hz. One possible explanation is that the large increase in \( \eta_{eff} \) with respect to bulk viscosity values, observed in the SFA experiments, may be accompanied by increasing slippage at the mica/hydrocarbon interface. In this case, the actual viscosity (and corresponding relaxation time) in the confined hydrocarbon system would be much larger than the observed \( \eta_{eff} \). Alternatively, this may indicate that, at low shear rates, a collective (rather than a single-particle) relaxation time controls the onset of the shear-thinning behavior and determines the magnitude of the viscosity in the confined system. While, at this stage, these remain speculative arguments, they make clear that identifying the relaxation process that controls the shear-thinning behavior is a crucial step toward developing a physical understanding of the SFA results.

V. CONCLUSION

We have performed molecular dynamics simulations of hexadecane between shearing plates with nanometer scale separations. The calculated effective viscosities depend strongly on the nature of the walls. We modeled the plates atomically with interaction strength that varied from typical values for hydrocarbons up to that for mica. In general, we find large slip at the fluid-wall interface. For hydrocarbon walls, the slip is practically complete and plug flow occurs. A consequence of this interfacial flow is that the effective viscosity increases with increasing plate separation in contrast to experiment\(^\text{5,7}\) and bead-spring simulations for short chains.\(^\text{17,18}\) This increase of the effective viscosity has been observed for simulations of entangled chains by Khare et al.\(^\text{24}\) We find that as the wall-fluid interaction is increased, the degree of slip decreases. The large slip occurs in the hexadecane system, because the fluid cohesion is relatively stronger than its adhesion to the wall. Consequently, shearing occurs more easily at the interface than in the fluid. As the wall is coupled more strongly to the fluid, more shearing is forced to occur in the bulk and the slip decreases.

The wall-fluid interaction also effects the calculated values of the scaling exponent of the viscosity. A stronger wall-
fluid coupling yields a larger exponent $\alpha$. For our strongest wall coupling, the confined hexadecane simulations yield $\alpha=0.4$, which is the same as our bulk NEMD value. The values of $\alpha$ are similar to that observed in experiments on hexadecane in confinement, where they were found to depend on the applied load.\textsuperscript{26} However, since the experimental shear rates are orders of magnitude smaller than the shear rates in our simulations, the corresponding values of $\alpha$ could apply to different regimes and may not be directly comparable. For the bead-spring chains as well as experiments on dodecane and OMCTS, the viscosity exponent $\alpha$ is approximately 2/3.

For confined fluids, the experiments find effective viscosities about 5 orders of magnitude larger than bulk. At much higher shear rates of our simulations, we find effective viscosities of order the bulk viscosity. This is consistent with extrapolating the experimental data to our shear-rate regime. In this matter, our hexadecane simulations are different from the earlier bead-spring simulations.\textsuperscript{17,18} However, we indicate that the bead-spring simulations correspond to a different phase point, lower in temperature, and using a time-temperature superposition argument, we have shown that the shear rates of the model simulations are shifted to correspond to the experimental one.

We have performed NEMD simulations in order to obtain bulk shear viscosity and compare its shear-rate dependence with the results in confined geometry. The Newtonian values of the bulk shear viscosity tend to be below the experimental values for the potential set used in this work. More work on potential development is clearly needed. The present work shows that the results of confined simulations can match the NEMD viscosities. The NEMD simulation yielded more accurate viscosity data, partly due to longer simulations allowed by a massively parallel computing platform, while the confined simulations were performed on workstations. Thus a comparison of the efficiency of the two methods cannot easily be made. To obtain reasonable results in the confined simulations, a strong wall-fluid interaction is required in order to observe Couette flow. Both methods require very long runs for the low shear rates where the Newtonian regime is observed.

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