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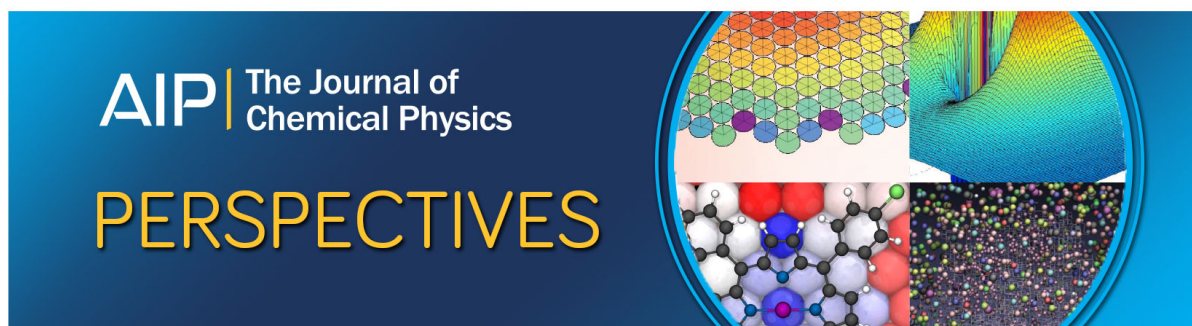
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Microscopic origin of the humidity dependence of the adhesion force in atomic force microscopy

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Water condenses between an atomic force microscope (AFM) tip and a surface to form a nanoscale bridge that produces a significant adhesion force on the tip. As humidity increases, the water bridge always becomes wider but the adhesion force sometimes decreases. The authors show that the humidity dependence of the adhesion force is intimately related to the structural properties of the underlying water bridge. A wide bridge whose width does not vary much with tip-surface distance can increase its volume as distance is increased. In this case, the adhesion force decreases as humidity rises. Narrow bridges whose width decreases rapidly with increasing tip-surface distance give the opposite result. This connection between humidity dependence of the adhesion force and the structural susceptibility of the water bridge is illustrated by performing Monte Carlo simulations for AFM tips with various hydrophilicities. © 2007 American Institute of Physics.

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I. INTRODUCTION

Water condensation between two adjacent surfaces is ubiquitous in the adhesion of solids and granular materials.^{1,2} If one of the adjacent surfaces is extremely sharp as in an atomic force microscope (AFM) *tip* with a 10–100 nm radius, a nanoscale water bridge forms. This bridge serves as a channel for molecules to flow from the tip to the substrate in dip-pen nanolithography (DPN).³ It also gives rise to a significant adhesion force (on the order of nanonewtons) which must be supplied to retract an AFM tip initially contacting a *surface*.^{4–10} Various experiments have reported that the adhesion force (commonly referred to as the pull-off force) is sensitive to changes in humidity.^{6–10} Conventional Laplace-Kelvin theory,¹¹ however, predicts little humidity dependence to the adhesion force. By taking into account the non-spherical tip shape^{6,10} and the effects of liquid evaporation,¹² one can significantly improve the continuum theory to reproduce the experimental results. Some of the most interesting predictions of this approach¹⁰ occur for tip structures that are defined with nanometer resolution, which is where an atomistic description of the tip and the bridge could be important.

As an alternative to the use of continuum theory, we have been studying the use of lattice-gas models and Monte Carlo calculations to describe bridge behavior.^{13–16} This approach provides molecular level insight into the description of the bridge that is missing in the continuum description. In

addition, for small tips and small tip-surface separations there are important differences compared to continuum theory predictions in bridge structure and stability. In particular, the bridge is very unstable when it is only a few molecules in diameter, and this leads to a minimum bridge width for small tips,¹³ and a sudden “snap-off” of the bridge when the AFM tip is retracted more than a critical distance from the surface. Molecular density functional theory¹⁷ (DFT) provides an alternative molecular level approach that has been widely used to study the phase behavior in confined spaces. This mean-field theory neglects long-ranged density correlations and is limited in its ability to describe fluctuations of the water bridge,^{13,14} so the Monte Carlo approach is more useful in the present context.

Despite its importance in AFM experiments and DPN, our understanding of the adhesion force at the molecular level is far from complete. More to the point, we do not clearly understand what structural aspect of the bridge determines the humidity dependence of the adhesion force. As humidity rises, the water bridge becomes wider and bigger. It seems likely that a bigger bridge should yield a larger adhesion force. However, experiments tell us that the adhesion force sometimes gets smaller as humidity rises. In this work, we show that it is the change in the bridge volume with respect to tip retraction that determines the humidity dependence of the force. There are two opposing contributions to the volume change of the bridge as the tip retracts from the surface. One is the increase in volume that occurs because of increased height of the bridge. The other is the decrease in volume because of the narrowing of the bridge width during

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the tip retraction. It is then the *susceptibility* of the bridge width to the tip retraction that determines the relative importance of each contribution to the volume change. For a bridge with a large susceptibility in width, the latter contribution (narrowing of the bridge) dominates to give a decreased bridge volume in the course of the tip withdrawal. If the water bridge is wide and has small susceptibility in width (which is the case for a strongly hydrophilic tip at a high humidity), however, the bridge volume can expand by elongating the tip-surface distance. When this occurs, the adhesion force decreases with humidity rise. We illustrate this by performing Monte Carlo simulations for AFM tips with various wettabilities (hydrophilicities) on a hydrophilic surface.

This paper is organized as follows. Section II describes the details of our molecular model and Monte Carlo simulation. In Sec. III, we analyze the geometry of the water bridge and derive an equation which relates the susceptibility in width of the water bridge to the humidity dependent adhesion force. Section IV illustrates how this force-bridge relationship manifests itself for tips with different hydrophilicities. We elucidate why the adhesion force decreases with increasing humidity for a strongly hydrophilic tip. We conclude in Sec. V.

II. SIMULATION DETAILS

The present Monte Carlo simulation is based on a lattice-gas model of water.^{13-16,18} This coarse-grained model has successfully explained the phase behavior of water confined in a carbon nanotube.^{18,19} It also reproduced the typical magnitude of the experimental pull-off force and its humidity dependence.¹⁵ Our system geometry imitates a hemispherical AFM tip above a planar surface (Fig. 1). Water molecules can occupy cubic lattice sites confined between the tip and surface. Lengths are in units of the *lattice spacing* l , which is taken to be the molecular diameter of water, 0.37 nm.¹⁸ The radius of the tip R is 30 lattice spacings (11 nm), and the horizontal range of our system is $-30 \leq x, y \leq 30$. The first quadrant ($x \geq 0, y \geq 0$) of the system is simulated by using a Monte Carlo method, and the remaining quadrants are taken to be mirror images of the first with respect to the XZ and YZ planes, and the Z axis. Invoking this reflecting boundary condition yields nearly identical results compared with a full simulation.^{14,16}

A water molecule interacts with its nearest-neighbor molecules with an attraction ϵ and has its own chemical potential μ . When it is the nearest neighbor of one of the sites of the tip and surface boundaries, it feels binding energies b_T and b_S , respectively. The system Hamiltonian is

$$H = -\epsilon \sum_{i,j=nn} c_i c_j - b_T \sum_{i=tip} c_i - b_S \sum_{i=surf} c_i - \mu N, \quad (1)$$

where c_i is the occupancy (1 or 0) of the i th site, and the first summation runs over nearest-neighbor pairs, the second is for the sites next to the tip boundary, and the third for the sites right next to the surface boundary. N is the number of molecules in the system. Using the Hamiltonian, Eq. (1), we performed grand canonical (μVT) Monte Carlo simulations.¹³⁻¹⁶ For given values of μ , V , and T , we have

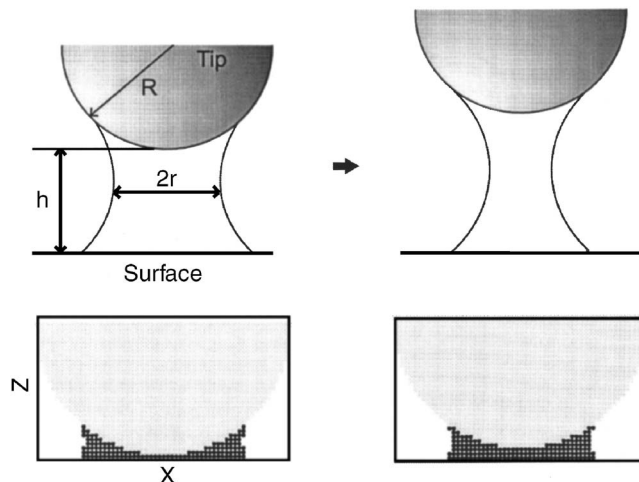


FIG. 1. (Top) A schematic diagram illustrating the structural change in the water bridge during tip retraction. Shown on the left is a concave water bridge formed between a spherical AFM tip and a flat surface. R is the tip radius, h the tip-surface distance, and r the half width of the bridge waist. Shown on the right is a new bridge that results from the tip retraction. Its height h increases but its half width r decreases. (Bottom) Monte Carlo snapshots of the structural change in the water bridge as a result of the tip retraction. Both the AFM tip and the surface are hydrophilic. Filled circles represent water molecules, and the gray area is the tip. The planar surface is a square lattice located at $Z=0$. We show a two dimensional ($Y=0$) cross section of the water bridge at a relative humidity of 79%. As the tip-surface distance increases from 2 (left) to 4 (right) lattice spacings, the bridge width shrinks but the height of the bridge increases.

performed 40 000 Monte Carlo moves (trials to change c_i) for every site. The *relative humidity* s is defined as $s = \exp[(\mu - \mu_c)/k_B T]$, where μ is chemical potential and $\mu_c (= -3\epsilon)$ is the chemical potential at the bulk gas-liquid transition.²⁰ This definition of relative humidity is the ideal gas limit expression for the system pressure relative to the bulk saturation pressure. The bulk critical temperature T_c for the lattice gas is given by $k_B T_c / \epsilon = 1.128$. Identifying our liquid as water ($T_c = 647.3$ K) sets $\epsilon = 4.771$ kJ mol⁻¹. The temperature is fixed at $T/T_c = 0.46$, corresponding to water at room temperature. If we use the above physical values for ϵ and l , our force unit is $\epsilon/l = 0.021$ nN. We have taken the same binding energy of the surface as in the previous work, $b_S/\epsilon = 1.594$, so that the surface is completely wet by water.²⁰ The surface is therefore classified as *strongly hydrophilic*. We considered four different tips with $b_T/\epsilon = 0.75, 0.95, 1.30,$ and 1.59 . The tips with $b_T/\epsilon = 0.75$ and 0.95 are called *weakly hydrophilic* because the tips are partially wet by water.²⁰ Tips with higher values of b_T/ϵ are called *strongly hydrophilic*. In calculating the bulk density ρ , we use mean-field DFT.²¹ With this approach, the grand potential per unit volume Ω_{DFT}/V is given by

$$\Omega_{\text{DFT}}/V = k_B T [\rho \log \rho - (1 - \rho) \log(1 - \rho)] - 3\epsilon \rho^2 - \mu \rho. \quad (2)$$

The equilibrium density is determined by the condition $\delta(\Omega_{\text{DFT}}/V)/\delta\rho = 0$. We checked the validity of DFT by running several simulations for the bulk system, and quantitative agreement with Monte Carlo simulations was found.

Ash *et al.*²² have shown that the adhesion force F between the tip and surface separated by a distance h is given by

$$\left(\frac{\partial F}{\partial \mu}\right)_{h,T} = \left(\frac{\partial N_{\text{ex}}}{\partial h}\right)_{\mu,T}, \quad (3)$$

where N_{ex} is the excess number of molecules with respect to bulk ($N_{\text{ex}} = N - N_{\text{bulk}}$). This remarkable relationship results from a Maxwell relationship in the presence of surfaces. In our simulation, we calculate F vs h by numerically integrating Eq. (3) with respect to μ (for details, see Ref. 17). Starting from a sufficiently low μ that gives zero values for $(\partial N_{\text{ex}}/\partial h)$, we integrate Eq. (3) by using Simpson's rule. $(\partial N_{\text{ex}}/\partial h)$ at intermediate μ values is evaluated as $\partial N_{\text{ex}}/\partial h = [N_{\text{ex}}(h+1) - N_{\text{ex}}(h)]/l$, where $N_{\text{ex}}(x)$ is the excess number at a tip-surface distance x . We then find the *pull-off distance* h_{min} defined as the tip-surface distance at which $F(h)$ is a minimum (most attractive). The maximal adhesion force (*pull-off force*) is given by the magnitude of F at $h = h_{\text{min}}$, $-F(h_{\text{min}})$. In most cases, h_{min} is found to be either two or one lattice spacing. At a fixed temperature T and chemical potential μ , F is a function of h . A typical F is negative (attractive) for small h 's and approaches zero as h increases. Our simulation shows that F sometimes can be repulsive [$F(h) > 0$] when the tip is in contact with the surface, $h = l$. This is the case when contact of the tip with the surface squeezes many molecules out of the confined space between the tip end and the surface.²³ An attractive $F(h)$ means that the system is more stable (lower value of the grand potential) at the tip-surface distance h than at the distance $h+l$. This makes sense because as h decreases, the liquid gets more confined between the tip and the surface, and thus it feels stronger surface fields. Decreasing h from $2l$ to l , however, squeezes molecules out of the confined space between the tip and surface (molecules just cannot exist at the tip-contact area defined as the area where the tip-surface contacts the surface). When this "squeezing-out" of liquid is substantial (usually at a high humidity), the force becomes repulsive.

III. THE STRUCTURAL SUSCEPTIBILITY OF THE WATER BRIDGE

We now analyze the humidity dependence of the adhesion force. A natural quantity to focus on is the derivative of the pull-off force with respect to humidity s . Using the definition of s above and Eq. (3), we can write $-\partial F(h_{\text{min}})/\partial s = -(k_B T/s)(\partial N_{\text{ex}}/\partial h)$, where $-\partial N_{\text{ex}}/\partial h$ is evaluated at $h = h_{\text{min}}$. A positive (negative) value of $\partial N_{\text{ex}}/\partial h$ at $h = h_{\text{min}}$ means a decreasing (increasing) pull-off force with respect to increasing humidity. Since the bulk contribution to N_{ex} is negligible ($N \gg N_{\text{bulk}}$ because the bulk is the vapor phase), we can identify N_{ex} as N . Then, $\partial(\text{pull-off force})/\partial s \approx -(k_B T/s)(\partial N/\partial h)$. If the density of the water bridge is constant (which is true for our lattice model), N is proportional to the volume of the water bridge V_b . Therefore, the humidity dependence of the pull-off force is governed by $-\partial V_b/\partial h$, i.e., the susceptibility of the bridge volume with respect to an increase in the tip-surface distance,

$$\left(\frac{\partial(\text{pull-off force})}{\partial s}\right)_T \approx -(\rho_b k_B T/s) \left(\frac{\partial V_b}{\partial h}\right)_T, \quad (4)$$

where ρ_b is the number density of the bridge, and the derivative with respect to h is evaluated at the pull-off distance corresponding to the force minimum, $h = h_{\text{min}}$. According to Eq. (4), the pull-off force is an increasing (decreasing) function of humidity if the water bridge decreases (increases) in volume with increasing tip-surface distance. In general, there are two competing parts to the change in V_b as the tip retracts. As h increases, the height of bridge increases (see Fig. 1), and therefore its volume expands. At the same time, an increase in h narrows the bridge width $2r$ (see Fig. 1) and thus reduces its volume. This competition can be clearly seen by considering a cylindrical bridge with a radius r and a tip-surface distance h (the case where the bridge in Fig. 1 has no curvature). Inspection of the geometry gives dV_b/dh for the cylindrical bridge as (see the Appendix for its derivation)

$$(1/\pi R r)(dV_b/dh) = r/R - (-2dr/dh) \times (h/R + 1 - \sqrt{1 - r^2/R^2}). \quad (5)$$

In Eq. (5), the first term on the right hand side, r/R , represents the increase in V_b as h increases. On the other hand, the second term, containing $-2dr/dh$, is negative and corresponds to a decrease in V_b during tip retraction from the surface. Equation (5) indicates that dV_b/dh is determined by a sum of these two competing terms. As r/R increases due to a humidity rise, both the first and second terms on the right hand side in Eq. (5) increase in magnitude. It is then the value of $-2dr/dh$ that determines the sign of dV_b/dh .

Note that the dimensionless quantity $-2dr/dh$ is the susceptibility of the bridge width to an increase in the tip-surface distance. A large $-2dr/dh$ means that the corresponding water bridge shrinks rapidly as the tip is retracted. A bridge with a small $-2dr/dh$ on the other hand is stable with respect to the tip withdrawal. The susceptibility of a thermodynamic variable is usually related to the fluctuation of that variable. For example, the susceptibility of N to μ is directly proportional to the fluctuation in N , $\partial N/\partial \mu \propto \langle(N - \langle N \rangle)^2\rangle$.²⁴ However, it is difficult to relate the susceptibility of the bridge width $-2dr/dh$ to the fluctuation (or instability) in the bridge width. This is due to the fact that the Hamiltonian, Eq. (1), is not a linear function of the bridge width $2r$.²⁴

IV. RESULTS AND DISCUSSION

We have considered four tips with different affinities for water, $b_T/\epsilon = 0.75, 0.95, 1.30, \text{ and } 1.59$. By continuously varying the humidity from 0 to 80% in our simulation, we have calculated the susceptibility in width, $-2dr/dh$ (Fig. 2). To do such a calculation, we checked the water bridge width by varying the tip-surface distance for a given humidity. For a given snapshot of the liquid obtained from the Monte Carlo simulation, we determine the width of the water bridge by first counting the number of columns that are continuously occupied by molecules from the site just above the surface to the site right below the tip boundary. Such a collection of columns forms an approximate circle when viewed along the

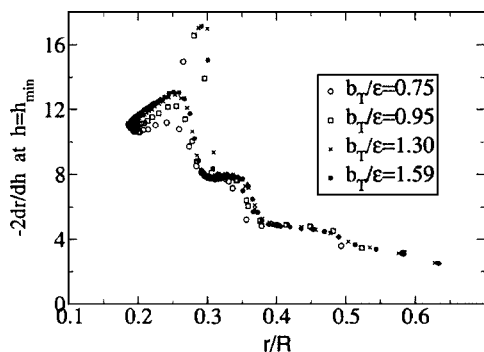


FIG. 2. The susceptibility of the water bridge width to an increase in the tip-surface distance. For four different tips ($b_T/\epsilon=0.75$, 0.95, 1.30, and 1.59), we calculated $-2dr/dh$ at the pull-off distance h_{\min} by varying humidity from 0 to 80%. Calculated $-2dr/dh$ (dimensionless quantity) is plotted as a function of the half-width of the bridge relative to the tip radius, r/R .

Z axis, and the number of columns is proportional to the circle area. The water bridge width (for this liquid snapshot) is then defined as the diameter of the circle. If the bridge has a concave shape, this width for a given snapshot corresponds to the bridge width at its neck. The bridge width $2r$ in Eq. (5) is taken to be the average of 20 000 snapshot-dependent bridge widths defined above. Then, $-2dr/dh$ is defined as the difference in the bridge width as h changes from h_{\min} to $h_{\min}+l$ (h_{\min} =pull-off distance) divided by l . We have already described the method to determine the pull-off distance h_{\min} in Sec. II. In Fig. 2, we plot $-2dr/dh$ as a function of r/R . Overall, the susceptibility $-2dr/dh$ varies from 2 to 18, and it becomes small as the bridge gets wider (r/R goes up), especially for strongly hydrophilic tips ($b_T/\epsilon=1.30$ and 1.59). Note that a narrow bridge ($r/R<0.3$) is sensitive to tip withdrawal, and thus its susceptibility significantly depends on tip hydrophilicity. In contrast, a wide bridge is relatively stable in its width with respect to tip retraction, and its susceptibility does not depend much on the tip hydrophilicity (one can see a converging behavior of the susceptibility for $r/R>0.3$). Note that near $r/R=0.3$, the structural susceptibility is quite sensitive to change in the binding energy of the tip, b_T . Then, Eq. (5) predicts that the humidity dependence of the pull-off force at $r/R=0.3$ should vary significantly from tip to tip. $r/R=0.3$ corresponds to a humidity of 29% for $b_T/\epsilon=1.59$ in our simulation. These observations can be related to the fact that the humidity dependence of the pull-off force at near 30% humidity is quite different depending on the tip hydrophilicity (as found in Ref. 15). We have also checked how the susceptibility depends on relative humidity and found a similar behavior as in Fig. 2: At low humidities ($<40\%$), the susceptibility becomes sensitive to the tip hydrophilicity. Overall, as humidity increases (as the bridge becomes wide), the susceptibility becomes small.

In most cases, the susceptibility in the bridge width $-2dr/dh$ is large so that the second term in Eq. (5) leads to a negative dV_b/dh . As a result, the pull-off force is an increasing function of humidity. For a wide bridge with small $-2dr/dh$, however, the second term can be smaller in magnitude than the first term. The pull-off force in that case decreases with increasing humidity. To illustrate the above

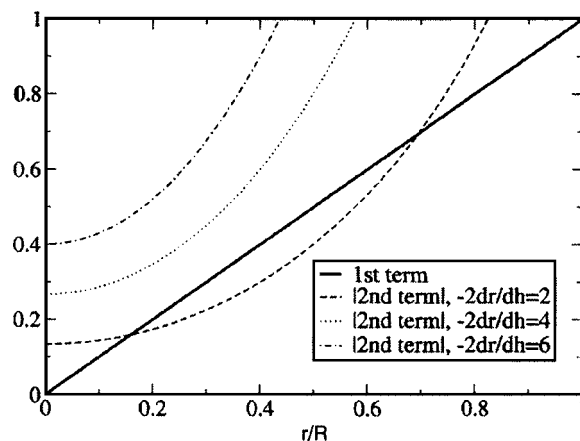


FIG. 3. The two competing terms in the volume change of a cylindrical liquid bridge with respect to an increase in the tip-surface distance. The first and second terms on the right hand side of Eq. (5) are plotted as a function of r/R , where R and r are the radii of the tip and bridge, respectively. R and h are 30 and 2 lattice spacings, respectively. The magnitude of the second term is plotted for three different values of $-2dr/dh$ ($=2, 4$, and 6).

points, we have plotted in Fig. 3 each term of the right hand side of Eq. (5) (which is dimensionless) for three different values of $-2dr/dh$ ($=2, 4$, and 6). h/R is chosen to be a typical value for our simulation, $h=2$ and $R=30$ (in units of lattice spacings). One can see that for $-2dr/dh=4$ and 6 , the second term prevails regardless of r/R , making dV_b/dh negative. For the smallest susceptibility of the figure, $-2dr/dh=2$, however, the first term becomes larger than the second in magnitude for $0.16 \leq r/R \leq 0.69$. This indicates that the pull-off force switches its humidity dependence at $r/R=0.16$, and becomes a decreasing function of humidity. Interestingly, the humidity dependence of the pull-off force switches its behavior again at $r/R=0.7$. This is, however, beyond the humidity range (0% – 80%) considered in our simulation because we have not found such a wide water bridge.

We conclude our analysis by presenting Monte Carlo calculations of the pull-off force versus humidity for tips with different binding energies b_T 's for water, $b_T/\epsilon=0.75$ (circles), 0.95 (squares), 1.30 (triangles), and 1.59 (stars). Figure 4 shows that for the weakly hydrophilic tips, $b_T/\epsilon=0.75$ and 0.95, the pull-off force increases with increasing humidity. As shown above, this can be attributed to the fact that water bridges for these tips rapidly shrink in width if the tip is retracted (large $-2dr/dh$). This makes the pull-off force increase with increasing humidity. In contrast to this, the pull-off force for strongly hydrophilic tips ($b_T/\epsilon=1.30$ and 1.59) increases up to a certain humidity ($\sim 32\%$ for $b_T/\epsilon=1.59$ and $\sim 41\%$ for $b_T/\epsilon=1.30$) but decreases with further increasing humidity. This is consistent with the above analysis (Fig. 3). For strongly hydrophilic tips, the water bridge at a high humidity is wide [large r/R in Eq. (5)] and is not strongly dependent on the tip-surface distance [small $-2dr/dh$ in Eq. (5)]. This leads to the decreasing pull-off force with increasing humidity. Note also in Fig. 4 that the slope of the pull-off force with respect to humidity tends to get smaller as humidity increases. This is due to the inverse humidity term ($1/s$) in Eq. (4).

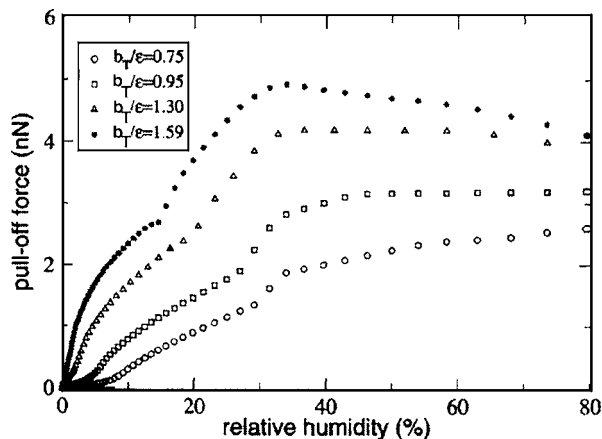


FIG. 4. Pull-off force vs humidity for tips with different binding energies b_T for water, $b_T/\epsilon=0.75$ (circles), 0.95 (squares), 1.30 (triangles), and 1.59 (stars). For weakly hydrophilic tips, $b_T/\epsilon=0.75$ and 0.95, the pull-off force always increases with increasing humidity. The pull-off force for strongly hydrophilic tips ($b_T/\epsilon=1.30$ and 1.59) increases up to a certain humidity but decreases with further increasing humidity.

We assumed a cylindrical shape for the water bridge because it is amenable to a simple and physically clear analysis. Also, simulated bridges are not much different from a cylinder in shape (see Fig. 1). It should be pointed out, however, that Eq. (5) does not quantitatively predict the humidity dependence from the Monte Carlo simulation shown in Fig. 4. One might try to generalize Eq. (5) to the case of a liquid bridge with a concave meniscus. In addition to this geometric aspect, a complete theory of the humidity dependence should also evaluate the susceptibility of the water bridge width, $-2dr/dh$ in Eq. (5). This susceptibility came from Monte Carlo simulations in the present work. One can imagine using a continuum thermodynamic theory instead. We are concerned, however, about the validity of continuum theory for such narrow and small water bridges. The simple cylinder model qualitatively explains the origin of the humidity dependence of the pull-off force, so it is adequate for a simple analysis.

V. CONCLUDING REMARKS

The humidity dependence of the adhesion force measured by AFM is related to the structural properties of the underlying water bridge, as determined by the variation of the bridge volume with tip-surface distance. An increase in the tip-surface distance makes the bridge thicker, increasing its volume. The same increase in the tip-surface distance, however, narrows the bridge width and this reduces the bridge volume. These two opposite contributions compete to determine whether the adhesion force increases or decreases as humidity rises. The susceptibility of the bridge width to tip retraction emerges as a deciding factor for the humidity dependence. For strongly hydrophilic tips at high humidities, the water bridge becomes wide and has a small susceptibility so that the bridge volume expands as the tip is pulled away from the surface. When such a case arises, the adhesion force becomes a decreasing function of humidity. These results can be used to understand the typical behavior of the pull-off force for hydrophilic surfaces (e.g., mica, silicon oxide).⁵⁻¹⁰

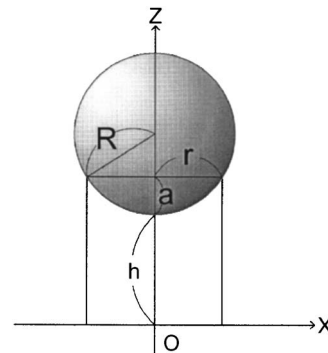


FIG. 5. A diagram illustrating the geometry of the liquid cylinder that connects a sphere to a flat surface located at $Z=0$. A two dimensional cross section (XZ plane) of the geometry is shown. The sphere and the liquid cylinder have radii of R and r , respectively, and the sphere-surface distance is h . The portion of the sphere immersed in liquid is a truncated sphere with a height of a .

The present Monte Carlo treatment of the pull-off force assumes that the velocity of tip retraction is slow compared to the adsorption and desorption rates of water. That is, adsorption equilibrium is maintained as the tip retracts from the surface. If the tip retraction is fast compared to the time constants for adsorption-desorption, one might need a more general treatment that considers the kinetic aspects of the experiment as well.

ACKNOWLEDGMENTS

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APPENDIX: DERIVATION OF EQUATION (5)

Let us consider a sphere with radius R separated by distance h from a flat surface located at $Z=0$ (Fig. 5). Suppose a liquid cylinder connects the sphere to the surface. Then, the portion of the sphere immersed in the liquid is a truncated sphere. Let us denote the height and volume of the truncated sphere by a and V_{trunc} , respectively. Inspection of Fig. 5 tells us that the liquid volume V_b is given by $V_b = \pi r^2(h+a) - V_{\text{trunc}}$, where r is the radius of the cylinder. Note that a is expressed as $a = R(1 - \sqrt{1 - r^2/R^2})$ due to the relation $r^2 = (2R - a)a$. V_{trunc} is given by $V_{\text{trunc}} = \int_h^{h+a} \pi x^2 dz$, where z is the Z position of the sphere-liquid interface, and x is the vertical distance of the liquid-sphere interface from the Z axis. The above integral for V_{trunc} can be evaluated to give $V_{\text{trunc}} = \pi(Ra^2 - a^3/3)$. Then, the desired liquid volume V_b is given by

$$V_b/\pi = r^2h + r^2R(1 - \sqrt{1 - r^2/R^2}) - R^3(1 - \sqrt{1 - r^2/R^2})^2 + (R^3/3)(1 - \sqrt{1 - r^2/R^2})^3. \quad (\text{A1})$$

Taking the derivative of Eq. (A1) with respect to h , we get dV_b/dh as in Eq. (5).

- ¹L. Bocquet, E. Charlaix, S. Ciliberto, and J. Crassous, *Nature (London)* **396**, 735 (1998).
- ²T. C. Halsey and A. J. Levine, *Phys. Rev. Lett.* **80**, 3141 (1998).
- ³D. S. Ginger, H. Zhang, and C. A. Mirkin, *Angew. Chem., Int. Ed.* **43**, 30 (2004).
- ⁴J. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1992).
- ⁵H. Choe, M.-H. Hong, Y. Seo, K. Lee, G. Kim, Y. Cho, J. Ihm, and W. Jhe, *Phys. Rev. Lett.* **95**, 187801 (2005).
- ⁶X. Xiao and L. Qian, *Langmuir* **16**, 8153 (2000).
- ⁷M. He, A. S. Blum, D. E. Aston, C. Buenviaje, R. M. Overney, and R. Luginbuhl, *J. Chem. Phys.* **114**, 1355 (2001).
- ⁸D. L. Sedin and K. L. Rowlen, *Anal. Chem.* **72**, 2183 (2000).
- ⁹D. B. Asay and S. H. Kim, *J. Chem. Phys.* **124**, 174712 (2006).
- ¹⁰H.-J. Butt, M. Farshchi-Tabrizi, and M. Kappl, *J. Appl. Phys.* **100**, 024312 (2006).
- ¹¹L. R. Fisher and J. N. Israelachvili, *J. Colloid Interface Sci.* **80**, 528 (1981).
- ¹²C. Gao, *Appl. Phys. Lett.* **71**, 1801 (1997).
- ¹³J. Jang, G. C. Schatz, and M. A. Ratner, *Phys. Rev. Lett.* **92**, 085504 (2004).
- ¹⁴J. Jang, G. C. Schatz, and M. A. Ratner, *J. Chem. Phys.* **116**, 3875 (2002).
- ¹⁵J. Jang, G. C. Schatz, and M. A. Ratner, *J. Chem. Phys.* **120**, 1157 (2004).
- ¹⁶J. Jang, G. C. Schatz, and M. A. Ratner, *Phys. Rev. Lett.* **90**, 156104 (2003).
- ¹⁷P. B. Paramonov and S. F. Lyuksyutov, *J. Chem. Phys.* **123**, 084705 (2005).
- ¹⁸L. Maibaum and D. A. Chandler, *J. Phys. Chem. B* **107**, 1189 (2003).
- ¹⁹G. Hummer, J. C. Rasaiah, and J. P. Noworyta, *Nature (London)* **414**, 188 (2001).
- ²⁰R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B* **26**, 5112 (1982).
- ²¹M. J. De Oliveira and R. B. Griffiths, *Surf. Sci.* **71**, 687 (1978).
- ²²S. G. Ash, D. H. Everett, and C. Radke, *J. Chem. Soc., Faraday Trans. 2* **69**, 1256 (1973).
- ²³J. Jang, M. A. Ratner, and G. C. Schatz, *J. Phys. Chem. B* **110**, 659 (2006).
- ²⁴T. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).