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Thermally induced suppression of friction at the atomic scale

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Atomic-scale friction, as accessed in tip-based experiments, is investigated theoretically in the full range of surface corrugations, temperatures, and velocities. Emphasis is given to the regime of thermal drift, when the regular stick-slip behavior is completely ruined by thermal effects. The possibility of nearly vanishing friction ("thermolubricity") is predicted even for strong (overcritical) surface corrugations, when traditional models would predict significant friction. The manifestation of this effect in recently published experimental data is demonstrated.

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The seemingly simple phenomenon, *friction*, remains poorly understood. Generally, friction is concerned with dissipation of momentum. However, a variety of dissipation channels can be in action, depending on the time and space scales concerned. Friction force microscopy (FFM) [1] allows direct atomic-scale access to the friction force: an object (the tip) is dragged along a surface by an external "arm" (the cantilever), which is at the same time used to measure the friction force experienced.

A very recent and really remarkable discovery in this field is concerned with direct observations [2,3] of nearly vanishing friction. This phenomenon, predicted theoretically under the name superlubricity [4], can be understood using a simple mechanistic approach to the problem, referred to as the Tomlinson model (for details, see, e.g., [5]). When the effective lateral corrugation of the tip–surface interaction is reduced to a certain critical value, the model predicts the transition from tip motion with stick-slip character (typically observed in FFM experiments) to nondissipative continuous sliding along the surface. The experiments of Ref. [3] seem to be consistent with the theory: reducing the normal load, and hence the lateral surface corrugation, one observes a transition from nearly regular stick-slip behavior to a nearly continuous sliding. In contrast, experiments of Ref. [2] exhibit a larger degree of irregularity even in the stick-slip regime [see Fig. 1(a)], and an absolutely irregular, stochastic behavior of the tip in the nearly frictionless regime [see Fig. 1(b)]. This suggests a very pronounced role of thermal effects in the second case.

An important role of temperature in friction was anticipated many decades ago [6], but is still far from being understood. Recent investigations have been restricted to the stick-slip regime [5,7–10] and the transition to the viscous drag regime at higher velocities [9]. Thermally activated jumps of the tip over small potential barriers preceding the "mechanistic" slips were shown to lead to a certain variation in positions of the slip events seen in FFM scans [see, e.g., Fig. 1(a)], and to explain a weak logarithmiclike decrease of friction with decreasing velocity [7]. However, the existing theory tacitly neglects the possibility of thermally activated slips over "high" potential barriers experienced by the tip at most of the positions of the support. Actually, this is reasonable only for sufficiently strong surface corrugation and/or low temperature, and/or high velocity, but little if anything is known about what the actual restrictions are.

In our work, atomic friction is for the first time investigated theoretically in the full range of surface corrugations, temperatures and scanning velocities. Analysis of all possible regimes will be given in a full size paper. In this letter we concentrate on the regime of thermal drift, when the regular stick-slip behavior is completely ruined by thermal effects. As the main result, we predict the possibility of nearly vanishing friction in the case of a relatively strong (overcritical) surface corrugation, when the traditional mechanistic approach would prescribe a sizable friction. As an alternative to the "mechanistic" superlubricity, the effect can be called *thermolubricity*. We demonstrate the manifestation of this effect in the experimental data of Ref. [2]. Finally, having obtained the value of the only free parameter of the theory from

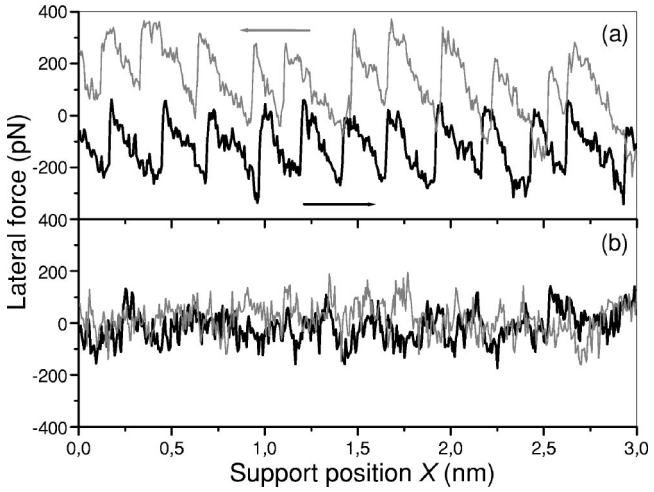

FIG. 1. Characteristic lateral-force loops at two different relative surface corrugations, measured in the FFM experiment reported in [2]: (a) $\gamma=4.96$, (b) $\gamma=2.46$.

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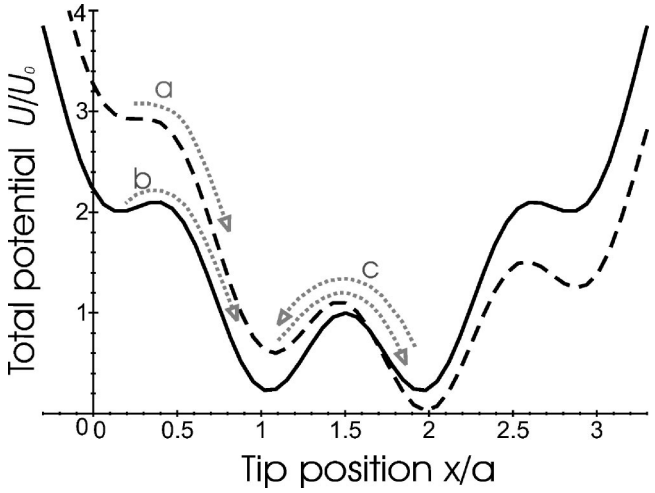

FIG. 2. Total potential U vs tip position x, for $\gamma=10$ and for two support positions, $X=1.5a$ (solid) and $X^{(c)}=1.82a$ (dashed). Arrows (a, b, c) show different types of slips.

comparison with experiments, we indicate two puzzling questions, stimulating further theoretical and experimental work towards understanding the microscopic mechanisms of dissipation.

Describing motion of the FFM tip along the surface, we follow the usual assumption that the measuring system can be characterized by one effective spring constant, K, which accounts for both the flexibility of the cantilever and that of the tip. Implying one dimensional motion, assuming the tip–surface interaction potential to be sinusoidal, with amplitude U_0 and period a, and introducing the tip and support coordinates, x and X, respectively, we write the total potential experienced by the tip as

$$U(x,t)=\frac{U_0}{2}\left[1-\cos\left(\frac{2\pi x}{a}\right)\right]+\frac{1}{2}K(x-X)^2, \tag{1}$$

where $X=Vt$, with V the scanning velocity. The instantaneous lateral force is $F=-K(x-X)$, while the friction force is given by its time average. Introducing the dimensionless, relative surface corrugation

$$\gamma=2\pi^2\frac{U_0}{Ka^2}, \tag{2}$$

one distinguishes between two essentially different cases. If $\gamma>1$, the total potential (1) contains several wells (see Fig. 2), which periodically appear and disappear due to the motion of the support, while if $\gamma<1$ there is only one well, at any position of the support. This is the origin of the transition from the dissipative stick-slip motion to the case of superlubricity at the critical corrugation $\gamma_c=1$, within the Tomlinson model. With $\gamma>1$, the tip sticks in its original well until it disappears at a certain critical position of the support, and the tip slips to the neighboring well [Fig. 2(a)], etc. Assuming complete dissipation of the excess of energy in every slip event, one finds a nonzero averaged lateral force, i.e., friction. With $\gamma<1$, the tip exhibits continuous sliding along the surface; the mean lateral force is zero and the motion is frictionless. Note that for large K this situation can occur even for strong surface corrugation.

On a more microscopic level, one should explicitly consider interaction of the tip with thermal excitations of the substrate (e.g., with phonons), introducing an element of nonequilibrium statistical mechanics. Particular trajectories of the tip can be simulated using Langevin dynamics, while average behavior of the system can be described by a kinetic equation (e.g., of the Fokker-Planck type [11]) for the probability density to find the tip at a certain time at a certain position x and in a certain energy state. However, at the modest velocities used in FFM, the problem can be substantially simplified by the fact that the inherent motions of the tip are fast with respect to the scanning velocity. This allows us to average over these fast processes by going over from the probability density to the simple probabilities $p_i(t)$ to find the tip at a certain time in a certain well i (see Fig. 2). In this way, the kinetic equation is reduced to a system of continuity equations for $p_i(t)$ in discrete space:

$$V\frac{dp_i}{dX}=-(r_i^+ + r_i^-)p_i + r_{i-1}^+ p_{i-1} + r_{i+1}^- p_{i+1}. \tag{3}$$

Here, the role of time is played by the support coordinate $X=Vt$. The number of wells involved in the problem increases with γ, as can be easily derived from (1).

In Eq. (3) we have assumed that only single jumps to neighboring wells can take place. Coefficients r_i^+ and r_i^- are the rates of activated jumps from well i to the right and to the left, respectively, which can be written as

$$r_i^\pm = r_0 \exp\left(-\frac{U_{bi}^\pm}{k_B T}\right), \tag{4}$$

with U_{bi}^+ and U_{bi}^- the potential barriers from well i to the right and to the left, which depend on the support position X (see Fig. 2). Expressions for $U_{bi}^\pm(X)$ follow from (1) in a straightforward manner.

The prefactor r_0 in (4) is not known in advance. One could follow transition state theory and relate it to the frequency of vibrations in the well, $r_{0i}=\nu_i$. Then the dependence of ν_i on X could be derived directly from (1) although absolute values would not be obtained since the effective mass is not known. Actually, the prefactor can be *lower* than ν_i, as predicted by kinetic theories of activated processes (see, e.g., Ref. [12]) which explicitly take into account the coupling with the substrate bath. On the other hand, in our case the prefactor can be substantially *increased* by a thermodynamic factor concerned with a collective effect [13], dependent on the number of atoms of the tip in contact with the surface. With this in mind, we leave the prefactor r_0 to be the only free parameter of the theory. We assume here that it is independent of the support position X (and hence, of i), although this is not necessarily correct.

Equation (3), with initial conditions $p_i|_{X=0}=\delta_{io}$, with o denoting the starting well, completely determines the behavior of the system. The ensemble averaged lateral force as a function of the support position can be found as $\overline{F}=-K(\overline{x}-X)$, with the mean position of the tip $\overline{x}=\Sigma x_{\min}^{(i)} p_i$. Here $x_{\min}^{(i)}$ are the X-dependent minima of the total potential (1). The

friction force F_{fric} is found by averaging $\overline{F}$ over X.

In addition to the Tomlinson parameter γ, Eq. (3) brings out another dimensionless parameter of the system

$$\beta = \frac{V}{ar_0}\exp\left(\frac{U_0}{k_B T}\right), \tag{5}$$

the ratio of the characteristic values of the left-hand side (lhs) and right-hand side (rhs) in (3). This parameter shows how fast or slow the scanning process is with respect to the characteristic rate of thermally activated jumps as shown in Fig. 2(c). Clearly, the stick-slip regime corresponds to the case $\beta \gg 1$. In this regime a first approach is to completely neglect thermal effects. With $r_i^{\pm}=0$, (3) leads to $p_i=\mathrm{const}$. This means that the tip resides (with probability unity) in the original well as long as the well exists, then it moves to the adjacent well, etc. This is just the description of the mechanistic Tomlinson model. However, this approximation is never justified. The terms on the rhs are small with respect to the lhs almost everywhere but not in the vicinity of the critical positions of the support, where the barriers U_{bi}^{+} are small and the jump rates become large. Hence the activated slips in the vicinity of the critical points [as shown in Fig. 2(b)] are always important. This is the origin of both a weak velocity dependence of friction and a statistical distribution in positions of slips in the stick-slip regime, as was already discussed in [5,7,8,10] on the basis of an approximate solution of an equation of the type (3).

In the opposite limiting case, $\beta \ll 1$, while the support passes one lattice spacing a, the tip exhibits many activated jumps, back and forth, between the potential wells. This regime can be called *thermal drift.* The tip drifts with a mean position $\overline{x}$ which moves with X. The difference $(X-\overline{x})$ determines the mean lateral force. Meanwhile, instantaneous lateral force exhibits rapid fluctuations of the order of the maximum surface force, since the change in the tip position in one jump, i.e., the distance between the wells, is of the order of the lattice spacing a. In the intermediate case, say at $\beta \sim 1$, the tip exhibits on average one activated jump per interatomic distance passed by the support. The behavior of the instantaneous lateral force in this case should be regarded as irregular or stochastic stick slip.

Since the stick-slip regime is relatively well understood, we first of all concentrate on the thermal drift regime, $\beta \ll 1$. If β is small, the system of Eq. (3) can be solved analytically, expanding p_i in a power series in β. In this way, in any order in β, the problem is reduced to a system of linear algebraic equations, and solution is straightforward. Leaving details for a full-size paper, we briefly report the most important results of our calculations. First of all, one observes that in the zeroth-order approximation in β, the friction force is exactly zero, $F_{\mathrm{fric}}^{(0)}=0$. This means that friction vanishes in the limiting case of zero velocity, $F_{\mathrm{fric}}|_{V\to 0}=0$. The result is important, since earlier simulations [14,15] for the case $T=0$ suggested a nonzero friction in the zero velocity limit. The effect of temperature observed here is that at nonzero T, for any given U_0, the activated slips of the tip will have enough time to completely destroy the stick-slip motion, provided scanning is sufficiently slow. Somewhat analogous physics was discussed earlier [16] with respect to static friction.

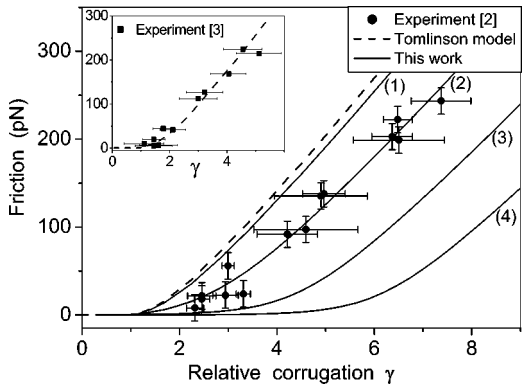

FIG. 3. Friction force as a function of relative surface corrugation γ for $V=30$ nm/s, $a=0.25$ nm, and $K=1.8$ N/m. Solid curves: present theory for (from left to right) $V/ar_0=7.5\times 10^{-n}$ with $n=1,2,3,4$. Dashed curve: Tomlinson model. Experimental points retrieved from Ref. [2]. Inset: experimental points retrieved from Ref. [3] ($V=3$ nm/s, $K=1.3$ N/m, $a=0.5$ nm).

To first order in β, the friction force is close to $F_{\mathrm{fric}}^{(1)} \sim V(K/r_0)(U_0/k_B T)\exp(U_0/k_B T)$. In the thermal drift regime friction increases linearly with V, and the increase is very steep. This is in contrast to the weak logarithmic increase characteristic for the stick-slip regime [5,7,8,10]. Furthermore, there is a strong, exponential dependence on U_0/T. Consequently, even a small decrease in surface corrugation or a small increase of temperature will lead to a substantial decrease in friction. In this low-velocity regime temperature acts as a lubricant.

Realization of a certain regime—stick-slip ($\beta \gg 1$), intermediate ($\beta \sim 1$), or thermal drift ($\beta \ll 1$)—depends on U_0 and T, and also on V, a, and r_0. Variable-temperature and low-velocity FFM experiments are still lacking in order to directly address all the regimes predicted. However, variation of the effective surface corrugation in a wide range has been the subject of recent experiments [2,3]. To visualize the possible role of thermal effects for different surface corrugations, the friction force is plotted in Fig. 3 as a function of γ (values of T, V, a, and K are taken from the experiment [2]). The dashed curve is the prediction of the Tomlinson model (thermal effects completely ignored). The solid curves represent our numerical solution to Eqs. (3) and (4) in the entire range of β for four values of the prefactor r_0, each time increasing by one order of magnitude. Our calculations show that even at low values of r_0 the friction force is decreased noticeably with respect to the Tomlinson value (dashed curve). At no γ value do our results approach the dashed curve, but the ratio between our results and the Tomlinson value does approach unity in the limit of high γ.

From Fig. 3, we conclude that friction can be negligibly small even when the surface corrugation is large enough to produce substantial friction in traditional mechanistic theory. In analogy with *superlubricity* that takes place at $\gamma<1$, the effect of substantial reduction in friction at $\gamma>1$, due to the transition from the stick slip to the thermal drift regime, can

be called *thermolubricity*. We predict that upon decreasing the surface corrugation, thermolubricity should occur prior to superlubricity. At higher temperatures and/or at lower velocities the γ range of thermolubricity will be wider. At low temperatures, high velocities, and/or low prefactor r_0, the system will switch nearly directly from the stick slip to the superlubric regime without a distinguishable, intermediate role of thermal effects.

The experimental data retrieved from Ref. [3] (see inset of Fig. 3) follow the stick-slip regime down to $\gamma=1$, without any visible manifestation of thermally activated slips. The same can be inferred from the very regular stick-slip behavior of the lateral force $F(X)$ seen in the scans with $\gamma=5$ and $\gamma=3$ in Ref. [3], and at lower γ [17]. We are forced to conclude that the prefactor of activated jumps, r_0, in the system used in these experiments was below 2×10^2 s^{-1}. We will return to this value later.

Figure 3 also shows data from the experiments described in Ref. [2]. Like our calculations, these experimental data deviate strongly from the Tomlinson model—more than a factor 2 at low γ—and suggest a pronounced role of thermally activated jumps. From the comparison with the calculated curves, we find that there is excellent agreement between theory an experiment over the full experimentally addressed range of γ values for a prefactor of $r_0=1.6\times10^3$ s^{-1} (second solid curve).

Additional support for these conclusions can be drawn from the shape of the scans in Fig. 1 (which correspond to one of the higher and one of the lower points in Fig. 3). In the upper scan one can clearly see irregular stick slips, with on average about one thermally activated slip per atomic period passed, as should be expected in the intermediate regime, $\beta\sim1$. In the lower scan one can see several large fluctuations of the lateral force per atomic period. This suggests β to be on the order of 0.1, close to the thermal drift regime. Both observations are in agreement with the positions of the corresponding points in Fig. 3. In summary, the experiments of Ref. [2] seem to clearly demonstrate "thermolubric" behavior in the range of $\gamma>1$.

The values of the prefactor r_0 obtained from the comparison with experiments are puzzling, at least in two respects. First, what is the reason for the order of magnitude difference between the prefactors for the two experiments? One possible answer involves a collective, entropic effect of the type proposed in Ref. [13] for the gliding diffusivity of large atomic clusters. There was a graphite flake attached to the tip in Ref. [2], and hence the number of atoms in contact with the surface was indeed considerably larger than in Ref. [3].

Second, the effective spring constant in both cases (~1 N/m) was of the order of the stiffness of atomic bonds, suggesting that the flexible part of the tip is formed by a small group of atoms at the apex. This means that the effective mass which actually probes the surface is atomically small. Consequently, one would expect the prefactor to be in the range of atomic frequencies, rather than the kHz regime. Further theoretical and experimental work is needed to solve these puzzles, which will contribute to a full understanding of the truly microscopic mechanisms of dissipation.

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