Quantification of the meniscus effect in adhesion force measurements

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(Received 16 December 2005; accepted 7 February 2006; published online 28 February 2006)

Adhesion forces between a gold sphere and flat gold substrate are studied using atomic force microscopy in different environments. The pull-off force measured in a vacuum is found to be a small fraction of that in ambient air or nitrogen atmosphere. Calculations of capillary condensation forces, including the effects of elastic deformation of the contacting bodies and of adsorption layers, reveal that the meniscus force is the dominant source of the observed difference in pull-off forces. The experimental data show that nitrogen purge does not eliminate the meniscus contribution to the pull-off force. [DOI: 10.1063/1.2181200]

The interaction between surfaces at the nanoscale is of recent interest due to its effect on technology of micro and nanosystems and medical applications.[1–3] Since the advent of atomic force microscopy (AFM), it has become possible to measure frictional[4] and adhesion interactions[5–8] with nanoNewton sensitivity and nanometer spatial resolution. So-called snap-on and pull-off forces are extracted from force-distance curves measured between surfaces and probes.[7,8] Pull-off forces are usually used as a measure of adhesion.

Adhesive forces are composed of several contributing elements, such as van der Waals force, electrostatic force, meniscus force, and other interaction forces, originating from the physics and chemistry of the surfaces. There have been several attempts to isolate these components.[9–13] In ambient conditions, the dominant force appears to be the meniscus force associated with the formation of a small liquid capillary between the two surfaces. A common way to study meniscus effects is to measure pull-off forces at different relative humidity (RH) levels. Literature data[9,10,12,14] exhibit various behaviors of pull-off force as a function of RH, and it is an open question whether the pull-off force measured in nitrogen atmosphere is free of a meniscus contribution. It should be pointed out that the interaction forces are more complicated in the presence of a meniscus[15] so that the measured adhesion force might not be a simple addition of the contributing forces. The van der Waals force, for example, can be reduced in the presence of meniscus.[15,16] The meniscus force could trigger additional elastic or even plastic deformations of the surfaces.[17]

In this letter, we report our study of adhesion in different environments: ambient air, nitrogen atmosphere, and vacuum. The experiments performed in a vacuum should eliminate meniscus, allowing us to investigate the effectiveness of a nitrogen purge in removing the meniscus effect. We selected micrometer-radius spheres of known radii, instead of nanometer-sharp AFM tips, as probes, which made possible a direct quantitative comparison of the experimental data with model calculations that include the effects of elastic deformation of the contacting bodies and of adsorption layers. The use of micrometer spheres also reduces contact pressure, which is especially important in studies of soft materials.[7,8]

The experiments were carried out using an ultrahigh vacuum (UHV) AFM system (RHK Technology, UHV3500) (Ref. 18) at 1×10^{-10} mbar, an ambient AFM (Veeco Metrology, Multimode) and a home-built adhesion tester that used an optical fiber as a cantilever.[19] All three instruments were located in the subbasement of the Advanced Measurement Laboratory at the National Institute of Standards and Technology under controlled air cleanliness (Class 1000), temperature (21.0 °C±0.1 °C), and humidity (45%±5%). The instruments were supported on structures with additional vibration isolation systems.

We chose gold as the probe and substrate materials to minimize effects of surface contamination and of electrostatic force due to contact potential difference. Gold spheres, of 13 μm and 12 μm radius, were glued onto an AFM cantilever and a piece of optical fiber, respectively, and used as probes (see Fig. 1). Atomically smooth gold film on mica (Georg Albert PVD-Beschichtungen, Heidelberg, Germany) was used as the substrate. The spring constants of the AFM cantilever and optical fiber were measured using a TriboIndenter (Hysitron) (Ref. 20) to be 26 N/m and 1.7 N/m, respectively.

During force-distance curve measurements, the loading conditions were carefully controlled in order to stay within the elastic contact regime. The gold sphere was examined by scanning electron microscopy before and after measure-

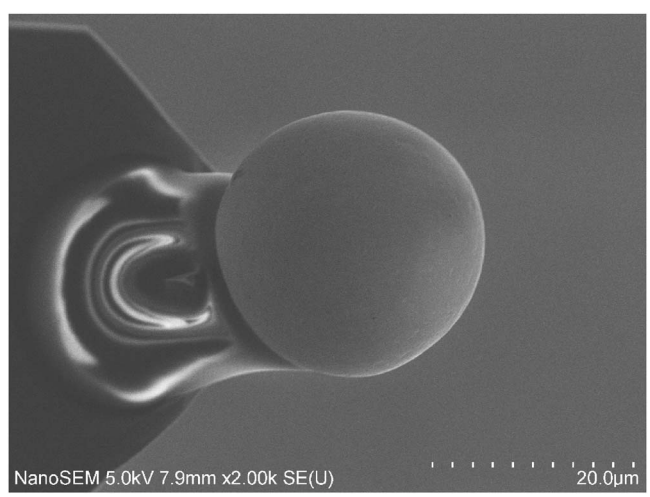

FIG. 1. Scanning electron micrograph of a gold sphere attached to the end of an AFM cantilever. Radius of the sphere is 13 μm.

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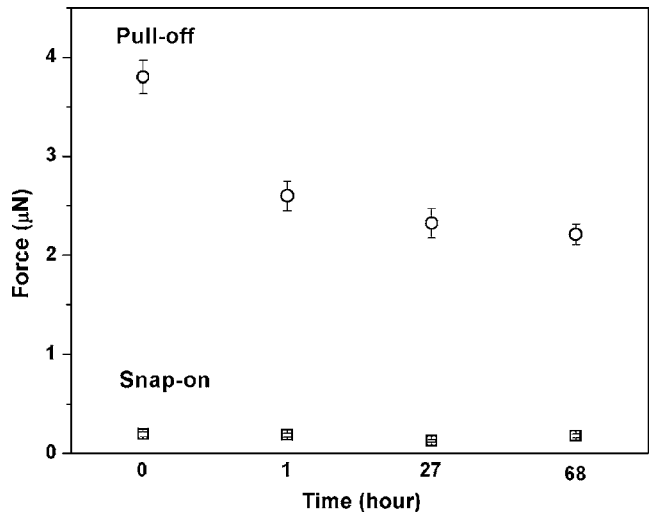

FIG. 2. Snap-on and pull-off forces measured by AFM in ambient air (0 h) and after continuous nitrogen purge for 1 h, 27 h, and 68 h.

ments, and no plastic deformation was observed. The speed for the approach and retraction was set at 150 nm/s in all the measurements. Both the probe and substrate were grounded to remove electrostatic interactions. Ten force-distance curves were recorded at each location and repeated at five locations of the substrate for each environment to ensure the reproducibility of the measurements.

Figure 2 presents snap-on and pull-off forces measured in ambient air (45% RH) and nitrogen atmosphere (<1% RH) using the ambient AFM. The snap-on force values are much smaller than the pull-off force values, consistent with other observations.[7,8] The snap-on forces do not vary substantially. In contrast, the pull-off forces measured in nitrogen atmosphere are lower than that in ambient air, and a slow decrease is observed as the time of nitrogen purge increases.

Snap-on and pull-off forces measured using different instruments and in different environments are presented in Fig. 3. The snap-on forces measured by AFM in ambient air (0.19 μN±0.03 μN), nitrogen atmosphere (0.18 μN±0.02 μN), and vacuum (0.21 μN±0.01 μN) are essentially the same within the experimental uncertainties.[21] The absence of a strong environmental effect in the snap-on force is not surprising because a meniscus can only be

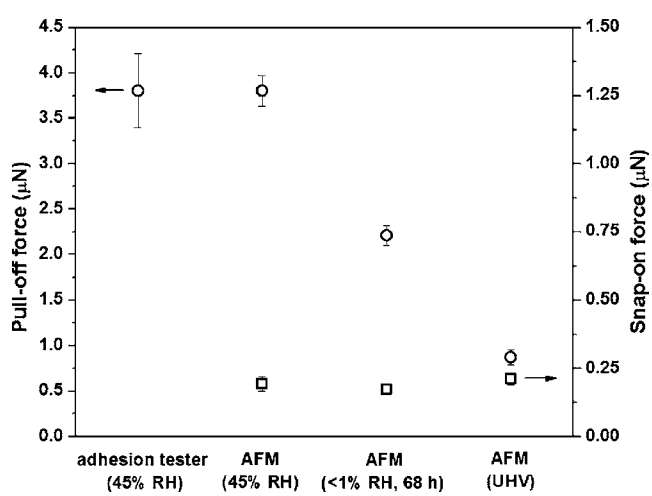

FIG. 3. Comparison of snap-on and pull-off forces measured using different instruments and under different environments.

formed after the probe snaps on. It should be pointed out that the measurements in an UHV were performed for an "as-loaded" probe and substrate, without any vacuum cleaning procedure. The observation of a consistent value of snap-on force provides evidence of similar probe and substrate surface conditions in the three environments.

There was no significant difference in the pull-off forces measured using the adhesion tester and the ambient AFM, both at 45% RH, although two types of instruments with different force-measurement mechanisms were used. The pull-off forces are 3.80 μN±0.41 μN in ambient air, 2.21 μN±0.11 μN after nearly three days of nitrogen purge, and 0.87 μN±0.09 μN in a vacuum. A common probe sphere was used first in ambient AFM, then in UHV AFM, and finally in ambient AFM again. Consistent data were obtained in ambient AFM measurements before and after UHV experiments, suggesting an absence of permanent change on the gold surfaces when placed in vacuum.

The difference between the pull-off forces in ambient air and UHV is 2.93 μN±0.42 μN and between nitrogen environment and UHV is 1.34 μN±0.14 μN. Humidity in ambient air is known to cause condensation near small objects, and there can be no condensation in UHV so that these differences in pull-off forces can be attributed mainly to a meniscus force. While previous studies have shown the dominant nature of meniscus effects on adhesion measurements in ambient air,[9–13] this letter reports a comparison of adhesion measurements in ambient air, nitrogen atmosphere, and UHV. Our data show that the pull-off force in nitrogen atmosphere (2.21 μN) is far from the value in UHV (0.87 μN), suggesting a substantial meniscus effect in nitrogen atmosphere.

In its simplest form, the force between a solid sphere of radius R and a flat solid substrate arising from liquid meniscus of radius $r_c \ll R$ is

$$F_c = 4\pi\gamma_{LV} R \cos\theta, \tag{1}$$

where $\gamma_{LV}$is the liquid-vapor surface tension and θ is the solid-liquid contact angle. Meniscus force is calculated to be 2.57 μN using Eq. (1) based on the literature value[14] of γ_{LV}=72.8 mN/mand measured values of R=12 μm and θ=78° (using contact angle instrument, First Ten Angstroms, FTÅ200). Equation (1), however, does not consider contact deformation between the probe and substrate and also ignores adsorption layers on the surfaces. Hence, we model the capillary interaction based on the classical capillary model with the inclusion of both effects. We choose to use the Hertzian contact theory instead of adhesive contact theories, because the modified van der Waals force in the presence of adsorption layer should be small.[15,16]

A schematic drawing of the contact with the capillary condensation is shown in Fig. 4. Adsorption layers, between the solid surfaces within a contact region, thickness D, and on the solid surfaces outside the contact, thickness e, are indicated. The sphere and meniscus radii are related by $R \gg r_2 \gg r_1$, such that

$$r_K = -\frac{\gamma_{LV} v}{kT \ln(P_v/P_{\text{sat}})} = \frac{r_1 r_2}{r_1 + r_2} \cong r_1, \tag{2}$$

where r_K is the Kelvin radius of the liquid, P_v is the vapor pressure, P_{sat} is the saturation pressure, and v is the molar volume of water. For a given value of RH, P_v/P_{sat}, values of

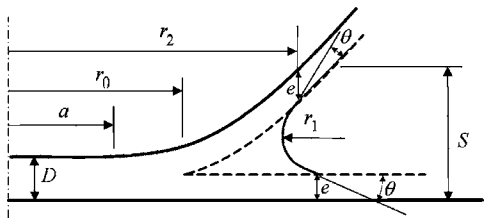

FIG. 4. Schematic drawing of capillary condensation. r_1 and r_2 are the meniscus radii in the vertical and horizontal planes respectively, a is the radius of the solid contact, e is the thickness of the adsorption layer, and D is the thickness of the confined layer. Vertical dimension exaggerated for clarity.

r_K and thus r_1 are specified. Within the meniscus, a Laplace pressure, $P_L = \gamma_{LV}/r_K$, acts to draw the sphere onto the surface over a radius r_0, where adsorption layers begin to overlap. The capillary has an annular projection and the capillary contact force, F_c, is thus

$$F_c = P_L \pi (r_2^2 - r_0^2) = \frac{\gamma_{LV}}{r_K} \pi (r_2^2 - r_0^2). \tag{3}$$

Mechanical equilibrium prescribes the separation, S, of the solid surfaces outside the contact due to the capillary forces as[22]

$$S = D + \frac{a^2}{\pi R}[(x^2-1)^{1/2} + (x^2-2)\tan^{-1}(x^2-1)^{1/2}], \tag{4}$$

where $x = r/a$ and a is the contact radius. Thermodynamic equilibrium between the solid, liquid, and vapor phases prescribes the separation S in terms of the meniscus height,

$$S = 2r_K \cos\theta + 2e. \tag{5}$$

Overall equilibrium is achieved by simultaneous, self-consistent solution of Eqs. (4) and (5) using Eq. (3) and setting $x = r_2/a$. An iterative, numerical scheme was used to do this and calculate meniscus forces for values of D and e.

We consider surface adsorption layers, which are estimated to be a single or double molecular layers based on van der Waals wetting theory.[15] During the contact formation, this layer is partially squeezed out, resulting in a single confined layer in contact area.[23] The capillary force under these considerations ($D = 0.25$ nm and $e = 0.35$ nm) is calculated to be 2.68 μN at 45% RH.

The calculated values of 2.57 μN and 2.68 μN at 45% RH using different assumptions agree with the measured difference in the pull-off forces between ambient air and vacuum (2.93 μN$\pm$0.42 μN) within the error range. The good quantitative agreement supports the idea that the difference is mainly due to meniscus force. The small residual difference between the experimental data and computed values is within the experimental uncertainty. It is noted that the van der Waals force components in ambient air and in UHV might be somewhat different[15,16] so that the meniscus force might be a little different from 2.93 μN.

Our calculations show small changes of capillary forces ($<10\%$) for RH between 5% and 90%. The existing theories based on continuum mechanics are not sufficient for precise computations of capillary forces at very low RH values.

In summary, our experimental and theoretical studies of adhesion between a gold sphere and a flat gold substrate indicate that the meniscus force dominates the pull-off force in ambient air (3.80 μN) and is not eliminated even after a few days of continuous nitrogen purge (2.21 μN). A much smaller pull-off force (0.87 μN) is measured in a vacuum where the meniscus is absent. In contrast, the snap-on forces measured in ambient air, nitrogen atmosphere, and a vacuum are essentially the same.

One of the authors (D. K.) acknowledges partial support by the Postdoctoral Fellowship Program of Korea Science and Engineering Foundation (KOSEF).

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