Velocity Dependence of Friction and Hydrogen Bonding Effects

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We show that the friction force varies with the sliding velocity in a manner that depends on the chemical nature of the interface. Surfaces terminated with the hydrogen acceptor and donor moieties capable of forming H-bond networks exhibit a friction that decreases with sliding velocity, a behavior that is opposite to that of surfaces where no such networks can form. We explain the results with a model where the domains of glassy H-bond networks are disrupted at a critical applied stress leading to slippage.

The classic laws stating that friction is proportional to the applied load, independent of the apparent contact area and sliding velocity [1], have been questioned in systems with dimensions approaching the nanometer. New tools such as the atomic force microscope (AFM) and the surface forces apparatus have made it possible to reexamine these laws in detail. One of the first successful contributions was the confirmation of the proportionality between friction and contact area down to the nanometer level. This area changes with load following the laws of classical elasticity, extended by the introduction of adhesive energies [2–4].

The question of the velocity dependence of friction has been scrutinized also, giving rise to a number of diverging findings. A velocity independent friction has been reported for silicon tips sliding over carbon surfaces [5], while a logarithmic increase with velocity has been observed on mica [6], NaCl [7], and self-assembled films [8–11]. The increase was explained as a consequence of the thermal agitation of the atoms in the contact. At low velocity the atoms at the interface remain for a long time in the minima of their interaction potential and thus have a higher probability of being thermally activated to jump over neighboring sites. External forces, normal and shear, distort the shape of the potential so that the barrier is lowered more in the forward direction, thus biasing the direction of the jumps [6–8,12–14]. Molecular dynamics simulation on a layer of absorbed molecules between two crystalline surfaces also predicts an increase of friction with velocity and load [15–18].

While this model explains the logarithmic increase of friction with velocity when the formation and rupture of the contact is fast enough for the interface structure to reach equilibrium between stick and slip events, the same argument can explain the reverse effect of a decrease of friction with velocity. This could occur when thermal activation favors interface restructuring to more stable configurations. For example, molecules at the interface might form organized structures such as ordered self-assemblies, networks of intermolecular bonds, etc., that

minimize energy for a given contact geometry. Such structures might be disrupted by high applied stress (load or shear) leading to a slip event. As the stress is released in the slip event, the interface will reorganize by nucleation and propagation at a characteristic speed. If the sliding velocity is too high the reorganization might not reach completion, leading to a less stable interface structure and a smaller friction force.

In this Letter, we report AFM observations of velocity dependent friction in systems that exhibit increases and/or decreases as a function of sliding speed. The main finding is that friction decreases with velocity in systems with the potential of forming cross-linked structures at the interface with linkage energies that are easy to overcome at the applied loads. They include surfaces terminated with groups such as -OH, -COOH, and $-NH_2$ that are capable of forming networks of H-bonds. In systems where the surface is terminated with chemically saturated species, like -O- (mica, dry SiO_2), and $-CH_3$, that cannot form such a network, or that are too strongly bound to be disrupted by moderate applied loads (-O- in oxides), the friction is found to increase with sliding velocity.

The experiments were performed at ambient conditions with a homemade AFM with an RHK-tech controller. Si_3N_4 cantilevers (NanoProbe^{TM}) with spring constant of 0.34 N/m and tip radius of roughly 500 nm (determined from profiles of sharp features) were used. The AFM head was housed inside a chamber for humidity control. A few experiments were also carried out in an RHK-tech ultra-high vacuum instrument to eliminate the possibility of water adsorption. All the experiments were performed at loads sufficiently low that no wear occurred, as checked by inspection of AFM images. Samples were prepared as follows. A CH_3 terminated film on mica was produced by dip coating in a chloroform solution of hexadecylamine [19]. A SiO_2 layer (>400 nm thick) on a Si wafer was cleaned in an ozone plasma for 5 min and rinsed in chloroform, hexane, acetone, and propanol solvents to produce a surface with no or very few, silanol groups [20]. A highly hydroxylated silica (on a Si wafer) was prepared by dip-

ping in a piranha solution [a 3:7 (v/v) mixture of 30% H_2O_2 and H_2SO_4] [21], followed by ultrasonication and rinsing with Milli-Q water [22]. Secondary ion mass spectroscopy measurements have shown that treating silica with hydrochloric acid generates silanols with a density of 4.1 nm^{-2} [23]. An amino-propyl-silane (APS) monolayer exposing -NH_2 groups [24] was prepared by dipping mica in a 1 g/l APS aqueous solution for 2 h, rinsing with Milli-Q water and drying with nitrogen. Polyethylenimine (PEI) (MW 2000, 50% water solution, Sigma) is a branched polyelectrolyte with numerous -NH groups. A flat (<0.3 nm rms roughness) monolayer was obtained by immersing mica in a 2 g/l aqueous solution of PEI for 12 h, water rinsing and nitrogen drying [25,26]. Finally a -COOH terminated monolayer was prepared by the Langmuir-Blogett technique from a chloroform solution of stearic acid (0.3% w/w) on a water subphase [27].

Two types of friction-velocity (F-V) relationships were observed. When sliding over surfaces such as bare mica, SiO_2 and films with methyl termination, friction increased with velocity as shown in Fig. 1. An approximately logarithmic increase was measured in the velocity range from 0.018 μm/s to 55 μm/s, beyond which it tended to level off. The same dependence (albeit enhanced) was observed at increasing loads. The experiments on SiO_2 were performed in ultrahigh vacuum. On surfaces coated with APS [Fig. 2(a)], PEI [Fig. 2(b)], and on acid-treated SiO_2 [Fig. 2(c)] friction was found to behave in the opposite way, i.e., to decrease with sliding velocity. The decrease is approximately logarithmic. While the behavior was similar at all loads investigated, the slope of the F-$logV$ curves was higher for the higher loads. Experiments on surfaces covered with stearic acid monolayers (COOH surface termination, not shown here), indicated a similar decrease of friction with velocity. We did not observe clear stick-slip features in the friction curves, except for noise peaks.

The -NH_2, -NH-, -OH, and -COOH functionalities are active species that can form networks of H-bonds. No such organized structures can form on -CH_3 terminated films, bare mica or bare SiO_2. We thus propose that the observed decrease of friction vs velocity is the result of the rupture and reformation of domains of H-bonded moieties. The model is similar to that of solidlike to liquidlike phase transitions in thin liquid films [28] and to the more general pinned domain model that has been proposed to explain stick-slip friction [29]. In the model the cross-linked network is the minimum energy configuration where the surfaces stick together. Indeed, molecular dynamics calculations of alkylthiol monolayers on gold show that the -OH terminated surfaces form a hydrogen bonded network with glassy character [30]. At a certain critical value of the applied stress however, the H-bonds break causing a local "melting" of the network and slippage of the interface. At low velocity, after stress release by the slip event, domains of H-networks can reform by nucleation and growth until
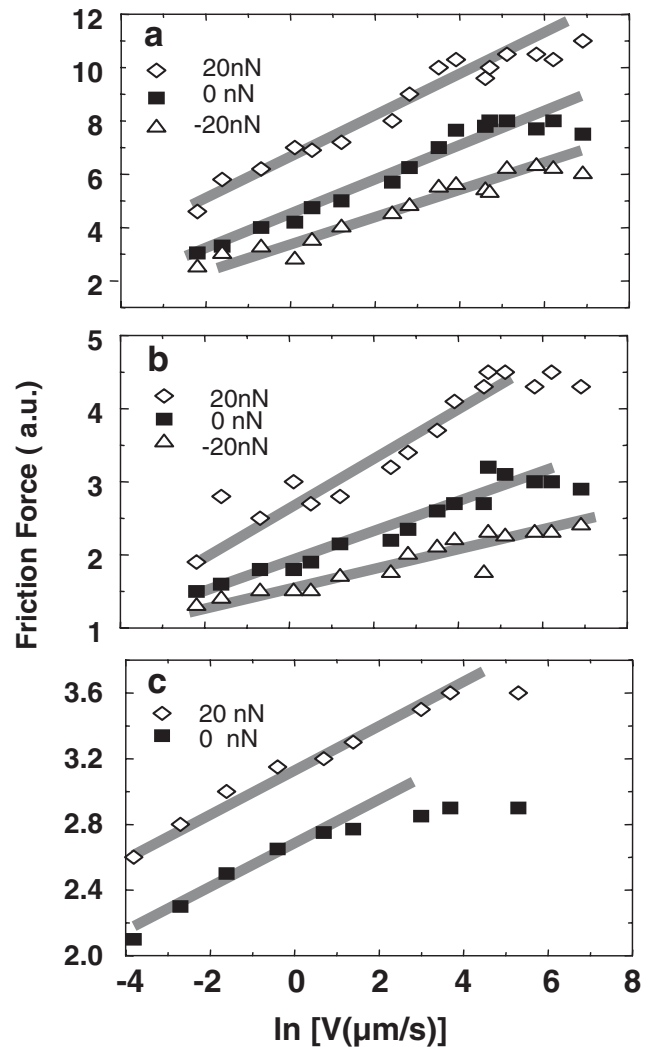

FIG. 1. Semilog plot of the friction force vs sliding velocity for various applied loads between a Si_3N_4 tip and samples of: (a) bare mica surface; (b) monolayer of hexadecylamine with methyl group termination; (c) bare SiO_2 surface. For samples A and B the experiments were performed in ambient conditions (Relative humidity: 35%, temperature 22°). For sample (c) the experiment was performed in vacuum (10^{-10} torr). Negative loads are used to counteract adhesion requiring pull-off forces of −45 to −50 nN. The plots have all the same arbitrary friction force scale.

they become large enough to arrest the motion. If the sliding velocity is too high reorganization will not be complete, leading to a less stable interface structure and a smaller friction force. Rottler *et al.* have simulated the glassy systems and found that the yield strength of the glassy layer increases logarithmically with aging time [31], thus the yield stress will drop logarithmically with velocity.

To test our assumption we deliberately disrupted the H-network by placing a drop of hydrochloric acid (1 M) on the -NH_2 terminated APS surface for 2 h. Formation of $NH_3^+Cl^-$ is a well know reaction that suppresses intermo-
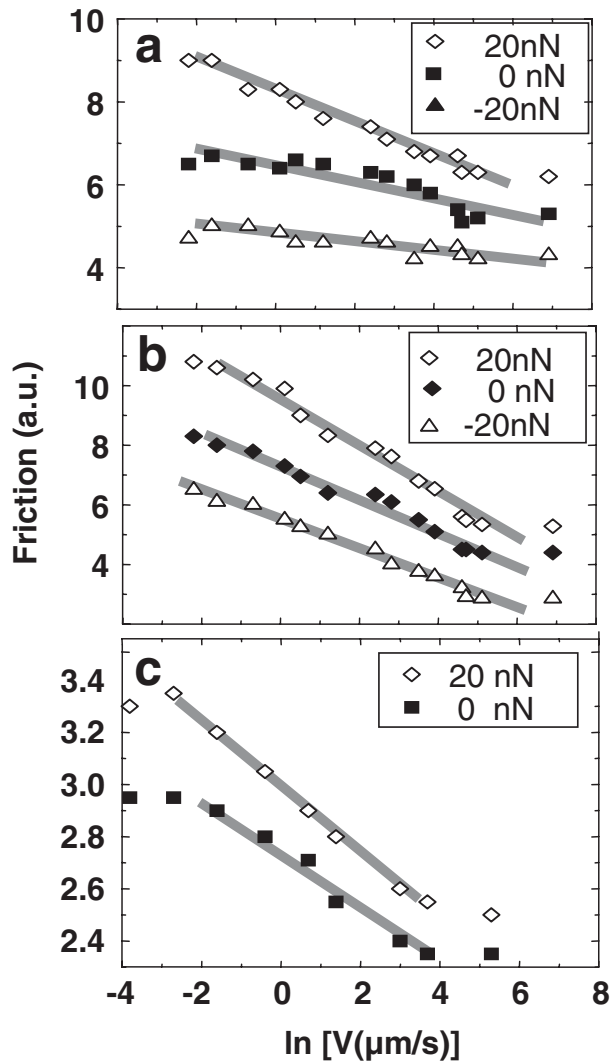
FIG. 2.   Semilog plot of the friction force vs sliding velocity between a Si_3N_4 tip and samples of: (a) APS monolayer on mica; (b) polyethylenimine monolayer on mica; and (c) acid-treated SiO_2 to produce a saturated layer of hydroxyl groups. For (a) and (b), the experiments were performed in ambient conditions (Relative humidity: 35%, temperature 22°). (c) was performed in vacuum (10^{-10} torr). The plots have the same arbitrary friction force scale.

lecular hydrogen bonding. After this treatment an increased friction vs velocity behavior (Fig. 3) is observed, opposite to that of the original APS surface [Fig. 2(a)].

We also employed cantilevers that were modified by alkylsilane (C_{12}-CH_3) or APS (-NH_2) to determine if the effect was dependent on the particular chemistry of the tip. The results showed that in every case the trends in the F-V relationship remain the same as with the unmodified cantilevers, although the absolute friction values differed, being higher for -NH_2 and lower for -CH_3 terminated tips.

Riedo *et al.* observed a logarithmic decrease of friction on glass sheets and attributed it to the formation of water bridges between the rough and hydrophilic surface and the
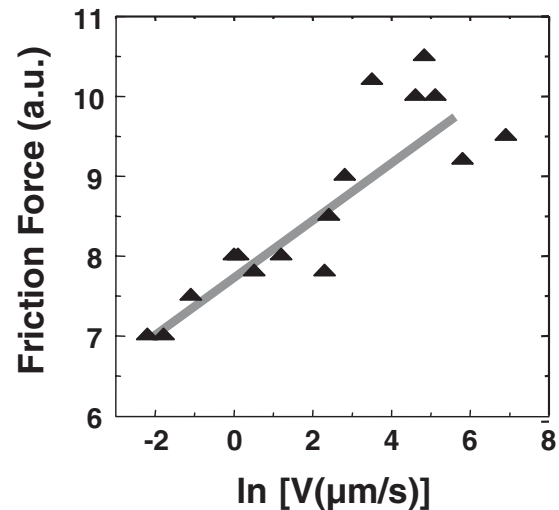

FIG. 3.   Semilog plot of the friction force vs sliding velocity between a Si_3N_4 tip and the APS coated mica sample after treatment with hydrochloric acid at 0 nN normal force (pull-off force approx. -50 nN). The friction-velocity behavior is reversed relative to that of the untreated APS film shown in Fig. 2. Experiment performed in ambient conditions.

AFM tip [32,33]. This explanation however does not apply in our case since our surfaces were very flat (root mean square roughness <0.3 nm), which does not lead to multiple asperity contact. To further ascertain that capillarity did not play a role in our case, friction experiments on SiO_2 were performed in ultrahigh vacuum. The results show unambiguously that a decrease in the friction vs velocity still occurs [Fig. 2(c)]. In experiments performed in air, humidity does affect the slope of the friction-velocity curve, as shown in Fig. 4 for the acid-treated SiO_2. Although the increased normal force exerted due to capillary condensation effects can explain the observed increase
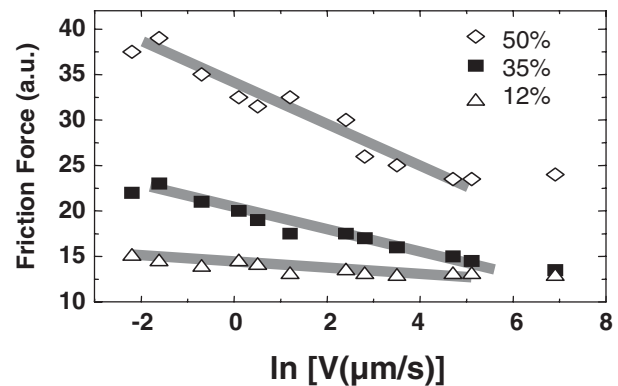

FIG. 4.   Semilog plot of friction force vs sliding velocity between a Si_3N_4 tip and an acid-treated SiO_2 surface (OH-saturated) at different relative humidity: 50%, 35%, and 12%. The normal force exerted on the cantilever is 40 nN.

in friction with humidity, the trend of decreasing friction with velocity persists.

The absence of stick slip in our friction traces points to the presence of several small domains in the contact that are formed and disrupted at different times [29]. For the tip radii and loads used in this study a contact diameter of roughly 25 nm can be estimated from hertz contact mechanics, which can accommodate several domains of nanometer size.

In conclusion, we have shown that the sliding properties of interfaces depend on their chemical nature, with friction increasing or decreasing with velocity depending on the ability of surface groups to form domains of cross-linked H-bonds that can be disrupted at a critical stress. The network is reconstituted after release of the stress and grows until sufficiently large domains are formed to arrest motion of the surfaces. Out findings indicate that the propagation velocity of the reaction boundary at room temperature should be of the same order as the scanning velocity of the tip ($\sim 10^{-6}$ m/s).

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