Very Low Friction State of a Dodecane Film Confined between Mica Surfaces

A. Jabbarzadeh,[1] Peter Harrowell,[2] and R. I. Tanner[1]
[1]*School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, New South Wales 2006, Australia*
[2]*School of Chemistry, The University of Sydney, New South Wales 2006, Australia*

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The existence of a very low friction state of a lubrication film is demonstrated in nonequilibrium molecular dynamics simulations of a six-layer dodecane film between mica walls. We argue that this low friction state is thermodynamically stable with respect to the well documented high friction film, the latter being a metastable state. These results are in striking accord with the recent report of Zhu and Granick [Phys. Rev. Lett. **93**, 096101 (2004).]. The extreme low friction is the result, not of wall slip, but of layer sliding throughout the film, a mechanism similar to solid lubrication.

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Over the last 15 years, a number of groups [1] have reported increases in the effective viscosity of liquid films confined between sliding mica surfaces by a factor of between 10^4 and 10^6 as the film thickness is reduced from infinity to 4–6 molecular diameters. The transition appears to be quite general. At temperatures well above their freezing points, thin films of spherical molecules [e.g., octamethylcyclotetrasiloxane (OMCTS)], linear alkanes (e.g., *n*-hexadecane and *n*-dodecane), or branched alkanes (e.g., squalene) have been observed to exhibit a substantial increase in viscosity with the transition taking place over only a few molecular layers [1,2]. The ubiquity of this transition to rigidity has been challenged recently by Zhu and Granick [3,4] who have suggested that artifacts arising from surface preparation and a failure to properly equilibrate the film may be responsible for the observed onset of rigidity in the thin films.

While the origins of the dramatic increase in viscosity remain unclear, there is considerable interest in exploring strategies to avoid this film ''stiffening'' and retaining the low friction of the lubricating film down to very small surface separations. In this Letter we present results of nonequilibrium molecular dynamics (NEMD) simulations of thin dodecane films which include clear evidence that, alongside the high friction behavior seen experimentally [2] and in previous simulations [5,6], there exists a second state of the film characterized by a very low friction, even smaller than the bulk viscosity. This low friction state is stable at rest with a free energy significantly lower than that of the high friction state.

Wall slip offers one route to low friction behavior. The observation of the slip of a shearing liquid against the adjacent wall has been well established for high viscosity liquids for some time [7]. The term ''superlubricity'' has been coined to describe another type of wall slip [8]. Here, low friction is observed between two phases whose structures are incommensurate with respect to one another. In this context, incommensurate means that no extended registry of structures is possible so that shear motion results in no overall change in that registry, and hence little to no friction results. This behavior has been observed for a variety of systems including silicon [9] surfaces and monolayers of adsorbates on metals [10]. Superlubricity, as defined here, is a direct consequence of structural rigidity. As one allows one or both phases to soften, there is an increase in local registry and, hence, friction [8]. Given the importance of film rigidity in producing superlubricity, it is not clear how significant this phenomenon is with regards to lubrication films. Barrat and Bocquet [11] have argued that structural mismatch between a liquid and a solid surface can result in a significant reduction in the interfacial friction and hence enhance wall slip. We are unaware of any results indicating the consequences of this structural mismatch in a thin lubricating film.

Most recently, Zhu and Granick [3,4] have demonstrated that, if mica surfaces are freshly cleaved immediately prior to the experiment without the use of a hot platinum wire, extremely low friction is observed in equilibrated films of OMCTS [3] and squalene [4]. Furthermore, the viscosity of these low friction films appears to be independent of film thickness down to 1 nm. This result is in sharp contrast with the previous observations of very high friction behavior in the same films where the mica surfaces had been prepared using the hot wire [2]. Using the fresh cleaved surfaces, Zhu and Granick have shown that for unequilibrated films the viscosity increases significantly with decreasing film thickness, similar to the previously reported behavior [2]. We suggest here that these observations indicate a new route to low friction behavior that is distinct from those already described here. Our justification for this distinction constitutes one of the main results presented here.

We present results of NEMD studies of a thin film of dodecane confined between model mica surfaces. Computational details can be found in Ref. [12]. A total of 96 molecules of *n*-dodecane are modeled using the intermolecular potential due to Siepmann and co-workers [13] with a cutoff of ~1 nm (2.5σ in terms of the potential parameters) for all potentials. The experimental Newtonian viscosity reported for dodecane is 1.34 mPa s

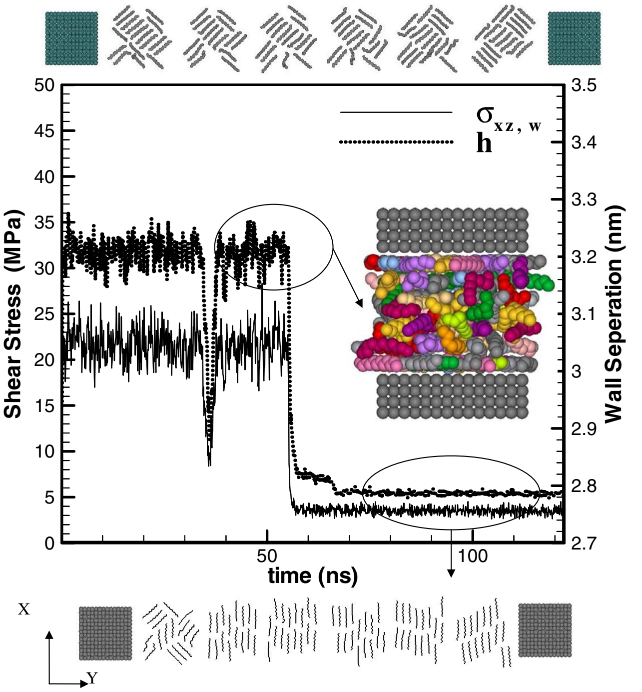

FIG. 1 (color online). Shear stress and film thickness of a six-layer dodecane film that is undergoing shear at shear rate 10^{11} s^{-1}. The results are shown against time, where $\sigma_{xz,w}$ and h are the shear stress calculated from the lateral force on the wall and the wall separation. The snapshots on the top, inset, and bottom, respectively, show equilibrated film configuration before applying the shear, the disordered film structure after application of shear at high friction regime, and orientation of the molecules in the layers after transition to the low friction regime.

for $\rho = 746$ kg/m^3 and 0.91 mPa s for $\rho = 727$ kg/m^3 [14]. The calculated bulk Newtonian viscosity from our simulations of the model dodecane is 1.6 mPa s and 0.95 mPa s for densities of 750 and 725, respectively. The wall is made of four (100) layers of a face centered cubic lattice with the atoms fixed at their lattice sites. The properties of the wall were selected to closely model the mica-alkane interface as in previous studies [5]. The lateral dimensions of the simulation cell are 3.6 nm × 3.6 nm. The initial configuration for dodecane was taken from an isothermal equilibrium simulation of the bulk liquid at a density of 750 kg/m^3 and a temperature of 300 K. Relaxation of the confined film between the two aligned mica walls was carried out over a run equivalent to 37.7 ns under a fixed normal load maintained using the Nosé-Hoover algorithm [15]. Unless otherwise indicated, all simulations have been carried out at a constant normal load of 1 atm and at 300 K. This protocol produced a film roughly 2.72 nm thick and comprising six well defined molecular layers. Within each layer, the molecules were found to have assembled into a mosaic of (roughly) square domains, exhibiting an imperfect registry with domains in adjacent layers. Each domain had a dimension roughly equal to the length of a single extended dodecane chain and consisted of molecules aligned along one of the two close packed (110) directions of the 100 surface. This pattern, which has been reported previously by Cui *et al.* [5,6] and Gao *et al* [16], is very similar to that characterized 20 years ago by Baumgärtner [17] in short semiflexible polymers on a 2D lattice. In the nonequilibrium simulations we applied a steady shear by moving the walls in opposite directions to produce shear rates covering the range 10^7–10^{11} s^{-1}. The shearing films were thermostatted using a homogeneous profile unbiased thermostat [15]. The streaming velocity at a position along the interface normal was obtained by averaging over the velocity of particles in the plane parallel to walls. Unless otherwise indicated, all shearing runs were begun with the relaxed stationary film configuration.

At the shear rate of 10^{11} s^{-1} we ran the simulation for 75 ns (16×10^6 time steps). The steady state at this shear rate exhibits a considerable dilation with a separation between walls of 3.8 nm, as compared with 2.7 nm at rest. The mosaic structure of the liquid film is completely disrupted for all layers except those adjacent to the walls, and there is a substantial reduction of layering in the center of the film. After 57 ns of shearing, we observed a spontaneous and irreversible transition to a new low stress state (see Fig. 1). This transition to low shear stress was accompanied with a sudden decrease of the film thickness to 2.8 nm. (To test the dependence of this observation on the potential cutoff we carried out similar calculations for a four-layer film with a cutoff of 5.0σ. We found an analogous transition to the low friction state here as well and conclude that our choice of cutoff does not significantly influence our results.) Further simulations for another 47 ns showed no signs of a return to the high stress state. This transition from the high friction (HF) state to the low friction (LF) state of the film was accompanied by a nematiclike alignment among the molecules. As shown in the configuration "snapshot" in Fig. 1, the alignment in the LF state in this case involved five of the six layers and was parallel with the shear flow direction. In other runs we have observed the alignment in the LF state to involve from two to five adjacent layers with the alignment either parallel or 45° to the flow direction. (The transition to 45° alignment was observed only in simulations at the lower shear rate of 10^{10} s^{-1}.)

In Fig. 2, we present the shear viscosity as a function of strain rate. The viscosity of the confined liquid has been calculated from the lateral forces on the wall atoms. The viscosity of the film in the HF state is well described by a power law $\eta \propto \dot{\gamma}^{-0.71}$ over the whole range of shear rates studied. These values are in good agreement with the simulation results of Refs. [5,6] for the same model. They are also consistent with the measurements of the six-layer dodecane film by Hu *et al.* [2] who reported a crossover to nonlinear behavior at $\dot{\gamma} \approx 10$ s^{-1} and a subsequent power law $\eta \propto \dot{\gamma}^{-0.66}$.

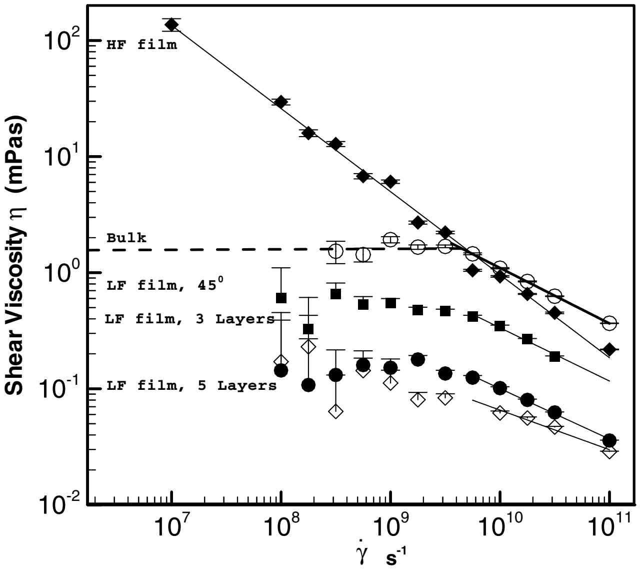

FIG. 2. The shear viscosity is plotted against the shear rate for a bulk and confined dodecane films. The confined dodecane shows two distinct regimes of low and high viscosity for a six-layer film. The bulk simulations are conducted at fixed density of 750 kg/m^3 and the same temperature. The results are shown for high friction film (solid diamonds), bulk (open circles), low friction film with 45° aligned layers (solid squares), low friction film with three of the six layers aligned (solid circles), and five of the six layers aligned (open diamonds) in the flow direction. The slopes of the shear thinning regime are -0.71, -0.47, -0.46, -0.43, and -0.34, respectively.

To characterize the various LF states, we started with configurations generated at high shear rates and then examined their rheology over a range of lower shear rates. The LF states are all characterized by viscosities lower than that of the bulk dodecane and with the crossover to apparent Newtonian behavior at roughly the same shear rate, $\dot{\gamma} \approx 10^9$ s^{-1}, at which the crossover occurs in the bulk. In this Newtonian regime, the LF states have viscosities in the range 0.2–0.7 mPa s, significantly lower than the bulk viscosity of 1.6 mPa s, also in the Newtonian regime. The viscosity of the LF state is found to decrease with an increasing degree of molecular alignment along the flow direction. We note, however, that even the 45° alignment appears to behave linearly at the lowest shear rates. Based on this observation it is unlikely that any LF state will exhibit a static friction.

If we assume, based on the experimental data, that the HF state exhibits Newtonian behavior for $\dot{\gamma} < 10$ s^{-1}, then the viscosity in the low shear rate limit would be similar to that observed experimentally [2], roughly 10^6 mPa s, over 6 orders of magnitude larger than the value in the LF state. Monitoring the average film thickness of the HF and LF states as a function of strain rate we found the rapid increase in thickness in the HF state for $\dot{\gamma} > 10^{10}$ s^{-1}. We assume that it is this increase in dilation that drives the transition to the LF state at high strain rates. This conclusion is supported by our observations that the HF → LF transition occurs at lower strain rates at high normal loads.

Once formed, the LF state was found to be stable at all shear rates including zero shear. Using the configuration depicted at the bottom of Fig. 1 as the initial state, the film was simulated at rest for 47 ns with no sign of any significant structural change. (Over this time interval, molecules in the LF state moved an average of 50σ and 3σ parallel and perpendicular to the direction of molecular alignment, respectively.) The total energy of the LF state at rest was found to be -3.587 kJ/mol as compared with a total energy of 0.042 kJ/mol for the HF state at rest. We can estimate an upper bound on the difference in configuration entropy between the HF and LF films at rest to be $T\Delta S = T(S_{\mathrm{LF}} - S_{\mathrm{HF}}) = -1.035$ kJ/mol [18]. Even though the film thickness is allowed to fluctuate, the constraint of an integer number of layers in the film effectively constrains the film at zero shear rate to a thermodynamic state best represented by the canonical ensemble. The difference in the Helmholtz (canonical) free energy is $\Delta A = A_{\mathrm{LF}} - A_{\mathrm{HF}} = \Delta E - T\Delta S = -2.594$ kJ/mol. We conclude that the LF state has a lower free energy than that of the HF state.

To summarize, we have established that there exists a low friction state of the six-layer dodecane film between mica surfaces. Free energy estimates suggest that the LF state is thermally stable with respect to the HF state. We have found no sign of the film spontaneously adopting the LF state at rest during our simulations, suggesting that the ordering processes at rest are too slow to be observed in our simulations. The metastable HF film

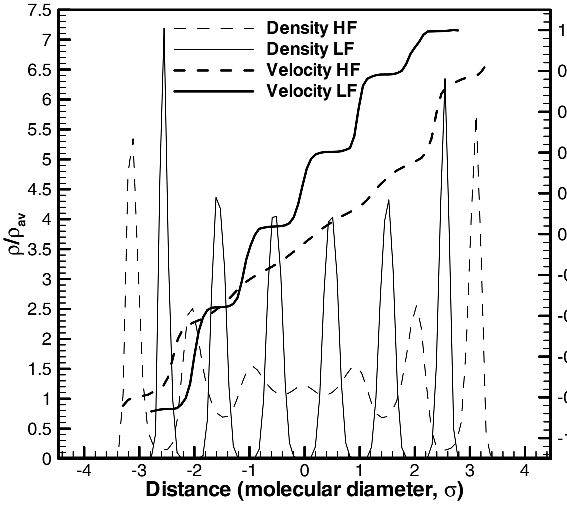

FIG. 3. Velocity and density profiles across the six-layer dodecane film at high and low friction regimes at a shear rate of 10^{11} s^{-1}. While for the disordered HF film the velocity is almost linear at the middle of the film, for the LF film the velocity profile is stepwise, indicating the slip happening between the layers of the film.

generates the rheological behavior already well established from both experiment and simulation. All of the features listed above are shared by the low friction state reported by Zhu and Granick [3] using clean mica surfaces. While we have generated our LF film via a method quite different from that used in Ref. [3], we believe that our nonequilibrium route essentially accelerates the kinetics of the transition rather than generating a completely distinct state from that obtained at rest. We propose that the similarities in the properties of the LF films outlined above justify the proposal that our new LF state is the analogue of that reported in Ref. [3].

How does the LF state achieve its low friction? Superlubricity, suggested in Ref. [3] as the explanation, is associated with wall slip. In Fig. 3 we compare the average velocity and density profile through the HF and LF films at a strain rate of 10^{11} s^{-1}. Neither state exhibits any sign of significant wall slip. Instead, we see that the aligned LF state involves layer slippage throughout the dodecane film while the HF state exhibits a uniform shear gradient. Slipping between layers is also observed in those LF films with only partial alignment or with alignment 45° to the flow direction. (This result is system dependent. Gao *et al.* [19] do see wall slip in simulations of hexadecane films confined between gold surfaces.) Lubrication involving sliding layers is more characteristic of solid lubricants (e.g., graphite or MoS_2) than liquid ones.

In conclusion, we have shown for the first time that a confined film can support multiple rheological states. The newly discovered LF state represents the state of lowest free energy found so far for the confined liquid. In this regard, our LF state is similar to the low friction films observed by Zhu and Granick [3,4] following slow equilibration between clean surfaces. We present evidence to suggest that the low friction state resembles a solid lubricant in its characteristic sliding layers dynamics. Perhaps this is the characteristic of the ideal lubricant—a fluid lubricant that wets the solid surfaces and, under strong confinement, transforms itself continuously into something resembling a solid lubricant.

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[18] The configurational entropy of the HF state was calculated assuming that each layer adopted a chess-board-like array of domains, each domain consisting of four aligned molecules. This gives 48 distinct choices for the origin of the domain array in a layer. We assume that each domain can adopt one of two possible directions of alignment independently of that adopted by neighboring domains. This introduces a multiplicative factor of 2^n, where n is the number of domains per layer and equals 4 in our simulations. We consider each of the six layers to be uncorrelated. This gives a total number of $(48 \times 2^4)^6$ configurations. Since we are interested in an upper bound on the entropy difference, we have taken the configurational entropy of the LF state to be zero.

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