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Effect of relative humidity on onset of capillary forces for rough surfaces

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ABSTRACT

Atomic force microscopy (AFM) was used to investigate the effect of relative humidity (RH) on the adhesion forces between silicon nitride AFM probes, hydrophilic stainless steel, and hydrophobic Perspex® (polymethylmethacrylate, PMMA). In addition, AFM-based phase contrast imaging was used to quantify the amount and location of adsorbed water present on these substrates at RH levels ranging from 15% to 65% at 22 °C. Both the adhesion forces and the quantities of adsorbed moisture were seen to vary with RH, and the nature of this variation depended on the hydrophobicity of the substrate. For the Perspex®, both the adhesion force and the amount of adsorbed moisture were essentially independent of RH. For the stainless steel substrate, adsorbed moisture increased continuously with increasing RH, while the adhesion force rose from a minimum at 15% RH to a broad maximum between 25% and 35% RH. From 35% to 55% RH, the adhesion force dropped continuously to an intermediate level before rising again as 65% RH was approached. The changes in adhesion force with increasing relative humidity in the case of the stainless steel substrate were attributed to a balance of effects associated with adsorbed, sub-continuum water on the cantilever and steel. Hydrogen bonding interactions between these adsorbed water molecules were thought to increase the adhesion force. However, when significant quantities of molecular water adsorbed, these molecules were expect to decrease adhesion by screening the van der Waals interactions between the steel and the cantilever tip, and by increasing the separation distance between these solid surfaces when they were 'in contact'. Finally, the slight increase in adhesion between 55% and 65% RH was attributed to true capillary forces exerted by continuum water on the two solid surfaces.

1. Introduction

In many industrial applications where populations of micro-scale (or smaller) particles are involved, humidity has a controlling effect on process performance [1,2]. It is well-known that liquid bridges form between surfaces in close contact, depending on the system relative humidity (RH), and the local topography of the interacting surfaces. Capillary forces result from accumulation of continuum water which leads to liquid bridges [3]. Capillary forces contribute to the overall surface interactions and are larger in magnitude than both van der Waals and electrostatic forces. The liquid bridges are beneficial in certain applications, such as in wet granulation, where they contribute to the nucleation of granules, or in nanolithography where they are used to transport molecules between surfaces [4,5]. In other cases, they produce damaging effects, such as caking and flow resistance during powder processing or stiction in MEMS [6].

The behavior of adsorbed water molecules has been studied via adsorption isotherms, ellipsometry, NMR, surface force apparatus (SFA), and various other techniques [7,8]. Atomic force microscopy (AFM) allows for the accurate probing and investigation of the effects of adsorbed or condensed moisture. An AFM uses a scanning probe to obtain high resolution topographical images of surfaces or to make adhesion force measurements. These measurements can resolve the effects of adsorbed moisture, either in molecular or continuum form, with resolution down to the pN-scale [9,10]. In order to better understand the adsorption or condensation of water from the vapor phase onto a solid surface, phase contrast imaging can be used to evaluate the presence of moisture on the surface in a semi-quantitative manner as environmental conditions change. The presence of adsorbed moisture on a surface can be observed via phase imaging in tapping mode using amplitude modulated AFM (AM-AFM). This technique can also document the presence of water on a surface while simultaneously collecting topographical data. Combined with AFM-based adhesion force measurements, AM-AFM phase imaging relates surface heterogeneity at the nano-scale, adsorbed water, and adhesion forces [7,10,11].

Water molecules in humid air will minimize their free energy by adsorbing to rough surfaces at low humidity and by condensing into crevices on the surface at higher humidity [8,12]. Most studies of these effects have used highly idealized surfaces while neglecting surface roughness [8,13–15]. In AFM-based studies of adhesion

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forces between AFM cantilevers and smooth and rough surfaces at varying RH, a large variability was observed in the measured forces [14]. This was attributed to a multitude of factors which affected the capillary forces, forces between adsorbed molecular water layers, and the overall probe-sample interactions. These include the radii of curvature of the menisci of any condensed moisture and the cantilever tip, the thickness of any adsorbed molecular water films, the surface roughness, the cantilever tip size and shape, and the contact angles of water on both the probe and the substrate (i.e., the surface energies of the probe and substrate) [13]. A silicon nitride cantilever with a nanoscale probe tip was used in a representative study to measure adhesion forces against a nominally smooth SiO_2 surface over a range of RH. The measured adhesion force was observed to be independent of humidity until RH exceeded ~30%. As humidity continued to increase, the force rose until it reached a maximum at roughly 70% RH, after which the force dropped rapidly as 100% RH was approached. This study concluded that the drop in force at high RH could be explained based on the behavior of continuum water on the interacting surfaces, but that the behavior at low/intermediate RH could only be explained if water was assumed to exist in a molecular form on the surface [14].

A common trend observed in various humidity studies for hydrophobic surfaces is a weak dependence of adhesion forces on RH [2,8,14,15]. This can be attributed to the fact that the surface energy of hydrophobic substrates generally prevents water from condensing or adsorbing in molecular form.

Despite the fact that numerous studies have been devoted to finding a relationship between adhesion force and RH, AFM phase imaging has not been paired with adhesion force measurements as a means to relate directly the presence of moisture on the surfaces to the adhesion force. The main objectives of this work are as follows: (1) to use phase contrast microscopy to document and quantify, to the extent possible, the presence of moisture on substrates as a function of varying RH, (2) to investigate the effect of RH levels on measured adhesion forces, and (3) to correlate the RH, the corresponding phase contrast observations, and the adhesion forces in an attempt to interpret observed effects of humidity on the adhesion.

2. Adhesion forces

There are several forces of interest within this study, including van der Waals forces, capillary forces, and hydrogen bonding forces [3,16]. Electrostatic forces were minimized in this work by the application of a Staticmaster® polonium wand [8]. This wand was placed in the vicinity of the interacting surfaces during force measurement, where it acted to ionize the air. The ions subsequently adsorbed on the interacting surfaces to neutralize any surface charge, effectively eliminating electrostatic forces. The hydrogen bonding and capillary forces vary significantly with RH, such that they may be substantially weaker or stronger than van der Waals interactions depending on the environmental conditions and the surface energies of the interacting materials. When the air is "dry" (i.e., RH < 15%), van der Waals forces are generally dominant [17–19].

For macroscopic liquid bridging in idealized environments, the continuum model that is used to describe the meniscus is calculated using the Young–Laplace equation. The macroscopic pressure difference (ΔP_L) across a curved liquid–vapor interface in equilibrium is known as the Laplace pressure [20]. The shape of the liquid bridge can be described by two radii of curvature and is defined by:

$$\Delta P_L = \gamma\left(\frac{1}{r_p} + \frac{1}{r_n}\right) = \frac{\gamma}{r_k} \tag{1}$$

where r_p and r_n are the two principle radii of curvature of the liquid bridge (in-plane and normal to the surface), r_k is the effective radius of curvature or Kelvin radius, and γ is the surface tension at the liquid–vapor interface. If this liquid droplet bridges the space between two solid surfaces, then a capillary force will act to draw the surfaces together. The adhesion force arises when the pressure acts over a specific area of the two surfaces in contact with the liquid bridge [15]. For a sphere and flat surface composed of the same material, the capillary forces can be calculated by:

$$F_{cap} = A\Delta P_L = A\frac{\gamma\cos\phi}{r_k} \tag{2}$$

where A is the cross-sectional area of contact of the bridge and the sphere and ϕ is the contact angle between the liquid and the surface material. Assuming that water vapor and condensed liquid water are in equilibrium, one can develop the commonly-known Kelvin equation:

$$r_k = \frac{\gamma\cos\phi V_m}{RT}\frac{1}{\ln(P_v/P_{sat})} = \frac{\gamma\cos\phi V_m}{RT}\frac{1}{\ln(RH)} \tag{3}$$

where P_{sat} is the saturation pressure of the water vapor at the temperature and pressure of interest, P_v is the vapor pressure of water in the gas phase at the conditions of interest, and V_m is the molar volume of liquid water. In the case of incomplete wetting of a surface, the condensed liquid favors confined spaces such as surface crevices with width less than a critical distance D_c described by [15]:

$$D_c = 2r_K\cos\phi \tag{4}$$

While the Kelvin equation is of great utility for macroscopic, continuous systems, its application is problematic on the nanoscale because it requires the liquid medium to be continuous, the meniscus shape to be circular, and the radii of the interacting surfaces to be much greater than either of the meniscus radii. For example, at 50% RH and 20 °C, the Kelvin critical distance for water is 1.4 nm on stainless steel. Since water has an effective diameter of 0.37 nm, the water would have to form a circular meniscus with less than four molecules for Eq. (3) to be valid. Therefore, the Kelvin equation cannot completely describe the dependence of the adhesion force on RH in this study.

Alternatively, hydrogen bonding between adsorbed, sub-continuum water molecules can be used to describe interactions between the cantilever tip and a substrate at low RH as noted by [21,22]. At RH levels below 60–65%, molecularly adsorbed moisture may exist between solid surfaces in near-contact, and this water may form hydrogen bonding networks that bridge the two surfaces. Such interactions would enhance the existing van der Waals interactions between these surfaces. The strength of hydrogen bonding interactions can be approximated by:

$$E_{HB} = \frac{\alpha}{D^{3.8}} \text{ or } F_{HB} = \frac{-3.8\alpha}{D^{4.8}} \tag{5}$$

where E_{HB} is the potential energy of the hydrogen bonding interaction between two molecules, α is a fit function, D represents the separation distance between the interacting molecules, and F_{HB} is the force of the hydrogen bonding interaction between two water molecules [17]. Hydrogen bonding between water molecules has been estimated to have a dissociation energy of ~220 meV/molecule, with hydrogen bond lengths ~2.9 Å [18].

This is congruent with recent studies [22–24]. As observed using attenuated-total-reflectance infrared spectroscopy (ATR-IR), ice-like layers of adsorbed water form on a silicon dioxide surface due to the strength of interaction between water and silicon dioxide. These ice-like layers of water grow to be approximately 3 molecules thick (~0.8 nm) at 30% RH and influence the orientation of subsequent water layers until 60% RH where the adsorbed water