

January 01, 2003

## A mechanism for lubrication between surfaces with atomic level roughness

J. B. Sokoloff  
*Northeastern University*

---

### Recommended Citation

Sokoloff, J. B., "A mechanism for lubrication between surfaces with atomic level roughness" (2003). *Physics Faculty Publications*. Paper 4. <http://hdl.handle.net/2047/d20000357>

This work is available open access, hosted by Northeastern University.

# A Mechanism for Lubrication between Surfaces with Atomic Level Roughness

J. B. Sokoloff

*Physics Department and Center for Interdisciplinary Research on Complex Systems, Northeastern University, Boston, MA 02115.*

(February 2, 2008)

It is proposed that lubricant molecules adsorbed on an interface between two asperities in contact, which is rough on the atomic scale, can switch the interface from the strong to weak pinning regime, resulting in a large reduction in the static friction. This is proposed as a possible mechanism for boundary lubrication.

In recent years there have been extensive studies, both in the form of experiment[1] and simulations[2], of the behavior of liquids at an interface between two solid surfaces as the surfaces are squeezed together, which leads to the liquid molecules being partially driven out from the interface. In the high pressure limit, the liquid is reduced to a bilayer. One goal of these studies is to understand how boundary lubrication might occur. In boundary lubrication, there is a very thin layer of a lubricant which is able to both protect the surfaces against wear and to reduce the static and sliding friction. These studies, however, have not provided a physical mechanism for how such a thin layer of a liquid separating two surfaces is able to reduce friction. In this letter, I will propose a possible mechanism for the reduction of static friction by a thin liquid lubricant pressed between two disordered solid surfaces, based on the theory of collective pinning[3]. In collective pinning theory, there are two regimes. There is a strong pinning regime, in which the elastic medium is able to distort a good deal so as to be able to nearly minimize the disordered potential, and there is a weak pinning regime, in which the elastic medium is only able to distort over a length  $L$ , known as the Larkin length, and as a consequence the interaction of the disordered potential with the elastic medium is only minimized within domains of length  $L$ , known as Larkin domains. Although we are interested in a disordered interface between two three dimensional solids, it is reasonable to expect that the study of an elastic solid in contact with a rigid disordered substrate will give results not qualitatively different from the problem of two elastic solids in contact at a disordered interface.

Collective pinning theory has been applied to the friction problem by Caroli and Noziere[4] and by Persson and Tosatti[5] using a model for asperity interaction which puts the interface in the weak pinning limit in which the Larkin length is very large. It was shown by the present author[6] that this model is at its critical dimension, which means that the interaction energy between the elastic solid and the substrate is minimized for a Larkin length comparable to the size of the interface for weak pinning and a Larkin length comparable to an atomic spacing in the strong pinning limit. For the case of a disordered interface between two solids, it is clear that the strength of the random potential due to the inter-

face will increase as the two surfaces are pushed together with larger and larger forces, because the hard cores of the surface atoms are pushed together. When the potential is sufficiently strong, the system must switch over to the strong pinning regime, at which point, the Larkin length switches over from being comparable to the interface size to atomic dimensions[6]. In the weak pinning regime it was shown that the force of static friction per unit area decreases as the square root of the interface area, whereas in the strong pinning limit, it will be independent of the interface area. The mechanism proposed here for lubrication is that the lubricant molecules at the interface will get squeezed under pressure into regions of the surfaces which for un-lubricated surfaces were not in contact. By doing so the normal force pushing the two surfaces together gets supported over a larger area of contact. The reason that this can put the system into the weak pinning regime is that the elastic forces between neighboring pinning sites will be made larger relative to their interaction with the second surface.

Recently He, et. al., and Muser and Robbins[7] have shown for clean weakly interacting two dimensional incommensurate interfaces that the force of static friction per unit area falls to zero as  $A^{-1/2}$  in the thermodynamic limit, where  $A$  is the interface area. Even identical solids are incommensurate if their crystalline axes are rotated with respect to each other. It is well known from studies of the one dimensional Frenkel-Kontorova model[1] that two incommensurate crystal lattices in contact with each other can slide with respect to each other with no static friction if their interaction is sufficiently weak compared to typical elastic energies, but if their mutual interaction is increased, above a critical value they make a transition (known as the Aubry transition [8]) to a state in which they do exhibit static friction. If two crystal lattices, consisting of atoms that do not interact chemically, are pushed together, their mutual interaction will increase because the hard core repulsions of the atoms in the two crystals will increase. Lancon[9] has studied the Aubry transition for a two dimensional model. Simulations by Muser and Robbins[7] and by Muser[10] for two incommensurate surfaces pushed together with a normal force corresponding to pressures comparable to those occurring at contacting asperities at a typical sliding interface (i.e., of the order of a 10 GPa's) do not undergo an Aubry

transition, and hence do not exhibit static friction. As discussed earlier, disorder, however, can pin contacting solids, just as it pins sliding charge density waves and vortices in a superconductor[3].

As a first step towards understanding how collective pinning theory, as described above, can provide a possible mechanism for boundary lubrication, let us consider the following likely but simple model for surface roughness at the sub-asperity level: Consider two identical three dimensional solids with atomically flat surfaces rotated with respect to each other, like those studied in Ref. 2. Let us now select atoms at random in the top layer of each surface and remove them. The atomic positions for this model of the top sub-layer of atoms are illustrated for a submonolayer with half the number of atoms as occurs in a full monolayer in Fig. 1. Now let us imagine placing two of these surfaces in contact and pressing them together with a load per unit area of the interface  $P$ . If the load is sufficiently high, we may safely assume that the force between a pair of surface atoms from the two surfaces which are in contact is dominated by the hard core interaction. Then, a good estimate of the magnitude of the mean force acting between a pair of surface atoms from the two surfaces that are in contact is  $P/n$ , where  $n$  is the number density per unit area of surface atoms. This is an estimate of the component of force normal to the interface, but since such atom pairs are rarely lined up so that one is exactly on top of the other, there will be components of force of comparable magnitude along the interface as well. Let us now imagine adding atoms to each of the outer layers until they each form a complete monolayer. Our model is then identical with the model studied in Refs. 6, 7, and 10. In this model it was reported in these references that even for loads per unit area as high as a GPa, there was no static friction between the surfaces. As the concentration of surface atoms is reduced from a complete monolayer on each surface by removing atoms chosen at random, there will certainly be a concentration at which the interface switches over from the weak pinning limit, in which the elastic energy dominates over the substrate potential (which in our case represents the second surface), to the strong pinning regime, in which the opposite is true.

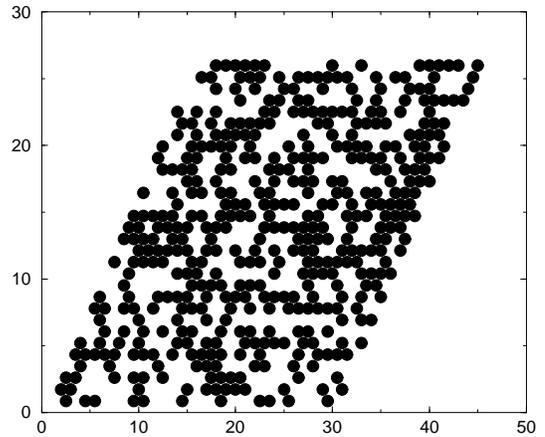


FIG. 1. The atomic positions are shown for a random submonolayer for a triangular lattice containing half of the number of atoms in a complete monolayer. The atomic positions are chosen at random. Distances are given in units of a lattice constant.

Following Ref. 6, scaling methods, like those used by Fisher for charge density waves (CDW)[3], are used to study static friction for disordered interfaces. This can be accomplished by minimizing the potential energy of the solid in contact with a rigid disordered substrate at  $z=0$  with respect to the size of a Larkin domain[3], which is expected to give qualitatively correct results for the problem of two elastic disordered solids in contact. Given that the energy density of the elastic solid is given approximately by

$$(1/2)E'|\nabla_t \mathbf{u}|^2 + (1/2)E'' \left| \frac{\partial \mathbf{u}}{\partial z} \right|^2 + V(\mathbf{r})\delta(z), \quad (1)$$

where  $E'$  and  $E''$  are elastic moduli,  $V(\mathbf{r})$  is the potential per unit area of the disordered substrate,  $\mathbf{u}(\mathbf{r})$  is the local displacement of the solid, and  $\nabla_t = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y})$ . Let us assume that  $\nabla \mathbf{u}(\mathbf{r})$  only differs significantly from zero over domains of length and width  $L$  parallel to the surface and height perpendicular to the surface equal to  $L$ . Then, following the discussion in Ref. 6, the energy of a single domain is given by

$$E = (1/2)L'L^2E'|\nabla_t \mathbf{u}'|^2/L^2 + |\partial \mathbf{u}'/\partial z'|^2/L^2 - V_0 c^{1/2}(L/a), \quad (2)$$

where  $a$  is an atomic length scale (e.g., a lattice constant),  $c$  is the concentration of surface atoms in contact with the substrate and  $V_0$  is a typical value of the substrate potential energy felt by an atom in contact with the substrate. In arriving at Eq. (2), we have assumed that since by definition of a Larkin domain,  $\mathbf{u}(\mathbf{r})$  within a domain is small compared to  $a$ , the interaction of the substrate potential with a domain is random and hence

the integral of this potential over a domain is proportional to the square root of the number of surface atoms in contact with the substrate (which is of the order of  $c(L/a)^2$ ). Here, we assume that  $\mathbf{u}(x, y, z)$  is equal to the function  $\mathbf{u}'(x', y', z')$ , where the function  $\mathbf{u}'$  varies by an amount of the order of atomic length scales when  $x'$ ,  $y'$  and  $z'$ , defined by  $(x', y', z') = (x/L, y/L, z/L)$ , each vary by an amount of order unity. The total potential energy due to the interaction of the solid with the substrate and the elastic distortion energy is the product of  $A/L^2$ , the number of domains along the interface, where  $A$  is the area of the interface, and Eq. (2). When the resulting expression is minimized with respect to  $L'$  one finds that  $L' \approx L$  and the energy per unit area at the interface is given by

$$E/A \approx [(1/2)E'|\nabla'_t \mathbf{u}'|^2 + (1/2)E''|\partial \mathbf{u}'/\partial z'|^2 - V_0 c^{1/2}/a]/L, \quad (3)$$

(where we use the average value of  $|\nabla'_t \mathbf{u}'|^2$  here). By the above arguments concerning the hard core interactions, it is clear that the magnitude of the mean force exerted on a surface atom by the substrate  $f_0$ , is given by  $n f_0 \approx P$ . Then  $V_0 \approx Pa/n \approx Pa^3/c$ , where  $a$  is a lattice constant. Then, the term in square brackets on the right hand side of Eq. (3) becomes  $[(1/2)E'|\nabla'_t \mathbf{u}'|^2 + (1/2)E''|\partial \mathbf{u}'/\partial z'|^2 - Pa^3/c^{1/2}]$ . When this quantity is positive, the interface energy is minimized for large  $L$  (i.e., comparable to the interface size) and when the square bracketed expression is negative, it is minimized for small values of  $L$  (i.e., comparable to atomic dimensions). Thus, it is clear that as  $c$  decreases, the interface will switch from weak pinning (if it was already in the weak pinning regime) to strong pinning. In the latter regime, by the arguments given in the last paragraph, the surfaces will be pinned together (i.e., there will be static friction). Thus for surfaces with sufficient roughness so that they are only in contact at a sufficiently dilute concentration of random points of contact, we are in the strong pinning regime, and hence, there must be sizable static friction.

Let us now place molecules of some a lubricant on these surfaces, which attach themselves strongly to the surfaces. This is the important property that these lubricant molecules must have in order to be good lubricants[11]. Then, let us assume that the attractive force between a lubricant molecule and a surface atom is much greater than the attraction between two lubricant molecules. These can be either single atoms or chains. If they are chains, we consider how the individual monomers position themselves on the interface. Simulations done for two flat surfaces in contact[2] show that under GPa pressures such a lubricant will get squeezed out until at the highest pressures we are left with a bilayer. In our case, where the surface is not smooth, we expect there to be a bilayer coating the steps (i.e., on the places on the outer layer at which there are surface atoms). The regions in

which there are no top submonolayer atoms present will also get filled in with lubricant molecules. The reason for this is that as the surfaces are squeezed together, some of the lubricant molecules that are driven from the steps will be pushed into these regions. I propose that this is a possible mechanism for boundary lubrication. This mechanism depends on there being a strong attraction between the surface and lubricant molecules, which causes the lubricant molecules to become trapped in one atomic layer deep "valleys" in the outer surfaces of the solids. We can see from Fig. 1 that the second layer of lubricant molecules that we propose to be present inside the valleys can easily be trapped there by lubricant molecules which are adsorbed on the tops of islands of top surface atoms (since they are assumed to be strongly attached to them). I have performed a simple Montecarlo calculation to illustrate this. A lubricant, consisting of 245 spherically symmetric molecules interacting with a Lennard-Jones potential is placed between the two surfaces. The lubricant molecules interact with each of the surfaces with a Steele potential [12]. Since when a molecule is sufficiently strongly pressed into one of the surfaces (because of the high pressures) the corrugation term in the Steele potential, which is the part that depends on  $x$  and  $y$ , dominates over the one that only depends on  $z$ , the potential can become unstable. This defect of the Steele potential is compensated for by making the corrugation term level off before it exceeds the term dependent only on  $z$ . The energy parameter  $\epsilon$  in the Lennard-Jones potential  $-4\epsilon[(\sigma/r)^6 - (\sigma/r)^{12}]$  was chosen to be a tenth of the energy parameter  $\epsilon_{gs}$  in the Seele potential [12]. The potential minima are taken to lie on a triangular lattice of lattice spacing  $a=2.88 A^o$ . The bottom surface contains a hexagonally shaped hole of semi major and semi minor axes 7.6 and 6.6  $A^o$  respectively. The surfaces are circular with radii equal to  $6a\sqrt{3}/2$  where  $a$  is taken to be 2.885  $A^o$ . If  $V_s(x, y, z)$  represents the potential due to this surface for values of  $x$  and  $y$  outside the hole (where the  $z$ -axis is normal to the interface),  $V_s(x, y, z + z_0)$  is taken to be the potential inside the hole. Here  $z_0$ , the depth of the hole, is taken to be equal  $a(2/3)^{1/2}$ , the depth that the hole, resulting from removing atoms in the surface layer, would have on the surface of a hexagonal close packed (hcp) lattice with its  $c$ -axis normal to the surface or a face centered cubic lattice with its (111) surface parallel to the surface. The calculation is started with the lubricant molecules placed in an hcp lattice five atomic layers thick with lattice constant  $a$  between the two surfaces and centered over the hole. The initial separation of the surfaces is 15 $A^o$  which is just enough for the initial crystal of lubricant molecules to fit without being compressed. The surface is kept at that separation for  $2 \times 10^6$  iterations. The separation is then reduced by  $0.5 \times 10^{-7}$  for every Montecarlo iteration until the separation reaches 9.84 $A^o$ . The interface pressure at this separation was found to be  $3.27 \times 10^{11} \text{ dyn/cm}^2$ , which is larger than the pressure at the area of contact of two asperities used in Ref. 6. For smaller separations the

total potential energy of the lubricant becomes large and positive, indicating that the film is becoming highly compressed. Results of these calculations for a  $k_B T = 20\epsilon$  (where  $k_B$  is Boltzmann's constant and  $T$  is the absolute temperature) are shown in Fig. 2. The radius of the shaded sphere used to represent a lubricant molecule was chosen to be approximately equal to the radius used in the simulation in b and c but not in a (for clarity). As can be seen, the film gets compressed into a bi-layer outside of the hole and the hole gets filled with a high concentration of lubricant molecules one monolayer thick, which could support load over the region in which the hole occurs. The interface between the two layers of lubricant will be an interface which will shear quite easily compared to an interface between unlubricated surfaces, as the only interaction acting across this interface is the interaction between pairs of lubricant molecules, which was chosen to be much weaker than the interaction between the two bare surfaces.

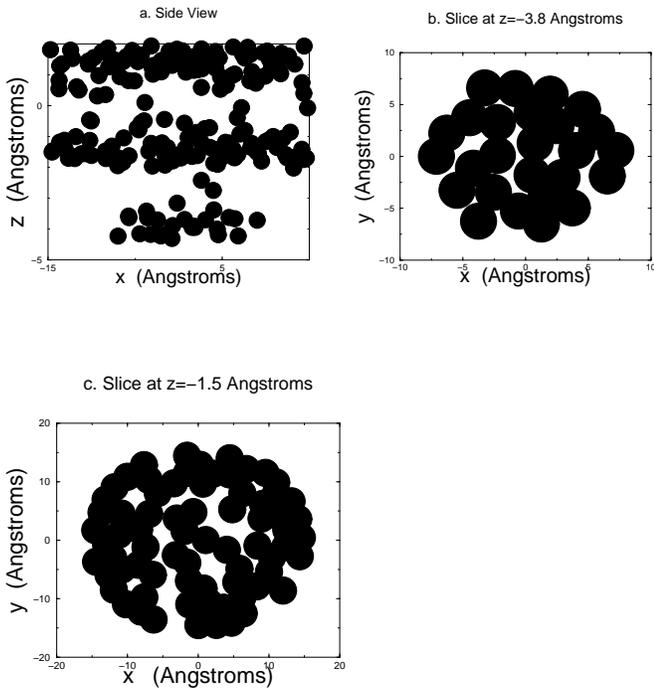


FIG. 2. In a, there is a side view of the distribution of molecules between the two surfaces. In b, the molecules in a slice of width equal to  $1A^\circ$  centered around  $z = -3.8A^\circ$  is shown, which are clearly located inside the hole. In c, the molecules in a slice of width equal to  $1A^\circ$  centered around  $z = -1.5A^\circ$  is shown, which are clearly located in one of the layers outside of the hole.

In contrast to the valleys in the outer surface assumed to occur at the interface between two asperities, lubricant molecules are not expected to get trapped in the space between micron scale asperities, because the depth of such regions is much too great to allow the attractive

force between surface atoms and lubricant molecules to reach the lubricant molecules in most of this region. As a result, most of the lubricant found here remains liquid[2]. The mechanism for boundary lubrication suggested here should be applicable at the pressures that occur at the contact area between two asperities, which can reduce the lubricant concentration down to a monolayer or less[2].

The idea of lubricant molecules filling in valleys in the top layer of each surface and thus making the top surface more smooth at first sight seems like a familiar idea, but here we have provided a mechanism for how "smoothness" results in low friction. The idea that by doing so, the interface switches from the strong pinning regime, in which there is large static friction to the weak pinning regime in which there is little static friction[6,7] provides a mechanism for how such "smoothing" of the surface with lubricant molecules can lead to low friction.

## ACKNOWLEDGMENTS

I wish to thank the Department of Energy (Grant DE-FG02-96ER45585).

- 
- [1] Chan D. Y. C., and Horn R. G., *J. Chem. Phys.* 83 (1985) 5311; Israelachvili J. N., *J. Colloid Interface Sci.* 110 (1986) 263; Reiter G., Demirel A. L., and Granick S., *Science* 263 (1994) 1741; Israelachvili J. N., *Intermolecular and Surface Forces* (Academic Press) 1992 2nd edition; Bhushan B., Israelachvili J. N. and Landman U., *Nature* (London) 374 (1995) 607; Granick S., *Science* 253 (1991) 1374.
  - [2] Gao J., Luedtke W. D. and Landman U., in "Physics of Sliding Friction," ed. B.N.J. Persson and E. Tosatti (Kluwer Academic Publishers) 1995, p.325; Gao J., Landman U. and Luedtke W. D., *Tribology Letters* 9 (2000) 3; Thompson P. A. and Robbins M. O., *Science* 250 (1990) 792.
  - [3] Larkin A. I. and Ovchinnikov Yu. N., *J. Low Temp. Phys.* 34 (1979) 409, Fukuyama H. and Lee P. A., *Phys. Rev.* B17 (1977) 535; Lee P. A. and Rice T. M., *Phys. Rev.* B19 (1979) 3970; Fisher D. S., *Phys. Rev.* B31 (1985) 1396; *Phys. Rev. Lett.* 50 (1983) 1486.
  - [4] Caroli C. and Noziere Ph., *European Physical Journal* B4 (1998) 233.
  - [5] Persson B. N. J. and Tosatti E. in *Physics of Sliding Friction*, ed. B. N. J. Persson and E. Tosatti (Kluwer Academic Publishers) 1995, p. 179.
  - [6] Sokoloff J. B., "Static Friction between Elastic Solids due to Random Asperities," *Phys. Rev Letters* 86 (2001) 3312; 'Sokoloff J. B., "Explaining the Virtual Universal Occurrence of Static Friction," *Physical Review* B65 (2002) 115415.

- [7] He G., Muser M. H. and Robbins M. O., *Science* 284 (1999) 1650; Muser M. H. and Robbins M. O., *Physical Review B* 61 (2000) 2335; Muser M. O., Wenning L. and Robbins M. O., *Physical Review Letters* 86 (2001) 1295.
- [8] S. Aubry, in *Solitons and Condensed Matter*, ed. A. R. Bishop and T. Schneider (Springer) 1978, p. 264.
- [9] Lancon F., *Europhysics Letters* 57 (2002) 74.
- [10] Muser M., *Tribology Letters* 10 (2001) 15.
- [11] B. Bhushan in the *Handbook of Micro/Nano Tribology*, ed. B. Bhushan (CRC Press, Boca Raton, 1999), p. 357.
- [12] Steele W., *Surface Science* 36 (1973) 317.