

Origin of Adhesion in Humid Air

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The origin of adhesion in humid air is investigated by pull-off force measurements between nanoscale contacts using atomic force microscopes in controlled environments from ultrahigh vacuum through various humidity conditions to water. An equivalent work of adhesion (WOA) model with a simplified interface stress distribution is developed, combining the effects of screened van der Waals and meniscus forces, which describes adhesion in humid air and which self-consistently treats the contact stress and deformation. Although the pull-off force is found to vary significantly with humidity, the equivalent WOA is found to be invariant. Increasing humidity alters the nature of the surface adhesion from a compliant contact with a localized, intense meniscus force to a stiff contact with an extended, weak meniscus force.

1. Introduction

Water plays a key role in the interactions between surfaces in nature. A familiar example is that we can easily bind wet grains of sand together to build everything from small structures on the beach up to huge sand castles.^{1,2} On the other hand, excessive water can disintegrate these structures; the most prominent example is from geophysics in which landslides are caused by the saturation of water in soil due to extreme rainfall or rapid melting of ice.³ In nanotechnological applications, not only liquid water, but moisture in the environment, can also influence the interaction between surfaces. Moisture present in humid air condenses to form nanometer-scale water menisci in the narrow gaps between contacts^{4–6} and introduces an additional force component at contacts that alters the adhesion mechanism.⁷ The nature and detailed effects of the adhesive meniscus are not well understood, although the significance of meniscus forces in technological applications involving nanoscale contacts is most obvious.^{8–10} There have been a number of studies to understand the transition that occurs from an equilibrium state of a condensed meniscus to another equilibrium state after the meniscus disappears in the process of separation of nanoscale contacts. These studies consider the phase transition,¹¹ viscosity effects,^{12,13} and evaporation¹⁴ of the meniscus during separation. It is evident from these studies that the process involves a high degree of complexity and unrevealed physics.

However, it is well-known that a condensed water meniscus increases the adhesion force between contacting surfaces in the presence of humidity. The maximum adhesion occurs at the point of separation where transition effects between meniscus equilibria are not significant. However, theoretical studies have shown the limitations in predicting the maximum meniscus force from contact area alone.^{15,16} Other studies have proposed an exact description of the meniscus component of the adhesion force but failed to incorporate the solid–solid adhesion component.^{17,18}

We describe here adhesion force measurements between nanoscale contacts using atomic force microscopes (AFM) in controlled environments from ultrahigh vacuum (UHV) through various humidity conditions to water. The aim of the measurements was to study the maximum adhesion force exerted by menisci at nanoscale contacts via pull-off measurements and understand the results based on a new approach defining the work of adhesion (WOA) incorporating the meniscus Laplace pressure. Our focus was to explain the maximum adhesion force (pull-off force) as a function of relative humidity (RH) in terms of the contact deformation via continuum contact mechanics incorporating the Laplace pressure and surface energy.

2. Theory

On a fundamental level, it is the surface-specific WOA that is required for the design of small components for nanotechnology applications. For a homogeneous system, the WOA, w , is defined as the work required to separate two surfaces of unit area, 1 and 2, from contact to infinity in a medium, 3, and is described by the Dupré equation:¹⁹

$$w_{132} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (1)$$

where γ_{13} , γ_{23} , and γ_{12} are excess interface free energy densities. For two identical solids eq 1 reduces to $w_{131} = 2\gamma_{13}$. Tabor showed that adhesion depends not only on the surface energies, but also on the surface roughness and the mechanical properties

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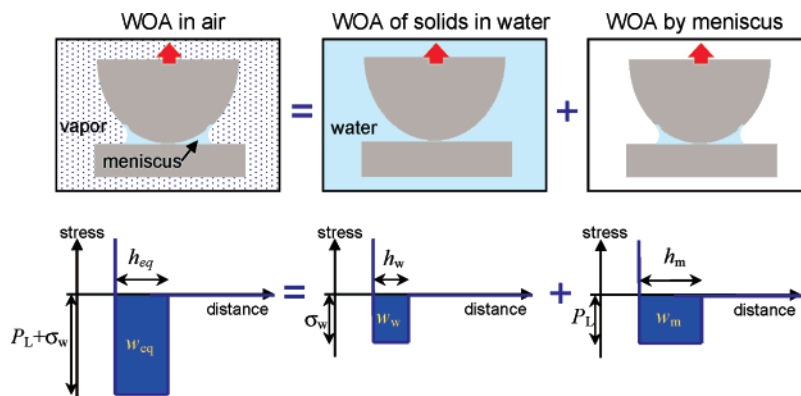


Figure 1. Schematic of the proposed WOA model. WOA in ambient condition is described as the sum of the WOA of solids in water medium and the WOA due to the meniscus. The corresponding constant stress field is shown schematically below. Note that the area of the squares represents the magnitude of the WOA.

of solids.²⁰ Established elastic theories for spherical contact, JKR²¹ and DMT,²² prescribe the adhesion force, F , in two different ways as $F = \frac{3}{2}\pi R w$ and $F = 2\pi R w$, respectively (R = sphere radius), based on different attractive stress distributions. The debates on the validity of these two theories continued until Maugis showed that these two competing models are the limiting cases of his self-consistent transition model.²³ This model adopts an adhesive potential between the surfaces exterior to the contact that exerts a constant stress, σ , until a critical separation h is reached (Dugdale approximation).²⁴ Typically the value of h is chosen such that $w = \sigma h$ matches that of a potential describing van der Waals interactions between the surfaces.

For surfaces interacting via discrete contacts in ambient conditions the validity of eq 1 is not obvious as the homogeneity of the medium is broken by the formation of water meniscus. Hence, neither the Dupré equation nor elastic continuum theories in present form can be used to describe a meniscus-mediated contact. The equilibrium meniscus radius is described by the Kelvin equation, $r_K = \gamma_{LV} v / kT \ln(p/p_S)$, where γ_{LV} is the surface tension of water (72 mN m^{-1}), v is the molar volume of water, k is the Boltzmann constant, T is temperature, and p/p_S is the relative vapor pressure.¹⁹ The validity of the equation was experimentally verified by Fisher and Israelachvili using a surface force apparatus, where the effect of surface roughness is minimized by using smooth mica surfaces.^{25,26} The results imply that the Laplace pressure, $P_L = \gamma_{LV}/r_K$, acting inside a meniscus results in the capillary force between two contacting bodies. Although a decrease in the contact area was observed as the relative vapor pressure increased, the elastic deformation of the solids due to the Laplace pressure inside the meniscus was not considered in their work. The meniscus around a spherical contacting body also results in a surface tension force. However, calculations of capillary meniscus forces for rigid bodies with point contacts show that the surface tension force is much smaller than Laplace pressure force except for very small contacting spheres in higher RH conditions,^{15,27} and hence here we consider only the Laplace pressure force. There have been attempts to describe elastic deformation by a meniscus using the transition

model, but these also remained incomplete as the solid–solid interaction across the liquid meniscus was ignored.^{18,28}

In order to understand the adhesion in humid air, there is a need for a comprehensive theory that includes the solid–solid interaction, elastic deformation, and the meniscus itself. In this article we propose a unified model that incorporates continuum contact mechanics and the thermodynamics of capillary condensation to explain adhesion in humid air. We propose a new approach that treats independently the effect of the solid–solid interaction and the effect of meniscus on the WOA as shown in Figure 1. As the solid–solid interaction is mainly working within the meniscus, it can be modeled as if it were in a homogeneous water medium. WOA by the solid–solid interaction in the water environment ($w_w = \sigma_w h_w$) can be described by the Dugdale approximation using screened van der Waals interactions. The same model can also describe WOA due to the meniscus (w_m) as the Laplace pressure is constant within the meniscus height, h_m . An equivalent WOA, w_{eq} , and critical separation, h_{eq} , under ambient conditions are defined by $w_{eq} = w_w + w_m$ and $h_{eq} = w_{eq}/(\sigma_w + P_L)$, respectively. The adhesive effects are all assumed to exhibit the constant stress distribution of the transition model.

3. Materials and Methods

Pull-off measurements²⁹ were carried out using AFM in UHV, water, and air of various relative humidities (RH, $= p/p_S \times 100$). Experiments in water and in controlled humidity were performed using a Multimode Nanoscope III microscope (Veeco, Santa Barbara, CA),³⁰ and UHV experiments were performed at pressure less than 2×10^{-8} Pa using a UHV 3500 (RHK Technology, Troy, MI). A liquid cell (Veeco Metrology Inc., Santa Barbara, CA) was used for pull-off measurements in water. Control of RH at the experimental site was achieved by purging a chamber (enclosing the AFM head) with dry nitrogen gas passed through distilled water. A Si_3N_4 probe tip (Veeco, Santa Barbara, CA) was used for the measurements in order to avoid wear and deformation and to maintain consistency in the data. No noticeable change in tip geometry was observed after the experiments. The tip (radius $R \approx 10 \text{ nm}$) was attached to an AFM cantilever with spring constant 0.14 N m^{-1} calibrated by an instrumented indenter, TriboIndenter (Hysitron, Minneapolis, MN). Pull-off measurements were carried out using the tip against two samples, namely, a Si surface (Virginia Semiconductor Inc., Fredericksburg, VA) and atomically smooth Au film on mica (Georg

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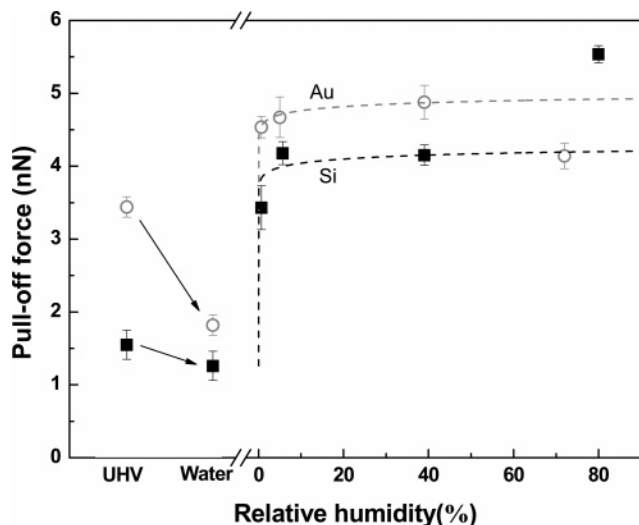


Figure 2. Pull-off forces measured in vacuum, water, and air of various RH (<1%, 5%, 40%, and 72% for Au, and <1%, 5%, 40%, and 80% for Si). The arrows are drawn as a guide to the eye. The dashed lines are pull-off forces based on constant equivalent WOA, 79 and 67 mJ m^{-2} for Au and Si, respectively.

Table 1. Comparison of Measured and Estimated Pull-Off Values^a

	UHV		water	
	measured (nN)	estimated (nN)	measured (nN)	estimated (nN)
Au	3.44 ± 0.12	5.1–5.3	1.82 ± 0.14	1.3–2.4
Si	1.55 ± 0.21	2.1–2.2	1.26 ± 0.23	0.4–0.5

^a Estimation is based on Hamaker constants of Si_3N_4 , Au, and SiO_2 in vacuum and water using $H_{12} = (H_{11}H_{22})^{1/2}$ (ref 19) and $H_{\text{Si}_3\text{N}_4\text{-vacuum-Si}_3\text{N}_4} = 17.4 \times 10^{-20}$ J (ref 34), 19.2×10^{-20} J (ref 33), $H_{\text{Si}_3\text{N}_4\text{-water-Si}_3\text{N}_4} = 6.1 \times 10^{-20}$ J (ref 33), $H_{\text{Au-vacuum-Au}} = 40 \times 10^{-20}$ J (ref 19), $H_{\text{Au-water-Au}} = 7 \times 10^{-20}$ J, 25×10^{-20} J (ref 35), $H_{\text{SiO}_2\text{-vacuum-SiO}_2} = 6.82 \times 10^{-20}$ J (ref 36), $H_{\text{SiO}_2\text{-water-SiO}_2} = 0.66 \times 10^{-20}$ J (ref 36), 1×10^{-20} J (ref 37).

Albert PVD-Beschichtungen, Heidelberg, Germany). In order to maintain the surface state throughout the experiments in all environments, no oxide-layer removal process was used for the Si. The same tip and samples were used for all measurements. All force–distance curves were recorded using the same cantilever retraction speed (150 nm s^{-1}). The probe and samples were electrically grounded to exclude the possibility of electrostatic interactions, and this was confirmed from the nature of the force displacement curve.

4. Results and Discussion

Pull-off forces measured in water, UHV, and ambient conditions are shown in Figure 2. The pull-off force was the smallest for both samples in water, increasing moderately in UHV, and considerably under ambient conditions. The behavior of pull-off forces with RH presented here is fully consistent with the earlier studies using smooth mica contact in the presence of cyclohexane vapor.^{25,26} Moreover, data for low RH including UHV agree well with our previous experimental work on meniscus effects on adhesion at microscale contacts.⁷ In water the adhesion force was due mainly to van der Waals interactions between the probe and surface, screened by the water medium.³¹ The pull-off forces measured in UHV were greater as the van der Waals interactions were unscreened and hence greater than those acting in water. The capillary force associated with water menisci formed around the contacts dominated the adhesive interactions under

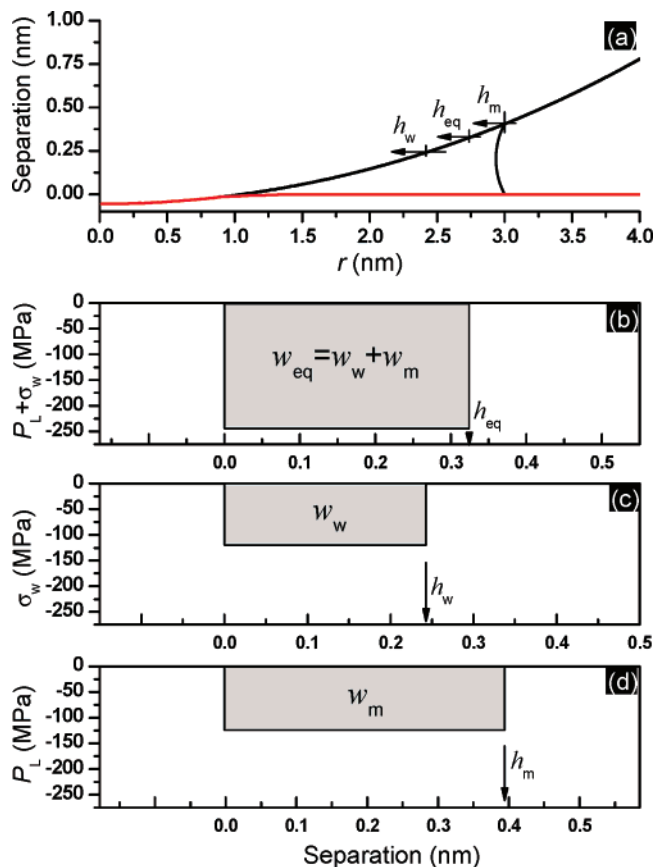


Figure 3. (a) Cross-sectional diagram of a contact at 40% RH, showing the contact deformation consistent with the equivalent stress distribution, shown in (b). The components of the equivalent stress distribution are the screened van der Waals stress (c) and the meniscus stress (d).

ambient conditions even at very low RH (dry condition achieved by the nitrogen purging) leading to large pull-off forces.⁷ These pull-off forces were the result of the contributions from the screened van der Waals interaction acting through the water within the meniscus and the meniscus itself.

The WOAs were calculated from the measured pull-off forces using the self-consistent transition model.²³ The critical separation for van der Waals interactions is $h_w = 0.97z_0$,²³ where $z_0 = 0.25$ nm was assumed as the interatomic separation within the contact. Solution of the transition equations gave the screened van der Waals stress, $\sigma_w = 120$ MPa (Au) and 84 MPa (Si), and WOA, $w_w = 29$ mJ m^{-2} (Au) and 20 mJ m^{-2} (Si). The WOA values in UHV were $w_{\text{UHV}} = 56$ mJ m^{-2} (Au) and 25 mJ m^{-2} (Si). These latter values are much smaller than those previously observed for “pure” Au and Si, as here the measurements in UHV were performed on “as-loaded” samples. Samples were deliberately not cleaned to retain the water overlayer,^{32,33} formed during exposure to ambient conditions. This layer is only a few molecular layers¹⁹ thick and helps to passivate the chemical bonding forces of the surfaces and enabled measurement of only the van der Waals forces. Estimated pull-off forces based on Hamaker constants, H , using the relationship²³ $w = H/16\pi z_0^2$ confirm that van der Waals interactions were dominant in UHV and water (Table 1).^{34–37} The parameters describing the ambient van der Waals stress field were taken to be invariant with humidity and were evaluated from the pull-off forces in water (and therefore in the absence of a meniscus).

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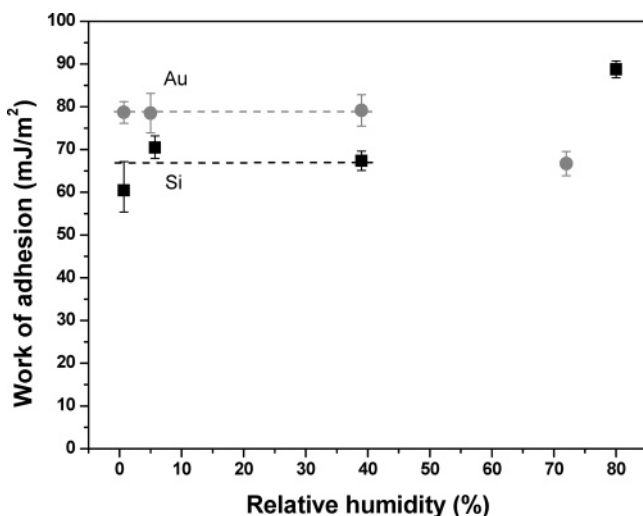


Figure 4. WOA calculated corresponding the pull-off forces in various RH (<1%, 5%, 40%, and 72% for Au, and <1%, 5%, 40%, and 80% for Si). The dashed lines are indicative of constant WOA calculated as 79 and 67 mJ m^{-2} for Au and Si, respectively.

With the assumption of $h_m \ll R$, the meniscus height is given by $h_m = 2r_K \cos \theta$ where θ is the assumed water contact wetting angle for both surfaces. Simple multiplication of the meniscus height and Laplace pressure, P_L , gives the WOA of the meniscus as $w_m = 2\gamma_{LV} \cos \theta$ and is a function of surface tension of the liquid (γ_{LV}) and the wettability of the surfaces (θ). It should be noted that the equivalent WOA under ambient conditions is specified by the wetting angle. This implies a constant WOA, as long as θ is invariant with RH.

On the basis of the equivalent WOA, the transition model describes the contribution of solid interaction and the meniscus to adhesion in various RH conditions. For illustration a profile of the deformed contact and meniscus calculated at 40% RH using the transition model and an equivalent stress field representing the combined effects of the van der Waals and meniscus stresses is shown in Figure 3. Knowing the contact angle, the equivalent WOA under ambient conditions was calculated for different humidity conditions and plotted in Figure

4. It can be seen that except for very high RH, the WOA is a constant (79 and 67 mJ m^{-2} for Au and Si, respectively). Pull-off forces estimated from WOA are shown in Figure 2. At very high RH, the validity of the suggested model using the Kelvin equation is questionable due to the presence of excessive water. The results confirm that the WOA is constant although the pull-off force varies significantly with RH, which is consistent with the proposed model.

In order to further confirm this result, we invoked thermodynamic and mechanical equilibrium conditions in the meniscus-mediated contact. The WOA for a spherical contact in air is the sum of the WOA for the contact in water and the WOA due to the meniscus,

$$w_{\text{eq}} = w_w + w_m = w_{\text{IL2}} + 2\gamma_{LV} \cos \theta \quad (2)$$

noting that eq 2 assumes that liquid–vapor equilibrium exists by establishment of the appropriate Kelvin radius for the meniscus. If this equilibrium assumption is extended to the solid–liquid–solid interface, such that the Dupré equation in a liquid, eq 1, pertains, and to the solid–vapor–liquid interfaces, such that the Young equation ($\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$)³⁸ pertains, the two terms in eq 2 can be rewritten to give

$$w_{\text{eq}} = \gamma_{1V} + \gamma_{2V} - \gamma_{12} \quad (3)$$

Equation 3 is nothing but the Dupré equation in the vapor medium and suggests that the equivalent WOA for a “dry” (non-meniscus) contact is identical to that for a “wet” (meniscus) contact and that the WOA for wet contacts does not depend on the details of the meniscus and contact geometry and should therefore be invariant with humidity. This second implication is, of course, consistent with our experimental findings.

Care should be taken in interpreting the equality of eqs 2 and 3: thermodynamic and mechanical equilibrium are assumed for all configurations, and the equivalent WOA is considered, not the extensive work required to separate two surfaces, for which the characteristic contact area is required ($\text{WOA} = \text{work}/\text{area}$). Nevertheless, it is clear from eq 3 that the WOA in humid air is fundamentally related to the surface and interfacial energies of the contacting solids alone. For identical solids, $w_{\text{eq}} = 2\gamma_{SV}$,

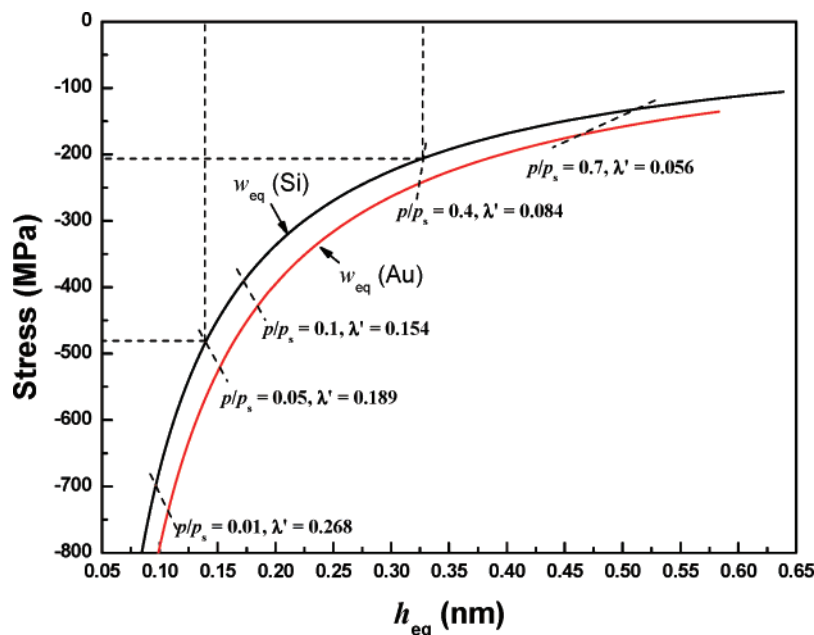


Figure 5. Map of the parameters defining the equivalent stress distribution between contacting surfaces under various humidity conditions. Solid lines are contours of constant WOA for Au and Si in air.

which implies that the pull-off force in humid air is ultimately due to the solid–vapor free energy change on increasing surface area.

The variation in the pull-off force with RH can be described in terms of the stress distribution using the transition model. The parameters describing the equivalent stress distribution, h_{eq} and w_{eq} , are used as coordinates in Figure 5: the two solid lines in the figure are contours of constant WOA for Au and Si. Variations in RH lead to motion along contours, as indicated in the figure for the experimental measurements performed on each material, corresponding to changes in the contact stress distribution. As we move along the contour (change in RH), the WOA described by the area of the rectangle remains invariant. However, the shape of the rectangle continuously varies indicative of variation in the stress distribution which is responsible for the change in pull-off force. At low RH there is a large stress with small critical separation (and as a consequence considerable contact deformation), and at high RH there is a small stress with a large critical separation (and little contact deformation). This change can be characterized by the dimensionless parameter $\lambda' = 2(P_L + \sigma_w)(\pi w_{\text{eq}} K^2/R)^{-1/3}$, where K is the reduced elastic contact modulus. This is similar to the λ in transition model, but modified by including the effect of the meniscus. Variation of λ in the transition model results in a transition between the limiting extremes of contact behavior.²³ There is an analogous transition with increasing RH, as reflected

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in the variation of λ' shown in Figure 5: increasing RH is described by a decrease in λ' that corresponds to an increase in meniscus size. In surface and contact mechanics terms, the growth of the meniscus changes the nature of the contact from a compliant, high surface-energy system to a stiff, low surface-energy system.

5. Summary and Conclusions

An equivalent WOA model was developed that included the effects of screened van der Waals and meniscus forces and that described the variation of pull-off forces with RH for nanoscale contacts in air. The equivalent WOA was found to be invariant with RH, a result consistent with the assumptions of full solid–liquid–vapor equilibrium at contacts containing a meniscus. Although the WOA was found to be invariant, the adhesion force increased significantly with RH from a base value observed in experiments in water. The change in adhesion force as a function of humidity is due to the change in stress concentration in the contact due to variation in the meniscus size with humidity. The WOA invariance implies that WOA due to the meniscus and WOA due to the surface forces balance each other to keep the WOA constant. Under thermodynamic and mechanical equilibrium conditions with a meniscus, our results indicate that the WOA depends only on the solid–vapor surface energy revealed by the resultant Dupré equation. The results are important as it explains the basic mechanism of adhesion in air since humidity is a key factor that affects the performance of nano- and microscale devices that operate in ambient conditions. An implication of this work is that adhesion between surfaces can be tuned by controlling the solid–vapor interfacial energy.

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