Capillary forces

Resultant Laplace pressure induces the liquid to flow away from the tip apex toward its sides. The net thickness of the fluid at the tip apex is thus very small, on the order of 7 nm, as found from subsequent experiments, while the bulk of the liquid accumulates on the sides of the tip. As an unmodified AFM tip approaches a substrate, it experiences negligible attraction until it is very close to the substrate. The van der Waals and/or other short-range forces cause the tip to jump into contact with the substrate as soon as the force gradient acting upon the tip exceeds the cantilever spring constant. This kind of cantilever instability is ubiquitous in AFM studies and typically occurs at distances of ∼2 nm of tip-substrate separation. The larger jump-in distance during the second and subsequent contacts occurs due to the coalescence of the liquid on the AFM probe and the small amount of liquid left behind at the substrate during the rupture of the capillary bridge in the preceding scan. When such a coalescence occurs, capillary forces act on the tip pulling it toward the substrate from a distance much larger than that observed with van der Waals forces.

During the retraction of the probe, various force distance responses are observed depending upon the surface energy of the substrate. Typically, ductile capillary bridges are formed on hydrocarbon and fluorocarbon surfaces, whereas a highly nonductile bridge is formed on a silica surface. Because of the ductile nature of the liquid bridges on hydrocarbon and fluorocarbon surfaces, it is possible to advance and subsequently retract the AFM probes through the liquid bridges without rupturing them.

Once the initial tip-substrate contact is ruptured, the surface tension force acting through the liquid meniscus is not large enough to counteract the restoring force of the cantilever, when the tip jumps out of contact. The limited liquid meniscus present between the tip and the silica substrate may, however, be the cause for the large adhesive force observed on this surface.

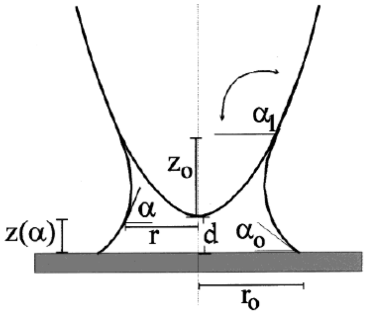

Figure 1: Schematic of a liquid bridge between an AFM tip and a flat surface.

The capillary forces acting on an AFM tip has 2 components. The first is the Laplace force arising from the difference between the pressures acting on the inside and outside of the liquid bridge. The second is the surface tension force that acts alongside the free surface of the liquid. Generally, the mean curvature of the free liquid surface can be described by Equation (1), where z and r define the coordinate of the free surface. The Laplace pressure difference is proportional to the mean curvature H of the free surface, and its magnitude would be zero (H=0) when a mechanical equilibrium is achieved between the liquid present in the bridge and on the tip.

$$2H = \frac{d^2z/dr^2}{(1+(dz/dr)^2)^{3/2}} + \frac{dz/dr}{r(1+(dz/dr)^2)^{1/2}} \ (1)$$

Negligible hysteresis in the force-distance scan indicate that this mechanical equilibrium is likely, therefore the mean curvature H is equal to zero so that the force acting on the tip results from surface tension alone. By setting (H=0), the above equation can be integrated to obtain Equation (2-3).

$$r\sin(\alpha) = r_0 \sin(\alpha_0) \ (2)$$

$$z(\alpha) = r_0 \sin(\alpha_0)\, In\left(\frac{\tan(\alpha/2)}{\tan(\alpha_0/2)}\right) \ (3)$$

The surface tension force acting on the tip is:

$$F = 2\tau r\gamma \sin(\alpha) = 2\tau r_0 \gamma \sin(\alpha_0) \ (4)$$

The replacement of the term $r_0 \sin(\alpha_0)$ into Equation (3) yields:

$$z(\alpha) = \frac{F}{2\tau\gamma} In\left(\frac{\tan(\alpha/2)}{\tan(\alpha_0/2)}\right) \ (5)$$

Whether or not the mean curvature attains a negative value depends on the detailed geometry of the tip. However, when the zero mean curvature condition prevails, Equation (5) above predicts an inverse relationship between capillary extension and the contact angle of the liquid on the solid substrate, α_0. To illustrate the above point, let us rewrite equation above in the following form:

$$d + z_0 = \frac{F}{2\pi\gamma} In\left(\frac{\tan\left(\frac{\alpha}{2}\right)}{\tan\left(\frac{\alpha_0}{2}\right)}\right) \ (6)$$

When the liquid-coated AFM tip contacts a substrate, the liquid spreading is governed by the advancing contact angle. When the tip is retracted, the contact angle at first changes from the advancing to the receding mode without the movement of the contact line. However, even though the liquid cannot spread by viscous motion, a rough calculation shows that the molecules can still spread at an appreciable rate on the surface by diffusion. Once the initial contact is broken, there is not enough surface tension force acting within this meniscus to offset the restoring force on the cantilever, and the tip jumps out of contact with the silica substrate. The forces between the AFM tip and silica surface cannot be modeled in the same way as it is done on fluorocarbon and the hydrocarbon surfaces due to the nonequilibrium drainage of liquid. Here the negative Laplace pressure within the liquid bridge is somewhat governed by the disjoining pressure (Π) within a PDMS film that spreads ahead of the liquid as a precursor film. This disjoining pressure can be estimated using the following equation, where A is the haymaker constant, δ is the film thickness.

$$\Pi = \frac{A}{6\pi\delta^3} \ (7)$$

The general understanding of the capillary interaction between the liquid-coated AFM tip and a substrate gained from the above studies can be used to control the deposition of nanoscopic drops on a surface. Deposition of these nanodrops requires a liquid bridge between the tip and the substrate that could be extended and ruptured, thus leaving behind a significant volume of material on the substrate

[Malotky, D.L. and Chaudhury, M.K., 2001. Investigation of capillary forces using atomic force microscopy. *Langmuir, 17*(25), pp.7823-7829.]

Several forces, such as van der Waals (VdW) or dipole-induced forces, electrostatic forces, and capillary forces influence the strength of adhesion (Beaudoin et al. 2015). Capillary forces caused by capillary condensation are of particular interest because they tend to dominate the adhesion interaction when present (Zimon 1982; Zarate 2010; Xu et al. 1998; Sedin and Rowlen 2000; Thundat et al. 1993; Podczeck 1998). The emphasis in the literature is on nanoparticle adhesion in the presence of water vapor due to the ubiquitous nature of water in all but the most meticulously controlled environments. However, capillary condensation and capillary forces can occur with a variety of adsorbates, such as organic solvents (Fisher and Israelachvili, 1981a, 303; Fisher and Israelachvili, 1981b, 528; Christenson, 1988; Asay et al., 2010) or incompletely miscible fluid–fluid mixtures (Christenson 1985), with or without a high vapor pressure (Butt and Kappl 2009).

When two solid bodies are in close contact and lyophilic (able to attract the adsorbate), a liquid bridge (i.e., meniscus) can form by either the spontaneous condensation of a vapor, otherwise known as capillary condensation; or, for non-volatile liquids, by the combination of adsorbed layers on the two surfaces which are drawn into a meniscus (Butt and Kappl 2009). A meniscus minimizes its surface excess energy by forming a curved liquid–vapor interface between two solid surfaces. This results in a more stable system and increases the work necessary to separate the two solid bodies. Hence the adhesion between two solid surfaces is greater because of the meniscus. The increases in adhesion due to these menisci are capillary forces. There are two components to the capillary force. The first is the capillary pressure force F_p, which is the product of the pressure difference across the liquid–vapor interface ΔP (Laplace pressure) and the wetted area of the particle A_w:

$$F_p = A_w \Delta P \quad (8)$$

DP is known as the Laplace pressure and is typically dominated by the magnitude of the pressure inside the meniscus and not the ambient pressure (Pakarinen et al., 2005). It is related to the mean curvature of the meniscus *J* through the Young–Laplace equation (Adamson and Gast, 1997; Leal, 2007; Israelachvili, 2010), where γ is the liquid-vapour surface tension.

$$\Delta P = \gamma J \quad (9)$$

The second component to the capillary force is the surface tension force F_S. It pulls the contact line between the meniscus and the upper solid toward the contact line between the meniscus and the lower solid (Pakarinen et al. 2005) and is characterized by the Young equation and the contact angle (Hughes et al. 2015). F_S is determined by multiplying the wetted perimeter l_w (the three-phase contact line) of the particle by the component of the surface tension normal to the two interacting surfaces (Pakarinen et al., 2005), where α_n is the angle of inclination of the liquid meniscus from the vertical axis.

$$F_S = \gamma l_w cos\alpha_n \quad (10)$$

A general form of the total capillary force FC is then (Pakarinen et al. 2005; Beaudoin et al. 2015; Butt and Kappl 2009):

$$F_C = F_p + F_S = A_w \frac{RT}{V} In\left(\frac{P}{P_0}\right) + \gamma l_w cos\alpha_n \ (11)$$

F_S is often neglected in the treatment of capillary forces because it is typically much smaller than F_p for lyophilic surfaces (Israelachvili 2010). Butt and Kappl (2009) provide an excellent review of the capillary force equations for smooth systems of many common geometries, such as plane–plane, sphere–plane, cone–plane, sphere–sphere, and cone–cone systems.

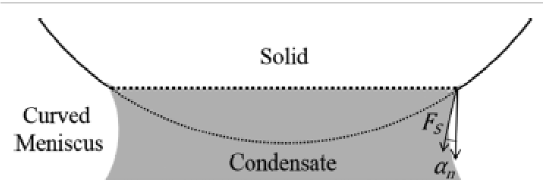

Figure 2: A condensate forms a curved meniscus between a spherical particle and a flat surface. F_S is the surface tension force and α_n is the angle of inclination of the liquid meniscus from the vertical axis.

The hydrophilic nature of adhering surfaces determines the existence of capillary forces. For example, when either or both of the surfaces are hydrophobic, the force of adhesion is generally independent of RH (Farshchi-Tabrizia et al. 2008; Ptak et al. 2011; Zarate et al. 2013; Jones et al. 2002; Jang et al. 2004; He et al. 2001; Eastman 1996; Bhushan and Sundararajan 1998; Knapp and Stemmer 1999). These results suggest that the hydrophobicity inhibits capillary condensation and all of the attractive forces can be attributed to other factors such as VdW interactions and surface topography. Contrastingly, when both surfaces are hydrophilic and liquid bridges form more readily, the force of adhesion can monotonically increase, monotonically decrease, exhibit a maximum, step-wise increase, or remain constant as the RH increases. Therefore, the hydrophilic surfaces clearly enable capillary forces to be a contributing factor to the overall adhesion. Yet with such a variety of observable trends, it is reasonable to conclude that surface hydrophilicity merely creates the circumstances necessary for the existence of capillary forces, but is insufficient to describe how these forces will behave with a change in RH.

A common assumption in capillary force studies is that the liquid bridge is a one component system (e.g., pure water). However, labile ions from ionic substrates or surface contaminants can diffuse into a liquid bridge and thereby alter the properties of the condensed vapor, such as the surface tension. Yet, the presence of deposited, involatile material after evaporation (Christenson and Israelachvili 1987) and a significant shift in the refractive index of water in these liquid bridges (Christenson 1985; Israelachvili 1973) in SFA studies suggest that dissolved surface contaminants are present and can significantly change bulk water properties. The leaching of ions and surface contaminants into liquid bridges has also been observed for silica (Derjaguin et al., 1974) and CaF2 (He et al., 2001). Even though ion transport is limited, the small amount of surface ions in the liquid bridge alter the surface tension of the bulk liquid. Therefore, the diffusion of ions into the liquid bridge can even cause a hydrophobic surface to exhibit hydrophilic adhesion tendencies.

The surface roughness of the particle and the substrate is often a controlling factor in the strength of adhesion. This is true for both the VdW and the capillary forces because the surface roughness determines the degree to which two adhering surfaces complement each other. The lower the complementarity between the two surfaces, the lower the VdW force because the actual area of contact has decreased. The capillary force also decreases because the nano-asperities limit the size of the menisci, at least until the RH reaches a critical value at which the condensed moisture fully encompasses the nano-asperities (Ata et al. 2002; Jones et al. 2002; DelRio et al. 2007; van Zwol et al. 2008; P. van Zwol et al. 2007). Indeed, if the complementarity of the particle and the substrate is low, the force of adhesion will fall well below theoretical predictions (Jones et al. 2002).

To model the contact area, the rigidity of the system or its proclivity toward deformation must be properly understood as well. Less rigid systems will deform more readily to a strong attractive force than will a stiff system. This means that an increase in the capillary force will likely increase the amount of deformation in the system, though it will likely influence the strength of the VdW attraction as well, which could lead to more deformation and a wider, more stable capillary bridge. In the end, the system will deform until an equilibrium between the attractive and repulsive forces is reached, but it must be noted that it is difficult to know the capillary force without the deformation and vice versa. It is reasonable to expect, however, that the capillary force will likely be larger in less rigid, lyophilic systems than in more rigid, lyophilic ones. This is because the actual area of contact will increase in the less rigid system and will encourage larger, more stable liquid bridges to form.

The dependence of the capillary force on the shape and size of the particle can be mitigated by normalizing the force by the ROC of the tip, but not eliminated. First, the shape of the AFM tip must be properly represented by a sphere or circle for the normalization by the radius of curvature (ROC) to be meaningful. Since the shape of the AFM tip or colloidal probe can easily change through the course of the experiment (FarshchiTabrizia et al. 2008), this assumption may not be accurate for all measurements. Second, smaller, sharper tips are more susceptible to local surface roughness than larger, flat ones (Çolak et al. 2012; Çolak et al. 2014), thereby producing more scatter in the data. Also, some of the large SiO2 colloidal probes exhibit normalized forces that are well below the typical values (~0.003) (He et al. 2001; Bhushan and Sundararajan 1998), presumably because the adhesion is not governed by the macroscopic shape, but by the nanoscale roughness on the surface of the particle, thus skewing the normalization. In summary, the size (i.e., mass) of the particle will dictate the general magnitude of adhesion; the local roughness and shape will dictate the actual force measurement.

Whatever the governing mechanism of meniscus formation, it has been shown theoretically and experimentally that smaller particles/asperities have a lower kinetic barrier toward meniscus formation. For example, colloidal probes (i.e., micrometer-sized particles) require contact times longer than 1 s and can require contact times on the order of 1000s (Rabinovich et al. 2011; Sirghi et al. 2006; van Zwol et al. 2008; Xu et al. 1998) to reach the equilibrium capillary force. Sharp AFM probes (ROC < 50 nm), on the other hand, only require contact times on the order of milliseconds (Butt and Kappl 2009; Sirghi et al., 2006; Fukunishi and Mori 2006). The relationship between the size of the particle and the required contact time is a result of the time required to fill the meniscus to its equilibrium volume (Sirghi et al. 2006; Rabinovich et al. 2011). This volume is larger for larger particles or asperities.

As a result, the kinetics of meniscus formation between two surfaces is not negligible in capillary force studies. For AFM experiments, this means that force-curves must be performed slowly to obtain the equilibrium capillary force. The typical acquisition range for conventional force-curve measurements (colloidal probes) is between 0.01 to 10 s (Haugstad 2012). Moreover, force-curve acquisition speeds are between 0.01–1 ms for dynamic AFM modes (i.e., tapping mode) and 0.01–1 ms for force-curve mapping

(Haugstad 2012). Thus, the acquisition speed must be pre-determined based on the size of the particle=tip and the acquisition method so that the time-independent and equilibrium assumptions may be employed. Longer contact times unfortunately may contribute to surface modification of the probe or surface as indicated in the previous sections

[Harrison, A.J., Corti, D.S. and Beaudoin, S.P., 2015. Capillary forces in nanoparticle adhesion: a review of AFM methods. *Particulate Science and Technology*, *33*(5), pp.526-538.]