

Sliding Velocity Dependence of Adhesion in a Nanometer-Sized Contact

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The influence of sliding velocity on the adhesion force in a nanometer-sized contact was investigated with a novel atomic force microscope experimental setup that allows measuring adhesion forces while the probe is sliding at continuous and constant velocities. For hydrophobic surfaces, the adhesion forces (mainly van der Waals forces) remain constant, whereas for hydrophilic surfaces, adhesion forces (mainly capillary forces) decrease linearly with a logarithmic increase of the sliding velocity. The experimental data are well explained by a model based on a thermally activated growth process of a capillary meniscus.

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The apprehension of friction mechanisms at the nanometer scale is of considerable interest for both scientific and technologic research fields. On the fundamental side, friction is a universal phenomenon that is manifested in many natural behaviors such as earthquake dynamics or physics of granular media [1–3]. On the technological side, the emergence of miniaturized mechanical systems and nanotechnologies [4] requires reducing energy dissipation due to friction to improve the system autonomy, durability, and to minimize their economical and environmental costs. However, phenomena involved in friction mechanisms are far from being well understood [5,6]. The development of techniques such as surface force apparatus (SFA) or atomic force microscopy (AFM) offers new opportunities to better comprehend the elementary mechanisms of friction at the nanometer scale. In particular, SFA experiments conducted on organic monolayers show that adhesion is velocity dependent [7,8]. In addition, AFM experiments conducted on various surfaces show that friction is strongly dependent on the sliding velocity [9–11]. Typically, for hydrophobic surfaces, the friction force increases linearly with a logarithmic increase of the sliding velocity, whereas for hydrophilic surfaces, it decreases linearly with the logarithmic increase of the sliding velocity [9,11,12]. These behaviors are explained by models that consider phenomena which are likely to occur at the nanometer scale, such as stick-slip motion and capillary nucleation [11]. Precisely, the nucleation of water bridges between surfaces close to each other and the growth of the capillary meniscus are both thermally activated processes in which the water vapor molecules have to overcome energy barriers (i) to initiate the formation of the capillary bridges or meniscus and (ii) to pass over surface defects constraining the meniscus growth [13]. For an AFM probe and a hydrophilic surface sliding contact, a capillary meniscus nucleates and grows at the vicinity of the contact area. The depression in the meniscus generates an adhesive force proportional to the contact wet area. This adhesive force acts as an additional normal load and is of the same order of magnitude as the external

applied load [14]. It plays, at least, an indirect role in the friction mechanisms. However, time is needed for the capillary meniscus to reach its equilibrium state. In particular, it was reported that the capillary forces depend on the contact time [15] and the nucleation time of a capillary bridge in a 1 nm gap formed between asperities in the case of a silicon AFM probe and a soda lime glass has been experimentally estimated to be in the ms time scale, for temperatures ranging from 299 to 332 K at a relative humidity of 40% [16]. Therefore, even if there is no direct experimental evidence that the capillary forces are sliding velocity dependent, it is now accepted that when the contact is submitted to high sliding velocities the relative displacement of surfaces disturbs the nucleation and growth of the capillary meniscus. As a result, for hydrophilic surfaces, an increase of the sliding velocity causes a decrease of the capillary force that leads to a decrease of the friction force. In this Letter, we present a direct nanoscale experimental investigation of the influence of sliding velocity on the adhesion force on both hydrophilic and hydrophobic surfaces, using an innovative custom AFM circular mode [17]. In particular, we report experimental evidence of the decrease of the capillary force on hydrophilic surfaces at high sliding velocities, and finally we show that the behavior observed for the adhesion force versus the sliding velocity is clearly explained by a model based on a thermally activated growth process of a capillary meniscus.

AFM allows measuring adhesion forces using the so-called force spectrum mode while the tip is not scanning the sample [18]. In the following experiments, force spectra are acquired while imposing a sliding motion of the probe-sample contact. Limitations encountered with the conventional back and forth scan mode are detrimental for our experiments, as capillary forces are supposed to be velocity dependent due to kinetics of capillary condensation. The alternations of the sliding and the rest periods resulting from conventional back and forth scan lead to a nonconstant capillary force due to the growth and

vanishing of the capillary meniscus during rest and sliding periods, respectively. Consequently, we have developed the AFM circular mode [17], that generates a circular horizontal displacement of the probe. Disregarding stick-slip events, this mode leads to a relative motion of the contact, without acceleration, deceleration, and any rest periods during sliding which necessarily occur with the conventional back and forth scanning mode. All the experimental results reported here are obtained combining the conventional force spectrum at low constant driving velocity of $0.1 \mu\text{m} \cdot \text{s}^{-1}$ with the circular mode that is set to a constant circular motion frequency of 100 Hz and with diameters varying in the range of 18 nm to $1.8 \mu\text{m}$, thus allowing the measurement of adhesion forces while the contact is sliding at a constant and continuous sliding velocity. Dependence of the adhesion force on the sliding velocity was investigated at room temperature and at constant relative humidity of 40%–50% with a homemade modified commercial AFM (Dimension 3100, Nanoscope V from Veeco) to generate the circular mode. The probe used was an AFM silicon nitride tip (DNP cantilevers from Veeco) whose radius R is 30–40 nm and the normal spring constant determined by the thermal noise method [19] is $0.3 \text{ N} \cdot \text{m}^{-1}$. We checked that no contamination or wear of the probe occurred after each experiment. Figure 1 reports typical force spectra obtained on a hydrophilic substrate [a chemically vapor deposited (CVD) gold layer on glass] and measured with the same probe, at low and high sliding velocities. The comparison of the two spectra clearly shows a significant decrease of the adhesion force as the sliding velocity V increases that is comparable to the

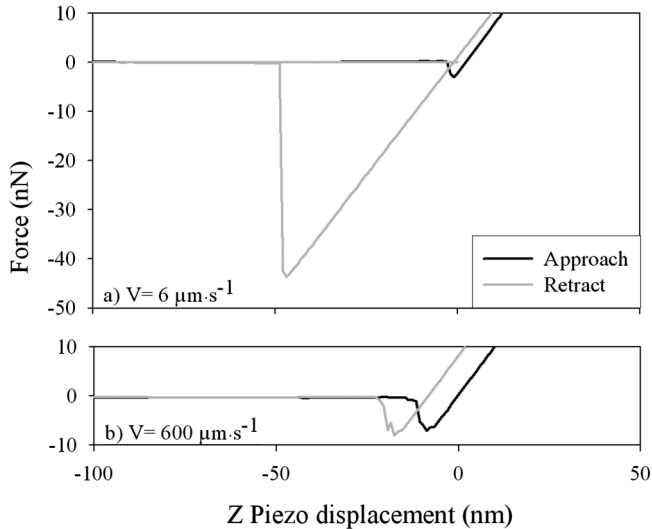


FIG. 1. Force spectra (on a CVD gold surface) at low (a) and high (b) sliding velocities (30% of relative humidity) obtained by combining AFM force mode to the circular mode in the experimental setup. For hydrophilic surfaces, the adhesion force (or snap off) decreases with an increase of the sliding velocity due to vanishing of capillary forces.

attractive forces (snap on) when the sliding velocity is high. This is evidence that the capillary forces are vanishing as the sliding velocity increases. Experiments performed on different hydrophobic surfaces [HOPG, methyl grafted silicon wafer (Si_{CH_3})] show that the adhesion force is constant whatever the sliding velocity (Fig. 2). This behavior is consistent with the adhesion force contributions for hydrophobic surfaces that are mainly due to van der Waals forces, which are velocity independent. On the contrary, for hydrophilic surfaces [CVD gold, mica, silicon wafer (Si), silicon nitride (Si_3N_4)], the adhesion force is velocity dependent due to capillary forces and follows three different regimes (Fig. 2). For low sliding velocities (regime I), the adhesion force remains constant and is equal to the adhesion force measured with no sliding. In this regime, we can assume that the capillary meniscus has enough time to form and to reach its equilibrium state. For high sliding velocities (regime III), the adhesion force is constant and equal to van der Waals forces. The capillary forces have completely vanished (Fig. 1). Finally, for intermediate velocities (regime II), we observe a linear decrease of the adhesion force with a logarithmic increase of the sliding velocity. We can define a threshold value for the sliding velocity, V_{start} . For sliding velocities $V > V_{\text{start}}$, the capillary meniscus can no longer reach its equilibrium state. To our knowledge, this trend has never been experimentally observed directly but it is predicted by the model proposed by Riedo *et al.* [11] to explain the logarithmic sliding velocity dependence of friction forces. Their model is based on the nucleation of capillary bridges that can form in the gap between distant asperities if the time of contact is sufficiently long. The

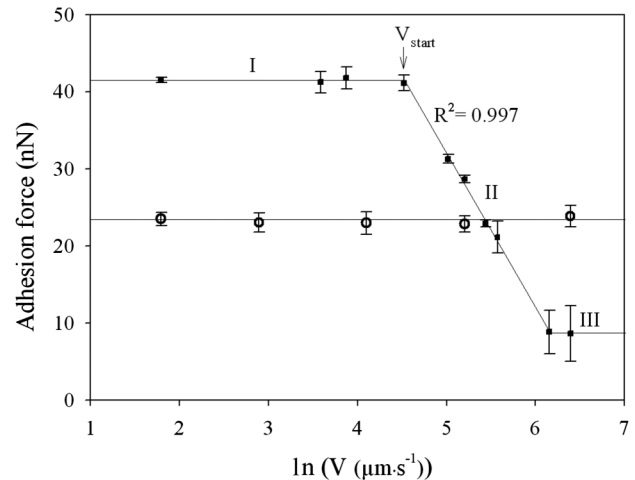


FIG. 2. Average adhesion force (computed from 10 spectra, error bars represent the standard deviation) as a function of the logarithm of the sliding velocity for a hydrophilic CVD gold surface (squares) and a hydrophobic HOPG sample (circles) (48% of relative humidity, tip radius is 30 nm). For hydrophilic surfaces, the adhesion force follows three regimes labeled I, II, and III.

nucleation of a liquid bridge of volume Ω between two asperities, at a temperature T and at a relative humidity R_H , costs a threshold free energy ΔE [20],

$$\Delta E = k_B T \ln \left[\frac{1}{R_H} \right] \rho \Omega, \quad (1)$$

where ρ is the molecular density of the liquid in units molecules/m³. Commensurate with this thermally activated process, Szoszkiewicz and Riedo [16] and Greiner *et al.* [9] have experimentally estimated the nucleation energy barrier of a capillary bridge in a gap of 1 nm height to be about 1 eV. If we consider a nucleation process, we can estimate, from the experimental value of ΔE reported in Ref. [16] and Eq. (1), the volume of water Ω of the capillary bridge to be 0.4 nm³. This volume corresponds approximately to a dozen water molecules, which is about 500 times smaller than the number of water molecules needed to form the complete water meniscus around a probe of 25 nm radius [16]. Still, this model supposes the existence of many asperities on the two surfaces in the vicinity of the contact between the probe and the sample whose contact radius is much smaller than the probe radius. However, our experiments conducted on an atomically flat mica surface have also shown a linear decrease of the adhesion force with the logarithmic increase of the sliding velocity. For such atomically flat surfaces, it is reasonable to assume that the contact between the probe and the sample is without asperities. Moreover, whatever the sample, the root mean square roughness R_q is very small (Table I), and as the surface roughness depends on the surface area [21], the roughness of the wet surface occupied by the meniscus is even smaller. Consequently, there is no evidence that the number of asperities is high enough to generate the nucleation of water bridges around the contact area. It is more reasonable to consider the probe-sample contact as a monoasperity contact or that the capillary meniscus nucleates and grows from the

probe-sample contact rather than from the formed gaps between asperities of the two surfaces. Moreover, the behavior of V_{start} with the hydrophilicity of the surface (Table I) shows that the growth of the capillary meniscus is disturbed at lower sliding velocities as the hydrophilicity of the surfaces, which governs the volume of the capillary meniscus at its equilibrium state, increases. Precisely, the higher the volume of the meniscus, the longer the time for the meniscus to reach its equilibrium state. All these considerations suggest that the beginning of the intermediate regime is size meniscus dependent or that the behavior of the adhesion force in the intermediate regime is rather related to the growth process of the capillary meniscus rather than to the nucleation one. Following this assumption, there is always evidence of the presence of a capillary meniscus in regime II that is unable to reach its equilibrium state. This is experimentally confirmed since the adhesion force values in regime II never decrease to the minimum force value reached in regime III that corresponds to the vanishing of the capillary meniscus. A growth process of the capillary meniscus which is also a thermally activated process could also explain this linear decrease of the adhesion force with the logarithm of the sliding velocity. The growth energy barrier $\Delta E'$ is influenced by local chemical heterogeneities, asperities, or atomic roughness of the surfaces (Fig. 3) [13,20,22–24]. $\Delta E'$ increases as the number of these defects increases. Thus, the value of $\Delta E'$ is supposed to increase as the edge of the capillary meniscus spreads onto the surfaces while growing. This suggests that, in a first approximation, $\Delta E'$ is proportional to the perimeter of the meniscus $2\pi R_l$, where R_l is the radius of the wet area of the surface, which can be estimated at the equilibrium by the following equation [14]:

$$R_l = \sqrt{2R_p R_k [\cos\theta_p + \cos\theta_s]}, \quad (2)$$

where R_k is the absolute value of the Kelvin radius, R_p the probe radius, θ_p and θ_s are the static contact angles with

TABLE I. Material parameters and experimental data. R_q is the root mean square roughness determined from a 1 μm^2 AFM tapping modeTM topographic image, θ is the static contact angle with water, V_{start} and V_{end} are, respectively, the sliding velocity at which the intermediate regime starts and ends in the same experimental conditions.

	R_q	$\theta(^{\circ}) \pm 5^{\circ}$	$V_{\text{start}} (\mu\text{m/s})$	$V_{\text{end}} (\mu\text{m/s})$
Hydrophobic samples				
HOPG	0.05	105		
Si _{CH3}	0.20	100		
Hydrophilic samples				
Mica	0.03	5	9	40
Si	0.16	60	60	279
Si ₃ N ₄	0.34	70	95	347
Gold	0.23	75	160	897

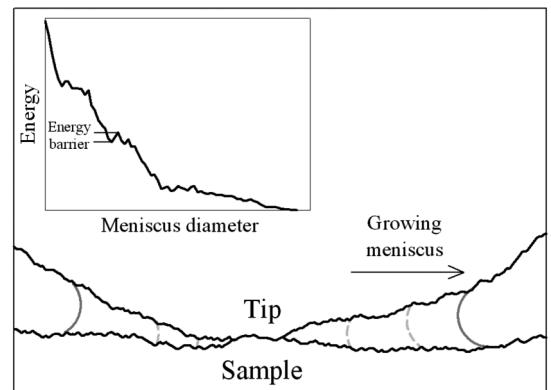


FIG. 3. Growing meniscus around the tip-sample contact. The energy barrier becomes higher as the number of surface defects increases during the meniscus growth.

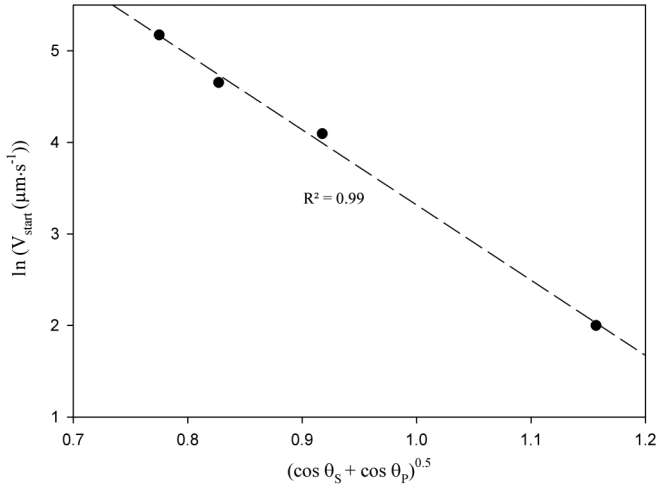


FIG. 4. $\ln(V_{\text{start}})$ as a function of $[\cos(\theta_s) + \cos(\theta_p)]^{0.5}$. All results are obtained at the same relative humidity and temperature and with the same tip (41% of relative humidity, $T \approx 25^\circ\text{C}$, and 30 nm tip radius). The linear behavior is in good agreement with a model based on a thermally activated growth process.

water of the probe and the surface, respectively. From the Arrhenius law, the resident time t to overcome the energy barrier $\Delta E'$ is given by

$$t = t_0 \exp\left[\frac{\Delta E'}{k_B T}\right], \quad (3)$$

where t_0 is a preexponential constant. Then, following this model, the velocity V is proportional to the inverse of the resident time of the meniscus at the vicinity of the defects:

$$V \propto \frac{1}{t} \propto \exp\left[\frac{-\Delta E'}{k_B T}\right]. \quad (4)$$

Combined with Eq. (2), when the meniscus reaches its equilibrium state (i.e., at $V = V_{\text{start}}$), we obtain at a given T

$$\ln(V_{\text{start}}) \propto \frac{-\Delta E'}{k_B T} \propto -R_l \propto -\sqrt{\cos\theta_p + \cos\theta_s}. \quad (5)$$

From Eq. (5), we expect that the logarithm of V_{start} is proportional to $-\sqrt{\cos\theta_p + \cos\theta_s}$. This is experimentally confirmed by Fig. 4 for four hydrophilic surfaces, that shows the linear trend predicted by this model. In conclusion, we have experimentally shown that on nanometer-sized contacts of hydrophobic surfaces, adhesion forces or mainly attractive forces remain constant with the sliding velocity. For hydrophilic surfaces, adhesion forces decrease logarithmically with the sliding velocity from a threshold value of the sliding velocity and vanish at high sliding velocities. This threshold value could be related to the meniscus size rather than to sample roughness. This behavior is also observed on a nanometer-sized contact between an atomically flat surface and a smooth probe, and the

kinetics of the capillary condensation is suggested to be related to a thermally activated process that find its origin in either the meniscus nucleation process or in the growth process. Further experiments with various model surfaces and probes are necessary to understand the influence of these two phenomena on the capillary growth. However, the model based on the growth process of the capillary meniscus is in good agreement with our experimental data.

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