

Adhesion Forces between Surface-Modified AFM Tips and a Mica Surface

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The adhesion force between modified AFM tips and a mica substrate has been studied using an atomic force microscope. The force–distance curves measured by the microscope show that the adhesion force is sensitive to the surface energies of the materials coated on the tips. The adhesion force between a gold-coated tip and a mica surface is much larger than that between a paraffin-coated tip and a mica surface. A simple calculation shows that this behavior of the adhesion forces can be accounted for by the van der Waals and capillary forces between the AFM tips and the substrate.

Introduction

Since its invention following that of the scanning tunneling microscope (STM),¹ the atomic force microscope (AFM) has been increasingly used in studying surface forces and surface structures of a wide range of materials.^{2–10} The heart of an AFM is a sharp tip that interacts with a sample surface at a distance of atomic dimensions. The interaction force with the sample sensed by the tip as it scans across the surface forms images of that surface. The interaction force between the tip and the sample is affected not only by the morphology of the sample surface but also by the materials that the tip and the sample are made of as well as by the environment.^{4,5,10} It is therefore important to understand and characterize the fundamental interactions between different tips and sample surfaces under different environmental conditions.

For a tip and a substrate that are composed of electrically neutral and nonmagnetic materials, the force between them would be mainly due to van der Waals and capillary interactions between the two. The capillary force would be absent if an AFM scanner is operated in a vacuum or a dry environment. A study of the interaction force between an AFM tip made of W and various substrates in a dry environment found direct correlation between the adhesion forces the AFM measured and the sample surface energies.¹⁰ Studying surfaces of many chemical and biological systems often requires samples being kept in an ambient or a controlled humidity environment. In these cases, the surface of the samples would be covered by a thin water film. The capillary force due to the water meniscus formed around the end of the tip would strongly influence the interaction between the tip and the surface. The capillary force is affected by the wettability of water

to the substrate as well as to the tip surface. For a hydrophobic substrate, the thickness of a water film formed on that is very limited, which would result in a relatively small capillary force. If the surfaces of both the substrate and the tip are hydrophilic, a large water meniscus can be formed around the tip, resulting in a strong capillary force between the two. Several recent studies have investigated the adhesion force between an AFM tip and different substrates as a function of humidity.^{11–13} The results of these studies show that the adhesion force depends strongly on whether the substrate is hydrophilic or hydrophobic.¹¹ However, it seems that attention has not yet been paid to how the surface energy of a tip would affect the adhesion force in different environments. In this study, we attempt to examine the adhesion forces between an AFM tip coated with different materials and a mica surface in a controlled humidity environment.

Materials and Methods

We systematically measured the force–distance forces on a mica surface with tips coated with different materials. We started with clean Si₃N₄ tips and then coated them with gold or paraffin thin films. Gold and paraffin have very different surface energies and thus completely different water wettabilities.¹⁴ We conducted the measurements in an environment with controlled humidity.

The force–distance curve measurements were made with a commercially available atomic force microscopy system (Explorer from TopoMetrix Inc.).¹⁵ The tip/cantilevers employed were also purchased from the same manufacturer.¹³ The cantilevers we used were made of Si₃N₄ and were pyramidally shaped with approximate dimensions of 5 μm per side on the base and 5 μm high.

The microscope was enclosed inside a container made of Plexiglas. The container, which had an internal volume of approximately 1.5 × 10⁻² m³, could be sealed so as to be nearly airtight. Dry nitrogen or other gas can be introduced into the container at a controlled rate. During the measurements, the plastic container was first flushed with dry nitrogen gas several times, and then the relative humidity inside the container was controlled by introducing either dry nitrogen or water vapor. The water vapor was generated from a distilled and deionized water source. The relative humidity (RH) was monitored using a relative humidity meter.¹⁶ The sensitivity of the RH meter is

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not satisfactory at humidity below 25% and above 90%, which limits the humidity range of our measurements.

The substrate used in this study is a piece of natural muscovite mica which is almost colorless when examined under an optical microscope. We cleaved the mica surface each time before it was installed into the Plexiglass chamber.

We conducted three sets of measurements. The first set of measurements was made with bare tips as supplied by the manufacturer.¹⁵ Right before the measurements, the tips were rinsed with acetone and then methanol to ensure relative cleanliness. The second set was made with the same tips after they were coated with thin gold films with a few hundred angstroms thickness. A SPI sputtering machine was used to coat the gold films to the tips.¹⁷ The tips were held pointing upward and DC sputtered with gold with a current of 2 mA, giving a deposition rate of 0.3 Å/s. A faster deposition rate was found to cause some changes in the cantilevers. The tips were used for measurements immediately after they were exposed to air. Lastly, a set of the measurements was made with the same tips after coating them with thin layers of paraffin. The paraffin wax, purchased from a local hardware store,¹⁸ was used as an evaporation source to coat thin layer films on the tips. The chemical composition and purity of the paraffin were not available to us.

The results obtained with the cleaned bare tips are reproducible. Occasionally the gold coated and paraffin coated tips would produce results which are almost the same as those produced by the bare tips. We speculate that in these cases the very end of the tips remains bare Si₃N₄, even though the rest of the tip was coated with gold or paraffin. In order to eliminate those results which are due to incompletely coating the end of the tip with the desired thin films, we measured the force–distance curves many times with the same tips repeatedly coated with gold or paraffin and only kept those results which could be reproduced by the same tip.

Results and Discussions

We have measured several hundred force–distance curves under different humidities and tip coatings. Figure 1 shows three typical force–distance curves measured with a bare Si₃N₄ tip and the tip coated with gold and paraffin. The force–distance curves are plotted as the photodetector current versus the distance moved by the z-piezo. The commercial AFM system we used was designed to achieve the highest possible force sensitivity; thus, the dynamic range of the force measurements is very limited. When a gold-coated tip is used, the large attractive adhesive force causes the cantilever to bend so much that the signal completely saturated the detector over a large portion of the curve. In order to reveal the entire force–distance curve, we had to purposely misalign the laser beam to decrease the sensitivity of force measurements. Such a measure could introduce some erroneous response if the laser beam is not reflected from the flat region on the back of the cantilever. Some of the erroneous features can be easily seen in the force–distance curves plotted in Figure 1. Because of these erroneous features, the absolute forces between a tip and the substrate measured with our AFM system were not very reliable. However, the distance over which the z-piezo has to retract in order for the tips to break away from the substrate was found to be independent of how we align the laser beam. To ensure that the paraffin films were not penetrated when the contact between the tip and the substrate was made, we limited the maximum distance the cantilever travels once it feels a repulsive force by setting a limit via software on the maximum signal current.

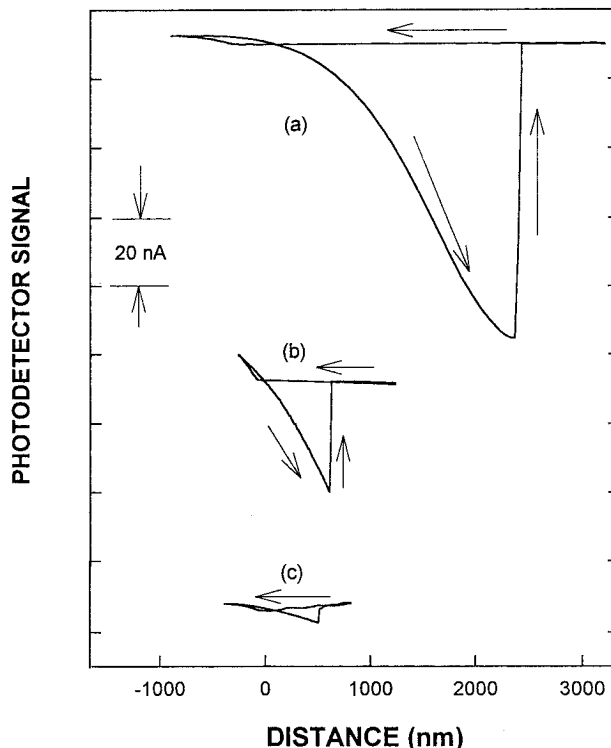


Figure 1. Force–distance curves plotted as the measured signal from the photodetector versus the z-piezo travel distance. (a) Force–distance curve measured with a tip coated with gold film. (b) Force–distance curve measured with a clean, bare Si₃N₄ tip. (c) Force–distance curve measured with a tip coated with paraffin film.

The main feature in Figure 1 is the dramatic difference in the force–distance curves measured with tips coated with different materials. For gold-coated tips, the distance at which the tip breaks away from the substrate is much larger than that measured with a bare Si₃N₄ tip or with a paraffin-coated tip. The difference indicates that the adhesion force for the gold-coated tip is much larger than that for bare and paraffin-coated tips. We use the break-free distance as a measure of the adhesion force between the tips and the substrate. The distance was measured from the point that the tip feels a repulsive force to the point where the tip breaks away from the substrate (the jump in the force–distance curve). Figure 2 plots the break-free distance in the force–distance curves measured with three different types of tips as a function of relative humidity. Each data point represents the averaged break-free distance measured within a 10% relative humidity range. The adhesion force between an AFM tip and a mica surface can be obtained by multiplying the break-free distance by the spring constant of the cantilever. The spring constants of cantilevers are quantities that are difficult to measure with certainty. We used a quoted value of 0.064 N/m from the manufacturer.¹⁵ However, it should be noted that the value is accurate only to an order of magnitude. Because of this uncertainty, we only compare the results obtained with the same tip.

As mentioned above, the adhesion force we measured here is mainly caused by the van der Waals and capillary interactions between a tip and the substrate.^{4,19} For a spherically shaped tip interacting with a flat substrate, the nonretarded van der Waals force can be approximated

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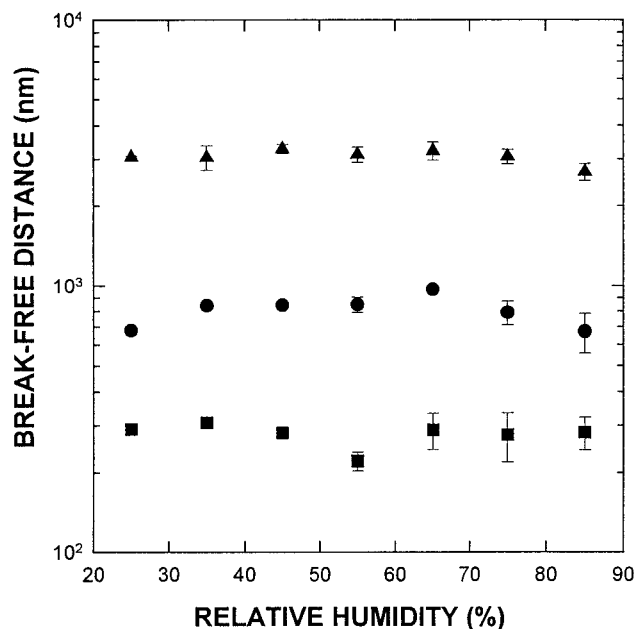


Figure 2. Break-free distance versus relative humidity: (▲) gold-coated tips; (●) bare Si₃N₄ tips; (■) paraffin-coated tips.

as²⁰

$$F = HR/6D^2 \quad (1)$$

where H is the nonretarded Hamaker constant, R is the radius of the tip, and D is the distance between the tip and the substrate. Here the Hamaker constant involves interaction between the tip and the substrate across a thin water film. It can be approximately obtained using the relation^{14,21}

$$H = H_{ts} - (H_{tw} + H_{sw} - H_{ww}) \quad (2)$$

where the subscripts t , s , and w stand for tip, substrate, and water, respectively, and H_{ts} , H_{tw} , H_{sw} , and H_{ww} are the Hamaker constants between the two media indicated by the subscripts across vacuum. The Hamaker constant is proportional to the square root of the product of the surface energies of each material and can be further related to the Hamaker constants for the individual media.¹⁸

The capillary force between a tip and a substrate in a humid environment is due to the existence of a thin layer of water molecules adsorbed on the surfaces. For a hydrophilic substrate, the thickness of the water film can be approximately described by a Frenkel–Hasel–Hill relation, $t = [kT\alpha \ln(p_s/p)]^{1/3}$, where α is related to the Hamaker constant between water and the substrate and the density of water ρ by $\alpha = H_{sw}/(6\pi\rho)$ and p and p_s are the partial vapor pressure and saturated vapor pressure of water.²¹ As an AFM tip approaches the substrate, the capillary force on the tip is initially near zero until the tip contacts the surface of the water film. When the contact is made, water wicks up around the tip to form a meniscus bridge between the tip and the substrate. The Kelvin radius of the meniscus is determined by $r = \gamma V/[RT \log(p/p_s)]$, where γ is the surface tension of water.¹⁴ As

relative humidity is less than 90%, both the water film thickness and the radius of the meniscus bridge are less than 100 Å,^{4,20} which is much smaller than the radius of the AFM tips used in this study. In this case the capillary force can be well described by^{14,20}

$$F = 4\pi R\gamma \cos \theta / (1 + D/d) \quad (3)$$

where θ is the contact angle between the water–vapor interface and the tip, D is the distance between the tip and the substrate, and d is the distance the tip extends into the water bridge. Because the cantilevers we used have a relatively small spring constant, the tip would jump-in to contact with the substrate once the capillary force comes into play and stay in contact until break away during tip retractions.

We calculated the van der Waals force and capillary force between the tips and the substrates and listed them in Table 1. The van der Waals forces were calculated using eq 1 and assuming that the tip–substrate distance before breaking free is 1 Å. The Hamaker constants were calculated using eq 2. Since the thickness of the gold and paraffin films coated on the tips was much larger than the tip–substrate distance before the tip break away, we assumed that the van der Waals interaction between a modified tip and a substrate is dominated by the material which coats the tip. The capillary forces were calculated using eq 3, assuming that D/d is small. The surface tension of water is 0.073 N/m ($T = 20^\circ\text{C}$).¹⁴ The contact angle between the surface of a gold-coated tip and water is 0° and that between the surface of a paraffin-coated tip and water is 110° .¹⁴ We do not have an accurate value for the tip radius. In Table 1, we choose an upper-bound value of 1000 Å, provided by the manufacturer, for the tip radius.¹⁵ It should be noted that such a choice might overestimate both the van der Waals and capillary forces by the same proportion and thus the rough agreement between the measured adhesion force and the sum of the van der Waals force and the capillary force for gold-coated tips may be accidental. Table 1 shows that the van der Waals force between gold-coated tips and mica substrate is five times larger than that between paraffin-coated tips and the same substrate, while the measured adhesion forces differ by a factor of more than 10 in the two cases. The results of the calculation indicate that the difference is due to the diminishing capillary force when a tip is coated with a hydrophobic material.

Figure 2 shows that the adhesion forces are insensitive to the humidity within the range of our measurements. For paraffin-coated and bare Si₃N₄ tips, if the water meniscus around the tip is absent, no dependence of adhesion force on humidity should be observed. In the case of gold-coated tips, the capillary force depends on the water film thickness and thus the measured adhesion force should vary with relative humidity. One possibility for our failure to observe the humidity dependence is that the thickness of water films formed on the mica substrate we used is actually limited and thus would not increase with relative humidity. This explanation is consistent with the results of recent measurements by a polarization force microscope⁹ and ellipsometry²⁴ indicating that, for humidities up to about 50%, the average thickness of the water film on the mica surface is still of molecular dimension. However, a recent study by Thundat *et al.*¹³ found that the adhesion force between a Si₃N₄ tip and a mica substrate increases by a factor of about two when relative humidity rises from 20% to 80%. The discrepancy

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Table 1. Comparison of Calculated Adhesion Forces and Measured Adhesion Forces between Different Tips and Mica Substrate^a

tip	Hamaker constants ^a (10^{-20} J)	van der Waals Force (nN)	capillary force (nN)	measured adhesion force (nN)
gold	5.5	92	92	192
Si ₃ N ₄	2.8	48		51
paraffin	0.93	15	-31	17

^a The Hamaker constants were calculated using eq 2. The Hamaker constants for individual media used in the calculation are as follows: gold,¹⁴ 40; water,¹⁴ 3.7; mica,¹⁴ 10; Si₃N₄,²³ 174; all in the unit of 10^{-20} J. We failed to find the value of Hamaker constant for paraffin, so we used the value for hydrocarbon (7.1×10^{-20} J) in the calculation.²⁰

might be due to different mica substrates used. As mentioned above, the mica substrate we used is a piece of natural muscovite mica. A fairly large amount of impurities (most of them are oxides) exist between two cleavage layers in the mica and thus stay on the surface after it is cleaved.²⁵ Thus it is possible that the mica substrate we used is actually hydrophobic and the thickness of the water film formed on it is limited even at higher relative humidity. It was observed that the adhesion force between an AFM tip and a clean Si substrate increases with humidity while the adhesion force between an AFM tip and a hydrophobic surface is independent of humidity.¹¹ The adhesion force between Si₃N₄ tips and a mica substrate obtained in this study seems to be consistent with the mean values of that reported in refs 12 and 13 with consideration of tips with different radius used.

Summary

In summary, we have studied the humidity dependence of adhesion forces between modified AFM tips and mica substrates. The results show that the adhesion force

depends strongly on the surface energies of the tip and the wettability of water to the tip surface in a humid environment. The measured adhesion force agrees with that calculated by assuming that the adhesion force is caused by van der Waals and capillary forces. Our results indicate that, by coating AFM tips with a layer of hydrophobic material, the adhesion force between the tip and substrate covered with a thin water film would be greatly reduced. The modification of AFM tips might provide improved results in imaging certain biological or chemical systems.

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