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Influence of Relative Humidity on Interparticle Capillary Adhesion

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\textbf{Abstract}

A homemade instrument is designed to directly characterize the adhesion between two rigid polymeric micro-spheres in the presence of moist air. The tensile load is measured as a function of approach distance at designated relative humidity (RH). The measurement is consistent with our model from the first approximation. The model is further extended to include a rough surface. Capillary adhesion force is shown to be monotonically increasing with RH for smooth surfaces but becomes more pronounced at low RH for rough surfaces. Moisture has a profound influence on interparticle adhesion which has significant impacts on a wide range of industrial applications.

\textbf{Keywords:} adhesion, humidity, particle, surface roughness, capillary

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1. Introduction

When two lyophilic surfaces are brought to proximity in the presence of vapor as an intervening medium, condensation results in a liquid meniscus at the narrow gap in the vicinity of the intimate contact. The phenomenon appears ubiquitously in many systems, such as granular materials, colloid particles and sandy soils. One inevitable consequence is the increase in interparticle adhesion in the presence of moisture, resulting in powder aggregation and coagulation. It is therefore crucial to investigate the influence of humidity dependent capillary force in, for instance, food processing, pharmaceutical mixtures, powder handling, aerosol suspension and biomaterial dehydration. Such studies are in fact fundamental to estimate the performance and lifespan of micro-/nano-electromechanical devices and nano-structures.

A number of advanced instruments are capable of quantifying adhesion, namely, surface forces apparatus - SFA, force feedback microscope, force traction device, and atomic force microscopy - AFM. AFM is by far the most prevailing technique to investigate nano- to pico-Newton range forces with nano-meter actuation displacement and is apt to measure the “pull-off” force or the critical tensile load to detach two adhered bodies such as a particle on a substrate. Equipped with an environmental chamber, adhesion in moist air can be accurately measured in systems such as microparticles on oxide surface, AFM tip interaction with a smooth or patterned surface, pollen on hydrophilic surfaces, micro-/nano-particle interactions. Despite the wide applications, AFM is limited to probes with nano-scale dimension. Governed by similar working principles, SFA measures the intersurface interaction force between the two approaching atomically smooth cylindrical surfaces by detecting the deflection of a cantilevered spring attached to one of the cylinders.
SFA allows measurements of large bodies in millimeter scale, as well as liquid bridge in sub-millimeter scale. SFA meets many successes in adhesion between rough surfaces, evaporation and condensation of the meniscus in slits and pores, and gecko-inspired microfibrillar surfaces. These celebrated instruments, however, have their intrinsic limitations. One major shortcoming is the inadequate capability to investigate capillary forces between two micron-scale bodies.

Theoretical models are available in the literature to discuss the influence of humidity on the critical “pull-off” to detach adhered solid bodies. In essence, the classical Kelvin equation describes the mean curvature of meniscus, and the Young–Laplace equation yields the Laplace pressure behind the meniscus. Several analytical models, i.e., first-order approximations describing the interrelationship between the meniscus profile and the separation distances of two spherical surfaces, are quite successful in fitting the measurement of adhesion force-displacement curve or mechanical compliance. Recent numerical models and simulations have offered more detailed considerations in the exact shape of the liquid bridge and the influence of van der Waals attraction. Several models incorporate surface roughness in the adhesion models, including liquid bridge capillarity between two rough parallel surfaces and particle-wall impaction subject to a range of humidity. Previous studies demonstrated that surface roughness plays a critical role in the humidity-dependency of the adhesion force because capillary mainly forms between asperities. However, the influence of surface roughness upon capillary force between two rigid spherical microparticles is yet to be fully addressed. Here “rigid” refers to negligible deformation of the microspheres when subject to sub-mN range external forces.

In this study, we develop a new homemade instrument to characterize the detachment of two adhered polymer microparticles in a controllable humid environment.
environment. A theoretical model is constructed to analyze the measurements based on the capillary force at variable RH as well as the influence due to surface roughness.

2. Experimental

2.1. Experimental Setup

A homemade instrument was designed to simultaneously measure applied force and displacement between two particles held together by a meniscus bridge within a humidity chamber (Figure 1). An ultrasensitive force transducer probe (Aurora Scientific, 406A) with sensitivity in 10 nN range was driven by a micro-stepper stage (Newport, UTS 100CC with ESP301 Motion Controller) in the vertical or Z-direction with a resolution of 10 nm. Alignment of the particle along the same axis was achieved by an X-Y motorized stage (Prior Scientific, H117P1T4) with 100 nm resolution in both X and Y directions. A data acquisition system (National Instruments, SCC-68) was installed to receive simultaneous outputs from both the force transducer and the Z-stage to generate the force-displacement curves. A computerized control panel based on LabVIEW software (National Instruments, LabVIEW 2016) synchronized the X-Y stage movements and force sensing. The sample spheres as well as the actuator-force sensor unit was sealed inside an optically transparent chamber which regulated the RH by a humidity controller (ibidi GmbH, Gas Mixer M-323). An optical microscope equipped with an ultra-long focal length objective (Edmund Industrial Optics, VZM 450), a CCD camera (Sony, XC-ST50CE) and an image acquisition system monitored the loading-unloading process in-situ. The surveillance system allowed side-view with magnification up to 100× from outside the environmental chamber through a transparent acrylic window. The entire setup was mounted on an anti-vibration table (Wentworth Laboratories Ltd, ATV 702).
2.2. Experimental Procedure

Polymethyl methacrylate (PMMA) particles with a diameter in the range of 700 to 900 µm (EPRUI Biotech Co. Ltd, PRC) served as the sample spheres. Two such particles with similar dimensions (ca. 800 µm in diameter) were adapted for the present study. The top sphere was attached to a force transducer, while the bottom sphere was firmly glued to a planar glass slide to avoid undesirable sliding or rolling during the contact process. The two spheres were aligned by the X-Y stage along the loading axis. The long-focal CCD microscope was used to monitor the movement from the side-view in two orthogonal directions to ensure a pole-to-pole alignment. The top sphere was then lowered by the Z-stage and brought into contact at the poles (see Figure 2). The humidity controller regulated the RH in the chamber tile to reach a desirable RH ranging from 60 to 95%. The mechanical response of the detachment process was measured as the top sphere was retracted until the meniscus bridge broke and the two spheres separated.

2.3. Surface roughness measurement

Surface topography and roughness of the PMMA spheres were characterized by AFM tapping mode (Bruker, Innova) with a line-by-line scanning of 256 sampling points per line over a 5 × 5 µm² at a rate of 0.25 Hz. The silicon AFM cantilever had a spring stiffness of 3 N/m (Bruker, RFESP). Image processing, analysis, and root mean square (RMS) roughness were carried out by Gwyddion (Gwyddion, v2.56) and MATLAB (MathWorks, 2017b).

3. Data Analyses

3.1. First-order approximation
Based on the existing models, the meniscus surface parallel to the symmetry axis is a circular arc of radius $r$ between two identical spheres with radius $R_s$. Figure 3 shows the two principal radii $l$ and $r$ of the capillary with $R_s \gg l \gg r$. Gravity, other intersurface interactions between the sphere such as van der Waals, and compressive stress on the spheres due to Hertz contact deformation are ignored, in reminiscent of the classical Bradley model. The capillary force $F_{cap}$ is given by

$$F_{cap} = -\pi l^2 \Delta P + 2\pi \gamma l$$

(1)

The first term in equation (1) is the attraction force due to the Laplace pressure, $\Delta P < 0$, acting at the neck of the water bridge with a cross-section area of $\pi l^2$. The second term indicates the liquid-air surface tension $\gamma$, a tensile force pulling on the two spheres.

At thermodynamic equilibrium, the Young–Laplace equation requires

$$\Delta P = \gamma \left(\frac{1}{l} - \frac{1}{r}\right)$$

(2)

and the Kelvin equation

$$\bar{R}T \ln \frac{P}{P_0} = V_m \Delta P$$

(3)

with the gas constant $\bar{R} = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$, $T$ the absolute temperature, $P$ the vapor pressure, $P_0$ the saturation vapor pressure, RH = $P / P_0$, and $V_m$ the molar volume of liquid water. Combining equations (2) and (3), a Kelvin length, $\lambda_K$, is defined as:

$$\lambda_K = \frac{\gamma V_m}{\bar{R}T} = \left(\frac{1}{l} - \frac{1}{r}\right)^{-1} \ln \frac{P}{P_0}$$

(4)

At 25 °C, $P_0 = 3.17$ kPa, $\gamma_{water} = 71.99$ mN/m, and $\lambda_K = 0.52$ nm. For $R_s \gg l \gg r$, equation (4) reduces to

$$\lambda_K = r \ln \frac{P_0}{P}$$

(5)
At the triple junction of air-solid-liquid, or three-phase contact line, the filling angle $\beta$ and the liquid contact angle $\theta$ are defined in Figure 3. For simplicity, a convenient parameter is defined as

$$c = \cos(\theta + \beta)$$

(6)

Several limiting cases are noted: (i) In case of a clean hydrophilic surface, $\theta = 0$ and $c = \cos \beta$; (ii) for small contact circle compared to the sphere radius ($l << R_s$), $\beta = 0$ and $c = \cos \theta$; and (iii) in case of a clean surface and small contact area, $c = 1$. If the meniscus volume, $V_s$, is assumed to be constant, the capillary force becomes

$$F_{\text{cap}} = 2\pi \gamma c R_s \left( 1 - \frac{D}{\sqrt{\pi R_s + D^2}} \right)$$

(7)

with $D$ the axial pole-to-pole separation. Kohonen et al. 37 derived an approximation for the transient growth rate of the meniscus radius $r$ that leads to ultimate equilibrium

$$\frac{dr}{dt} = \frac{2D_d M_W P_0}{\rho R T R_s} \left( \frac{P}{P_0} - e^{-\frac{\lambda_k}{r}} \right)$$

(8)

with $D_d = 2.5 \times 10^{-5}$ m$^2$/s the diffusion coefficient of the surrounding vapor at 25 °C, $M_W$ the molar mass of the liquid molecules, and $\rho$ the liquid mass density. Approaching equilibrium, the meniscus growth grinds to a halt (c.f. equation (5)). As the spheres are now gradually pulled apart, $D$ increases, the capillary is stretched vertically, and $r$ exceeds $\lambda_k$ accordingly and temporarily. To reestablish equilibrium, the meniscus shrinks following equation (8) which requires $dr/dt < 0$. Maximum shrinking speed, $v_{\text{max}} = -(dr/dt)$ is reached when $r >> \lambda_k$. At RH = 95%, the predicted $v_{\text{max}} \approx 0.14 \mu$m/s. In our experiment, the top sphere retracted at 1 µm/s >> $v_{\text{max}}$. The liquid bridge volume is hereafter assumed to be a constant. Under fixed load, the two smooth spheres detach from each other when $D = 0$ at “pull-off”. Equation (7) requires the external tensile load to reach a threshold of
\[ F^* = -2\pi \gamma c R_s \]  

which depends on \( \gamma, R_s \), and \( c \) only. In case of \( \theta = 0 \) and \( l \ll R_s \), \( c = 1 \) and 
\[ F^* = -2\pi \gamma R_s, \]

which matches with the Derjaguin-Muller-Toporov (DMT) model \(^{38}\) of adhesion between two identical spheres. It is remarkable that \( F^* \) does not depend on RH and the size and volume of the meniscus due to the fact that low RH leads to small \( r \) and \( l \) but large \( \Delta p \) and the converse is true for high RH (c.f. equation (3)). It is noted that \( F^* \) is the last equilibrium state upon loading based on thermodynamic energy balance. If the two particles are pulled apart at a slow velocity, the water bridge continues to be stretched further while the external load diminishes until “pull-off” under fixed-grips.

3.2. Numerical model

The geometrical profile of the capillary bridge can be found using the Dörmann and Schmid (abbr. DS hereafter) model \(^{27,39}\). Center of upper sphere is set as the frame of reference, and the line connecting the two-sphere centers serves as the \( x \)-axis as shown in Figure 3. The two spheres separated by a distance, \( D \), are held by an external tension, \( F; F = -F_{\text{cap}} \). The meniscus spans \( 0 < y < R_s \sin \beta \) and \( D < h < R_s \cos \beta \) . Rather than assuming a circular arc, the meniscus is divided into a series of vertices connected by piecewise linear segments. A gradient is computed based on the neighboring vertices before it is integrated over the meniscus to yield the overall geometry, \( y(x) \). The angle \( \beta \) is given an arbitrary value as that in the first approximation. The triple junction is labeled vertex 1 with coordinates \( (R_s \cos \beta, R_s \sin \beta) \) in the 2-D cross-section. Gradient of the segment joining vertices 1 and 2 is 
\[ \nabla_1 = -\cot(\theta + \beta), \]

and vertex 2 is therefore given by \( (R_s \cos(\beta + ds), R_s \sin(\beta + \nabla_1 ds)) \), with \( ds \) the trajectory along the meniscus arc. The two principal radii of \( r_1 \) and \( r_2 \) of the meniscus is governed by the classical Young–Laplace equation (c.f. equation (2)) where \( r \) and \( l \)
are replaced by \( r_1 \) along the arc and \( r_2 \) from the symmetry axis in the \( x \)-direction. Radius of curvature \( r_1 \) is defined as

\[
r_1 = \frac{[1 + y''^2]^{3/2}}{y''}
\]

with the operator \( ' = \frac{d}{dx} \). Gradient of the segment connecting vertices \( i \) and \( i+1 \) is \( \nabla_i = \frac{dy}{dx} \big|_i \) for \( 1 \leq i \leq n \). The procedure iterates until the arc reaches the triple junction on the lower sphere surface where \( i = n \). The profile is symmetric about the \( x \)-axis such that \( x_i = x_n \) and \( y_i = -y_n \). Convergence is ensured with \( |y_i - y_{i+1}| < 10^{-11} \) m. The capillary volume \( V_{DS} \) is found by

\[
V_{DS} = \sum_{i=1}^{n-1} \frac{\pi}{3} (y_i^2 + y_{i+1}^2 + y_i y_{i+1}) (x_{i+1} - x_i) - 2 \times \frac{\pi}{3} R_s^3 (2 + \cos \beta) (1 - \cos \beta)^2
\]

where the summation is performed over the conical frustums of infinitesimal height from the lower to upper triple junctions. The second term corresponds to the volume of the upper and lower spherical caps of the solid spheres interacting with the meniscus. The computed \( V_{DS} \) is checked against \( V \) from the first-order approximation. In the case of \( V_{DS} > V \), a smaller value of \( \beta \) is chosen to recompute \( y(x) \) and \( V_{DS} \). The numerical process is iterated using a MATLAB (MathWorks, 2017b) code until \( V_{DS} \) converged to \( V \) within the limit (<10\(^{-22}\) m\(^3\)).

Attraction between the spheres is found in terms of the midplane radius at the bridge neck \( (r_{neck} = x_n/2) \), which is balanced by the applied tension on the particles

\[
F = \pi r_{neck}^2 \Delta P - 2\pi r_{neck} \gamma
\]

In the limit of \( r_{neck} \) approaching \( r \) from the first approximation, the second term becomes negligible and \( F \) reduces to equation (9) at “pull-off”. Running the algorithm with an increasing \( D \) as shown in Figure 4, the function of theoretical \( F(D) \) is established.
3.3. Influence of surface roughness

Adhesion force or pull-off force between the two adhering particles does not depend on RH in theory. However, the literature reports RH dependency\textsuperscript{15,32,40,41}, prompting the vital role of intrinsic roughness of the contacting surfaces. The Kelvin length $\lambda_K = 0.52$ nm for water meniscus is a logical gauge of surface roughness. Should the root-mean-square (RMS) roughness fall short of $\lambda_K$, area bounded by the meniscus is fully submerged in water, the particles are smooth and equation (9) is valid. Conversely, if surface roughness is of the same order of magnitude as $\lambda_K$, meniscus at the interface becomes fragmented at the asperities rather than a continuous sheet, which is particularly true at low RH. Thus, $P^*$ depends on the distribution of asperities over the contact surface and the associated volume of meniscus bridges. As RH rises, the scattered bridges coalesce resulting in a continuous water sheet at the interface.

Butt introduced a model to incorporate surface roughness into inter-particulate adhesion mechanics\textsuperscript{20}. Figures 5a, 5b and 5c show the schematic of the formation of capillary between two rough surfaces under different RH conditions. Here the capillary assumes cylindrical shape and vapor condenses at the interface for $D < 2cr$. For a specific surface, a roughness function, $\varphi$, is assigned, which is defined as the probability of finding an asperity with a height of $\delta$. It is apparent that $\int_{-\infty}^{\infty} \varphi_1(\delta) d\delta = 1$. For two contacting surfaces with $\varphi_1$ and $\varphi_2$, an effective interface roughness $\varphi(\varphi_1, \varphi_2)$ is defined.

A shape function $g'(h)$ is the probability of finding the surfaces to be perfectly smooth at $h$. A height distribution $g(h)$ is defined as the convolution of $\varphi(\varphi_1, \varphi_2)$ and the general surface shape function $g'(h)$.

$$g(h) = \int g'(\zeta) \varphi(\zeta - h) d\zeta$$  \hspace{1cm} (13)
An integrated height distribution $G(h)$ is related to the height distribution $g(h)$ by

$$G(h) = \int_{-\delta_{\text{min}}}^{h-\delta_{\text{min}}} g(\zeta) d\zeta \quad (14)$$

$\delta_{\text{min}}$ is the maximal asperity heights (c.f. Figure 5c). The external tension threshold thus becomes

$$F^* = -A_0 G(h) \frac{Y}{r} \quad (15)$$

where $A_0 = \pi R_s^2$ serves as a reference area. Without loss of generality, the two particles are taken to be identical such that

$$g'(h) = \frac{1}{R_s^2} (R_s - \frac{h}{2}) \quad (16)$$

It is further assumed that $\varphi_1 = \varphi_2$, the asperities are uniformly distributed and are characterized by height ranging from $-\delta_0/2$ and $\delta_0/2$ as shown in Figure 6a. The effective surface roughness thus becomes

$$\varphi(\delta) = \int_{-\delta_0/2}^{\delta_0/2} \varphi_1(\zeta) \varphi_2(\delta - \zeta) d\zeta$$

which yields

$$\varphi(\delta) = \begin{cases} \delta_0 + \delta & \text{for } -\delta_0 \leq \delta \leq 0 \\ \frac{\delta_0^2}{\delta_0^2} & \text{for } 0 < \delta \leq \delta_0 \end{cases} \quad (17)$$

Substituting equations (16-17) into (13), equation (14) becomes

$$G(h) = \begin{cases} \frac{h^3}{6\delta_0^2 R_s} & \text{for } 0 \leq h < \delta_0 \\ \frac{1}{6\delta_0^2 R_s} [h^3 - 2(h - \delta_0)^3] & \text{for } \delta_0 < h \leq 2\delta_0 \\ \frac{1}{R_s^2} [(R_s - h)(h - \delta_0) + 2\delta_0] \approx \frac{h - \delta_0}{R_s} & \text{for } h \geq 2\delta_0 \end{cases} \quad (18)$$

Substituting equations (5) and (18) into equation (15), $|F^*|$ can be found as a function of RH, provided the surface roughness is known.
4. Results and Discussion

Figure 7a shows the applied tension on the upper sphere measured as a function of distance, $F(D)$, at RH = 95%. At $D = 0$, the spheres were at point contact and were pulled together by the capillary force, while the applied load reached its maximum tension of $F^*$ or pull-off force under fixed load. For $D < 0$, the spheres were slightly compressed such that $|F| < |F^*|$. For $D > 0$, the spheres detached from each other but were held together by a meniscus pillar. At $D^\dagger$, the meniscus collapsed and $F$ vanished hereafter. The 1st order approximation (equation (7)) is fitted to the measured $F(D)$ by least-squares to determine $V$ and $c$, which are then inputted to the DS model to generate the meniscus geometry and the capillary force. Both models are consistent with the measurements.

Figure 7b shows the experimental $F(D)$ relations at specific RH. The applied load is normalized with respect to the classical DMT pull-off force $(F^*)_{DMT} = -2\pi R_s^* \gamma$ from equation (9), where separation $D$ is made dimensionless by $R_s^*$, the effective radius of the sample spheres, $R_s^* = \left(\frac{1}{R_s} + \frac{1}{R_s}\right)^{-1} = \frac{R_s}{2}$. Here $F^* = F(D=0)$.

Figure 8 shows the monotonic increasing measured $|F^*|$ in the range of RH = 60% to 95%. Fitting the surface roughness model to experiment using equations (15) and (18) yields a characteristic asperity height $\delta_0 = 0.77$ nm. At RH = 95%, $r \approx 10.14$ nm $>> \delta_0$, indicating submergence of all asperities by a water sheet within the nominal contact radius and $F^*$ is dominated by $R_s$ instead of surface roughness. Since $\beta/\theta < 0.01$, $c = \cos(\theta + \beta) \approx \cos \theta$. The contact angle of the three-phase solid-liquid-vapor interface is associated with material chemistry and topography, and by and large
remains constant regardless of RH \[^{42,43}\]. At RH = 95%, \( c = 0.27 \) and \( \theta = 74.48^\circ \), matching the literature value of 68° in PMMA-water interface \[^{44}\].

To map the topography / roughness of typical PMMA spheres over the curved surface using AFM Z-scan, a polynomial background leveling algorithm \[^{45}\] was implemented to correct the sphere curvature. Figure 9a shows typical AFM measurements. Figure 9b the corresponding RMS roughness maps in 8×8 pixels, where the area average RMS were calculated, for instance, Area 1 being 2.2±0.4 nm and Area 2 being 2.7±0.4 nm. The outliers of extreme hills and valleys (i.e., RMS > 15 nm) are rare and ignored in computing the area average RMS. Figure 9c shows Gaussian distribution of asperity height, contrasting the uniformity in Butt’s model. The standard deviation \( \sigma \) is calculated as 1.8 ± 0.4 nm (c.f. Figure 6b).

Figure 10 shows the theoretical effective surface roughness function \( \varphi_{\text{Butt}} \) based Butt’s uniform asperity approximation (c.f. equation (18)), contrasting our measurement \( \varphi_{\text{Exp}} \) based on convoluting two Gaussian functions with the expectation mean \( \mu = 0 \) and standard deviation \( \sigma = 1.8 \) nm. Discrepancy between \( \varphi_{\text{Butt}} \) and \( \varphi_{\text{Exp}} \) can be understood by noting

1. The AFM measurement shown in Figure 9c conforms better to a Gaussian distribution than Butt’s uniform distribution approximation.
2. Though PMMA possesses a relatively high Young’s modulus (ca. 3 GPa), elastic deformation of the asperities is inevitable due to the high local contact stress.
3. At low RH, when the gap \( D \) shrinks down to molecular scale, water molecules with a diameter of 2.75 Å behaves anomalously and ceases to behave as a continuum \[^{46}\]. Dimension of two water molecules bonded by a typical
hydrogen bond is roughly 0.84 nm, which is comparable with the Kelvin length $\lambda_K = 0.52$ nm.

Butt’s approximation predicts reasonably well the mechanical response $F(D)$. Our measurement verifies that the humidity-dependent adhesion force can be modeled by the surface roughness independently measured by AFM.

5. Conclusions

A homemade instrument was built to characterize adherence between two microspheres in the presence of moist air. The constitutive relation $F(D)$ to detach two identical spheres was measured as a function of RH and shown to be consistent with first-order approximation and the numerical DS model. Surface topography mapped by AFM was incorporated into a surface roughness model to account for adhesion behavior. We have shown that the adhesion force increases with RH. Moisture-induced adhesion between particles plays a crucial role in developing innovative materials, such as biologically inspired capillary adhesive materials 47.

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Figure captions

1. The schematic of the experimental setup (not to scale).

2. Micrographs of the PMMA spheres in contact.

3. Liquid bridge between two identical spheres with radius $R_s$ with the filling angle $\beta$ and contact angle $\theta$. The inner dark gray and outer light gray areas denote the capillary based on the first-order approximation and DS model respectively. First vertex in the computational model begins on upper sphere surface.

4. Flowchart to compute $F(D)$ based on DS model.

5. Capillary bridges (a) isolated bridge connecting asperities at low RH; (b) multiple isolated bridges at an intermediate RH; (c) bridges coalesced to form continuous water sheet at high RH.

6. (a) Uniform surface roughness function $\varphi_1$ and the effective surface roughness function $\varphi$ in Butt’s model. (b) Measured surface roughness fitted to Gaussian distribution with $\mu = 0$ and $\sigma = 1.8$ nm.

7. (a) Typical force-distance ($F$-$D$) measured at a constant retraction speed of 1 $\mu$m/s. Curve fits by DS model and 1st order approximation are represented by red and gray curves, respectively. Here $|F^*| = 48 \pm 2 \mu$N and $D^\dagger = 19 \pm 2$ nm. (b) Normalized mechanical response $F(D)$ computed for a few specific relative humidity RH, where the normalization constant for external load is $2\pi R_s^* \gamma = 90.48 \mu$N and that for separation is $R_s^*$.

8. Fixed-load pull-off force as a function of relative humidity, $F^*(\text{RH})$, compared with the theory based on $\delta_0 = 0.77$ nm.

9. (a) Typical AFM scans of surface topography of areas from two PMMA spheres (256 sampling points per line, $5 \times 5 \mu$m$^2$). (b) Corresponding root mean square (RMS) roughness. (c) Measured asperity height.
10. Comparison of $\varphi_{\text{Butt}}$ based on uniform surface roughness distribution with the effective $\varphi_{\text{Exp}}$ based on Gaussian distribution fitted to measurements.
Figure 3
Start

Input capillary volume $V$
and guessed $\theta$

Input distance $D$

Input guessed $\beta$

Using ODE solver ODE45 in MATLAB

to solve the governing equation

$$r_1 = \left[ 1 + \left( \frac{\alpha}{\beta} \right)^2 \right] \frac{\beta}{a_0}$$

repeatedly to determine the profile of the meniscus

Optimization by MATLAB toolbox fminsearch
for new value $\theta$

Convergence check by

$|y_1 - y_0| < 10^{-11}$ m

Calculation for $F_{mg}$ using current $\beta$ and $\theta$ input

Convergence check by

$|V - V_{fr}| < 10^{-3}$ m$^3$

Output calculated force $F$

Increase distance $D$ by a constant increment $dD$

Check distance $D$ by

$D < 20 \times 10^{-9}$ m

Output $F$-$D$ curve

End

Figure 4
Figure 6

(a) Surface roughness function $\varphi_1$ and Effective surface roughness function $\varphi$

(b) AFM experimental data and Gaussian distribution $\mu=0 \sigma=1.8$
Figure 7
Figure 10

- Butt’s effective surface roughness function $\varphi_{\text{Butt}}$
- Experimental effective surface roughness function $\varphi_{\text{Exp}}$

Asperity height distribution (nm$^{-1}$) vs. Asperity height (nm)