Interaction Potential and Hopping Dynamics Governing Sliding Friction

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The friction force on a nanometer-sized tip sliding on a surface is related to the thermally activated hopping of the contact atoms on an effective atomic interaction potential. A general analytical expression relates the height of this potential and the hopping attempt frequency to measurements of the velocity dependence of the friction force performed with an atomic force microscope. While the height of the potential is roughly proportional to the normal load, the attempt frequency falls in the range of mechanical eigenfrequencies of the probing tip in contact with the surface.

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Fundamental research [1] and applications [2] involve exceedingly small mechanically moving components. This requires an improved understanding of friction forces appearing at the relevant length scales. As one approaches atomic [3] or molecular [1] scales, the most natural picture for sliding friction is the one of atoms in the contact area moving on a corrugated potential, similar to surface diffusion of adsorbates [4,5]. However, only few experimental studies have attempted to establish a relationship between friction forces and the atomic interaction potential [6]. On the theoretical side, *ab initio* calculations have determined the corrugation of the interaction potential of a layer of Pd atoms moving across graphite [7]. There are numerous molecular dynamics studies of a nanometer-sized tip sliding on a surface [8–10], however, a link of friction forces with the interaction potential at different loads has not yet been established.

Recently, the importance of thermally activated processes in sliding friction has been emphasized by various experimental and theoretical studies [3,11–14]. In the case of stick-slip motion, these processes are thermally activated jumps of the atoms forming the contact. At a given temperature these jumps occur with a certain rate. The externally imposed sliding velocity introduces a second rate, competing with the first. This gives rise to a logarithmic increase of the lateral (or friction) force, F_L, with the sliding velocity, v. This behavior can be in principle traced back to an effective corrugation of the interaction potential E_0 between the atoms in the contact area, and to a characteristic attempt frequency f_0 of the system. So far, however, there has been no precise experimental determination of E_0, and the meaning of f_0 has remained unclear.

In this Letter, we establish the link between the friction force on a nanoscopic tip sliding on a surface and the thermally activated hopping of the atoms in the contact on an effective potential. We measure by means of an atomic force microscope (AFM) the friction force between a silicon tip and a mica surface as a function of the externally applied load and velocity. The ensemble of our data is consistently explained by a thermally activated hopping process of the tip on an effective periodic potential. The load dependence of the corrugation of this potential and the attempt frequency are determined. The attempt frequency is identified as the mechanical resonance of the probing tip elastically coupled with the surface. Moreover, similarly to the action of temperature, we externally activate the jumps by applying lateral oscillations to the cantilever at different frequencies during its sliding on the mica surface. When these oscillations are at a critical frequency in the range of f_0 the friction force dramatically decreases. Finally, we experimentally and theoretically find a velocity which marks the transition from logarithmic increase of $F_L(v)$ to a region where friction is constant since thermal activation ceases to be relevant. This velocity is analytically related to the potential corrugation, E_0, and f_0.

The starting point of our model is the relationship between the dynamic energy barrier, ΔE, which prevents the jump of the tip from a stable equilibrium position on the surface into the neighboring one, and the instantaneous lateral force, f_L. Gnecco *et al.* [3] observed that the logarithmic velocity dependence of the mean value of the lateral force corresponding to the tip jump, F_L, can be explained assuming a linear relationship between ΔE and f_L: $\Delta E \sim (\text{const.} - f_L)$. However, this approximation is only valid in a limited velocity range and it lacks validity when the jump occurs very close to the critical point given by $\Delta E = 0$. Sang *et al.* [11] deduced that the correct relationship is $\Delta E \sim (F^* - f_L)^{3/2}$, where F^* is the friction force at zero temperature. In the following this result is applied to derive an analytical expression for the velocity dependence of friction without limitations in the velocity range. We note that the result of Ref. [11] has been derived for small contact areas while for large contact areas ΔE may be more accurately described by a linear dependence [15].

The energy barrier ΔE is defined as $\Delta E(t) = V(x_{\max}, t) - V(x_{\min}, t)$, where $V(x, t)$ is the sum of tip-surface interaction potential and cantilever spring

potential. The quantities $x_{\min}(t)$ and $x_{\max}(t)$ correspond to the first minimum and maximum of the combined potential at the time t, which are determined by the condition $\partial V/\partial x = 0$ [16]. Note that $x_{\min}$ coincides with the equilibrium position of the tip. At zero temperature, the lateral force required to make the tip jump from one potential minimum to another is $F_L = F^*$ (i.e., the force corresponding to $\Delta E = 0$). At finite temperature T the occurrence of thermally activated transitions between two minima when $\Delta E > 0$ leads to $F_L < F^*$ and the probability that the tip does *not* jump $p(t)$ is described by the master equation [3]:

$$\frac{dp}{dt} = -f_0 \exp\left[-\frac{\Delta E(t)}{k_B T}\right] p(t). \tag{1}$$

As outlined above, we assume that

$$\Delta E(t) = \frac{1}{\beta}(F^* - f_L)^{3/2}, \tag{2}$$

where β depends on the shape of the potential profile $V(x, t)$. Under this assumption, the condition for the maximum probability of jumping, $d^2p/d^2f_L = 0$, leads to the following expression for the mean friction force F_L [17]:

$$\frac{1}{\beta k_B T}(F^* - F_L)^{3/2} = \ln\frac{v_0}{v} - \frac{1}{2}\ln\left(1 - \frac{F_L}{F^*}\right), \tag{3}$$

where v_0, β, F^*, and f_0 are related by the expression:

$$v_0 = \frac{2 f_0 \beta k_B T}{3 k_{\text{series}} \sqrt{F^*}}. \tag{4}$$

The quantity k_{series} is the effective stiffness of the contact, which can be deduced from the slope of the lateral force vs distance curves [18,19]. In the present case, we measured $k_{\text{series}} = 1.2$ N/m, without significant variations in the range of applied loads.

The relationship between β and F^* depends on the shape of the interaction potential. While Eqs. (3) and (4) describe the general case of an arbitrarily shaped potential, we now briefly discuss the case of a sinusoidal potential, where an analytical relationship can be derived. In such a case $V(x, t)$ is described by

$$V(x, t) = -\frac{E_0}{2}\cos\frac{2\pi x}{a} + \frac{k}{2}(vt - x)^2, \tag{5}$$

where a is the surface lattice constant and E_0 is the corrugation of the interaction potential. From this we obtain

$$\frac{\partial V}{\partial x} = F^* \sin\frac{2\pi x}{a} - k(vt - x), \tag{6}$$

where

$$F^* = \pi E_0/a. \tag{7}$$

We have assumed that the tip-sample interaction is stronger than the cantilever elasticity, as usually observed experimentally [16]. Expanding Eq. (6) in Taylor's series around the critical point $x^* = a/4$ we find

$$\Delta E(t) = \frac{2\sqrt{2}}{3} E_0 \left(1 - \frac{kvt}{F^*}\right)^{3/2}. \tag{8}$$

The instantaneous lateral force is $f_L \simeq kvt$, so that by comparison with (2) we obtain

$$\beta_{\sin} = \frac{3\pi\sqrt{F^*}}{2\sqrt{2}a}. \tag{9}$$

The previous equations relate the velocity dependence of F_L to fundamental quantities such as E_0 and f_0. We have measured the velocity dependence of the friction force at different normal loads, F_N. With these measurements the validity of our model is confirmed and we determine for the first time, in a friction force experiment, the load dependence of E_0 and the hopping attempt frequency.

Our experiment was performed on a freshly cleaved and atomically smooth muscovite mica surface with a relative humidity of 30%. The friction forces and the surface topography of the film were investigated at room temperature by means of an AFM AutoProbe™ M5. We used V-shaped silicon cantilevers, and silicon conical tips with a nominal radius of curvature of 10 nm [20]. We define $F_N = 0$ nN at the point where the cantilever is not bent. Force calibration is achieved by the standard procedure described in [21]. The normal and torsional stiffnesses obtained in this way are $k_{\text{lever},n} = 0.35$ N/m and $k_{\text{lever},t} = 75$ N/m. The velocity dependence of friction was investigated by varying the scan frequency at fixed scan size (300 nm).

Our experimental results are presented in Fig. 1 showing F_L vs $\ln v$ for different normal loads F_N. Two regimes can be discussed, a roughly logarithmic increase of F_L with v up to a critical velocity $v_c \gtrsim v_0$, and a plateau of F_L for $v > v_c$ [22]. These two limiting cases are indeed predicted by Eq. (3). The prediction and the experimental confirmation of the plateau for $v > v_c$ is an important finding. It eliminates the unphysical meaning of v_0 as an upper velocity limit, which is implicit in the model in Ref. [11], and, since at the plateau the friction force takes on the value F^*, it enables direct experimental access to this quantity. We have fitted our experimental data with Eqs. (3) and (4) using as free parameters f_0, F^*, and β. The fits perfectly reproduce the data with the parameters reported in Table I. It is seen that F^* varies roughly linearly with F_N. Furthermore, in the approximately linear part of the F_L ($\ln v$) curves we observe an increase of the slope (i.e., an increase of β) with increasing F_N. From these observations we can estimate E_0 and f_0 as a function of F_N. These quantities are crucial to the understanding of the nanometer-scale processes underlying sliding friction.

Assuming that the tip-surface potential has a sinusoidal shape, its corrugation E_0 can be obtained from Eq. (7). In Fig. 2 the load dependence of E_0 is shown, assuming a

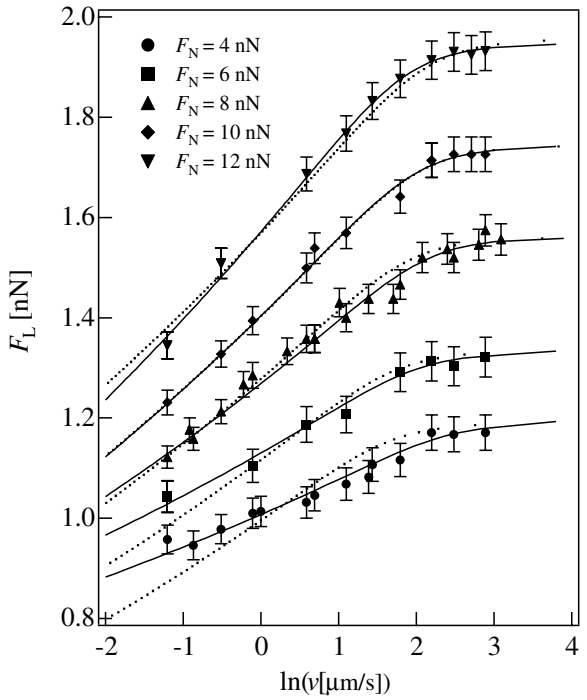

FIG. 1. Experimental friction force as a function of ln$v$ on mica for loads between 4 and 12 nN. The curves obtained from fitting the data with Eqs. (3) and (4) and f_0, β, and F^* as free parameters are shown as solid lines, while for the dotted lines we fixed f_0 to the value 19.5 kHz found in Fig. 3.

lattice constant of $a = 0.52$ nm [23]. Molecular dynamics simulations of AFM tips sliding on atomically flat surfaces showed that in the range of forces applied, few interacting atoms are expected [9]. The number of these atoms and F_L increase linearly with the applied load. The velocity range considered by molecular dynamics is above the velocities accessible by AFM experiments, therefore we can directly identify our measured F^* with the simulated F_L. The roughly linear increase of the energy corrugation E_0 reported in Fig. 2 is consistent with this result, considering the proportionality between F^* and E_0. The corrugation per atom of 0.1 eV is of the order of magnitude of barriers for surface diffusion [4,5].

The corrugation of $V(x, t)$ determines the behavior of β, i.e., the slope of the approximately linear part of the $F_L(\ln v)$ curves. When the interaction potential is more corrugated, for a fixed v, ΔE takes more time to decrease to zero and, as a consequence, thermal activation can have a stronger influence in the hopping process leading to an increased slope of the $F_L(\ln v)$ curves [see also Eq. (2)]. Since we found that the corrugation increases with the load we expect that also β increases with increasing loads. This is indeed found as reported in Table I. We can gain insight into the shape of the interaction potential through a comparison of the measured values of β with calculated values β assuming a certain profile of the interaction potential and using F^* as derived from the plateau. In Table I we show $\beta_{\sin}$ derived from Eq. (9) for the case of a sinusoidal potential using the experimental values of F^*. $\beta_{\sin}$ increases with F_N as β does, but it is smaller and it increases less rapidly with increasing F_N. This disagreement clearly shows that the effective potential has not a perfect sinusoidal shape. In addition, the shape of the effective potential may well vary as a function of normal load. For instance, it is feasible that upon increasing the load more details of the complicated unit cell of mica become apparent.

The order of magnitude of f_0 as determined from the fit (Table I) suggests that this prefactor in the Boltzmann term describing the intrinsic hopping rate of the nanocontact is related to mechanical vibrations and not to phonons. The elasticity of a V-shaped cantilever in contact with a surface was studied by Drobek *et al.* [24,25]. They found that the normal resonance frequency of the cantilever, $f_{\text{lever},n}$, increases by a factor of 4.5 once in contact with the surface, whereas the torsional frequency, $f_{\text{lever},t}$, increases only slightly, namely, by a factor of 1.3. For our cantilever, the free normal and torsional frequencies are $f_{\text{lever},n} = 40$ kHz and $f_{\text{lever},t} = 250$ kHz, respectively; in contact we thus expect about 180 and 325 kHz, which are both 1 order of magnitude higher than the values of f_0 reported in Table I. Eigenfrequencies comparable to f_0 are found when thinking that the cantilever forms a mechanical ensemble with the contact, i.e., a system of two springs in series. Considering the elasticity of the contact, the lateral stiffness changes from $k_{\text{lever},t} = 75$ N/m for the free cantilever to $k_{\text{series},t} = 1.2$ N/m, as reported above. The torsional frequency of the system scales with the lateral stiffness as $f_t \sim \sqrt{k_t/m^*}$, where m^* is the effective mass which is associated with the lateral motion of the ensemble. Assuming that m^* does not change significantly when the tip jumps into contact, the torsional frequency is thus reduced of a factor

TABLE I. Results from fitting the experiment with Eqs. (3) and (4) and f_0, β, and F^* as free parameters.

Load [nN]	ln(v_0[μm/s])	F^*[nN]	f_0[kHz]	β ($\times 10^6$)[N$^{3/2}$/J]	$\beta_{\sin}$ ($\times 10^6$)[N$^{3/2}$/J]
4	0.54 ± 0.12	1.19	53 ± 10	0.42 ± 0.01	0.22
6	0.22 ± 0.15	1.33	28 ± 6	0.6 ± 0.2	0.23
8	0.42 ± 0.09	1.56	23 ± 4	1.0 ± 0.2	0.25
10	0.34 ± 0.13	1.74	16 ± 4	1.4 ± 0.2	0.27
12	0.26 ± 0.07	1.94	13 ± 2	1.64 ± 0.01	0.29

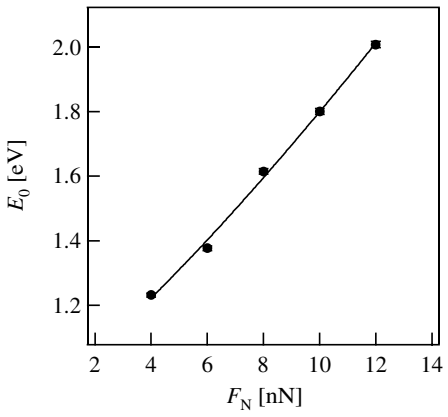

FIG. 2. Corrugation amplitude of the potential as a function of the normal load. A linear fit is shown as solid line.

$\sqrt{k_{\text{series},t}/k_{\text{lever},t}} \simeq 8$ with respect to the free cantilever, and thus it falls in the range of values reported in Table I.

The consistency of our results has been checked by independent measurements, which exploit the shear modulation technique introduced by Ge *et al.* [26]. Similarly to the thermal activation, we externally activate the jumps by applying lateral oscillations to the cantilever holder while sliding on mica. The frequency of the oscillations has been swept between 15 and 100 kHz. The amplitude of the oscillations was of the order of 1 nm, as confirmed by topography scans acquired at different frequencies across a nanosized impurity on mica. Below the critical value of the sliding velocity, v_c, the friction force appears dramatically reduced around the frequency $f = 19.5$ kHz (Fig. 3), independent of the applied load. This value is of the same order of magnitude as the frequencies reported in Table I. This shows the role of the resonance frequency in activating the tip jumps. We emphasize that the decrease of friction induced by external modulation is absent for $v > v_c$ which is exactly what is expected since there the mechanism of activated hops is no more relevant. For comparing the value of the attempt frequency directly measured in the experiment shown in Fig. 3 with the values of f_0 found indirectly by fitting the data in Fig. 1, we repeated the fit procedure with f_0 kept fixed at 19.5 kHz at all loads (see dotted lines in Fig. 1). The values of F^*, and hence E_0, are the same for the two fitting procedures for all loads. For the three largest loads the data are very well fitted also with f_0 fixed at 19.5 kHz, while the fits are not as good at 4 and 6 nN, however, only in the regime of small velocities. The essential result is that the value of f_0 has been measured with two independent experiments giving consistent results.

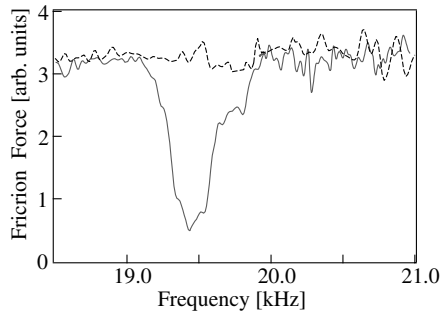

FIG. 3. Friction force vs frequency of the external oscillations at $v = 8$ μm/s (continuous line) and $v = 150$ μm/s (dashed line). The applied load is $F_N = 15$ nN in both cases.

In conclusion, a link between friction and thermally activated hopping of a silicon tip on a mica surface has been established. The height of the interaction potential increases proportionally to the external load. The attempt frequency is identified as a lateral resonance frequency of the probing tip in contact with the surface.

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