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Analysis of humidity-dependent adhesion between a probe tip and a surface

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ABSTRACT

Adhesive forces commonly exhibit a monotonic increase or a maximum with increasing relative humidity. However, anomalous behavior has been reported. Here, a numerical model of adhesive forces, comprised mainly of capillary and van der Waals forces, between a tip and a surface is established. It is described by a power law that considers the geometry, the liquid bridge wetting radius, the contact angle, and the separation distance. Capillary forces (sum of surface tension and Laplace pressure) and van der Waals forces are calculated. The latter cannot be neglected in the adhesion even at high humidity. Decrease in adhesion with increasing relative humidity can be attributed to a blunt tip shape, which is validated by experimental data. Specifically, the decrease in adhesion is attributed primarily to a transition from a rounded to a blunt tip shape. Structuring objects at the micro- or nanoscale can either increase or decrease adhesion as a function of relative humidity. This has a wide range of applications in robotic manipulation and can provide a better understanding of adhesion mechanisms in atomic force microscopy in ambient air.

Introduction

Adhesive forces underlie gripping mechanisms and can be used to align, assemble, or deform objects at the nanometer scale (Lambert & Delchambre, 2005; Ondarcuhu & Aime, 2013; Pepin, Rossetti, Iveson, & Simons, 2000). They must be maximized in gecko-like nanomaterials (Çolak, Wormeester, Zandvliet, & Poelsema, 2015), and minimized in electro-mechanical systems and in semiconductor wafer handling. In precise atomic force microscope (AFM) manipulations, nanometer-scale adhesive forces occur when pulling two solids apart. Small adhesive forces enable stable measurements during AFM scans (Vögeli & von Känel, 2000; Wan, Smith, & Lawn, 1992). However, the behavior of micro-scale objects cannot be predicted before performing experiments at the micrometer scale. Therefore, to control behavior at micro- or nanometer scales, numerical models of adhesive forces have to be established.

The effect of relative humidity on adhesive forces between a probe tip and a flat surface varies (Dörmann & Schmid, 2015; Köber et al., 2010; Pakarinen et al., 2005; Yaqoob, De Rooij, & Schipper, 2013). In many experiments, the adhesion exhibited a maximum or continuously increased with humidity (Ferreira, Gelinck, de Graaf, & Fischer, 2010; Paajanen, Katainen, Pakarinen, Foster, & Lahtinen, 2006). However, a counterintuitive decrease in adhesion between hydrophilic surfaces with increasing relative humidity was reported by Köber et al. (2010). The observations of Köber et al. (2010) were attributed to the hindered growth of the liquid meniscus at a truncated tip; only a blunted tip induced this behavior. However, other reports (Dörmann & Schmid, 2015; Ferreira et al., 2010; Paajanen et al., 2006; Pakarinen et al., 2005; Yaqoob et al., 2013) indicate that the growth of a liquid bridge is a function of not only tip shape but also contact angles and the tip-surface distance. Thus, a fundamental understanding of this counter-intuitive behavior is needed.

Here, we present a method to precisely calculate the adhesive force between a probe tip and a surface under ambient conditions, by considering the tip shape, the liquid bridge wetting radius, the contact angle, and the tip-surface separation. The force mainly consists of van der Waals and capillary forces (surface tension and Laplace pressure forces). Van der Waals forces are not negligible, and the adhesive force decreases monotonically with humidity for a blunted tip at a short separation distance ($\leq$0.3 nm). Numerical solutions of the proposed model are compared with experiments. When the tip shape changes from round to blunt (e.g., a flat punch),

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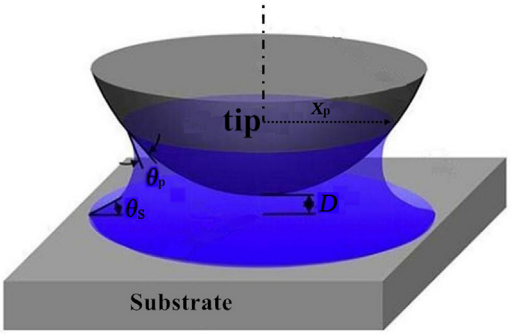

Fig 1. Schematic of the liquid bridge between an AFM probe tip and the substrate. θ_p is the contact angle of the liquid with the probe, θ_s is the contact angle of the liquid with the substrate, x_p is the horizontal distance of intersection between the meniscus and the probe tip (liquid bridge wetting radius), and D is the tip-substrate vertical separation distance.

the adhesive force changes from the cross over behavior to a monotonic decrease with humidity.

Theoretical model

Köber et al. (2010) performed adhesion measurements between a flat mica surface and silicon tip with three different shapes under humid conditions. In this study, we employed a concave-shaped liquid bridge model (Fig. 1) to describe their measurements between the hydrophilic surfaces (Yang, Nosonovsky, Zhang, & Chung, 2008). In our model, Deformation, surface roughness, and gravitational forces on the liquid were not considered (Butt & Kappl, 2009). Capillary (F_{cap}) and van der Waals (F_{vdW}) forces usually dominate others when a liquid bridge forms between a tip and a substrate (Fisher, 1926). Adhesive forces can thus be expressed as the sum:

$$F_{ad} = F_{cap} + F_{vdW}. \tag{1}$$

F_{cap} derives from capillary condensation, which can be expressed as (Xiao & Qian, 2000):

$$F_{cap} = 2\pi\gamma x_p \ \sin(\beta+\theta_p) + \pi x_p^2 \Delta p, \tag{2}$$

where $\gamma = 0.072$ N/m is the surface tension coefficient of water and x_p is the wetting radius of the liquid bridge, which is dependent on tip shape, separation distance, and humidity. β is the slope of tip contour at point x_p that describes the position of the contact line of the liquid on the tip. If $y(x)$ denotes the tip geometry, then β may also be calculated from $\beta = \arctan(y'(x))$ (Yang, Hu, & Qin, 2014). In Eq. (1), the surface tension component F_s of F_{cap} originates from surface tension at the interface between the fluid and gas phases, while the Laplace pressure force component F_p arises from the pressure differential Δp between the meniscus and the surrounding air. Δp is obtained from the Laplace Equation (Dörmann & Schmid, 2015):

$$\Delta p = \frac{\gamma}{r_k} = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{3}$$

here, r_k is the (negative) Kelvin radius, and r_1 and r_2 are the two principle curvature radii of the liquid bridge (in plane and normal to the surface, respectively), which are opposite to each other.

Assuming thermodynamic equilibrium, the Kelvin equation is (Nosonovsky & Bhushan, 2011):

$$r_k = \frac{\gamma v_m}{RT \ \ln(p/p_s)} = \frac{0.54}{\ln(p/p_s)} \tag{4}$$

where v_m is the molecular volume of water, R is the universal gas constant, T is the temperature (in K), p/p_s is the ratio of ambient to saturation pressures, and p/p_s is the relative humidity (RH). The value 0.54 assumes that the substrate is water at room temperature ($v_m = 0.018$ L/mol, $T = 300$ K, and $R = 0.082$ (L atm)/(mol K)) (Butt & Kappl, 2009). Based on the circular approximation, r_1 and r_2 can be given by:

$$r_1 = \frac{y(x_p) + D}{\cos(\beta+\theta_p) + \cos\ \theta_s}, \tag{5}$$

$$r_2 = x_p - r_1[1 - \sin(\beta+\theta_p)]. \tag{6}$$

For given values of RH and $y(x)$, the Kelvin radius r_k is calculated from Eq. (4), the wetting radius x_p, tip contour slope β can be calculated from Eqs. (3), (5), and (6), and F_{cap} is calculated from Eq. (2).

The classical expression for van der Waals forces is a pair-wise summation of Lennard–Jones potential energy (Hamaker, 1937). For simplicity, the capillary force in basic contact geometries (flat, sphere, cone, cylinder) is commonly used to describe adhesion between hydrophilic surfaces, and van der Waals forces are omitted or simplified in terms of the van der Waals equation for a sphere/plane geometry (Xiao & Qian, 2000). However, these simplified approaches would produce errors in the calculation of adhesive forces when tip shapes are not basic geometric shapes and the distance is short (Argento & French, 1996). From Hamaker (1937), surface element integration can be used to calculate the van der Waals interaction:

$$F_{vdW}(h) = \int V(h)dS(h), \tag{7}$$

where S is the wetted or dry area of the tip. The infinitesimal element of the surface dS on the end of the tip is $dS = 2\pi x dh$. V_{flat} is the interaction potential per unit area between surfaces:

$$V(h) = -\frac{H}{12\pi h^2}, \tag{8}$$

where H is the Hamaker constant, and $h = D + y(x_p)$ is the distance between surface elements. The potential consists of four terms (Yang et al., 2014) arising from the interaction energy between the wetted part of surface 1 and surface 2, that between the wetted part of surface 2 and surface 1, that between the dry part of surface 1 and surface 2, and that between the dry part of surface 2 and surface 1. The calculation of F_{vdW} is separated into the wet and dry surfaces of the tip. If the tip surface is wet for $0 \le y \le y(x_p)$ and dry for $y(x_p) \le y$, then:

$$F_{vdW} = \frac{H^{water}}{6}\int_0^{x_p} \frac{\partial S(x)}{\partial D}dx + \frac{H^{air}}{6}\int_{x_p}^{\infty} \frac{\partial S(x)}{\partial D}dx, \tag{9}$$

where H^{water} and H^{air} are the Hamaker constants for the wet (water) and dry (air) surfaces, respectively. F_{vdW} between an arbitrarily shaped tip and a substrate in the presence of a water bridge in the gap is given by:

$$F_{vdW} = -\frac{H^{water}}{3}\int_0^{x_p} \frac{x}{[D+y(x)]^3}dx - \frac{H^{air}}{3}\int_{x_p}^{\infty} \frac{x}{[D+y(x)]^3}dx. \tag{10}$$

Because there is no specified probe geometry, Eq. (10) yields the exact F_{vdW} on the probe.

Calculation of F_{vdW} requires only knowledge of $y(x)$, while x_p is determined by $y(x)$ and RH. A blunt tip is common in AFM experiments when the original tip is worn by tens or hundreds of consecutive measurements (Killgore, Geiss, & Hurley, 2011; Kopycinska-Müller, Geiss, & Hurley, 2006). In many tip-wear studies, the AFM tip shape is usually not ideal and may be described by a power-law function (Borodich, Keer, & Korach, 2003; Grierson, Liu, Carpick, & Turner, 2013; Han, Jiang, Jing, Prewett, & Jiang, 2011). Therefore, here, a tip with a slightly flattened apex can be described by the nonlinear power function $y(x) = |kx^n|$, where k is constant,

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