

Simulations of the static friction due to adsorbed molecules

Gang He and Mark O. Robbins

Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218

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The static friction between crystalline surfaces separated by a molecularly thin layer of adsorbed molecules is calculated using molecular dynamics simulations. These molecules naturally lead to a finite static friction that is consistent with macroscopic friction laws. Crystalline alignment, sliding direction, and the number of adsorbed molecules are not controlled in most experiments and are shown to have little effect on the friction. Temperature, molecular geometry, and interaction potentials can have larger effects on friction. The observed trends in friction can be understood in terms of a simple hard sphere model.

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I. INTRODUCTION

The last decade has seen great advances in techniques for measuring friction in contacts whose geometry and/or chemistry are controlled with atomic precision.¹⁻⁶ At the same time, increases in computational power have allowed increasingly realistic simulations of friction.^{7,8} These studies reveal unexpected behavior that raises questions about the molecular origins of static friction and the “laws” of friction that describe most macroscopic objects.

Friction is the lateral force needed to slide one object over another. The force needed to initiate sliding is called the static friction F_s . Its existence implies that the surfaces have locked into a local free energy minimum, and F_s represents the lateral force needed to displace them out of this minimum (Sec. II B).^{7,9,10} The force needed to maintain a constant sliding velocity v is called the kinetic friction $F_k(v)$, and it represents the force required to replace energy dissipated during sliding.

Macroscopic objects almost always exhibit a finite static friction and a kinetic friction that is smaller at low velocities. One puzzling result from many molecular scale theories of friction between bare surfaces is that the static friction almost always vanishes, and is not closely related to the kinetic friction.^{7,11} This indicates that some important feature is missing from these model systems, that must be included to make contact with macroscopic experiments. Of course real surfaces are generally not bare, but are coated with a layer of adsorbed molecules, as well as dust, dirt, and other debris. In this paper we explore the influence of a layer of molecules between two surfaces on friction forces, and show that including such layers naturally leads to behavior that is consistent with macroscopic measurements.

Over 300 years ago Amontons published two “laws” of macroscopic friction that are still taught and used today.¹² These state that the friction is proportional to the normal load L pushing two surfaces together, and independent of the apparent geometrical area of these surfaces A_{app} . Subsequent work^{3,4,13-18} is consistent with a more general friction formula that is based on the observation¹⁹⁻²¹ that the actual area of molecular contact between two surfaces A_{real} is much smaller than the nominal surface area A_{app} . The friction is assumed to be given by A_{real} times a local shear stress τ . If τ rises linearly with the local contact pressure P ,

$$\tau = \tau_0 + \alpha P, \quad (1)$$

then since $P = L/A_{\text{real}}$

$$F = \tau A_{\text{real}} = \tau_0 A_{\text{real}} + \alpha L. \quad (2)$$

This expression agrees with Amontons’s laws if A_{real} is proportional to L or if τ_0 is sufficiently small compared to αP . The former condition applies if the load is high enough to produce plastic deformation of the surfaces so that L/A_{real} remains equal to the hardness.¹⁹ It also holds for nonadhesive contacts between ideal elastic solids with random surface roughness.^{22,23} However, any adhesive bonding leads to friction in the limit of zero load and violates Amontons’s laws. For a piece of adhesive tape the first term in equation (2) dominates at low loads, and in many cases friction can be observed at negative loads.

Early attempts to explain Amontons’s laws and the existence of static friction were based on the idea that peaks on one surface interlock with valleys on the other surface.^{12,19} In order to slide, the top surface must then be lifted up a ramp formed by the typical slope $\tan \psi$ of the bottom surface. If there is no microscopic friction between the surfaces, then the minimum lateral force to initiate sliding is $F_s = L \tan \psi$. This result satisfies Amontons’s laws with a constant coefficient of friction $\mu_s \equiv F_s/L = \tan \psi$ that can span all possible values. However, this geometrical model for friction cannot explain many experimental observations. For example, coating a single monolayer of surfactant on a surface does not change its slope, but can reduce the friction by more than an order of magnitude. It is also well known that making surfaces too smooth actually leads to an increase in friction.^{19,24} A practical illustration of this is that magnetic hard disks are purposely roughened to reduce friction.

The fundamental problem with the above explanation for the origin of static friction is that there is no reason for the peaks from different surfaces to be correlated. In general one expects that at any instant in time some peaks will be moving up a ramp and an equal number of peaks will be moving down. The net lateral force will average to zero and there will be no static friction. A similar problem arises if one imagines that the interlocking peaks are individual atoms as in the “cobblestone” model discussed by Israelachvili and co-workers.^{17,25} If atoms are from two identical, aligned surfaces all of them will go up ramps simultaneously yielding

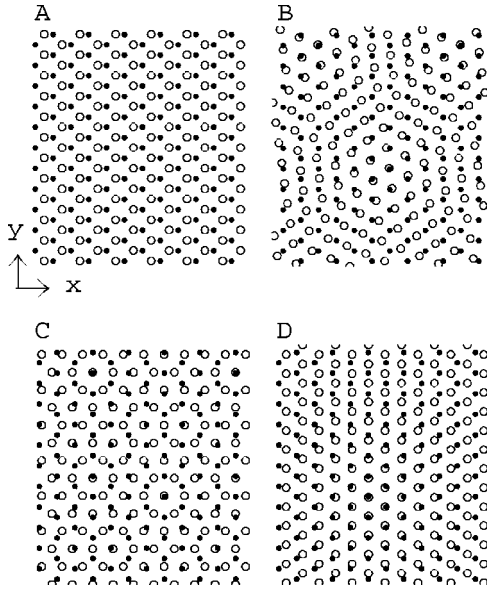


FIG. 1. Projections into the x - y plane of atoms from the inner surfaces of the bottom (solid circles) and top (open circles) walls. In A through C the two walls have the same structure and lattice constant, but the top wall has been rotated by 0° , 8.2° , or 90° , respectively. In D the walls are aligned, but the lattice constant of the top wall has been reduced by $12/13$. The atoms can only achieve perfect registry in the commensurate case A. The simulation cell was usually at least four times the area shown here.

Amontons's laws. However, friction measurements are usually made between misaligned surfaces or surfaces with different lattice constants. In this case the force from atoms moving up ramps should cancel the force from atoms moving downward, yielding a vanishing static friction.

A number of detailed analytic^{26–30} and simulation^{7,9,31–35} studies have concluded that F_s should generally vanish between bare crystalline or disordered surfaces. The exception is the case of commensurate surfaces that share a common periodicity in their plane of contact. In this case the free energy varies with the phase difference between the common Fourier components, and simulations of such surfaces^{36,37} find a static friction that rises linearly with pressure as in Eq. (1). However, the probability that two contacting surfaces are commensurate is infinitesimally small. Even identical surfaces are only commensurate when they are perfectly aligned.³¹ Any misorientation (Fig. 1) causes the surfaces to become incommensurate, i.e., have no common period. The free energy is then independent of translations and F_s is identically zero.^{27,28,30} If the interactions between the two surfaces are strong enough compared to interactions within the surfaces they may deform into a commensurate structure.^{9,27,28} However, this criterion is unlikely to be met for most of the surfaces around us, which have been chemically passivated by exposure to air. Indeed calculations for clean surfaces in vacuum find zero static friction between different facets of the same metal.^{30,31,34,38} Moreover, contacts that are known to be in the elastic limit exhibit static friction.^{3,4,16–18} Edge effects can lead to a finite static friction, but are not significant for the micron-sized contacts typically found between macroscopic objects.³⁹ Chemical

disorder and surface roughness are also unable to produce observed friction forces.^{23,39–41}

There are relatively few direct experimental measurements of the friction between bare crystalline surfaces. However, studies of adsorbed monolayers,^{42,43} small crystalline tips,⁴⁴ mica,⁴⁵ and molybdenum disulfide⁴⁶ support the conclusion that friction vanishes in this limit. A finite friction has been observed between clean metallic surfaces,^{19,47} but the surfaces were rough and the load appears to have been high enough to produce plastic deformation. Further work in this area would be of great value in testing the above theoretical models.

In recent papers^{9,39,48,49} we have suggested that the so-called “third bodies” that are present between most contacting surfaces^{50,51} can provide a general mechanism for static friction. These third bodies may take the form of wear debris, dust, or small hydrocarbon or water molecules that are adsorbed from the air. The interactions between such bodies are generally weaker than the interactions within the bounding solids. This frees them to rearrange at the interface to lower their free energy and lock the surfaces together. The layer of third bodies creates an immense number of metastable states, like that in a glass or granular medium. The third bodies can always fall into one of these states that is in registry with both bounding walls and thus produce static friction.⁵²

In this paper we report extensive studies of the static friction produced by layers of spherical or short-chain molecules between crystalline surfaces. We begin by describing different methods of measuring the static friction and establishing that it has a well-defined thermodynamic limit. Then the effect of temperature, wall geometry, interaction potentials, chain length, and areal density on the static friction are explored. In each case the static friction obeys equation (1) over the experimentally relevant pressure range. Factors that are not controlled in typical macroscopic experiments have little influence on τ_0 and even less effect on α , which dominates the friction at high loads. Such factors include wall geometry, sliding direction, and the length and density of adsorbed molecules. Increasing the temperature lowers τ_0 , but has relatively little effect on α . The value of α is strongly dependent on the interaction potential, particularly the effective hard sphere size of the molecules compared to that of wall atoms. All of our results can be understood in terms of a simple geometrical explanation^{39,49} for the origin of Eq. (1) (Sec. III F).

The following section describes the details of our simulations and the algorithms used to determine F_s . Section III determines the effect of each parameter in our simulations on the static friction and describes a simple geometrical picture that explains all of the observed trends. The final section summarizes the results.

II. SIMULATION METHOD

A. Potentials and geometry

We use a bead spring model⁵³ that allows us to explore the behavior of simple spherical molecules or short chains between bounding solids. Each molecule contains n spherical

TABLE I. Values of the orientation angle θ and the corresponding two-dimensional basis vectors and number of atoms per surface layer in the top wall. Both surfaces have hexagonal symmetry. The final column gives the percentage difference between the nearest-neighbor spacings in the two walls.

θ	\vec{b}_1/d_{nn}	\vec{b}_2/d_{nn}	Number of atoms	$(1 - d'_{nn}/d_{nn})$ (%)
0°	\vec{i}	$(1/2)\vec{i} + (\sqrt{3}/2)\vec{j}$	2304	0
2.02°	$(588/601)\vec{i} + (12\sqrt{3}/601)\vec{j}$	$(276/601)\vec{i} + (300\sqrt{3}/601)\vec{j}$	2404	-2.1
4.127°	$(192/193)\vec{i} + (8\sqrt{3}/193)\vec{j}$	$(84/193)\vec{i} + (100\sqrt{3}/193)\vec{j}$	2316	-0.3
6.3°	$(564/559)\vec{i} + (36\sqrt{3}/559)\vec{j}$	$(228/559)\vec{i} + (300\sqrt{3}/559)\vec{j}$	2236	1.5
8.2°	$(48/49)\vec{i} + (4\sqrt{3}/49)\vec{j}$	$(18/49)\vec{i} + (26\sqrt{3}/49)\vec{j}$	2352	-1.03
10.4°	$(564/571)\vec{i} + (60\sqrt{3}/571)\vec{j}$	$(192/571)\vec{i} + (312\sqrt{3}/571)\vec{j}$	2284	0.44
14.4°	$(564/589)\vec{i} + (84\sqrt{3}/589)\vec{j}$	$(156/589)\vec{i} + (324\sqrt{3}/589)\vec{j}$	2356	-1.1
19.1°	$(20/21)\vec{i} + (4\sqrt{3}/21)\vec{j}$	$(4/21)\vec{i} + (12\sqrt{3}/21)\vec{j}$	2268	0.79
25.2°	$(33/37)\vec{i} + (9\sqrt{3}/37)\vec{j}$	$(3/37)\vec{i} + (21\sqrt{3}/37)\vec{j}$	2368	-1.4
$30^\circ/90^\circ$	$(6/7)\vec{i} + (2\sqrt{3}/7)\vec{j}$	$(4\sqrt{3}/7)\vec{j}$	2352	-1.03

monomers. All monomers interact with each other through a truncated Lennard-Jones potential:

$$V(r) = \begin{cases} 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 - (\sigma/r_c)^{12} + (\sigma/r_c)^6], & r < r_c \\ 0, & r > r_c. \end{cases} \quad (3)$$

The parameters σ and ϵ are chosen as the units of length and energy, respectively. Combined with the monomer mass m , they determine the unit of time $t_{LJ} = (m\sigma^2/\epsilon)^{1/2}$. Typical values for hydrocarbons are: $\sigma \sim 0.5$ nm, $\epsilon \sim 30$ meV and $t_{LJ} \sim 3$ ps. We consider the case $r_c = 2^{1/6}\sigma$ to simulate a purely repulsive potential, and $r_c = 2.2\sigma$ is used to study the effect of adhesive forces.

Monomers are bound into chains by an additional strongly attractive potential between nearest neighbors on the same molecule,

$$V^{CH}(r) = \begin{cases} -\frac{1}{2}kR_0^2 \ln[1 - (r/R_0)^2], & r < R_0 \\ \infty & r \geq R_0, \end{cases} \quad (4)$$

where $R_0 = 1.5\sigma$ and $k = 30\epsilon\sigma^{-2}$. These parameters are chosen to prevent chain crossing as described in previous work.⁵³ We consider the case of spherical molecules ($n = 1$), and of short chains with $n = 3$ and 6. Based on mappings of the bead-spring model to real molecules,⁵³ this corresponds to alkane chains with up to roughly 16 carbons. Substantially longer molecules are unlikely to have sufficient volatility to contribute to the airborne contamination that is present on any surface. Polymers are often placed at interfaces intentionally to act as lubricants. We have not addressed the behavior of these much longer molecules.

Molecules are confined between two walls formed by the (111) surfaces of fcc crystals directed normal to the z axis. Wall atoms are connected to their lattice sites with springs of stiffness k_s in order to model elastic deformation in the simplest way.⁵⁴ We consider the completely rigid case, $k_s = \infty$, and $k_s = 840\epsilon\sigma^{-2}$ or $210\epsilon\sigma^{-2}$. Both of the latter values correspond to relatively compliant solids (Sec. III D). For ex-

ample, at $T = 0.7\epsilon/k_B$ the root mean squared (rms) displacements about lattice sites calculated from equipartition are about $.05\sigma$ and 0.1σ , respectively.⁵⁵

Wall atoms and fluid monomers also interact with a Lennard-Jones potential but with different characteristic energy and length scales σ_{wf} and ϵ_{wf} , respectively. These are varied to determine the effect of molecular size and chemistry on static friction. Direct interactions between atoms on different walls are not included in the simulations. They vanish identically for the short cutoff $r_c = 2^{1/6}\sigma$ used in most of our simulations, and have a very small effect on calculated quantities at larger r_c . Tests of the effect of wall-wall interactions are discussed briefly in Sec. III F.

Periodic boundary conditions are imposed in the plane of the walls. These periodic boundary conditions prevent us from considering truly incommensurate systems. However, the effect of commensurability rapidly decreases as the length of the common period increases.^{7,9,10,39} The degree of commensurability between the walls is varied in two ways. The first is to rotate the top wall by an angle θ about the z axis ($A-C$ of Fig. 1). Only the range of θ from 0 to 30° produces inequivalent results. The second is to retain the alignment of the two lattices ($\theta = 0^\circ$), but to change the ratio of the lattice constants of the bottom and top walls from unity to 12/13 (D of Fig. 1).

The simulation cell is a rectangle whose height along y is $\sqrt{3}/2$ times the length along x , and the [110] direction of the bottom wall is directed along the x axis. Special values of θ are chosen that allow both top and bottom surfaces to retain perfect triangular symmetry, and to have nearly the same nearest-neighbor spacings. Values for the percentage difference between the spacing on the bottom, d_{nn} , and on the top, d'_{nn} , walls are given in Table I. The difference is typically less than 2%, and no trends were seen with the sign or magnitude of this difference.

The system is thermostatted by coupling to a heat reservoir through Langevin noise and damping terms in the equation of motion.⁵⁶ Previous work shows that coupling along the direction of sliding produces a direct effect on the kinetic

friction, while coupling to the perpendicular components does not.^{7,35,57} Thus only the perpendicular components are thermostatted. Their equations of motion contain additional damping and noise terms that are not present for the parallel components,

$$m\ddot{x}_{\perp} = \vec{F}_{\perp} - m\Gamma\dot{x}_{\perp} + \vec{W}_{\perp}, \quad (5)$$

where F is the force from the interaction potentials, Γ is the damping constant that controls the rate of heat exchange with the reservoir, and W is the Gaussian-distributed random force acting on each monomer. The rms value of W is determined from Γ through the usual fluctuation-dissipation relation.⁵⁶ The equations of motion are integrated using a fifth-order, Gear predictor-corrector algorithm.⁵⁸ In most cases the time step $dt = 0.005t_{\text{LJ}}$ and $\Gamma = 0.4t_{\text{LJ}}^{-1}$. As discussed in Sec. III A, our measured static friction forces are insensitive to the choice of Γ .

The areal density of monomers is specified as the effective coverage on the separate surfaces before they are brought into contact. To avoid ambiguities in the definition of the monolayer density, we define the coverage as the number of adsorbed monomers divided by the total number of wall atoms in the surface layers of both walls. A coverage of 1/2 means that each wall had half as many adsorbed monomers as surface atoms before the walls were placed in contact. After contact the monomers from the two walls will produce about a monolayer between the walls, because the monomers and wall atoms have roughly the same size in our simulations. This definition assumes that the molecules lie flat between the two walls at coverages below 1/2. Simulations with realistic potentials⁵⁹ show that even when films are a few layers thick short alkane molecules lie flat along bounding walls.

To prepare initial configurations, we typically start with monomers in a crystalline state, or in the final state of a simulation for different conditions. The system is then heated to a temperature of $1.9\epsilon/k_B$ at a constant pressure of $4\epsilon\sigma^{-3}$ until the configuration has randomized (typically $500t_{\text{LJ}}$). Finally, the temperature and pressure are ramped to the desired value over $50t_{\text{LJ}}$ and allowed to equilibrate there for $450t_{\text{LJ}}$. Results for the static friction are not sensitive to changes in this procedure.

B. Determining the static friction

As noted in the introduction, static friction arises because the system has managed to lock into a local free energy minimum. The total energy needed to activate the system out of this free energy minimum increases with increasing system size.⁶⁰ However, for any finite system, thermal fluctuations will eventually lead to activated diffusion in the absence of any lateral force. This diffusion has been studied previously for the same model system used here.⁹ As discussed by these authors, the static friction is only well-defined if the limit of infinite system size is taken before the limit of long times. If the limits are taken in this order, then the static friction corresponds to the maximum derivative of

the free energy as the system is driven out of its local minimum.⁶⁰ If the order is reversed, the static friction is always zero.

Note that even in the infinite-size limit there may be rate dependence in the measured static friction. This is because the effective free energy surface depends on the degree to which monomers can diffuse between the walls. Based on our recent studies of kinetic friction, we expect that monomer diffusion will lead to a weak logarithmic dependence of static friction on measurement time.⁴⁹ This is analogous to the logarithmic rate dependence in the apparent yield stress of glassy systems.⁶¹

Two methods are used to find the static friction. We call them ‘‘ramp’’ and ‘‘search,’’ respectively. In both cases, simulations are done with the bottom wall fixed and the top wall under constant normal pressure P . A lateral or shear stress τ is then applied to the top wall at an angle ϕ relative to the x axis. The equation of motion for the lattice sites in the top wall is integrated in the same way as that for the monomers and wall atoms.⁶² All lattice sites move together with an effective mass equal to the number of wall atoms times m . When k_s is finite, the force acting on this mass is the sum of the spring forces and the external normal and shear forces. In the case of rigid walls, the force is the sum of the external forces and the interactions between wall atoms and monomers.

In the ramp algorithm, the shear stress is increased from zero at a constant rate until the wall begins to slide. The stress at which motion initiates is recorded, and the stress is then decreased at the same slow rate. The wall stops moving as the force decreases towards zero, and then begins to slide again in the other direction when the force is sufficiently negative. The magnitude of this depinning force is recorded, and the stress is increased once more. This oscillatory process is repeated at least 15 times to get a statistical sample of depinning forces. The stress is typically changed at a rate of $0.002\epsilon/\sigma t_{\text{LJ}}$. This rate must be slow enough that the wall has time to repin as the magnitude of the force drops. It also sets the accuracy on determining the depinning force, because a finite time is needed before motion of the top wall can be detected. In most cases the force is increased until the wall reaches a relatively high sliding velocity ($0.5\sigma/t_{\text{LJ}}$) and the depinning point is identified with the end of the last previous interval of $20t_{\text{LJ}}$ during which the wall moved less than 0.5σ .

In the search algorithm, we first guess upper and lower bounds for the static friction. Then a lateral stress equal to the average of these values is applied to determine whether sliding occurs.⁶³ The top wall is considered to be stuck if it moves by less than 1σ in $100t_{\text{LJ}}$ and to be sliding if it moves by more than 5σ . If it moves an intermediate distance, the motion is followed for another $100t_{\text{LJ}}$, and the wall is considered to be sliding if it moves by more than it did during the first $100t_{\text{LJ}}$. If the trial stress does not lead to sliding it becomes the new lower bound, and if sliding does occur the trial stress becomes the new upper bound. The system is then returned to an identical initial condition, and a stress midway between the two new bounds is applied. This process is repeated enough times (typically five) to obtain the threshold

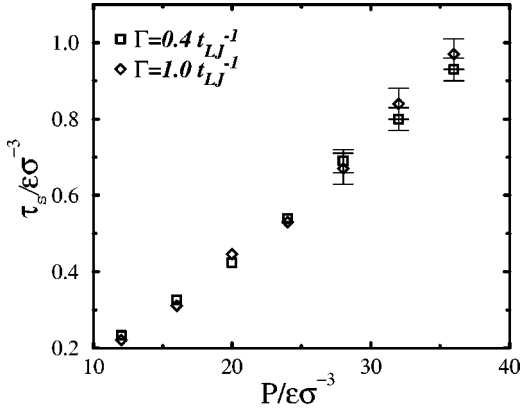


FIG. 2. Yield stress vs pressure for two values of the parameter Γ that controls the rate of heat exchange with the thermostat [Eq. (5)]. We observed no influence of the thermostat on the yield stress. For this data, the coverage is $1/2$, $\theta = 90^\circ$, $\sigma_{wf} = 1.0\sigma$, $\epsilon_{wf} = 1.0\epsilon$, $r_c = 2^{1/6}\sigma$, $d_{nn} = 1.2\sigma$, $T = 0.7\epsilon/k_B$, and $n = 6$. The search algorithm was used, and the simulation cell was 28.8σ by 24.9σ . Error bars are indicated when they are bigger than the symbol size.

stress with a precision of better than $\pm 0.02\epsilon\sigma^{-3}$. To get good statistics, different initial configurations are tried. These are generated by allowing sliding to occur for a distance of at least 5σ and then equilibrating the system at zero lateral stress for at least $100t_{LJ}$.

III. RESULTS

We first consider how technical details of the simulations may influence the results. These include the effects of thermostatting, system size, and the choice between ramp and search algorithms. Then the relevant physical parameter space is explored. First the variations with pressure, temperature, and wall stiffness are discussed. Then the effects of parameters that are not controlled in experiments are considered. These include the wall orientation θ , sliding direction ϕ , coverage, and chain length n . Finally, the effect of the potential parameters σ_{wf} , ϵ_{wf} , and r_c is explored.

A. Effect of thermostat

As described in the previous section, the wall atoms and monomers are coupled to a thermostat in order to maintain a constant temperature. The rate of heat transfer Γ is chosen to be small enough that the thermostat has little effect on the dynamics over the time scale required for the velocity autocorrelation function to decay to zero.

The main function of the thermostat is to remove heat generated by sliding friction. Previous work shows that the thermostat has little effect on kinetic friction if it is only coupled to the velocity components that are perpendicular to the sliding direction.^{35,57} Our focus here is the static friction. This should be even less sensitive to the thermostat since no heat is generated until sliding starts, and this is at a force greater than the static friction.

Figure 2 compares results for the static friction as a function of pressure P for $\Gamma = 0.4$ and $1.0t_{LJ}^{-1}$. The coverage was $1/2$ and the other parameters for these simulations were θ

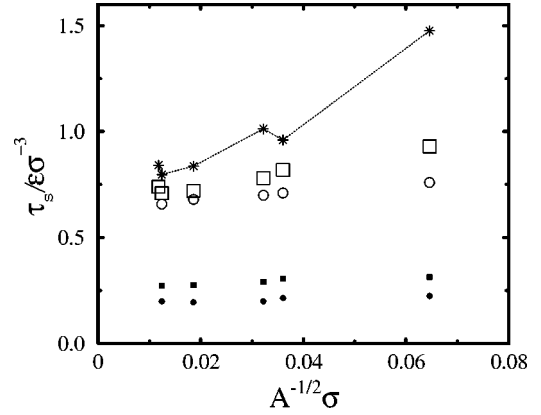


FIG. 3. Mean yield stress as a function of the inverse square root of the area A of the periodic simulation cell for the ramp (squares) and search (circles) algorithms at $P = 12\epsilon\sigma^{-3}$ (closed symbols) and $P = 28\epsilon\sigma^{-3}$ (open symbols). The maximum stress needed to initiate sliding from any initial condition at $P = 28\epsilon\sigma^{-3}$ is indicated by asterisks for the ramp algorithm. Simulations were done with rigid walls at $1/2$ coverage, $\theta = 90^\circ$, $\sigma_{wf} = \sigma$, $\epsilon_{wf} = \epsilon$, $r_c = 2^{1/6}\sigma$, $d_{nn} = 1.2\sigma$, $T = 0.7\epsilon/k_B$, and $n = 6$. Statistical errors are indicated by the symbol size.

$= 90^\circ$, $\epsilon_{wf} = \epsilon$, $\sigma_{wf} = \sigma$, $r_c = 2^{1/6}\sigma$, and $T = 0.7\epsilon/k_B$. Note that results for the two thermostatting rates are equal within our statistical error bars. Other tests show that equivalent results are obtained when only the wall atoms are coupled to the thermostat.

B. Effect of system size

The phenomenological expressions for friction described in the introduction assume that the static friction is given by a yield stress times the area of contact. The regions of direct molecular contact between macroscopic solids typically have diameters of order microns.^{19–21,24} It is important to establish that yield stresses calculated at the much smaller scales of our simulations are representative of larger contacts. It is also interesting to consider how friction forces would change if the contact dimensions were reduced to nanometer scales.

Figure 3 compares results from the ramp and search algorithms and shows how both scale with contact size. Values of the yield stress τ_s at $P = 12$ and $28\epsilon\sigma^{-3}$ are plotted as a function of the inverse width of the simulation cell. The latter is expressed as $A^{-1/2}$ where A is the area in the x - y plane. Given $\sigma \sim 0.5$ nm, the largest contact widths (smallest values of $A^{-1/2}$) correspond to 50 nm and the smallest widths to about 10 nm.

We first consider how contact area affects the variations in the stress needed to initiate sliding from different initial configurations. Points indicated by stars and squares indicate the maximum and mean forces needed to initiate sliding for $P = 28\epsilon\sigma^{-3}$ with the ramp algorithm. Note that the difference between the extreme and average yield stresses decreases rapidly with system size and is about 10% for the largest systems. This indicates that the distribution of yield stresses is well-behaved and can be thought of as arising from an incoherent sum of contributions from different re-

gions of the contact. The same trend is seen for the maximum and mean values from the search algorithm, but the fluctuations are slightly smaller.

In both algorithms the smallest system sizes tend to produce larger mean stresses. However, as assumed in phenomenological theories of friction,^{13,17,19} the mean values of the yield stress for all pressures and algorithms become independent of area as the contact size diverges. As shown in Fig. 3, finite size effects are larger for higher pressures. This may be because of the fact that the energy barrier for monomers to move between metastable states increases with pressure, making them more likely to get stuck in high-energy states. Finite-size effects also grow rapidly as the coverage decreases, since there are then fewer monomers at the same wall area.

Note that yield stresses from the ramp algorithm tend to be consistently higher than those from the search algorithm. At $P=28\epsilon\sigma^{-3}$ the difference appears to reflect larger finite-size effects for the ramp algorithm. However, the difference between the two algorithms is nearly independent of system size for $P=12\epsilon\sigma^{-3}$. The reason for this discrepancy is that it takes time for the wall to accelerate once the static friction is exceeded. One can only be sure that the wall has started sliding when it has moved by a few σ . With the ramp algorithm the force has increased to a higher value by this point. Attempts to extrapolate back to the onset of motion only partially corrected for this offset. Decreasing the ramp rate reduces the error, but also lengthens the simulation time proportionately. The search algorithm reduces the effective ramp rate to zero and efficiently converges on the yield stress.

For the above reasons the search algorithm is used for most of the following plots. Except where noted, the second to smallest system size of Fig. 3 is used. The surface of each wall then has 576 atoms and the simulation cell is 28.8σ by 24.94σ for the usual case of $d_{\text{nn}}=1.2\sigma$. Larger system sizes are used mainly at low coverage in order to ensure that the deviation of the yield stress from the thermodynamic limit is comparable to statistical uncertainties. Larger systems also allow a greater number of rotation angles θ to be studied.

C. Effect of temperature and pressure

Figure 4 shows the yield stress vs pressure for a coverage of 1/2 over a broad temperature range from $k_B T/\epsilon=0.3$ to 1.3. For reference, the triple point and critical temperature of Lennard-Jones monomers with $r_c \rightarrow \infty$ are about 0.7 and $1.3\epsilon/k_B$, respectively,^{58,64} and the zero-pressure glass transition temperature for short Lennard-Jones chains is between 0.4 and $0.5\epsilon/k_B$.⁶⁵⁻⁶⁷ The bulk melting temperatures of short-chain hydrocarbons are on the order of room temperature.

Note that τ_s increases linearly with pressure at each T , as assumed in Eq. (1). For representative values of $\epsilon=30$ meV and $\sigma=0.5$ nm, the unit of pressure $\epsilon\sigma^{-3} \sim 40$ MPa. Thus the highest pressures in Fig. 4 correspond to about 1.5 GPa. In those cases that we checked, linearity extended up to much larger pressures (at least $100\epsilon\sigma^{-3}$).

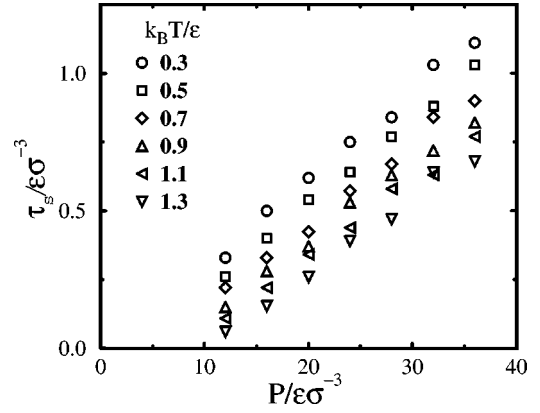


FIG. 4. Variation of yield stress with pressure at the indicated temperatures. In each case, τ_s rises linearly with P . The size of typical statistical errors is indicated by the symbol size. Errors are slightly larger at the highest pressures. Simulations were done with the search algorithm for rigid walls, 1/2 coverage, $\theta=90^\circ$, $\sigma_{wf}=\sigma$, $\epsilon_{wf}=\epsilon$, $r_c=2^{1/6}\sigma$, $d_{\text{nn}}=1.2\sigma$, and $n=6$.

However, these pressures were not routinely studied because a smaller time step is needed to integrate the equations of motion at larger pressures.

The plots of yield stress vs pressure at different temperatures in Fig. 4 are nearly parallel, but their intercepts shift rapidly with temperature. Results from fits to Eq. (1) are shown in Fig. 5. The slope α drops by only 16% with increasing T , while the intercept τ_0 is roughly proportional to T . Linear fits as a function of temperature give

$$\alpha = (-0.0057 \pm 0.0007) \frac{k_B T}{\epsilon} + (0.0338 \pm 0.0006),$$

$$\frac{\tau_0}{(\epsilon\sigma^{-3})} = (-0.214 \pm 0.013) \frac{k_B T}{\epsilon} + (0.015 \pm 0.011). \quad (6)$$

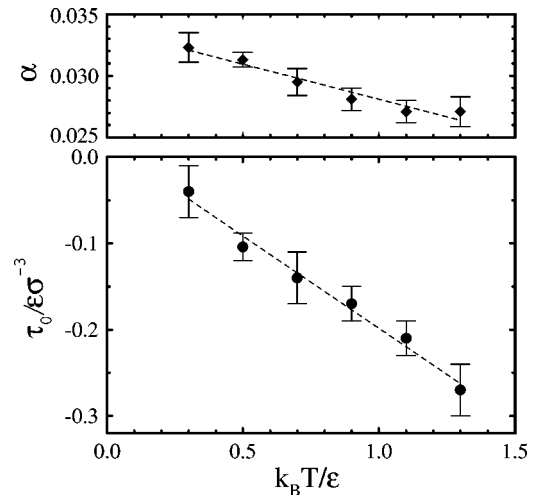


FIG. 5. Values of α and τ_0 as a function of temperature from fits of Eq. (1) to the data of Fig. 4. Dashed lines show the linear fits to the temperature dependence given in Eq. (6).

An explanation for the nearly constant value of α is presented in Sec. III F. In the remainder of this subsection we focus on the variation of τ_0 .

At each T , the linear fit for yield stress vs pressure crosses through zero at a threshold pressure $P_t = -\tau_0/\alpha$. Above this pressure we find a well-defined yield stress in the thermodynamic limit. Below P_t , the adsorbed layer acts like a lubricating liquid, with a shear stress that vanishes as the shear rate decreases.⁴⁹ In this regime, the bounding walls are far enough apart that molecules diffuse freely and do not lock the two walls into a local energy minimum. From the fit parameters in Fig. 6 we see that P_t rises roughly linearly with T . This is because the simulations used $r_c = 2^{1/6}\sigma$, which corresponds to the hard sphere limit. In this regime pressures are balanced only by entropic forces and thus must scale linearly with temperature. Attractive interactions are considered in Sec. III F

Most of the following simulations were done at $T = 0.7\epsilon/k_B$. Given the results just described, we expect that the same trends would be observed at other temperatures. It is important to note that static friction is observed at temperatures far above the bulk melting points of the adsorbed layers, since the temperature in real contacts may be well above the bulk melting point of short chain hydrocarbons.

D. Effect of wall stiffness

As described in Sec. II A, wall atoms were connected to lattice sites by springs with stiffness k_s , or fixed rigidly to these sites ($k_s \rightarrow \infty$). Decreasing k_s has two competing effects on the static friction. One is to make it easier for the two surfaces to deform into a structure with a common period. This tends to increase the yield stress. However, studies with bare walls found that unrealistically small values of k_s were needed to produce a finite static friction.⁹ Decreasing k_s also decreases the yield stress by allowing wall atoms to be pushed out of the way. In our simulations the second effect always dominates, and τ_s decreases as k_s decreases. This is consistent with a recent analytic theory for static friction.³⁹

Figure 6 shows results for systems *C* and *D* of Fig. 1 at $k_B T = 0.7\epsilon$. In each case, the yield stress rises linearly with pressure and decreases monotonically with k_s . The value of α drops by up to 50% as k_s decreases from infinity to $210\epsilon\sigma^{-2}$. Note that for $k_s = 210\epsilon\sigma^{-2}$ the rms displacement about lattice sites (Sec. II A) is near the usual Lindemann criterion for melting,⁵⁵ so much weaker values of k_s would be unphysical. To minimize computer time and the number of free parameters, we used rigid walls $k_s \rightarrow \infty$ in the following sections.

E. Effect of wall orientation, coverage, and chain length

Calculated values of the static friction for bare surfaces vary dramatically with wall geometry.^{7,34,68} The yield stress equals that of a bulk crystal for identical aligned surfaces ($\theta = 0^\circ$) and is identically zero for incommensurate orientations. Most experiments do not control the wall orientation, and yet measured friction coefficients between nominally dry surfaces vary by roughly 10% within the same laboratory

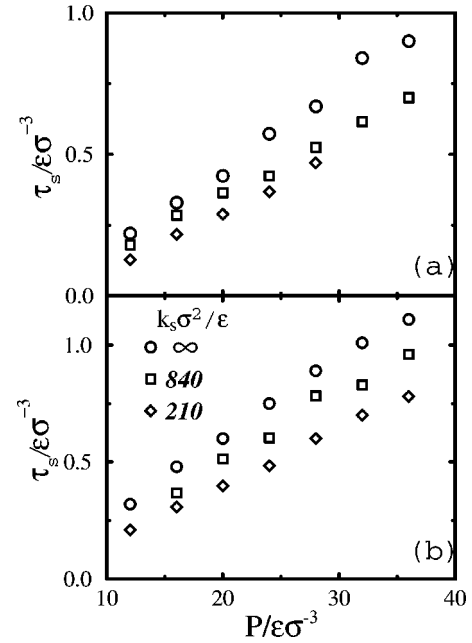


FIG. 6. Yield stress vs pressure for the indicated values of the stiffness k_s of the springs coupling wall atoms to lattice sites. The top panel shows results for $\theta = 90^\circ$ (*C* of Fig. 1) and the bottom panel shows results for $\theta = 0^\circ$ but $d_{nn}/d'_{nn} = 12/13$ (*D* of Fig. 1). In each case, decreasing the stiffness decreases the yield stress. These results are from the search algorithm with 1/2 coverage, $\sigma_{wf} = \sigma$, $\epsilon_{wf} = \epsilon$, $r_c = 2^{1/6}\sigma$, $d_{nn} = 1.2\sigma$, and $n = 6$.

and by 20% between laboratories.^{24,69} Another factor that is not controlled in most experiments is the density and chemistry of adsorbed molecules, although humidity is controlled in some cases. If adsorbed molecules are crucial in determining the static friction, the friction they produce must be relatively insensitive to the wall orientation, sliding direction, coverage, and chain length.

Figure 7 shows the yield stress as a function of pressure for the different walls shown in Fig. 1. At low coverages [Fig. 7(a)], the friction is nearly identical for all incommensurate walls. The friction for commensurate walls is roughly four times higher, but much less than the value for bare walls. At a coverage of 1/2 [Fig. 7(b)], the difference in the yield stresses for different incommensurate walls increases to roughly 20%. A similar variation with the direction of sliding ($\phi = 0$ or 90°) is seen. Most of this variation is due to changes in τ_0 and all the curves are nearly parallel. Fit values of α , which dominates the high-pressure friction, only change by about 5%.

The greater variability at coverage of 1/2 arises because this case corresponds to a dense monolayer between the surfaces. Molecules cannot pick and choose which portions of the surface to cover. As a result the friction is higher for geometries *B* and *D*, where there are larger regions where the walls look commensurate and molecules can easily lock into registry with both surfaces. The friction is smallest for geometry *C*, where there is almost no region where the two walls are in registry.

Figure 8 shows the yield stress vs pressure at different coverages for the extreme case of geometry *C* ($\theta = 90^\circ$).

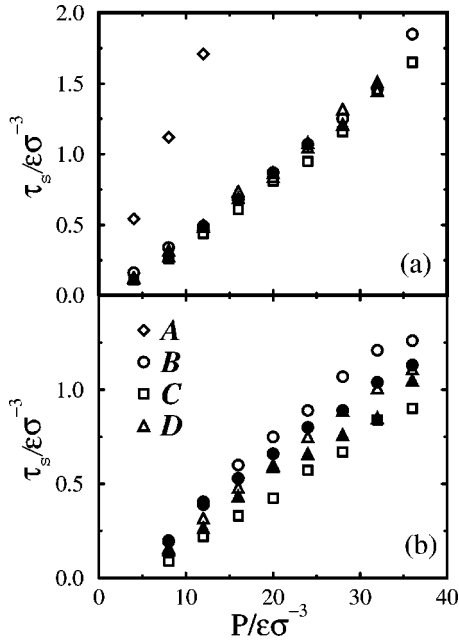


FIG. 7. Shearing direction and orientation dependence for (a) 1/8 coverage and (b) 1/2 coverage. The symbol shape indicates which of the geometries in Fig. 1 were used (see legend). Open and closed symbols are for lateral force applied along the x ($\phi=0^\circ$) and y ($\phi=90^\circ$) directions, respectively. The ramp algorithm was used in (a) and the search algorithm was used in (b). The potential parameters were $\sigma_{wf}=\sigma$, $\epsilon_{wf}=\epsilon$, $r_c=2^{1/6}\sigma$, $d_{nn}=1.2\sigma$, and $n=6$.

Note that the yield stress exhibits the usual linear pressure dependence at all coverages, and that most of the variation with coverage is in the intercept τ_0 . The value of α stays within 15% of the mean value 0.030. At each pressure, the friction decreases as the coverage rises from 1/8 to 1/2. During this increase in coverage, more and more of the sites with poor registry must be occupied. The friction goes down to a minimum value at a complete monolayer which corresponds

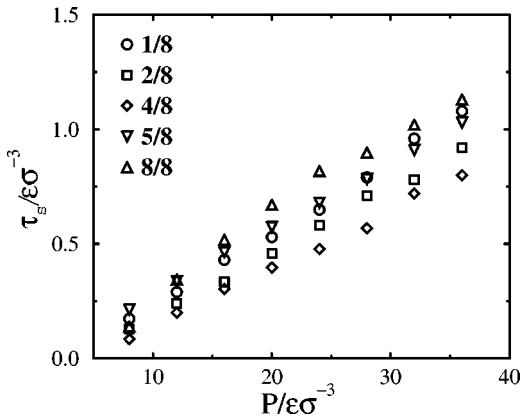


FIG. 8. Yield stress vs pressure for the indicated coverages with system C ($\theta=90^\circ$) where the largest variation was observed. Note that a coverage of 1/2 on each separated surface produces about a monolayer when the surfaces are placed in contact. Results are from the search algorithm with $\sigma_{wf}=\sigma$, $\epsilon_{wf}=\epsilon$, $r_c=2^{1/6}\sigma$, $d_{nn}=1.2\sigma$, and $n=6$.

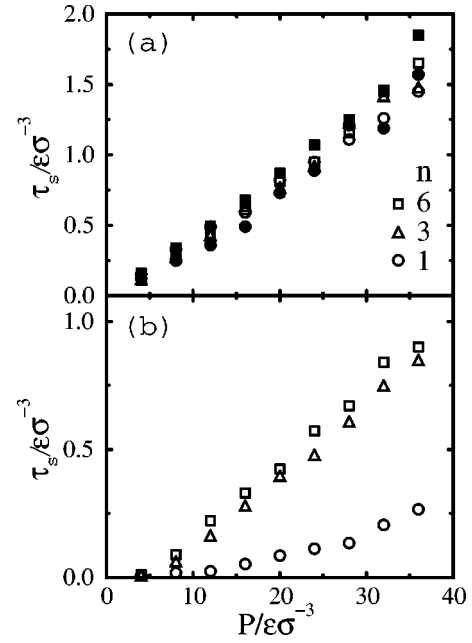


FIG. 9. Yield stress vs pressure for the indicated values of chain length n at coverage of (a) 1/8 and (b) 1/2. Open (closed) symbols are for system C (B). The potential parameters were $\sigma_{wf}=\sigma$, $\epsilon_{wf}=\epsilon$, $r_c=2^{1/6}\sigma$, and $d_{nn}=1.2\sigma$. Error bars are comparable to the system size and the ramp (search) algorithm was used for the top (bottom) panel. Except for spherical molecules at 1/2 coverage, the friction is insensitive to chain length.

to about 1/2 coverage. If the difference between the sizes of the monomers and wall atoms was bigger, locking would be frustrated even in the areas with good registry. This might lead to even smaller variations with coverage than those shown here.

As coverage rises from 1/2 to 1 (about two monolayers), the friction rises once more. The reason is that two layers of molecules have more internal degrees of freedom and can lock more easily into simultaneous registry with both walls. For this range of coverages yield continues to localize at the surfaces of the walls. Previous work on thicker films shows that yield can move into the film as thickness increases.^{62,70} In this limit τ_s approaches the bulk yield stress of the material making up the adsorbed layer, and eventually becomes independent of the coverage. Note that the bulk yield stress of polymeric materials is also found to follow the linear pressure dependence of Eq. (1).⁶¹

Figure 9 illustrates the interplay between the chain length and coverage dependence. At small coverages [Fig. 9(a)], there is little dependence on chain length or wall orientation. For a complete monolayer [Fig. 9(b)], chains with $n=3$ and 6 show nearly the same behavior, while spherical molecules ($n=1$) show a dramatically reduced friction and α . This suggests that the spheres are more constrained by their neighbors from locking into registry with the walls. This may reflect the fact that although all films contain the same number of monomers at a coverage of 1/2, the spheres are closer to their true equilibrium monolayer density than the chains. The reason is that the strong bonds within chain molecules lower the equilibrium spacing and thus increase the

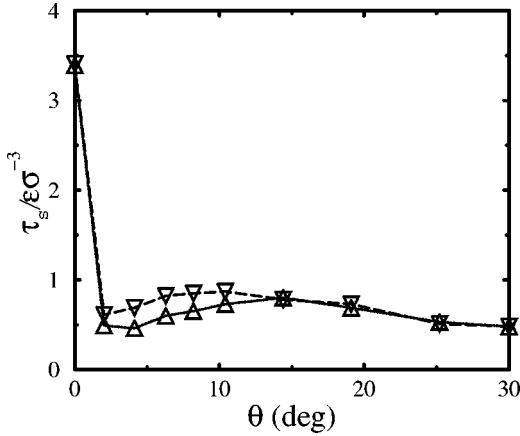


FIG. 10. Yield stress as a function of orientation angle θ at $P = 24\epsilon\sigma^{-3}$ for sliding along the x and y axes (down and up triangles, respectively). The commensurate case corresponds to $\theta=0$ and the smallest nonzero angle shown here is 2.02° . These results are from the search algorithm with 1/2 coverage, $\sigma_{wf}=\sigma$, $\epsilon_{wf}=\epsilon$, $r_c=2^{1/6}\sigma$, $d_{nn}=1.2\sigma$, and $n=6$. The simulation cell was 57.6σ by 49.9σ .

equilibrium density at a given pressure. The presence of two different types of bonds in chain molecules may also improve their ability to rearrange to lock into both surfaces. Another possibility is that chains produce a greater friction because of the strong intramolecular bonds. If one monomer in the chain is locked to the bottom wall and another is in registry with the top wall, the intramolecular bonds will lock the two walls together. This process has no analog for monomers and is particularly important as the coverage increases beyond a monolayer.

Figure 10 shows the static friction as a function of θ at a single pressure, $P = 24\epsilon\sigma^{-3}$. This large pressure was chosen to maximize the contribution of α to the yield stress. Only θ between 0 and 30° are shown because other angles are related by symmetry.

The commensurate case $\theta=0^\circ$ shows a much larger friction than any of the incommensurate systems. Even a 2° rotation reduces the friction to a value that is comparable to those at other values of θ . The same sharp transition was seen for coverages from 1/8 to 1. The data shown is for coverage of 1/2 where the variation of the yield stress at incommensurate θ has already been shown to be the largest. Even in this case the variation is less than $\pm 20\%$, which is comparable to experimental variations. The smaller variations of yield stress with θ at a coverage of 1/8 are comparable to our statistical error bars.

The sliding direction ϕ also has relatively little influence on the yield stress between incommensurate surfaces. Two orthogonal directions $\phi=0^\circ$ and 90° are shown in Fig. 10. The difference between them is most pronounced at small θ , where $\phi=0^\circ$ corresponds to pulling nearly parallel to the nearest-neighbor direction in each wall, and $\phi=90^\circ$ to pulling along the perpendicular direction.

Figure 11 shows the variation with ϕ in more detail for coverage of 1/2 and $\theta=10.4^\circ$, where the variation in Fig. 10 is large. The data are symmetric about $\phi=\theta/2$, which is the

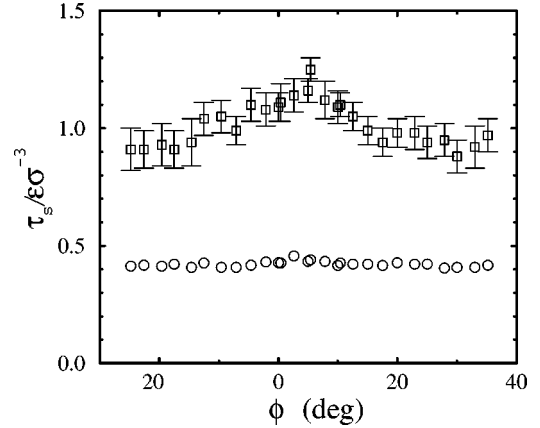


FIG. 11. The yield stress vs the angle ϕ between the applied stress and the x axis for $P=12\epsilon\sigma^{-3}$ (circles) and $32\epsilon\sigma^{-3}$ (squares). These results are from the search algorithm with 1/2 coverage, $\sigma_{wf}=\sigma$, $\epsilon_{wf}=\epsilon$, $r_c=2^{1/6}\sigma$, $d_{nn}=1.2\sigma$, and $n=6$. The simulation cell was 57.6σ by 49.88σ . Error bars are only shown when they are larger than the symbol size.

direction of a twofold axis. This direction gives the maximum friction, and the yield stress drops to a plateau value on either side. The variation is within our statistical errors at low pressures and is less than $\pm 20\%$ at the largest pressures studied. As in Figs. 7(b) and 10, sliding along the x axis leads to higher friction than sliding along y (equivalent to $\phi=0$ and 30° , respectively).

Note that when the yield stress is exceeded the top wall does not always move exactly in the direction of the applied force. This effect is most pronounced for the commensurate case, but is also seen at small θ .

F. Effect of interaction potentials

Experimental results for different sliding surfaces and different surface layers show much larger variations than the fluctuations for a given material system. Such changes in material would correspond to changes in the parameters in our interaction potentials such as the strength of the interaction between the wall and fluid ϵ_{wf} , the characteristic length of this interaction σ_{wf} , the range of the interaction r_c , and the nearest-neighbor spacing d_{nn} in the walls. Other structural properties and the elastic moduli and hardness of the solids may also be important, but are not easily included within our model.

The results shown so far were all for purely repulsive potentials, $r_c=2^{1/6}\sigma$. Increasing the cutoff to $r_c=2.2\sigma$ includes most of the attractive tail in the Lennard-Jones potential. This attractive tail leads to an adhesive force pulling the walls together in addition to the external pressure P . As shown in Figs. 12(a) and 12(c), the yield stress results for $r_c=2.2\sigma$ lie parallel to results for $r_c=2^{1/6}\sigma$ and could be obtained by shifting the zero of pressure to reflect the adhesive stress. The required shift increases with increasing coverage because the density of adsorbed molecules that contribute to the adhesive interaction increases.

When the above results are fit to Eq. (1), the value of α is independent of r_c , and the value of τ_0 increases with the

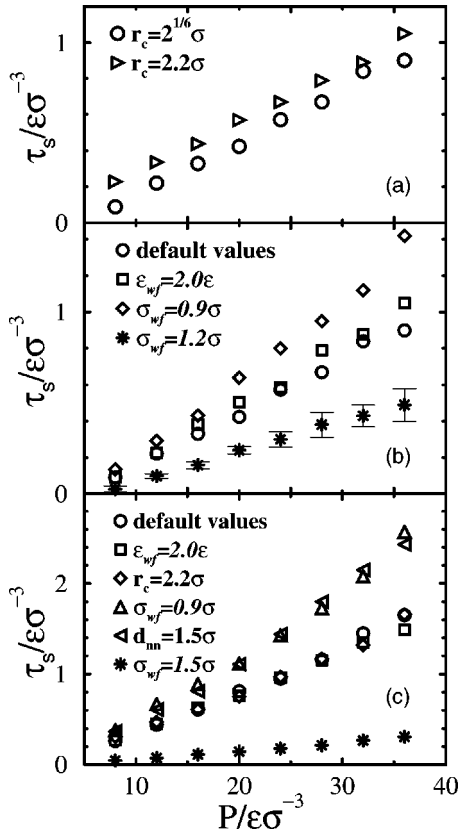


FIG. 12. Yield stress vs pressure for various choices of the potential parameters in system C with $n=6$. The coverage is $1/2$ in (a) and (b) and $1/8$ in (c). Unless noted, the default values of $\sigma_{wf} = \sigma$, $\epsilon_{wf} = \epsilon$, $d_{nn} = 1.2\sigma$, and $r_c = 2^{1/6}\sigma$ are used. Each of these parameters was changed in turn and the corresponding results are labeled by the changed value. The search algorithm was used for the data in (a) and (b), and the ramp algorithm was used in (c).

amount of adhesion. For purely repulsive interactions τ_0 is negative because a finite pressure is needed to lock the adsorbed layers in a glassy state (Sec. III C). When r_c is increased to 2.2σ , a glass forms at zero pressure, and the value of τ_0 is positive. Many authors refer to τ_0 as the adhesive contribution to friction, and it is obvious that τ_0/α represents the effective adhesive pressure that must be added to the external pressure to get strict proportionality between the friction and total load.

These simulations did not include the direct interactions between atoms from different walls. As noted in Sec. II A, the wall spacing is large enough ($>1.5\sigma$) that the direct interaction vanishes for $r_c = 2^{1/6}\sigma$. Even for $r_c = 2.2\sigma$, wall interactions have little effect. For example the extra adhesive pressure due to wall/monomer interactions is $\tau_0/\alpha \sim 5\epsilon\sigma^{-3}$ for $1/2$ coverage [Fig. 12(a)]. Direct calculation of the extra adhesive pressure due to interactions between atoms on different walls yields a value that rises from 0.4 to $1.3\epsilon\sigma^{-3}$ over the observed range of wall separations. Correcting the external pressure to account for this interaction would change α by less than 3%.

Panels (b) and (c) of Fig. 12 show that doubling the strength of the potential between the surfaces and monomers has almost no effect on the yield stress. The main factor that

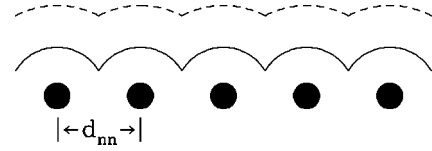


FIG. 13. Sketch of surface of closest approach for $D/d_{nn} = 0.7$ (solid line) and 1.3 (dashed line). The lateral force required to lift monomers up the ramps that these surfaces represent is given by the slope times the normal force.

changes α is the ratio between the characteristic separation between wall and fluid atoms σ_{wf} and the nearest-neighbor spacing between wall atoms, d_{nn} . The value of α rises monotonically as σ_{wf}/d_{nn} decreases. For the cases shown, α changes by an order of magnitude. Smaller values of α are obtained by increasing σ_{wf}/d_{nn} further, but it is difficult to increase α for this geometry. The reason is that the adsorbed molecules begin to penetrate into the wall when σ_{wf}/d_{nn} is too small. Other crystallographic orientations of the surface, such as (100), may produce larger values of α . Flat but disordered surfaces produce values of α as high as 0.3 .^{39,48}

The strong effect of σ_{wf}/d_{nn} and weak effect of ϵ_{wf}/ϵ suggest a geometric origin of α that is analogous to early geometric theories for Amontons's laws¹² and to Israelachvili and co-workers's cobblestone model.^{17,25} At pressures where the adsorbed layer acts like a glass, the repulsive part of the Lennard-Jones interaction dominates. The repulsive force between monomers and wall atoms at a separation r is given by $F_{rep} = 48(\epsilon_{wf}/\sigma_{wf})(\sigma_{wf}/r)^{13}$. The mean value of F_{rep} must scale as the pressure divided by the coverage. Hence, changing P or coverage by a factor of 2 only changes the typical separation between monomers and wall atoms by a factor of $2^{1/13}$ or 5%. Changing ϵ_{wf} by a factor of 2 leads to the same small change in separation. In contrast, the separation changes by a factor of $2^{12/13} \approx 1.9$ with a factor of 2 change in σ_{wf} . Thus monomers and wall atoms can be thought of as hard spheres whose diameter D is nearly independent of pressure and ϵ_{wf} , but directly proportional to σ_{wf} .

Figure 13 illustrates the effect of changing the ratio between the hard sphere diameter and the nearest-neighbor spacing d_{nn} . The hard-sphere repulsion leads to a surface of closest approach between a monomer and the wall. In order for the monomer to slide relative to the wall it must be lifted up the ramp formed by this surface. The lateral force required to move monomers up the ramp is just the normal load times the slope of the surface. Thus α will be proportional to some average of the slope over all monomers.³⁹ As D/d_{nn} decreases, monomers penetrate more deeply between the surfaces and both the slope and α increase. This is precisely the trend seen in Fig. 12. Thus the hard-sphere model explains the linear dependence of τ on pressure as well as the insensitivity to ϵ_{wf} and coverage, and the variation with σ_{wf} and d_{nn} .

IV. SUMMARY AND CONCLUSIONS

The results presented in this paper explore the effect of a specific type of third-body, small adsorbed molecules, on the

friction between the bounding solids. The effect of temperature, coverage, crystalline alignment, lattice constant, system size, molecular size, and interaction potential parameters were all examined.

The first important result is that static friction is observed for all systems—even when the static friction between bare walls is identically zero. The shear stress needed to initiate sliding approaches a constant value in the thermodynamic limit (Fig. 3) and follows the linear pressure dependence [Eq. (1)] seen in many experimental systems. Moreover, the shear stress is insensitive to parameters that are not controlled in most experiments, including crystalline alignment, coverage, and sliding direction. Even under conditions where the variations with these parameters are largest, the changes are comparable to typical experimental variations between different samples and laboratories.^{24,69} This is an important test of any molecular scale model for friction.

The value of τ_0 in Eq. (1) is increased by attractive interactions between the monomers and walls or between the two walls. The adhesive interaction was increased both by increasing coverage (Fig. 8) and by increasing r_c to increase the contribution from the attractive tail in the Lennard-Jones potential (Fig. 12). Increasing the temperature (Fig. 5) increases the entropic repulsion and lowers τ_0 .

For each system there is a pressure $P_t = -\tau_0/\alpha$ below which the adsorbed layer acts like a liquid lubricant (Sec. III C). When the attractive tail of the Lennard-Jones potential is included (large r_c), the value of P_t for submonolayer films is negative up to quite high temperatures. This implies that the film will be in a glassy state under any positive load, and explains the counterintuitive result that introducing a thin layer of “lubricant” produces static friction. Experiments^{3,4,17,18} and simulations^{7,8,59,62} with many different molecules show that films must be several monolayers thick before they change from glassy to liquid behavior and begin to provide lubrication. It would be interesting to explore whether lubricating behavior could be extended to submonolayer films through use of specially tailored molecules or elevated temperatures.

All of the observed trends in α can be understood in terms of a simple geometrical model where monomers act like hard spheres. Within this model, α only depends on the hard sphere diameter and the wall geometry. Parameters such as pressure, temperature, wall/monomer coupling energy, and r_c have almost no effect on the hard sphere diameter and thus α . In contrast, changes in σ_{wf} or d_{nn} produce direct changes in the geometry and change α dramatically (Fig. 12). Smaller shifts in α are produced by changes in coverage that alter the ability of the hard spheres to pack into a configuration that locks into both walls (Fig. 8).

Simple model potentials were used for the adsorbed molecules and surfaces in this study, in order to allow a wide range of parameters to be investigated. More realistic models will have more complex interactions and multiple atomic species. This will complicate the geometry, but one expects that the basic idea of an effective surface of closest approach defined by hard-sphere repulsions will still be valid at the pressures of interest. This naturally produces static friction and a shear stress that obeys Eq. (1). Indeed the same picture can be applied to larger particles between bearing surfaces such as dust, sand or wear debris.

While our geometric argument for α bears some similarity to earlier models based on interlocking of macroscopic¹² or atomic^{17,25} asperities, there is an important difference. These previous models envisioned asperities that were rigidly attached to their respective surfaces and would translate with them. The mobile atoms considered here and in previous work,^{9,39,48,49} rearrange to create interlocking configurations for any relative position of the surfaces. Not only does this explain why static friction can occur between surfaces with uncorrelated asperities, it also makes it possible to connect static and kinetic friction.

As pointed out by Leslie^{12,71} in 1804, interlocking of rigid asperities can explain static friction, but predicts vanishing kinetic friction. The reason is that the energy needed to move up ramps is recovered as the asperities move back down and the total work required to slide the surfaces vanishes. The situation is very different when the interlocking occurs dynamically through motion of adsorbed molecules. As shown in recent works,^{39,49} at any given instant almost all of the mobile molecules are trapped in local free energy minima. Since lateral motion of the walls increases their energy within this minimum they contribute to the friction. The kinetic and static friction are closely related because the distribution of molecules in free energy minima is nearly the same. The difference is that when the walls are moving at fixed velocity the local minimum holding each molecule eventually becomes unstable. It then pops forward rapidly to the nearest metastable state. Much of its energy is dissipated in this pop because molecules pop forward at different locations at different times in an incoherent manner and the potential they move to varies in a random way. It is not possible for them to move up and down over a rigid potential energy surface as in the models of fixed asperities considered by earlier researchers.¹² Instead, as envisioned by Leslie,⁷¹ “the upper surface travels over a perpetual system of inclined planes; but that system is ever-changing” so that, like Sisyphus, it “makes incessant yet unavailing efforts to ascend.”

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