Impact of Humidity on Adhesion between Rough Surfaces[†]

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The surface forces apparatus was used to study the variation with relative humidity of adhesion between mica and rough gold films coated with either a hydrophobic or hydrophilic self-assembled monolayer (SAM). Pull-off forces, as a function of relative humidity, were measured between mica and gold coated with either *n*-octadecanethiol or 1-hydroxylunicosanethiol. For the alcohol-terminated SAM, pull-off forces increase from 370 mN/m (dry conditions) to 845 mN/m (saturated conditions). For the methyl-terminated SAM, pull-off forces increase from 160 mN/m (dry conditions) to 643 mN/m (saturated conditions). A quartz crystal microbalance was used to obtain adsorption isotherms on the two different SAMs. Angstrom-level changes in adsorbed layer thickness are associated with marked changes in measured adhesion forces.

Introduction

Adhesion of particles to surfaces has sustained the interest of colloid scientists for the major part of the last century. While well-understood surface forces[1] are at the root of this sticking event, complications such as particle shape, surface roughness, and capillary condensation continue to obscure a complete scientific and practical knowledge of this technologically important phenomenon. Such knowledge is especially critical to new technologies, such as magnetic rigid disk memory systems and microelectromechanical systems (MEMS), which rely on preventing the adhesion of microstructures to surfaces and to one another. While such new systems have much to gain by making surfaces as smooth and microstructures as small as possible, these factors also exacerbate undesirable adhesion events. More generally, these systems are plagued with "stiction" problems, which cause two surfaces to have unusually high frictional forces, adhesive forces, or both on account of a variety of factors including the presence of thin liquid films between the contacting surfaces.[2]

Systems in which surfaces are in or near contact are always susceptible to capillary condensation as caused by exposure to humid environments. The propensity of hydrophilic surfaces, combined with the high meniscus tension of water, make this possibility both common and consequential. A well-known example of the importance of humidity comes from applications of the atomic force microscope (AFM); the presence of condensate between the probe tip and sample affects the forces measured as well as the resolution of images obtained.[3,4] In this case it is generally assumed that a single bridge of liquid forms between the microscopic tip and the opposing sample. Analysis is thus based on well-established predictions associated with an isolated mensicus as formed between two bodies.

As part of their own comprehensive work solving the Laplace−Young equation for axisymmetric menisci, Orr and co-workers[5] review the history of efforts dedicated to predicting the shape of pendular liquid rings and the associated capillary forces acting between two curved bodies. In short, the curvature of a mensicus gives rise to a capillary pressure force that is transmitted by liquid. The pressure jump across the meniscus is given by Young's equation

$$\Delta p = 2H\sigma \tag{1}$$

where σ is the surface tension and H is the mean curvature of the meniscus. In the limit of negligible liquid volume, the associated capillary force exerted between a rigid sphere of radius R in contact with a flat is given by

$$F/R = 2\pi\sigma(\cos\theta_1 + \cos\theta_2) \tag{2}$$

where θ_1 and θ_2 are the contact angles the liquid makes with each respective solid surface.

In unsaturated environments, the level of humidity controls the extent of capillary condensation as given by Kelvin's equation which dictates the curvature of menisci that are formed at a given relative humidity (i.e., at a given p/p_{sat}):

$$2H = \frac{RT}{V\sigma}\ln(p/p_{sat}) \tag{3}$$

Here V is the molar volume of condensate, R is the gas constant, T is absolute temperature, p is the vapor pressure, and p_{sat} is the saturated vapor pressure. Notably, application of the Kelvin equation to unsaturated conditions predicts mean radii of curvature at the nanoscopic level (e.g., at 50% relative humidity, $(2H)^{-1} \approx 0.8$ nm).

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The validity of the Kelvin equation in such conditions has, however, been experimentally verified by Fisher and Israelachvili.[6,7]

Interestingly, as long as eq 2 is assumed to hold (i.e., if liquid volumes are small enough), degree of humidity should not affect the capillary force exerted between two bodies in contact. In other words, as humidity is decreased, the volume of condensate becomes smaller but the meniscus curvature will be higher; the increase in pressure jump is offset by the decrease in wetted contact area leading to the same effective capillary force. This simplistic prediction has been supported by experimental measurements. In particular, Christenson[8] used the surface forces apparatus to investigate the effect of humidity on adhesion between smooth mica substrates. While a small variation of force with humidity was observed, the measurements could be explained by taking into account the macroscopic elastic deformations of the contacting bodies as put forward by Fogden and White.[9] (They conclude that the asymptotic force relation above, eq 2, applies in the limit of saturation, while it overestimates by 33% the capillary force in the limit of negligible humidity.)

The recent increased use of atomic force microscopy has heightened interest on the effects of relative humidity. At mentioned above, analysis is generally based on a liquid bridge which spans between the tip and nearby sample. In this case (in contrast to that of a liquid ring surrounding two contacting bodies) the force is predicted to increase with relative humidity, as the bridge thickens, to a maximum predicted by eq 2 above. This behavior has been experimentally verified by Thundat and co-workers;[4] they observe an approximately 2-fold decrease in capillary force as humidity is reduced.

A much more complex and technologically significant problem is the situation of contact between rough surfaces. Even the relatively smooth surfaces used in MEMS and magnetic recording media have nanometer-scale roughness features. Komvopoulos and Yan[10] have, for example, shown that liquid bridging at intermediate humidity is the dominating short-range attraction mechanism prevailing at MEMS interfaces. And it is known that head/disk stiction occurs at humidities greater than 80%.[2,11]

Contact between rough surfaces generates a bountiful landscape for micromeniscus formation about touching asperities as well as between opposing asperities in close proximity. Unlike the situation of contact between smooth surfaces, here adhesion can be acutely sensitive to changes in relative humidity. In fact, it is common to see a sharp increase in adhesion at some distinguishable humidity level, as observed by McFarlane and Tabor in one of the earliest experimental studies of capillary adhesion forces.[12] Effects of humidity are particularly acute when at least one of the two surfaces is highly hydrophilic. Thus, in practice, interface modification strategies which control surface wettability, such as application of self-assembled monolayers,[13] can provide important remedies to diminishing undesirable effects of capillary condensation at rough interfaces.

When the contact zone is completely flooded with liquid, so as to yield a macroscopic meniscus, the capillary force is predicted by the relation above (eq 2). In general, at humidities below saturation the exerted capillary force is less.[14] How much less depends on the number and extent of micromenisci existing about the microscopic asperities that are in, or near, contact (information that is difficult if not impossible to determine). Adhesion data reflect the process of interface "fill-up" as new micromenisci (i.e., microscopic bridges) form and existing bridges and rings thicken and coalesce. Some attempts have been made to develop models of contacting rough surfaces in the presence of lubricating films[11] and/or in humid environments.[10,15] Though numerical in nature and not easy to generalize, these models confirm some basic observations and intuitions. For example increasing roughness (e.g., texturing the surface) will diminish the undesirable adhesive effects of lubricating films and humidity (though from a practical point of view this remedy is often counterproductive to achieving other system performance goals).

All models of capillary forces recognize the influence of surface chemistry as manifested by contact angles (see eq 2). At the microscopic level, surface chemistry will regulate the adsorbed layer thickness at any given relative humidity. Adsorption provides a mechanism for interface fill up, as an increase in film thickness will trigger the formation of new bridges.[15] The notion that adsorbed film thickness is important is not new. The insightful Tabor[12] suggested that adhesion at rough interfaces would be significantly increased when the thickness of adsorbed liquid becomes comparable to the height of asperities. More recent studies find, indeed, that stiction is a maximum when the thickness of liquid films equals the head/disk gap[2] and that stiction at the head/disk interface becomes significant when the thickness of liquid is close to a critical thickness which is related to the magnitude of surface roughness.[16]

Significant advances in understanding adhesion between microscopically rough surfaces will rely on experiments in which surface wettability, relative humidity, and surface roughness can be independently controlled. In this paper, we report on a set of experiments designed with this ultimate goal in mind. The point of these particular experiments is to investigate the dependence of adhesion on humidity as surface wettability is changed without change in underlying roughness; furthermore we explore the relationship between variation of adhesion and variation in adsorbed water thickness. Our experiments take advantage of the unique capabilities of the surface forces apparatus (SFA), a device designed to measure the forces between, and associated deformations of, two gently curved surfaces in contact. A powerful feature of this technique is the use of multiple beam interferometry to measure macroscopic deformations as well as microscopic deformations within the contact zone.[17,18] We have previously used the SFA to examine the contact of rough gold films adhered to molecularly smooth mica.[18,19] As these polycrystalline films exhibit nanometer-scale roughness, they are good candidates for these studies. We have also shown how self-assembled monolayers formed on gold impact the adhesive forces as well as deformation me-

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chanics of this system.[20] With these behaviors now well characterized, we use these systems in the SFA to study dependence of adhesion on relative humidity. In particular, we compare the adhesion of mica to rough gold coated with a hydrophobic self-assembled monolayer (SAM) (n-octadecanethiol, $CH_3(CH_2)_{17}SH$) and to rough gold coated with a hydrophilic SAM (1-hydroxylunicosanethiol, OH-$(CH_2)_{21}SH$).

Experimental Section

The SFA technique as applied to studies using rough metallic films has been described in detail elsewhere.[17−21] Sheets of molecularly smooth muscovite mica (approximately $3-4\,\mu$m) were glued onto cylindrically curved ($R \approx 1$ cm) silica support disks used in the SFA. One disk is rigidly mounted; the other is affixed to the end of leaf spring of known spring contact. Prior to gluing, one mica sheet was coated with a silver film (glued silver-side down) as needed for application of multiple beam interferometry. After gluing, the other mica sheet was coated with a thin gold film of 500 Å thickness as prepared by thermal evaporation (≈ 4 Å/s; no external heating of the substrate). Polycrystalline gold films prepared in this manner are rough. Analysis by our AFM facility shows the gold films have a root-mean-square roughness of about 20 Å with an asperity density of about 2500 peaks/μm². Our interferometric measurements of contact between these gold films and mica suggest that the tallest peaks (which measure about 100 Å) regulate the intimacy of contact at the rough gold/mica interface. In particular, the effective thickness of dielectric medium (e.g., air) trapped within the gold/mica interface is about 60 Å.[18,19]

A focus of much of our previous work with these gold films has been the study of microdeformations at the contact zone as a result of applied forces[19,20] as well as surface forces acting alone.[17] As asperities deform (and trapped dielectric thickness thereby diminishes) the adhesion between the rough gold and mica increases. The act of pulling surfaces apart can also change (increase) the surface roughness.[17,22] While the presence of a SAM actually diminishes the extent of microdeformations,[20] it does not eliminate them. The load and time-dependent nature of microdeformation behavior (with consequent impact on adhesion) impedes using the same gold substrate for adhesion measurements at a series of humidities. Hence a freshly prepared gold film was used for each experiment. Moreover, each film was taken through the same loading/unloading regiment, consisting of application of 7.6 μN of force per second up to a compressive load of 0.025 N, at which point the load was retracted until the surfaces jumped apart. The deflection of the spring at the moment of separation is very nearly equal to the separation of the surfaces after the jump as determined by multiple beam interferometry. The strength of adhesion, as measured by the pull-off force, is simply equal to the deflection of the spring multiplied by the spring constant. In each experiment, the effective radius of curvature of the (undeformed) interacting surfaces is also measured by multiple beam interferometry. To allow comparison of one experiment to the next, and also to theory (e.g., eq 2), pull-off forces measured between the curved surfaces are scaled by (divided by) this radius of curvature.

Solutions of octadecaenthiol (Aldrich) and 1-hydroxyluni-cosanethiol (synthesized by one of us[23]) were prepared in ethanol through which nitrogen was bubbled. The concentration of each solution was 0.5 mM. The gold-coated mica substrates described above were placed in SAM solution under a nitrogen blanket for a period of 6−12 h. After being vigorously rinsed with ethanol and blown dry with a continuous stream of nitrogen, the SAM-modified gold disk was then mounted in the SFA.

The final step prior to experimentation involved inserting into the sealed chamber of the SFA a small vial of saturated salt solution to control humidity. The limit of zero humidity was
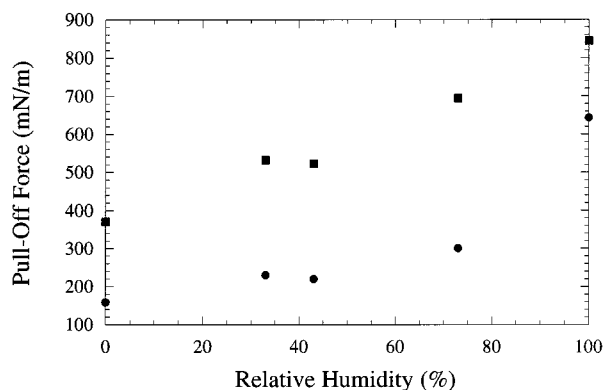
Figure 1. Pull-off forces (mN/m) as a function of relative humidity. Separate self-assembled monolayers were prepared for each data point: square symbols are for the alcohol-terminated SAM; circles are for the methyl-terminated SAM.

achieved using a small vial of desiccant and then purging with nitrogen gas for at least 0.5 h.

Adsorption measurements of water on SAM-coated gold were made using a home-built quartz crystal microbalance (QCM) described elsewhere.[24] SAMs on the gold electrodes of the QCM were prepared in the same fashion as SAMs on the gold films used in the SFA. Relative vapor pressure of water was controlled using a vapor dosing system.

Results and Discussion

The experimental protocol described in the previous section suffices to establish reasonably precise pull-off force measurements for SAM-coated gold against mica, thus making this study feasible. Experimental scatter is about 15% (unlike the case for uncoated gold for which scatter is substantially higher[19,20]). In dry conditions, as reported previously, the pull-off force for contact between octanedecanethiol-coated gold and mica is about 160 mN/m. For contact between 1-hydroxylunicosanethiol-coated gold and mica, pull-off forces measure 370 mN/m. Forces in the latter case are respectively higher because of the high surface energies of the hydrophilic SAM and the hydrophilic mica surface. As noted in the Experimental Section, a freshly prepared gold film (as well as fresh mica) was used for each experiment (i.e., at each humidity level); after the gold was coated with a monolayer, each experiment followed the same loading/unloading protocol so as to keep as constant as possible the microscopic deformations known to occur.[19,20]

The main result of this study is shown in Figure 1, which shows the pull-off forces for both the hydrophobic and hydrophilic SAMs as a function of relative humidity. As is readily seen for both systems, the pull-off force increases with relative humidity. At a given humidity, the adherence of the alcohol-terminated monolayer to mica is greater than that of the methyl-terminated monolayer. In both cases, the impact of humidity is significant, causing increases in adhesion well beyond the values in a dry environment.

The effects of relative humidity are quite apparent in our experiments. The nominal contact area of the deformed surfaces is greater for higher humidities, consistent with an increase in adhesion as measured directly through the pull-off force. The wavelengths of the interference fringes (which depend sensitively on the refractive index of dielectic material trapped between the surfaces) show a slight increase consistent with introduction of water within the contact zone.

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At saturated conditions, the pull-off force between 1-hydroxylunicosanethiol and mica measured 845 mN/m. That between octanedecanethiol and mica measured 643 mN/m. It should be realized that these are fairly strong adhesions. For example the pull-force required to separate two molecularly smooth mica sheets ranges from 600 to 1000 mN/m[25] and is relatively insensitive to humidity. The force required to separate gold from mica at the as-evaporated, intimate gold-mica interface is 1800 mN/m; subsequent contact of this extremely smooth ($\approx$4 Å root mean square roughness) gold to mica requires about 800 mN/m for separation.[22]

It is interesting to examine the applicability of the force relation, eq 2, which should be valid in the limit of saturation. Water wets mica giving a zero contact angle on this surface. Contact angles of water on SAMs of different termination are well characterized;[26] for sake of this analysis we take that on the alcohol-terminated SAM to be 0° and that on the methyl-terminated SAM to be 105°. From eq 2, the capillary adhesive force between the alcohol-terminated monolayer and mica is then predicted to be 905 mN/m and that between the methyl-terminated monolayer and mica is predicted to be 335 mN/m. While the former is within 7% of the measured value at saturation conditions, the latter is only half the measured value. If, instead, one uses the forces measured to calculate contact angles, one finds a value of 30° for the alchohol-terminated SAM and a value of 65° for the methyl-terminated SAM. It is conceivable that the hydrophilic surface may indeed exhibit such a value (see, for example, ref 27), but the corresponding result for the methyl-terminated SAM is unlikely. Of course forces of interaction other than capillary forces, if present, also contribute to the total force measured. It is difficult, however, to rationalize any such particular force that would give rise to the unpredictably large adhesion exhibited by the methyl-terminated SAM at saturation. Hence, we have no explanation for this particular data point. Finally, with respect to this limiting condition, we note that we did not notice, for either SAM, any evidence of a macroscopic meniscus as formed about the entire nominal contact zone. The interferometric technique employed allows such a meniscus to be readily discerned in certain situations, namely for symmetrically designed interferometers; since ours is not of this type we cannot rule out that such a meniscus did indeed form.

From the adhesion data presented in Figure 1, one may argue that the rate of force increase with relative humidity is fairly similar for both SAMs. This is especially true if one does not consider the limiting adhesion values at saturation. We now compare these "adhesion isotherms" to adsorption isotherms of water onto each type of gold-supported SAM. It has long been recognized that the variation of adhesion with relative humidity often parallels the corresponding variation of adsorbed water thickness.[12] Figure 2 shows the thickness of adsorbed water as a function of relative vapor pressure as obtained using a quartz crystal microbalance. Eight sets of independent experiments were performed as marked by different symbols (six for octanedecanethiol SAMs and two for 1-hydroxylunicosanethiol SAMs). Differences between the isotherms (for a given SAM) are small but noticeable; such differences probably arise from the variation of film to film. Nevertheless, at any relative humidity the hydro-
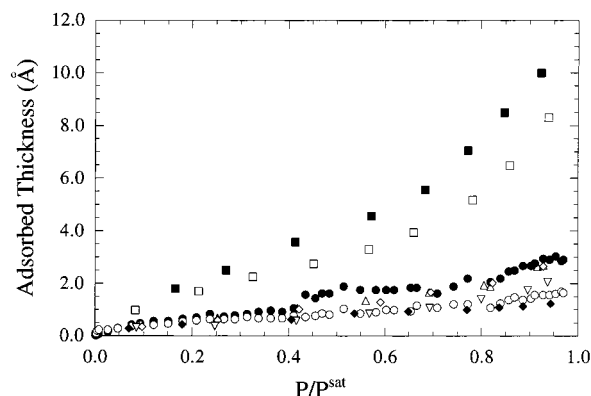
Figure 2. Thickness of adsorbed water (assuming $\rho = 1$ g/cm^3) on SAM surfaces as measured with a quartz crystal microbalance. Six separate adsorption isotherms (symbol for each separate SAM) are shown: square symbols correspond to the alcohol-terminated SAMs; other symbols correspond to methyl-terminated SAMs.

philic SAM adsorbs more water, as is intuitively expected. While our experiments cannot probe adsorption close to saturation, we note that the uptake of water on the methyl-terminated film shows no signs of a sharp increase (adsorption behavior that is consistent with the nonwetting characteristics of the surface).

On comparison of adsorption to adhesion, it is clear that mere angstrom-level increases in film thickness appear sufficient to affect measured forces. It is also interesting to compare the thickness of adsorbed water to a measure of the interface roughness. We do not know the thickness of water on mica, but recent studies[28] show that the maximum thickness reaches only 14 Å at 90% relative humidity. Hence, the total effective thickness of adsorbed water (adding that on SAM to that on mica) only reaches at most 25 Å at conditions near saturation. As previously reported[18,19] the interferometric technique permits us to characterize in situ the effective interface roughness in terms of the effective thickness of air trapped within the nominal contact zone. For the substrates used in this study, this thickness is about 60 Å. Our studies thus suggest that capillary forces are significant even when the thickness of adsorbed liquid is a fraction of the height of asperities. Last, it also clear that, at best, the shapes of adsorption isotherms only qualitatively match the shape of adhesion isotherms. The lack of exact correspondence was also found in the modeling work of Tian and Brushan;[15] they showed that sharp increases in adhesion at about 90% relative humidity were associated with a gradual, exponential variation of adsorbed water thickness.

Conclusions

The strength of adhesive contact between rough solids can be significantly increased in humid conditions. The increase in adhesion arises from the formation of micromenisci within the nominal area of contact. Capillary forces can be strong enough to yield adhesion strengths similar to those measured between smooth surfaces. The impact of humidity on adhesion depends, as might be expected, on the wettability of the interacting surfaces. While qualitatively similar, we found no explicit correspondence between the variation of adhesion with humidity and the variation of adsorbed water thickness with humidity. On the other hand, angstrom-level changes

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in adsorbed water thickness lead to marked increases in adhesive forces. The systems examined herein are characterized by nanometer-scale roughness features, similar to surfaces used in MEMs other devices. Adhesion between these nearly smooth surfaces is not controlled by any one factor—roughness, surface chemistry, and relative humidity all play important, and interrelated, roles.

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