Non monotonic velocity dependence of atomic friction

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We study the velocity dependence of the frictional force of the tip of an atomic force microscope as it is dragged across a surface, taking into account memory effects and thermal fluctuations. Memory effects are described by a coupling of the tip to low frequency excitation modes of the surface in addition to the coupling to the periodic corrugation potential. We find that when the excitation mode frequency is comparable to the characteristic frequency corresponding to the motion of the tip across the surface, the velocity dependence of the frictional force is non monotonic, displaying a velocity range where the frictional force can decrease with increasing velocity. These results provide theoretical support for the interpretation of recent experiments which find a frictional force that decreases with velocity on surfaces covered with a monolayer.

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I. INTRODUCTION

In an atomic force microscope, the motion of the tip as it is dragged across a substrate provides an efficient way to probe atomic friction of surfaces. In fact, the moving tip can be regarded as a singleasperity which determines the frictional force between macroscopic surfaces. Under a constant load, the low-velocity motion of the tip on a surface exhibits stick-slip behavior as the moving tip hops over the corrugation potential defined by the substrate. For a quantitative description of friction at the microscopic level, theoretical understanding of the behavior of the tip on the substrate under different conditions is required. Recent studies have argued that due to thermal fluctuations, the lateral frictional force increases logarithmically with increasing sliding velocity. However, it is also found experimentally that the frictional force can have an opposite behavior, where it decreases with the sliding velocity depending on the ambient conditions and the nature of the substrate. The origin of this decreasing velocity dependence is not fully understood and it is possible that distinct effects need to be taken into account to explain different experimental conditions. Current explanations of this behavior for point contact friction are based on extensions of the simplest effective model, the generalized Tomlinson model, taking into account additional effects such as dissipation due to deformation of the AFM tip or the inclusion of additional time scales for reorganization of the surface during sliding. In particular, the interpretation of recent experiments on surfaces covered with a monolayer in terms of an additional time scale due to surface restructuring still lacks detailed theoretical support.

In this work, we study the velocity dependence of the frictional force within a simple theoretical model taking into account the coupling of the AFM tip to excitation modes of the surface in addition to the coupling to the periodic corrugation potential. We model the generic excitation modes by damped harmonic oscillators analogous to the model of an adsorbate coupled to phonon modes of the substrate. We find that when the excitation mode frequency is comparable to the characteristic frequency of the particle moving across the surface potential, the velocity dependence of the frictional force is non monotonic displaying a velocity range where the frictional force can decrease with increasing velocity. These results provide theoretical support within a simpler model for the interpretation of recent experiments which find a frictional force that decreases with velocity on surfaces covered with a monolayer.

II. MODEL

The lateral motion of the tip can be described by a model of a single particle in an external one-dimensional potential representing the substrate and coupled elastically to the moving support. The equation of motion for the particle is given by

\[ m\ddot{x} = -\frac{dV(R, x)}{dx} - m\gamma\dot{x} + f(t) \quad (1) \]

where the noise variables \( f(t) \) satisfy

\[ < f(t)f(t') > = 2m\gamma k_BT\delta(t - t') \quad (2) \]

and \( V(R, x) = V_p(x) + V_s(x, R) \) is the total potential including the interaction of the tip to the substrate with periodic potential

\[ V_p(x) = V_o[1 - \cos(2\pi x/a)] \quad (3) \]

and the elastic interaction between the tip and the moving support

\[ V_s(x, R) = \frac{1}{2}k(x - R(t))^2 \quad (4) \]
where $R(t)$ is the position of the support.

The friction damping parameter $\gamma$ in Eq. (1) results from the coupling of the tip to the surface excitations with a much shorter time scale than the motion of the tip (e.g., electronic excitations) which results in a $\delta$-function correlated random force $f(t)$ with instantaneous Markovian damping without memory as described by Eq. (2).

The microscope support is moving at constant velocity, $R(t) = vt$, where $v$ is the support velocity. The average force on the support due to the tip motion is then given by

$$ F = k < R(t) - x > $$

(5)

This is regarded as the frictional force with the substrate since without damping we should have $F = 0$ when averaging out the negative and positive force region of the periodic potential. For sufficiently large frictional damping, stick and slip motion is expected. As shown in Ref. 3, using this model the frictional force $F$ increases with increasing velocity $v$. At small $v$, it increases logarithmically but ultimately one would expect $F$ to be just $\gamma v$, for sufficiently large $v$.

We extend the model described by Eq. (1) by allowing the tip to couple to other excitations in the substrate which have a finite time scale. These other excitations are modeled by damped simple harmonic oscillators as done in Ref. 11. These excitations can be labeled by the mode index $\lambda = (i, l)$ where $i = 1, 2$ labels the symmetry group and $l$ runs from 1 to $N/2$ where $N$ is the total number of modes. Each mode is characterized by a displacement variable $u_{\lambda}$, which couples to the tip motion. The total Hamiltonian can be written as

$$ H = \frac{p^2}{2m} + V(x, R) - \sum_{\lambda} \frac{M \omega_{\lambda}^2}{2} W_{\lambda}^2(x) $$

$$ + \sum_{\lambda} \left[ \frac{p_{\lambda}^2}{2M} + \frac{M \omega_{\lambda}^2}{2} (u_{\lambda} + W_{\lambda}(x))^2 \right] $$

(6)

The third term in the above Hamiltonian represents a counterbalance term. This is added so that when the tip moves very slowly relative to all the time scales given by $2\pi/\omega_{\lambda}$, then at any instantaneous position of $x$, $u_{\lambda} = -W_{\lambda}$ and the actue effective potential felt by the tip is $V_p(x) - \sum \frac{M \omega_{\lambda}^2}{2} W_{\lambda}^2$ which is the adiabatic potential. However, when the tip is moving very fast relative to such time scales, then the substrate has no time to respond, and one recovers the rigid substrate potential $V_p(x)$. The explicit form of $W_{\lambda}(x)$ is chosen as

$$ W_{1,1} = \frac{2\pi \alpha V_o}{a \sqrt{\frac{N}{2} M \omega_{\lambda}^2}} \sin(2\pi x/a) $$

$$ W_{2,1} = \frac{2\pi \alpha V_o}{a \sqrt{\frac{N}{2} M \omega_{\lambda}^2}} \cos(2\pi x/a) $$

(7)

The coupling $\alpha$ in Eq. (7) depends on the frequency $\omega$ of the mode. This is chosen here to have the form $\alpha(\omega) \propto \omega$ so that the total effect of a finite number of damped oscillators corresponds to a continuum distribution of excitation modes with a density of states $\rho(\omega) \propto \omega^2$, analogous to that for 3-D phonons in the Debye model. The equations of motion for the tip and the mode displacement variables can be written in a dimensionless form as

$$ \ddot{x} = -2\pi \sin(2\pi x) + k(R(t) - x) - 2\pi \alpha_o \sum_{\lambda} \omega_{\lambda} f_{\lambda}(x) u_{\lambda} $$

$$ -\gamma \dot{x} + f(t) $$

$$ \ddot{u}_{\lambda} = \omega_{\lambda}^2 u_{\lambda} - \alpha_o \omega_{\lambda} g_{\lambda}(x) - \gamma_{\lambda} \ddot{u}_{\lambda} + \lambda_{\lambda}(t) $$

(8)

where the additional noise variables $\lambda_{\lambda}$ for the damped harmonic oscillator also satisfy a fluctuation-dissipation relation

$$ < \lambda_{\lambda}(t), \lambda_{\lambda}(t') > = 2\gamma_{\lambda} T \delta(t - t') \delta_{\lambda,\lambda}. $$

Without loss of generality, we can set $m = M$ for simplicity. In Eq. (8), $f_{1,1} = \cos(2\pi x)$, $g_{1,1} = \sin(2\pi x)$, $f_{2,1} = \sin(2\pi x)$, $g_{2,1} = \cos(2\pi x)$ and $\alpha_o = \pi k V_o / (a \sqrt{N/2})$. The lattice constant $a$ is taken as the unit of length, $V_o$ the unit of energy, and $\sqrt{ma^2/V_o}$ the unit of time.

### III. NUMERICAL RESULTS AND DISCUSSION

We have performed numerical simulations of the coupled dynamical equations (5) using Brownian molecular dynamics. The parameters for the spring and microscopic damping were fixed to $k = 3$ and $\gamma = 6$ and for damped harmonic oscillators, $\gamma_{\lambda} = 2\omega_{\lambda}$ and $\alpha_o = 2.5$. Time steps ranged from $dt = 0.001$ to 0.005. Numerical results for the velocity dependence of the friction force obtained from Eq. (5) assuming different angular frequencies $\omega$ for coupling to one odd or even mode are shown in Figs 1 and 2. They are qualitative similar and show that when the frequency of the excitation mode is sufficiently small the velocity dependence of the friction force is non monotonic. While at sufficiently small or large velocities it increases with velocity there is an intermediate range of velocities where the frictional force decreases as the velocity increases. The approximate linear decrease in the semilog plot of Figs 1 and 2, suggest that this decrease is logarithmic.

To understand this non monotonic behavior it should be noted that there are several important time scales in the problem. First, there is a velocity dependent time scale, $t_v = a/v$, which is the average time for the tip to traverse one lattice period of pinning potential. The pinning potential introduces a time scale, $t_0 = \sqrt{ma^2/V_o}$, the vibrational period of the tip in the well. In the stick and slip regime where the tip is stuck in the well and perform many vibrational oscillations before hopping to the next minima, we have $t_v \gg t_0$. The time for crossing the barrier is relatively fast, on the order of $t_v$. With the coupling to a new excitation mode of frequency $\omega$, another time scale $t_1 = 2\pi/\omega_1$ is introduced. We now consider what is the effect of varying $t_v = a/v$ on the
frictional force $F$. In the absence of the coupling to the excitation mode, the logarithmically increase of the friction force with velocity $v$ was obtained for velocities up to $t_v \approx t_0$. Now consider what happen if we choose an excitation mode such that $t_l$ is several times larger than $t_0$ ($\omega_l << \omega_0$) and we vary $t_v$. As far as the intrinsic frictional damping is concerned, when $t_v$ approaches $t_l$, the damping should increase and also becomes non-Markovian. Eventually, when $t_v$ becomes very large, the damping should saturate to a Markovian value. So based on this consideration, the effective $\gamma$ should increase and saturate as a function of decreasing $v$. The frictional force $F$ should exhibit similar behavior. In addition, the even mode can lead to a velocity dependent substrate relaxation that changes the effective potential as discussed previously. However, for the present choice of parameters, the velocity dependence of the effective non-adiabatic frictional force due to the coupling to the new excitation mode dominates as evidenced by the results in Fig. 1 and 2, showing similar results for coupling to an even or odd modes.

The effect of varying the temperature at fixed mode frequency $\omega$ is also of interest. As can be seen from Fig. 3, the qualitative non monotonic behavior remains but there is an increase in the magnitude of the negative slope of the velocity-force curve as the temperature decreases.

We have also performed additional calculations to check the effect of including more excitation modes to model a more realistic continuum model of substrate excitations. 6 independent damped harmonic oscillators with frequencies in a range $[\omega_{\text{min}}, \omega_{\text{max}}]$ with $\omega_{\text{min}} = \omega_{\text{max}}/6$ were included in these calculations. As can be seen from Fig. 4, the behavior for the velocity dependence for different maximum frequencies $\omega_{\text{max}}$ is qualitatively similar to the behavior in Fig. 1 at the same temperature. The main effect of the additional modes below $\omega_{\text{max}}$ is a tendency to saturation of the frictional force at lower frequencies.

IV. CONCLUSION

We study the velocity dependence of the frictional force of the tip of an atomic force microscope as it is dragged across a surface using a single particle model, taking into account memory effects and thermal fluctuations. In our model, there is an additional coupling of the particle to excitation modes of the surface modeled by damped har-
monic oscillators. We find that when the excitation mode frequency is comparable to the characteristic frequency of the motion of the tip across the surface potential, the velocity dependence of the frictional force is nonmonotonic displaying an intermediate velocity range where the frictional force can decrease with increasing velocity. Therefore, the sliding behavior on the surface depends on the nature of the surface through the characteristic frequency of such excitation modes. Recently, non-monotonic velocity dependence of friction was observed experimentally on surfaces covered with a monolayer. The experimental results were interpreted as resulting from the chemical nature of the surface, with friction increasing or decreasing with velocity depending on the presence of cross-linked H-bonds. It was argued that for higher sliding velocity there is not enough time for re-ordering to occur and the friction force should decrease logarithmically with velocity, while at lower velocities the breaking and reordering of the H-bonds contribute a new source of friction that increases with decreasing velocity. Our results provide theoretical support for this idea through an explicit calculation within a simple model. The breaking of glassy domains of H-bonds at a critical stress and reordering introduces a new time scale, which corresponds in our model to the inverse frequency of the additional excitation mode of the surface. The non-monotonic velocity dependence of the friction then follows naturally when the time scale of the motion of the tip across the surface becomes comparable to this new time scale for the excitation mode. However, since we find a non-monotonic behavior without invoking any glassy behavior, our results suggest that similar behavior should be found even on surfaces without disorder when additional excitation modes are present.

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