Molecular dynamics study of the nano-rheology of \(n\)-dodecane confined between planar surfaces

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Realistic molecular simulations agree with previously published surface force experiments that \(n\)-dodecane confined between mica surfaces displays shear-thinning starting at shear rate orders of magnitude less than in the bulk fluid. We probe the origin of this behavior by studying rotational and diffusional relaxations in the simulated fluid and find a freezing-out of the rotational degrees of freedom and a power-law diffusional relaxation, resulting in over seven orders of magnitude increase in the relaxation time. © 2003 American Institute of Physics. [DOI: 10.1063/1.1568084]

I. INTRODUCTION

Experiments with surface force apparatus (SFA) on the rheological properties of fluids confined by mica surfaces under an applied external shearing force have observed an orders of magnitude increase in viscosity compared to the bulk fluid when the film thickness is less than about eight molecular layers.\(^1\)\(^{3}\) To explain the fundamental origin of this phenomenon, early simulations with simple atomic fluids confined to nm gaps noted stick-slip behavior similar to that observed in experiment. However, the stick-slip frequency observed in experiment was of the order of Hz,\(^4\) while that from simulation was of the order of \(10^{12}\) Hz.\(^5\) In more recent studies, direct calculations of viscosity using bead–spring models\(^6\) and more realistic united atom models\(^7,8\) observed typical liquidlike viscous behavior.

The confined fluids in the SFA experiments exhibited shear-thinning behavior, in which the viscosity decreases with increasing shear rate. For \(n\)-dodecane, as shown in Fig. 1, this occurs at a shear rate greater than \(\sim 10\) s\(^{-1}\). Shear-thinning is a general phenomenon, well established both theoretically and experimentally for bulk fluids including simple fluids, chainlike alkanes, and polymers, which occur when the shear rate exceeds the rate at which stress can relax through rotational and translational molecular motion.\(^9,10\) For bulk alkane fluids, recent, accurate molecular simulations have shown that it is possible to predict accurately the shear rate at which the transition to shear-thinning occurs\(^11\)\(^{14}\) as the inverse of the longest relaxation time. For alkanes with 10–30 carbons, this is the rotational relaxation time and is in the range of 0.1–10 ns, corresponding to shear rates of \(10^8\)–\(10^{10}\) s\(^{-1}\). Thus, the observed transition at \(\sim 10\) s\(^{-1}\) in the SFA experiment on confined \(n\)-dodecane represents an increase in the longest relaxation time at least eight orders of magnitude over that in the bulk.

In recent molecular simulations of confined \(n\)-dodecane\(^15\) using an effective surface–fluid interaction that reproduces the surface energy of the mica surface, we found that the density of the confined fluid must increase over its bulk value for the confined fluid to have the same normal pressure as the hydrostatic pressure of the bulk fluid; and that the density increases with decreasing distance between the confining surfaces. (The phenomenon is dependent on the strength of the wall–fluid attractive interaction. The strong wall–fluid attraction in the mica–alkane system resulted in a density increase in the confined fluid. It is possible that weak wall–fluid attraction may result in reduced density in confined fluids. See Ref. 15 for details.) At a separation of six molecular layers, where experiments observed a dramatic increase of viscosity, an ordered structure was observed in the simulations characterized by the layering and parallel packing of molecules in two perpendicular directions in the plane parallel to the walls. In this article, we present results of MD simulations on the rheological behavior of confined \(n\)-dodecane and compare them with the previously published experimental results of Granick \textit{et al.}\(^1\) We find that the simulated fluid exhibits many of the features observed in experiments, including comparable shear-rate dependent viscosity and shear thinning at shear rate orders of magnitude lower than in the bulk fluid. By investigating the relaxation times in

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the confined fluid, we elucidate the dynamical process of molecular relaxation and suggest a mechanism by which the experimentally observed dramatic increase of the relaxation time and viscosity can be understood.

II. MOLECULAR MODELS AND SIMULATION METHODS

As in previous work, n-dodecane is described by a united atom model and the wall–fluid interaction by a Lennard-Jones potential derived from a model for the wall that reproduces the surface energy of mica, using a large cutoff distance of 5σ (σ = 3.93 Å) to accurately take into account the effect of the long-range interaction. Simulations were started from a previously equilibrated configuration of a 16.78 ns run, and the wall atoms were thermostatted at 300 K. We note that bulk n-dodecane forms a triclinic crystalline structure upon freezing. The planar confinement studied here prevents the n-dodecane from forming such triclinic crystalline structure. For full details of the simulation method and the structures of the confined n-dodecane film, the reader is referred to Ref. 15.

We calculated viscosity by three methods. (1) We applied an equal and opposite constant stress to the top and bottom walls at constant film thickness. We then measured the average wall velocity and hence the induced shear rate and calculated the viscosity as the ratio of shear stress to shear rate. (2) We moved the top and bottom walls at equal and opposite constant velocity, also at constant film thickness, and measured the average shear stress in the fluid and again calculated the viscosity as the ratio of shear stress to shear rate. Similar complementary methods have been applied to bulk fluids. (3) We repeated the second method, but at constant (approximately atmospheric) normal pressure rather than constant film thickness.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows the results of the molecular simulations described above. For comparison, we also plot the calculated viscosity in bulk at the same temperature and pressure, and the results of Granick et al. for the viscosity of n-dodecane from SFA experiments. We note that the experiments are limited to shear rates of 10⁵ s⁻¹ and less by the instability of the mica surfaces at higher shear rates, while the small, finite system simulations are limited to shear rates of 10¹² s⁻¹ and higher due to thermal noise.

First, we observe the clear difference in viscosity between bulk and confined fluids from simulation. The bulk fluid exhibits a transition from the Newtonian plateau to shear-thinning at ~1.1 × 10¹⁰ s⁻¹ and has a Newtonian viscosity ~0.80 cP, compared to the experimental value of 1.3 cP for bulk n-dodecane. This level of agreement is typical of the united atom model for which the dynamics are faster than the fully atomistic model. In a previous publication, we have shown that the plateau viscosity agrees with independently calculated zero shear rate viscosity using the Green–Kubo formalism, demonstrating that the plateau in the shear rate-dependent viscosity correctly extrapolates to the zero shear viscosity and that bulk alkane fluids exhibit Newtonian behavior in a large range of shear rate. The transition point correlates well with the inverse of the calculated rotational relaxation time of 100 ps for bulk n-dodecane (see below). The calculation cannot distinguish the effects of rotational from diffusional relaxation with a relaxation time of 170 ps and a transition shear rate of 0.59 × 10¹⁰ s⁻¹. The shear-thinning at higher shear rate is dominated by the orientation of the molecules. For the confined fluid, the viscosity continues to increase with decreasing shear rate to the lowest shear rate calculated, 7.1 × 10⁷ s⁻¹, already over two orders of magnitude lower than the transition point for the bulk fluid. This directly validates the experimental phenomenon of confinement-induced slowing down. The shear-thinning can be described by a power law with exponents ~0.55 and ~0.62, for constant film thickness and constant normal pressure simulations, respectively.

We now consider the dynamics of the confined fluid to see if the observed shear-thinning behavior can be explained in terms of relaxation processes that can be probed by molecular simulation. Figure 2(a) shows the rotational relaxation of the equilibrium, confined fluid as characterized by the orientational correlation function (ORCF) of the unit end-to-end vectors of the molecules from a very long 38.8 ns averaging time. After an initial relatively fast relaxation of about 5 ns, the ORCF plateaus at 0.963, correspond to a maximum rotation angle of ~15°. This implies that a confined molecule rotates ~15° before colliding with another molecule because of the tight packing. The inset shows the comparison between the bulk and the confined fluid. In bulk fluid, the ORCF exhibits an exponential decay, giving a rotational relaxation time of 100 ps. Figure 2(b) shows the mean squared displacement (MSD) of the center of mass of the confined molecules in directions normal and parallel to the surface vs time. The inset in Fig. 2(b) shows a comparison of the MSD between the bulk and the confined fluids. The nearly vanishing normal MSD of the confined fluid is
easily understood since the molecules are aligned in the in-plane direction and are constrained to move in the lateral direction. Additionally, the solid walls prevent collective motion of the molecules in the normal direction. However, significant diffusion does occur in the in-plane directions, showing a power law behavior

\[ \text{MSD} \sim t^\alpha \]

very similar to that of polymers described by the reptation model

\[ r_i(t) \sim t^{1/2} \]

signifying the effect of space constraint,

\[ \langle [r_i(t) - r_i(0)]^2 \rangle = \lambda t^\alpha, \quad (1) \]

where \( \lambda = 6.855 \) and \( \alpha = 0.409 \), with \( t \) in units of nanoseconds and MSD in \( \text{Å}^2 \). Since the rotational degrees of freedom are frozen out and there is very little molecular motion in the normal direction, we expect the in-plane diffusion to be the main relaxation process for dissipating stress when the confined fluid is strained by an external shear force. If we knew the characteristic length for the confined fluid, the power law behavior in Eq. (1) would allow us to estimate a relaxation time. In bulk polymer rheology, the size of the polymer molecule is commonly used to estimate the relaxation time. Using the length of an \( n \)-dodecane molecule as the characteristic length, we estimate a diffusion time for the bulk fluid of about 170 ps. But the in-plane order in the confined fluid implies intermolecular correlation in the motion of the confined molecules, leading to a longer order correlation length than the length of one molecule. In their original work to understand their experimental results, Hu et al. proposed that the increased relaxation time was due to collective motion of the confined molecules. By measuring the variation of viscosity with normal pressure, they found an activation volume of 80 nm\(^3\), giving an in-plane area of 34 nm\(^2\) when divided by the thickness of 2.4 nm of the 6-layer film, corresponding to a characteristic length of 5.8 nm. Using 34 nm\(^2\) in Eq. (1) as the in-plane mean square displacement, we estimate a relaxation time of \( 3.9 \times 10^{-3} \) s, leading to a transition shear rate of \( 2.6 \times 10^2 \) s\(^{-1}\), seven orders of magnitude lower than for bulk dodecane and remarkably close to the experimental transition shear rate of \( \sim 10 \) s\(^{-1}\). We emphasize that such dynamical slowing down arises from the strong wall–fluid interaction-induced structured order, not from the reduced dimensionality for the ultrathin film. Our calculations with a six-layer \( n \)-dodecane film confined between hydrocarbon-like surfaces show rotational and diffusional relaxation on a time scale similar to that of the bulk.

The dynamical slowing down becomes more pronounced as thickness decreases. Figures 3(a) and 3(b) show the rotational and diffusional relaxation for a three-layer confined \( n \)-dodecane film. The in-plane (full line) and normal (dashed line) MSD of the three-layer confined \( n \)-dodecane.

\[ \text{FIG. 2. (a) Rotational relaxation of the unit end-to-end vector for confined } n \text{-dodecane. Inset shows the dramatic slowing down of rotational relaxation for confined } n \text{-dodecane fluids compared to bulk. (b) In-plane (full line) and normal (dashed line) MSD of confined } n \text{-dodecane. The smooth dotted line is a fit to the power law behavior. Inset shows the slow change of MSD in confined } n \text{-dodecane fluids compared to bulk.} \]

\[ \text{FIG. 3. (a) The rotational relaxation of the unit end-to-end vector for a three-layer confined } n \text{-dodecane film. (b) In-plane (full line) and normal (dashed line) MSD of the three-layer confined } n \text{-dodecane.} \]
IV. CONCLUSIONS

In summary, we have performed realistic molecular dynamics simulations of \( n \)-dodecane narrowly confined between mica surfaces under shear. The orders of magnitude increase of the Newtonian viscosity and the shear rate at which the onset of shear-thinning occurs (which is equal to the reciprocal of the longest relaxation time) are remarkably close to those measured in previous SFA experiments. The relaxation time inferred from simulation, similar to that measured in the experiment, is seven orders of magnitude larger than that of the bulk fluid. The results predict even more dramatic effects for \( n \)-dodecane confined to smaller thickness, as observed experimentally.

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