Ordering of a Thin Lubricant Film due to Sliding

O. M. Braun*
Institute of Physics, National Academy of Sciences of Ukraine, 03650 Kiev, Ukraine
Centre for Chemical Physics, University of Western Ontario, London N6A 3K7, Ontario, Canada

M. Paliy
Department of Chemistry, University of Western Ontario, London N6A 5B7, Ontario, Canada

S. Consta
Department of Chemistry, University of Western Ontario, London N6A 5B7, Ontario, Canada
Centre for Chemical Physics, University of Western Ontario, London N6A 3K7, Ontario, Canada

(Received 13 January 2004; published 24 June 2004)

A thin lubricant film confined between two substrates in moving contact is studied using Langevin molecular dynamics with the coordinate- and velocity-dependent damping coefficient. It is shown that an optimal choice of the interaction within the lubricant can lead to minimal kinetic friction as well as to low critical velocity of the stick-slip to smooth-sliding transition. The strength of this interaction should be high enough (relative to the strength of the interaction of lubricant atoms with the substrates) so that the lubricant remains in a solid state during sliding. At the same time, the strength of the interaction should not be too high, in order to allow annealing of defects in the lubricant at slips.

DOI: 10.1103/PhysRevLett.92.256103 PACS numbers: 81.40.Pq, 46.55.+d

The problem of friction between two substrates in moving contact is very important technologically as well as very rich physically [1,2]. In recent years essential progress in understanding tribological phenomena has been achieved by the increase in the computational power that has made possible more realistic simulations of friction (see [2] and references therein).

Most mechanical devices use liquid lubricants to reduce friction, which typically provide friction coefficients of order $\mu \gtrsim 0.1$ in a smooth-sliding regime [1](the tribological friction coefficient is defined as $\mu = f/f_l$, where f is the driving force and f_l is the load). When the width of the lubricant film is reduced to a few atomic layers, e.g., because of squeezing the lubricant out of the contact region due to high load at the moments when the sliding stops, a thin film usually solidifies [1,2]. The lubricant structure, though, is strongly affected by the substrates, and the static frictional force f_s is generally nonzero. At a low driving velocity v_s the motion in such a system corresponds to stick slip, where short fast sliding events are separated by long sticking ones. The stick-slip motion is explained by the melting-freezing mechanism: the film melts during slip and solidifies again at stick [3,4]. When the driving velocity increases above some threshold value v_c, the sliding becomes smooth. The critical velocity of this transition is of atomic scale [5], $v_c \sim (0.03 - 0.1)c$, where c is the speed of sound (much lower v_c values observed at macroscopic experiments are due to the concerted motion of many contacts [6]).

On the other hand, the use of solid lubricants may be a very promising way, especially in microdevices, where conventional lubricants may often be ineffective or may even work like a glue. In an ideal case of the contact of two rigid crystalline incommensurate surfaces, the static frictional force f_s is zero (moreover, the same is true even for commensurate surfaces if they are not perfectly aligned [7,8]). Similarly, if the lubricant film has a crystalline structure and is confined between two flat substrates with an ideal structure, the friction coefficient in such a perfect-sliding system may be as low as $\mu \sim 10^{-3}$–10^{-2} or even lower [5]. The critical velocity of the transition from stick slip to smooth sliding is also quite small, $v_c \sim 10^{-2}c$, and the stick-slip motion is now explained by the inertia mechanism [5].

Unfortunately, such an ideal system can hardly be realized experimentally. Even specially prepared surfaces are not perfectly smooth on a mesoscopic scale, and a lubricant has typically numerous structural defects. As a result, the static frictional force f_s is large enough, and the solid lubricant melts at the onset of sliding. Then, at stick, the film solidifies back, but, again, either into an amorphous state or into a state with many defects, because the cooling of the confined film is very rapid due to very good thermal contact with the substrates. According to simulation [5], in such a system one finds $\mu > 0.1$ and $v_c \sim 0.1c$; i.e., the tribological characteristics are of the same order as (or even worse than) those of liquid lubricants.

The aim of the present work is to explore whether the system itself may approach the desired perfect-sliding regime for a suitable choice of the solid lubricant. As is well known, the energy pumped into the system due to external driving has finally been converted into heat. Therefore, the effective lubricant temperature T^* must increase during sliding. It is this increase of the temperature that leads to the melting of the lubricant in the melting-freezing mechanism of stick slip [3,4]. However, if T^* remains lower than the melting temperature T_m, the lubricant film could remain solid and, at the same time, its structure may become more ordered due to the annealing of structural defects, especially if T^* is close to T_m. Because T_m is determined by the interactions within the lubricant, one may tune the parameters of interaction looking for a situation where $T_m \gtrsim T^*$. In what follows we show that, indeed, a suitable choice of the parameters may lead to the desired self-ordering of the lubricant and consequently to the low values of the frictional forces.

Model.—In this study we use molecular dynamics based on Langevin equations with a coordinate- and velocity-dependent damping coefficient as described in [5]. Each of the substrates is made of two layers of 24 × 11 atoms organized into lattices of square symmetry, where the outermost layers are rigid, while the atoms belonging to the layers in contact with the lubricant are allowed to move in all three spatial directions. The outermost layer of the bottom substrate is kept fixed, while the outermost layer of the top substrate is driven with a velocity v_s through an attached spring of elastic constant $k_s = 3 \times 10^{-4}$. Between the substrates we put $N = 480$ lubricant atoms as shown in Fig. 1. In the x and y directions we use periodic boundary conditions (PBC).

All the atoms interact via the Lennard-Jones potential function, $V(r) = V_{\alpha\alpha'}[(r_{\alpha\alpha'}/r)^{12} - 2(r_{\alpha\alpha'}/r)^6]$, but the parameters $V_{\alpha\alpha'}$ (the amplitude of interaction) and $r_{\alpha\alpha'}$ (the equilibrium distance) are different for different kinds of atoms: for the interaction between atoms of the substrate the parameters are $V_{ss} = 3$ and $r_{ss} = 3$, for the lubricant-substrate interaction, $V_{sl} = 1/3$ and $r_{sl} = \frac{1}{2}(r_{ss} + r_{ll})$, and for the interaction between lubricant atoms, $r_{ll} = 4.14$ (an "incommensurate" case), while the amplitude of interaction V_{ll} is varied from 0.1 to 1. This variation covers the whole range between the two limiting cases described in the introduction, namely, the cases of a liquid ("soft") lubricant and of a solid ("hard") lubricant. The atomic masses are $m_l = m_s = 1$. Throughout this Letter we use dimensionless units (for transformation to dimensional units see [5]). Some of the simulation results for the cases of $V_{ll} = 1/9$ (soft) and $V_{ll} = 1$ (hard) lubricants have been presented in [5,10].

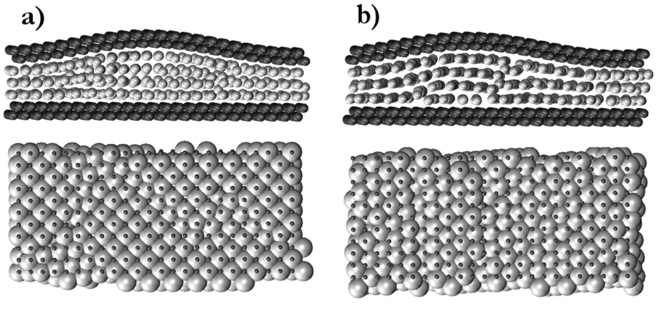

FIG. 1. The model: the light spheres show the lubricant atoms, and the dark spheres show the substrate atoms. The atoms in the outermost layers of the substrates correspond to the rigid parts of the substrates while the dynamics of the other substrate atoms is fully simulated. The load and shear are applied to the rigid part of the top substrate. The rigid part of the bottom substrate is fixed. (a),(b) The configuration before and after reordering, correspondingly (at the beginning and at the end of the dependence shown in Fig. 3) for the system with $V_{ll} = 0.5$ driven with the velocity $v_s = 0.1$. Each panel has side and bottom views; in the latter there is only one layer of substrate shown, and the atomic radii are adjusted in order to visualize clearly the (in)commensurability between the lubricant and the substrate. (The figures were produced with Visual Molecular Dynamics software [9].)

Unfortunately, in such a model with PBC, the results could be too sensitive to the number of lubricant atoms N: if N does not match exactly the number of atoms in closely packed layers, then extra atoms (vacancies) will produce structural defects, especially in small systems accessible in the simulation. To reduce uncertainties due to this difficulty, we used a geometry with a curved top substrate [11] as shown in Fig. 1, when the z coordinate of the rigid layer varies along the x direction by $\Delta z = \frac{1}{2} r_{sl}(1 - \cos 2\pi x/L)$, where L is the size of the substrate. Such a geometry is close to real experimental situations, where the surfaces are always rough, and our model describes, in fact, a single contact (asperity) between the substrates.

As an initial configuration, we always take the melted one driven with the high velocity $v_s = 1$ that corresponds to the smooth-sliding regime. Then the driving velocity was decreased and increased again by the steps $v_s = 1$, 0.3, 0.1, 0.03, 0.01, 0.03, 0.1, 0.3, 1, and 3, every step was simulated for time 2.1×10^4, and the system dynamics was analyzed. All the results presented below are for zero substrate temperature and the normal force $f_z = -f_l = -0.1$, which corresponds to the compression of the lubricant (all forces in the text and figures are per one substrate atom). We checked that our results do not change for a nonzero substrate temperature, as long as it does not exceed effective lubricant temperatures induced by sliding [5,10,12].

Results.—Typical dependencies of the spring force f on time are presented in Fig. 2. When the stage moves with a low velocity v_s, the spring elongates and the force increases linearly with time until it reaches the static frictional force f_s. At this moment the top substrate begins to slide and catches up with the stage, so that f decreases, the substrates stick again, and the whole cycle is repeated. This is the stick-slip regime shown in Figs. 2(a) and 2(c). On the other hand, at a high stage velocity, the smooth sliding is observed, Figs. 2(b) and 2(d), and the spring force is equal to the kinetic frictional force f_k.

The mechanism of sliding, however, is different for soft and hard lubricants. In the soft-lubricant case [e.g., for

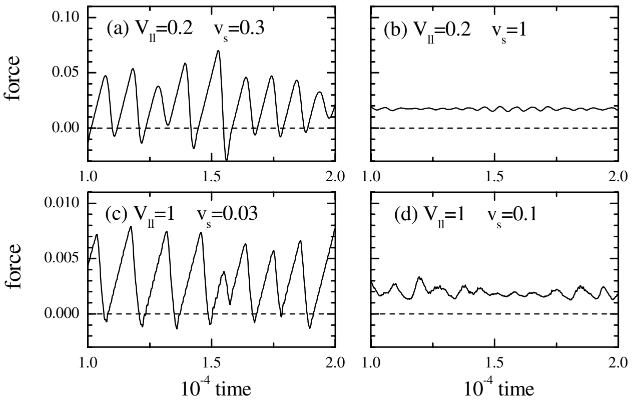

FIG. 2. Typical time dependencies of the spring force for regimes of stick-slip motion [(a) and (c)] and smooth sliding [(b) and (d)] for the soft lubricant [$V_{ll} = 0.2$ (a),(b)] and the hard lubricant [$V_{ll} = 1$ (c),(d)]. The driving velocities are the following: (a) $v_s = 0.3$ and (b) $v_s = 1$ for the soft lubricant, and (c) $v_s = 0.03$ and (d) $v_s = 0.1$ for the hard lubricant.

$V_{ll} = 0.2$ shown in Figs. 2(a) and 2(b)], the effective lubricant temperature T^* increases above the melting temperature T_m at the sliding ($T_m \approx 0.15$ for the soft lubricant [10]), both in the smooth-sliding regime and at slips in the stick-slip regime. During sliding the lubricant is liquid, and the kinetic frictional force $f_k \sim 0.02$ only weakly depends on the sliding velocity v. Thus, for the soft lubricant, the stick-slip regime is due to the melting-freezing mechanism as was first described by Thompson and Robbins [3].

In the hard-lubricant case, on the contrary, although the lubricant temperature T^* also increases due to sliding, it remains lower than the melting temperature T_m [e.g., see Figs. 2(c) and 2(d) for the $V_{ll} = 1$ case, when $T_m \gtrsim 0.4$ [10]]. Therefore, the lubricant does not melt during sliding, but remains in the solid state with the structure that it had at the onset of sliding (i.e., with numerous defects). For the hard lubricant, the stick-slip regime is due to an inertia mechanism (similar to the bistability of an underdamped driven atom in an inclined periodic potential [13]). Note that now the kinetic frictional force f_k essentially depends on the sliding velocity v (e.g., at low velocities f_k scales with v as $f_k \propto v^5$ [5]).

Now recall that the melting temperature of the lubricant film is proportional to the interaction amplitude V_{ll} [4,10]. Therefore, for an appropriate choice of V_{ll} one can find a situation where $T^* \lesssim T_m$, i.e., where the sliding-induced heating brings the system close to but lower than the melting temperature. In this case the lubricant will remain solid during sliding, but its structure may reorder due to the annealing of the defects. Although the sliding-induced heating also gives rise to a concurrent process of thermal generation of new defects, one could expect that for a suitable choice of V_{ll} the annealing will be more important and the system will approach the ideal case of perfect sliding.

Simulations show that indeed this is the case. An example is shown in Fig. 3 for the case of $V_{ll} = 0.5$ with the driving velocity $v_s = 0.1$: the system is in the stick-slip regime at the beginning, but during slips the solid lubricant is heated and reordered, the structural defects (such as vacancies, interstitials, grain boundaries, etc.) are annealed, and the regime changes to the smooth-sliding one. The configurations before reordering and after it are shown in Figs. 1(a) and 1(b), respectively. In the former configuration, the lowest lubricant layer is highly commensurate with the substrate, so that the sliding begins at the middle of the lubricant by destroying the structural defects. On the contrary, in the latter configuration, the lubricant body is more ordered, while the lowest lubricant layer is now incommensurate with the substrate, so that the sliding easily occurs at this interface.

The friction force for different values of the interaction amplitude V_{ll} is presented in Fig. 4 [12]. We emphasize that, because we do not use an artificially prepared initial configuration but a realistic one, the system chooses by itself during annealing and sliding; the values f_s and f_k are not unique but may change from run to run. This is indicated by "error bars" in Fig. 4, which just show deviation of the corresponding values in different runs. For the small enough system used in the simulation, the concentration of structural defects can fluctuate significantly, so that the deviations of frictional force may be

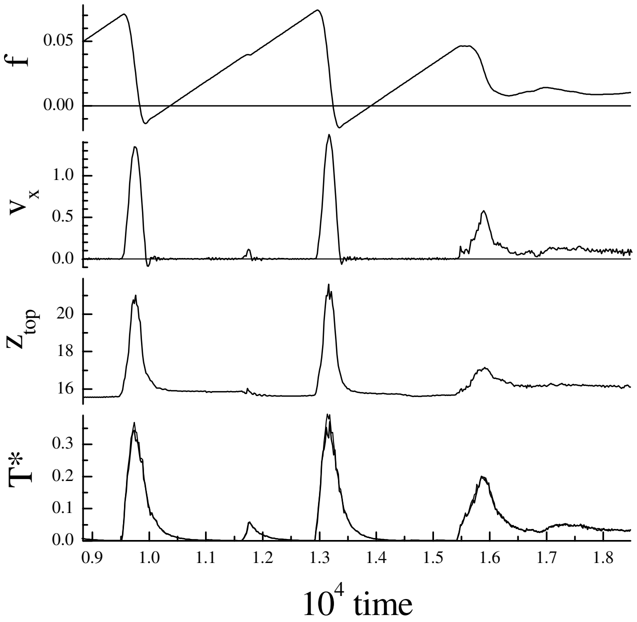

FIG. 3. Reordering of the lubricant: spring force, velocity of the top substrate, lubricant width, and effective lubricant temperature as functions of time at $v_s = 0.1$ for the $V_{ll} = 0.5$ system. Configurations before reordering (at stick in the stick-slip regime) and after it (at smooth sliding) are shown in Fig. 1 top and bottom, correspondingly.

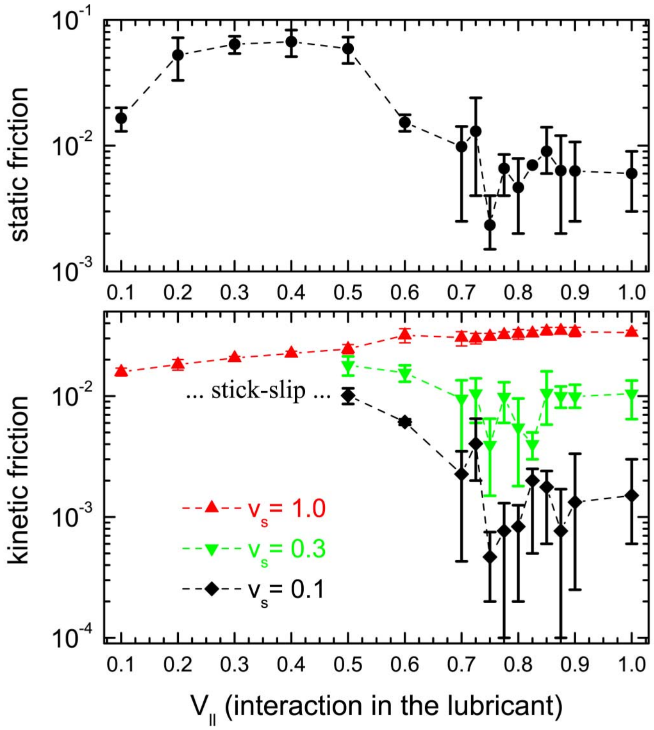

FIG. 4 (color online). Static f_s and kinetic f_k frictional forces for three values of the driving velocity ($v_s = 0.1$, 0.3, and 1 as shown in legend) as functions of the interaction amplitude V_{ll} in the semilogarithmic scale. The "error bars" show deviation of the simulation results in different runs.

quite large, although the experimentally observed characteristics that are macroscopically averaged should be well defined. One can observe two clear-cut features of the behavior of the frictional force. First, as one can judge from the dependence of f_k on v_s, the mechanism of the stick-slip motion changes from the melting-freezing to the inertia mechanism at $V_{ll} \gtrsim 0.5$, i.e., for $V_{ll}/V_{sl} \gtrsim 1.5$. Most importantly, one can observe that for $V_{ll} \approx 0.8$ the kinetic frictional force f_k achieves a minimum as low as $f_k \approx 10^{-4} - 10^{-3}$. The friction coefficient in this case takes values of order $\mu \lesssim 10^{-2}$, which are more than 1 order of magnitude lower than those attainable with conventional liquid lubricants.

Thus, we have shown that there exists *the optimal choice of the strength of interatomic interaction* V_{ll} *within the lubricant*, which leads to *the minimization of the kinetic friction* as well as to the low critical velocity of the stick-slip to smooth-sliding transition. The optimal value of V_{ll} should be high enough (relative to the amplitude V_{sl} of the interaction of lubricant atoms with the substrates) so that the lubricant remains in a solid state during sliding. At the same time, the value of V_{ll} should not be too high, in order to allow annealing of the structural defects in the lubricant. For the parameters used in the simulations, the optimum was achieved at $V_{ll} \approx 2.5 V_{sl}$.

O. B. was partially supported by the NATO Collaborative Linkage Grant PST.CGL.980044. S. C. and M. P. thank NSERC and Premier's Research Excellence Grant for support, and Canadian Foundation for Innovation (CFI) for the grant used to build computer facilities employed in this work.

---

*Electronic address: obraun@iop.kiev.ua

[1] B. N. J. Persson, *Sliding Friction* (Springer-Verlag, Berlin, 1998); Surf. Sci. Rep. **33**, 83 (1999).
[2] M. O. Robbins and M. H. Müser, in *Handbook of Modern Tribology*, edited by B. Bhushan (CRC Press, Boca Raton, 2000).
[3] P. A. Thompson and M. O. Robbins, Science **250**, 792 (1990); M. O. Robbins and P. A. Thompson, Science **253**, 916 (1991).
[4] B. N. J. Persson, J. Chem. Phys. **103**, 3849 (1995).
[5] O. M. Braun and M. Peyrard, Phys. Rev. E **63**, 046110 (2001).
[6] O. M. Braun and J. Röder, Phys. Rev. Lett. **88**, 096102 (2002).
[7] M. Hirano and K. Shinjo, Phys. Rev. B **41**, 11 837 (1990); M. Hirano, K. Shinjo, R. Kaneko, and Y. Murata, Phys. Rev. Lett. **78**, 1448 (1997); M. Dienwiebel *et al.*, Phys. Rev. Lett. **92**, 126101 (2004).
[8] M. H. Müser and M. O. Robbins, Phys. Rev. B **61**, 2335 (2000).
[9] W. Humphrey, A. Dalke, and K. Schulten, J. Mol. Graphics **14**, 33 (1996); http://www.ks.uiuc.edu/Research/vmd/.
[10] O. M. Braun and M. Peyrard, Phys. Rev. E **68**, 011506 (2003).
[11] B. N. J. Persson and P. Ballone, J. Chem. Phys. **112**, 9524 (2000).
[12] A more detailed presentation of simulation results will be given elsewhere.
[13] H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1984).