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Dry Friction due to Adsorbed Molecules

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Using an adiabatic approximation method, which searches for Tomlinson model-like instabilities for a simple but still realistic model for two crystalline surfaces in the extremely light contact limit, with mobile molecules present at the interface, sliding relative to each other, we are able to account for the virtually universal occurrence of "dry friction." The model makes important predictions for the dependence of friction on the strength of the interaction of each surface with the mobile molecules.

Muser and co-workers have argued that clean surfaces should not exhibit static friction [1], but the presence of mobile molecules (so called "third bodies") at the interface can lead to static friction. This is a surprising result because one usually expects such lubricant molecules to reduce rather than enhance friction. On the other hand, if the mobile molecules are much more strongly attached to one surface than the other, they will act as randomly distributed pinning sites belonging to the surface to which they are strongly attached, and it was argued in Ref. 2 that molecular level random defects on the surface will not lead to static friction. Thus, an important ingredient in these molecules' leading to static friction is the relative strength of the interactions of the lubricant molecules with the two surfaces. We have done simple calculations which demonstrate that when the interaction of a molecule with the two surfaces is nearly of equal strength, the system exhibits multistability (i.e., the molecule can have two or more possible equilibrium positions for a given relative displacement of the two wells, one of which becomes unstable). This opens the exciting possibility that the relative strengths of the bonding to each of the surfaces of molecules trapped at an interface can be responsible for whether the molecules reduce or increase friction. It was argued by Caroli and co-workers [4] that without multistability there is no static or dry friction. There have been recent molecular dynamics studies of slow speed kinetic friction which relate their results to the mechanism of Ref. 4, both in one dimensional and two dimensional models[5]. The present work differs from Ref. 5 in that we have developed an adiabatic approximation method for locating Tomlinson-like potential instabilities which result in "dry friction" in the Muser-Robbins picture[1]. We feel that our adiabatic approximation method is more suited to the "dry friction" problem than molecular dynamics because it is better able to deal with the slow speed sliding limit.

The model we have have studied consists of two rigid surfaces with a dilute concentration of particles trapped between them. To zeroth order, we neglect the particle-particle interactions. The surfaces are represented by two identical two dimensional periodic potentials, which are rotated relative to each other at an arbitrary angle, as this is the usual situation at an interface. We model

the potential function acting on a mobile molecule due to each surface by the Steele potential[6] in the limit in which the molecule is not too close to either surface (compared to a lattice constant). For one surface (surf1), it is given by

$$v_1(x, y) = v_0 \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} =$$

$$v_0 \{ 2\cos[(2\pi/a)x] \cos[(2\pi/3^{1/2}a)y] + \cos[(4\pi/3^{1/2}a)y] \}, \quad (1)$$

where the vectors \mathbf{G} denote the smallest reciprocal lattice vectors of a triangular lattice of lattice constant a and v_0 is the strength of the potential. This approximate potential is valid if the surfaces are just barely touching (but this is not contactless friction). We chose for the potential of the second surface (surf2), the potential given in Eq. (1) rotated by ϕ and translated by $(\Delta x, \Delta y)$. Then this potential is given by $v_2(x, y) = v_1(x', y')$, where $x' = (x + \Delta x)\cos(\phi) + (y + \Delta y)\sin(\phi)$ and $y' = -(x + \Delta x)\sin(\phi) + (y + \Delta y)\cos(\phi)$, where, ϕ is the rotation angle, and the displacement parameters Δx and Δy are given by: $\Delta x = s_0\cos(\theta) + b\sin(\theta)$ and $\Delta y = s_0\sin(\theta) - b\cos(\theta)$. Here, $s_0 = vt$ where v is the velocity of sliding of surf2 relative to surf1 along a direction making an angle θ with the x-axis. The minimum at the origin of surf2 is moving along a path displaced a distance b , the distance of closest approach, normal to the path with respect to the minimum at the origin of surf1.

Since we are neglecting intermolecular interaction, we study a single molecule placed at random within the Wigner Seitz unit cell of surf1 containing the origin, for an arbitrary value of b . We assume that each molecule will move to the nearest minimum of $v_1 + v_2$. The resulting potential minimum reaches its smallest value when the two surfaces have slid until the two minima are at their distance of closest approach b . Therefore, the resulting potential minimum can only become unstable and disappear after this point, since before it the minimum is getting deeper. Thus we need only begin our search for instabilities for wells that are at their distance of closest approach. Because this potential is a function of time, the existence of these minima is time dependent. As

the minimum disappears, the particle will drop to another potential minimum of lower energy, resulting in a gain of kinetic energy, which is assumed to get quickly transferred to phonons and electronic excitations of the surfaces. This is the mechanism for frictional energy dissipation. We have studied Eq. (1) using this method, but it is equally applicable to any two periodic or disordered potentials, representing the two surfaces.

In order to locate minima, and to track their positions and stability as our surfaces slide past one another, we first place a particle at a random position at the interface and use a Montecarlo routine to move it to the nearest potential minimum. In order to predict where the minimum will move during sliding, we use the fact that the force on a particle at the potential minimum $(x_0(t), y_0(t))$ remains identically zero for all time in the adiabatic approximation to find velocity at which the minimum is moving. Then, we have

$$\frac{d}{dt} \frac{\partial v}{\partial x}(x_0(t), y_0(t), t) = \frac{\partial^2 v}{\partial x^2} \Big|_0 \frac{dx}{dt} + \frac{\partial^2 v}{\partial x \partial y} \Big|_0 \frac{dy}{dt} + \frac{\partial^2 v}{\partial x \partial t} \Big|_0 = 0, \quad (2a)$$

$$\frac{d}{dt} \frac{\partial v}{\partial y}(x_0(t), y_0(t), t) = \frac{\partial^2 v}{\partial y^2} \Big|_0 \frac{dy}{dt} + \frac{\partial^2 v}{\partial x \partial y} \Big|_0 \frac{dx}{dt} + \frac{\partial^2 v}{\partial y \partial t} \Big|_0 = 0. \quad (2b)$$

We then solve the above equations for the instantaneous velocities of the minimum as the surfaces slide as follows:

$$\frac{dx}{dt} = \frac{1}{D_0} \frac{\partial^2 v}{\partial x \partial y} \Big|_0 \frac{\partial^2 v}{\partial y \partial t} \Big|_0 - \frac{\partial^2 v}{\partial y^2} \Big|_0 \frac{\partial^2 v}{\partial x \partial t} \Big|_0, \quad (3a)$$

$$\frac{dy}{dt} = \frac{1}{D_0} \frac{\partial^2 v}{\partial x \partial y} \Big|_0 \frac{\partial^2 v}{\partial x \partial t} \Big|_0 - \frac{\partial^2 v}{\partial x^2} \Big|_0 \frac{\partial^2 v}{\partial y \partial t} \Big|_0. \quad (3b)$$

Multiplying the velocity by the time step gives us the approximate new position of the minimum after sliding. The term in both dominators above, which we have designated as D_0 , is given by

$$D_0 = \frac{\partial^2 v}{\partial x^2} \Big|_0 \frac{\partial^2 v}{\partial y^2} \Big|_0 - \left| \frac{\partial^2 v}{\partial x \partial y} \right|_0^2. \quad (4)$$

It plays a critical role in our algorithm. It is known as the Gaussian curvature (for extrema points). When $D_0 = 0$ an instability occurs. Furthermore, Eqs. 3 depend on the inverse of D_0 . For this reason, the time step between successive relative displacements as the surfaces slide must be scaled by D_0 as we approach a minimum.

The 2nd order Taylor series expansion of the potential, assumed to be with respect to the location of the nearest minimum,

$$v(x, y) = v(x_0, y_0) + \frac{\partial v}{\partial x} \Big|_0 \Delta x + \frac{\partial v}{\partial y} \Big|_0 \Delta y + (1/2) \frac{\partial^2 v}{\partial x^2} \Big|_0 \Delta x^2 + (1/2) \frac{\partial^2 v}{\partial y^2} \Big|_0 \Delta y^2 + (1/2) \frac{\partial^2 v}{\partial x \partial y} \Big|_0 \Delta x \Delta y, \quad (5)$$

is now used to determine more accurately the location of the new minimum. The first order derivatives vanish, since we assume that we are expanding about the true minimum. The second order derivatives can, to 2nd order, be replaced by the second order derivatives at the present position of the particle, provided we are close to the actual minimum. The quantities $\Delta x = (x_0 - x_{pp})$ and $\Delta y = (y_0 - y_{pp})$ are then the approximate distances, along the x and y directions, between the particle's present position (pp), and where the actual minimum is. In order to use the force components felt by the particle at it's present location to find Δx and Δy , we differentiate the above 2nd order approximation with respect to both x and y, obtaining an approximation for the force components near the true minimum.

$$\frac{\partial v}{\partial x} = \frac{\partial^2 v}{\partial x^2} \Big|_{pp} \Delta x + \frac{\partial^2 v}{\partial x \partial y} \Big|_{pp} \Delta y, \quad (6a)$$

$$\frac{\partial v}{\partial y} = \frac{\partial^2 v}{\partial y^2} \Big|_{pp} \Delta y + \frac{\partial^2 v}{\partial x \partial y} \Big|_{pp} \Delta x. \quad (6b)$$

Eqs. (6a) and (6b) are solved for Δx and Δy to give

$$\Delta x = \frac{1}{D} \frac{\partial^2 v}{\partial y^2} \Big|_{pp} \frac{\partial v}{\partial x} \Big|_{pp} - \frac{\partial^2 v}{\partial x \partial y} \Big|_{pp} \frac{\partial v}{\partial y}, \quad (7a)$$

$$\Delta y = \frac{1}{D} \frac{\partial^2 v}{\partial x^2} \Big|_{pp} \frac{\partial v}{\partial y} \Big|_{pp} - \frac{\partial^2 v}{\partial x \partial y} \Big|_{pp} \frac{\partial v}{\partial x}, \quad (7b)$$

where D is the quantity given in Eq. (4) but evaluated at the point (x_{pp}, y_{pp}) . The derivatives in Eq. (7) are found from the potential $v_1 + v_2$ defined in Eq. (1) and in the discussion under it. If the particle is close to the minimum, this procedure converges very quickly to the true minimum. How quickly it converges, however, is dependent on the size of the quantity D.

In our algorithm, we compute D_0 . The second derivatives of the potential form a two dimensional 2nd rank tensor, which can be diagonalized for appropriate orientation of the coordinate axes. D_0 is equal to the product of these diagonal elements. The xx component defines a parabola along the x-direction, and the yy component defines another along the y-direction. If both components are positive, one has a minimum, if both are negative, a maximum, and if one is positive and one is negative, then one has an instability, if the third order term in the Taylor series of Eq. (5) is nonzero and a minimum otherwise. When the minimum first becomes unstable, one of the eigenvalues, and hence D_0 , goes to zero, we may have an instability. A typical instability is illustrated in Fig. 1, which shows a potential minimum which has become unstable, in the sense that one wall of the well minimum has disappeared, allowing a particle located in this minimum to flow into a neighboring minimum, which is also shown in this figure.

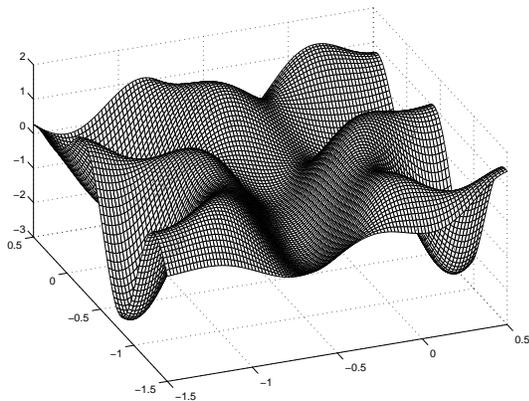


FIG. 1. An unstable potential minimum and a lower energy stable minimum are shown. The x and y axes are in units of a and the potential is in units of v_0 .

Our method allows us to track the position of a minimum until it becomes unstable, at which point we can locate the new minimum into which an unseated particle will next fall into. This allows us to calculate the drop in potential energy that such a particle would undergo, that we associate with the energy loss due to friction. The total frictional energy loss between our two surfaces would then be the sum of the energy drop for each particle every time it experiences an instability. Instead of doing a full simulation of many particles at an interface, which would be highly time consuming in the slow speed sliding limit, we have chosen to examine the motion in the adiabatic approximation of a single particle for various rotation angles ϕ and angles of sliding θ . Then, a simple average is taken over the possible energy drops that occur for the various instabilities, in order to find the average energy loss between two surfaces, as a result of their sliding motion, for any number of particles. An absolute minimum of the total potential is a result of the coalescence of two minima, one from each surface. Because of the periodicity of the surfaces, as these two minima slide past one another (for fixed values of ϕ and θ), only one parameter is needed to describe the behaviors for the resulting potential minimum, the distance of closest approach b defined above. Because of this, we can examine all possible behaviors of a minimum of the total potential for fixed values of ϕ and θ by considering the behavior of the minimum that results from the overlap of the two central minima as a function of the parameter b . The results will give us all possible instabilities a single particle may undergo anywhere on the surface for a given rotation angle ϕ and angle of sliding θ . From these results we can determine the average energy lost per particle per instability, and from this we can estimate the average frictional force between the two surfaces. Our results for one value of θ and ϕ are illustrated in the first two columns of table 1. Runs were made for all values of $0 < b/a < 0.5$ with a spacing of 0.02. Values of b/a

for which no instabilities were found are not listed in the table.

In order to estimate the force of friction, we first find $\langle \Delta E \rangle$, the mean value of the energy drop in an instability for each value of θ and ϕ . For example, for the values given in table 1, we obtain $\langle \Delta E \rangle = 0.0667v_0$. The mean value of the force of friction is given by the $\langle \Delta E \rangle / \langle \Delta x \rangle$, where $\langle \Delta x \rangle$ denotes the mean distance that the two surfaces must be slid in order to find an instability. Since $\langle \Delta x \rangle$ is of the order of a lattice spacing, which is of the order of $3 \times 10^{-8} \text{cm}$, and since the potential strength V_0 is of the order of 0.01980 eV[6,7], we obtain a force of friction per molecule at the interface of the order of $7.044 \times 10^{-8} \text{dyn}$ for $\theta = 0.327$ rad and $\phi = 0.1309$ rad. The values of $\langle \Delta E \rangle$ for other values of θ and ϕ that we considered were of similar magnitude. If a unit cell area of a surface is of the order of 10^{-15}cm^2 and there is a concentration of molecules (i.e. the number of molecules per unit cell) of 0.01, we obtain a frictional stress (i.e., the force of friction per cm^2 of contact area) of $7.044 \times 10^5 \text{dyn/cm}^2$. Then an interface of total area 1cm^2 with an area of contact (at asperities) which is 2 percent of this value, will exhibit a force of friction of 0.02cm^2 times the frictional stress, or about 10^4dyn or about 0.1 N, which is a reasonable value.

We have repeated our procedure for the case in which the strengths of the potentials of the two surfaces, denoted above by v_0 differ. Our results for one set of values of θ and ϕ are given in the last two columns of table 1. Column 3 gives the maximum amount that v_0 for surf1 can be increased and still get instabilities and column 4 gives the maximum amount that v_0 can be increased for surf2 and still get instabilities. (There is an asymmetry between the surfaces because the angles between the direction of sliding and the axes of the two surfaces differ.) We find that once the strengths of the two surface potentials differ by at most 0.3 percent, instabilities are no longer found. This implies that at least at zero temperature, there will be no kinetic friction at slow sliding speeds. As mentioned earlier, for large differences in potential strengths this is not an unexpected result because in that case the mobile molecules at the interface are much more strongly attached to one surface than the other. This is essentially the case of two surfaces in contact at randomly placed points of contact, which was considered in Refs. 1-3. There it was found that there is no static friction. Since the existence of static and kinetic friction require that there be instabilities[4], and since it was shown in Refs. 1-3 that there is no static friction, it is also likely that there will be no slow speed kinetic friction in this case. The lack of instabilities, and hence slow speed kinetic friction, when the potential strengths differ by small amounts, comes as a surprise. Since we did find near instabilities (i.e., a potential wells bounded by a very low ridge in one direction) for case of surfaces whose potential strengths differ by only a few percent, the possibility still exists that there will still be friction once Boltzmann's constant times the temperature becomes comparable to

these low potential ridges bounding nearly unstable potential wells. An earlier treatment of this problem for two surfaces which consist of a random or periodic array of rotationally symmetric Gaussian potential wells[8] shows that the minima of the net potential acting on a mobile molecule at this model interface will always become unstable as the surfaces slide relative to each other. Furthermore, a Gaussian potential well placed at random on one surface, to represent a local defect, can always result in an instability, if its depth is greater than v_0 [9]. Therefore, we concluded that for this model, there will always be dry friction for any nonzero temperature.

TABLE I. Results for $\phi = 0.1309rad$ and $\theta = 0.3927rad$.

b/a	$\Delta E/v_0$	$(\Delta v_1/v_0) \times 10^2$	$(\Delta v_2/v_0) \times 10^2$
0.0	0.0669	0.285	0.295
0.02	0.0571	0.246	0.308
0.04	0.0507	0.194	0.304
0.06	0.0366	0.132	0.283
0.08	0.0162	0.064	0.247
0.24	0.0169	0.249	0.064
0.26	0.0373	0.287	0.131
0.28	0.0510	0.307	0.191
0.30	0.0571	0.306	0.241
0.32	0.0649	0.280	0.279
0.34	0.0993	0.228	0.302
0.36	0.1332	0.0	0.0
0.38	0.1665	0.0	0.0
0.40	0.2667	0.0	0.0
0.42	0.2341	0.0	0.0
0.44	0.1997	0.0	0.0
0.46	0.0565	0.0	0.0
0.48	0.1255	0.0	0.0

Our conclusion is that although the array of Gaussian potentials treated in Ref. 8, which could represent imperfections of the surfaces, appears to always exhibit dry friction, the model potential considered in this work, which should describe two perfectly periodic surfaces, only exhibits significant dry friction when the strengths of the two surface potentials are nearly equal. We have also performed molecular dynamic simulations which support the conclusions of the procedure used in this work[9].

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