Modeling and Analysis of Capillary Force Interaction for Common AFM Tip Shapes

Amir Farrokh Payam, Mehran Jalalifar and Morteza Fathipour

1School of Electrical and Computer Engineering, Faculty of Engineering, University of Tehran, 11365/4563, Iran
2Islamic Azad University, Fereydan Branch, Isfahan, Iran

Abstract: This paper presents an analytical method to calculate the capillary force between AFM tip and the sample surface. For this purpose, several tip/substrate interactions including sphere/substrate, cone/substrate, truncated cone/substrate and two-sphere/substrate interactions are considered. Both equal and non-equal contact angles for liquid/solid interfaces are examined. Analytical models based on the energy method, for the capillary force between AFM tip and sample surface are developed and the efficiency of these models is investigated. Furthermore, the effect of several important parameters such as humidity, tip surface distance, tip geometry and contact angles on the meniscus force is studied. Experimental measurements confirm the precision and accuracy of the proposed models.

Key words: Capillary force • tip shape • humidity • contact angles

INTRODUCTION

Rapid development of high precision force measuring devices, such as atomic force microscope (AFM) and surface force apparatus (SFA), has attracted much attention particularly in nanoscience and nanotechnology where adhesion forces can play a significant role in the operation of such instruments. Thus accurate understanding and modeling of the capillary force is of much interest. Many works have been carried out on the modeling and simulation of the capillary force. The non-linearity of the capillary equation in combination with a variety of substrate geometries lead to a large number of solutions to the problem. Hence, several models and methods have been derived to describe the wet adhesion between several tip shapes and particles. There are two major approaches to model capillary force. The first is based on the energy method in which energy is minimized for a given fixed liquid volume [1]. The second approach is based on a direct force calculation from the meniscus geometry obtained by the solution of the so-called Laplace equation [1]. The relation between humidity and capillary force has also attracted much attention in recent years [2-8].

Further expressions were proposed based on the circular approximation for the curvature of the liquid-vapor interface [7-11] and for the numerical computations of the curvature [4, 12, 13]. Circular approximation has been shown to be valid for small liquid bridges [14-17]. In [4] the exact meniscus profile has been numerically calculated from the Kelvin equation and it was found that a circular meniscus profile would give correct results in most cases. In [5, 18] using circular approximation, on the basis of models describing the wet adhesion of tips and substrates joined by liquid bridges, the influence of the tip shapes and various parameters on the magnitude of the capillary force is studied. In [7, 8] based on the circular approximation, the effect of different geometries and AFM tip parameters as well as humidity on the capillary force is studied. The accuracy of the proposed method [7, 8] is evaluated by comparing the results obtained from the model with those obtained by experimental measurement.

Methods presented for modeling and calculation of the capillary force for AFM studies are usually based on a number of approximations. For example, sphere/substrate geometry is usually considered for the capillary interaction of the AFM tip and substrate. In [1, 11, 19] only the contribution of the Laplace pressure term to the total capillary force was considered and the surface tension term was neglected. On the other hand, in [5, 7, 8] equal contact angles for tip/liquid and liquid/plane was assumed.

In this paper, we will employ the energy method to present appropriate models for capillary force for common AFM tip shapes. Moreover, this study is carried out for both symmetric and asymmetric contact angles. We then, investigate the effect of important
parameters affecting the capillary force. Finally, we compare the results with those of available experimental measurements for the capillary force provided in [7].

This paper is organized as follows: In section 2, we discuss formation of liquid bridge and the energy method. Then in sections 3-6 we calculate the capillary force for four common AFM tip shapes, i.e. cone, sphere, truncated cone and two-sphere shapes. In section 7 we investigate the effects of the tip/sample distance, humidity, contact angles and tip geometry on the capillary force for both symmetric and asymmetric configurations and provide the results of the numerical studies. The comparison between our calculations with the experimental measurement is given in section 8. Finally, in section 9, a conclusion is provided.

**CAPILLARY FORCE FORMATION**

Figure 1 shows schematically the geometry for the capillary force problem. A tip and plane are linked through a liquid (usually water) meniscus due to the humidity condensation. \( \theta_1 \) and \( \theta_2 \) are the contact angles for the two phases interface (tip/liquid and liquid/plane).

A meniscus will be formed when the radius of curvature of the nano-contact is below a certain critical radius. This critical radius is defined approximately by the size of the Kelvin radius:

\[
r_{ke} = \frac{1}{r_1} + \frac{1}{r_2}
\]

where \( r_1 \) and \( r_2 \) are the principal radii of the curvature. The Kelvin radius is related to the partial pressure \( P_s \), the saturation vapor pressure, by [7]:

\[
r_{ke} = \frac{\gamma V}{RT\log\left(\frac{P}{P_s}\right)}
\]

Assuming that liquid is formed by the water vapor, the surface tension \( \gamma \) is 0.072 (N/m), the gas constant \( R \) is 8.268 (J/Kmol), the temperature \( T \) is 298 (K), \( V_m = 18\times10^{-3} (m^3/mol) \) is the mol volume and \( P/P_s \) is the relative vapor pressure (relative humidity) [5]. To describe the shape of the liquid meniscus we use circular approximation [5-7, 14-17] and to calculate the capillary force, we use the energy minimization concept [13].

The energy of a liquid bridge is composed of three contributions: the liquid solid (\( \gamma_l A_s \)), the liquid-vapor (\( \gamma_{lv} A_{lv} \)) and the solid-vapor (\( \gamma_{sv} A_{sv} \)) interfacial energies, where \( \gamma \) and \( A \) denote the respective surface tensions and surface areas. The total interfacial energy \( W \) is given by:

\[
W = -\gamma_l A_s - \sum_{i=1}^{2} (\gamma_{ai} - \gamma_{ai}^i) A_i
\]

Following [5], we consider the attractive force to be positive. Using the Young-Dupré equation, interfacial energies can be replaced by contact angle and surface tension:

\[
\gamma_{sv} - \gamma_{lv} = \gamma_s \cos \theta_i \quad i=1,2
\]

Thus the energy equation becomes:

\[
W = -\gamma_s (A_s - A_{ai} \cos \theta_i - A_{ai}^i \cos \theta_i) = -\gamma_s A
\]

**CAPILLARY FORCE BETWEEN A CONE TIP AND A SOLID PLANE**

Figure 2 shows the geometry of a cone tip and a solid plane linked by a water meniscus.

In this figure, \( b \) is the radius of the water meniscus wetting the cone tip, \( \alpha \) is the cone half angle and \( D \) is the distance between tip and substrate. \( r \) and \( l \) are the outer and inner radii curvature of the liquid bridge, respectively.
Based on Fig. 2, we calculate the respective areas and volume of the liquid bridge and then by taking derivative of energy with respect to the AFM tip-substrate distance, the capillary force is obtained.

The volume of the liquid bridge \( V_l \) is obtained by rotating a circular arc of radius \( r \) about the \( y \) axis and subtracting the volume of the cone tip immersed in the liquid:

\[
V_l = \pi \int_{z_1}^{z_2} G(z) dz - V_s
\]

where the equation for the curve \( G(z) \) is:

\[
G(z) = r + 1 - \sqrt{r^2 - (z - r \cos \theta_1)^2}
\]

and the coordinates of points 1 and 2 in Fig. 2 are given by:

\[
x_1 = r + 1 - r \sin \theta_2, x_2 = b
\]

And

\[
z_1 = 0, z_2 = \frac{b}{\tan \alpha} + D
\]

For the case where the meniscus volume is known, based on (11), one can numerically calculate \( b \) from \( V_l \) and other known parameters. Then using the calculated wet circle radius, the capillary force may be calculated based on the method presented here. On the other hand, the area based of the Eq (8) is given by:

\[
A = 2\pi \int_{z_1}^{z_2} G(z) dz - A_{all} \cos \theta_1 - A_{all} \cos \theta_2
\]

Hence:

\[
A = 2\pi \left( r + 1 \right) \left( \frac{z_2^2 \cos(\alpha - \theta_1) \sin(\alpha - \theta_1)}{2(\sin(\alpha - \theta_1) + \cos \theta_1)} + \frac{r^2}{2} \sin^{-1} \left( \frac{\sin(\alpha - \theta_1)}{\cos \theta_2} \right) \right)
\]

\[
+ \pi \left( r + 1 \right) \left( -\sin \theta_2 \cos \theta_2 + \sin^{-1}(\cos \theta_2) \right) - \frac{n b^3}{3 \tan \alpha}
\]

To calculate the capillary force, we need to take the derivative from the energy with respect to the AFM tip-substrate distance:

\[
F = -\frac{\partial W}{\partial D}
\]

Therefore:

\[
F = \frac{\partial W}{\partial V_1} \frac{\partial V_1}{\partial \theta_1} + \frac{\partial W}{\partial V_2} \frac{\partial V_2}{\partial \theta_2} + \frac{\partial W}{\partial x_1} \frac{\partial x_1}{\partial D} + \frac{\partial W}{\partial x_2} \frac{\partial x_2}{\partial D} + \frac{\partial W}{\partial b} \frac{\partial b}{\partial D}
\]

\[
= \gamma \times \left( \frac{\partial A}{\partial \theta_1} + \frac{\partial A}{\partial \theta_2} + \frac{\partial A}{\partial x_1} + \frac{\partial A}{\partial x_2} + \frac{\partial A}{\partial b} \right)
\]

Note that \( \frac{\partial b}{\partial D} \) is calculated based on the condition:

\[
\frac{\partial V_1}{\partial D} = \frac{\partial V_1}{\partial \theta_1} \frac{\partial \theta_1}{\partial D} + \frac{\partial V_1}{\partial \theta_2} \frac{\partial \theta_2}{\partial D} + \frac{\partial V_1}{\partial x_1} \frac{\partial x_1}{\partial D} + \frac{\partial V_1}{\partial x_2} \frac{\partial x_2}{\partial D} + \frac{\partial V_1}{\partial b} \frac{\partial b}{\partial D} = 0
\]

Where:

\[
\frac{\partial \theta_1}{\partial D} = \frac{1}{\sin(\alpha - \theta_1) + \cos \theta_2} + \frac{1}{\tan(\alpha)(\sin(\alpha - \theta_1) + \cos \theta_2)} \frac{\partial b}{\partial D}
\]
From (16), the $\partial b/\partial D$ is obtained. Substituting $\partial b/\partial D$ in (15), the capillary force is calculated.

**CAPILLARY FORCE BETWEEN A SPHERE TIP AND A SOLID PLANE**

The schematic geometry of a sphere tip and a solid flat substrate is shown in Fig. 3.

In this figure $\phi$ is the filling angle, $R$ is the radius of the circle of the liquid bridge wetting the sphere and $r, l$ are the curvature radii of the meniscus bridge.

$$r = \frac{R(1 - \cos \phi) + D}{\cos (\phi + \theta)} + \frac{l \sin (\theta_1 + \phi) + R \sin \phi - r}{(21)}$$

The volume of the liquid bridge $V_l$ is obtained by (7), but the coordinates of contact points 1 and 2 are:

$$x_1 = r + l - \sin \theta_2, x_2 = b = R \sin \phi$$

And

$$z_1 = 0, z_2 = r \cos (\theta_1 + \phi) + r \cos \theta_2$$

So, the volume becomes:

$$V_l = \pi z_2 \left( (r + 1)^2 - r^2 \right) - \frac{\pi}{3} \left( r^2 \cos^2 (\theta_1 + \phi) + r^2 \cos^3 \theta_2 \right)$$

$$- \pi \left( r + 1 \right) \left( \cos (\theta_1 + \phi) \sin (\theta_1 + \phi) + \sin^{-1} \left( \cos (\theta_1 + \phi) \right) + \sin \theta_2 \cos \theta_2 - \sin^{-1} \left( -\cos \theta_2 \right) \right)$$

$$- \frac{\pi R^2}{6} \left( 3R^2 \sin^2 \phi + R^2 (1 - \cos \phi) \right)$$

Also, when $V_l$ is known, to calculate the capillary force, one can numerically obtain $\phi$ from (24) and use to calculate filling angle. The area of the structure in Fig. 3 is given by:

$$A = 2\pi z_2 \left( (r + 1) - \pi \left( \cos (\phi + \theta_1) \sin (\phi + \theta_1) + \sin^{-1} \left( \cos (\theta_1 + \phi) \right) + \sin \theta_2 \cos \theta_2 - \sin^{-1} \left( -\cos \theta_2 \right) \right) \right)$$

$$- \pi R^2 \left( (1 - \cos \phi)^2 + \sin^2 \phi \right) \cos \theta_1 - \pi x_1 \cos \theta_2$$

To calculate the capillary force, we need to take the derivative from the energy with respect to the gap distance between AFM tip and substrate. So that:

$$F = -\frac{\partial W}{\partial D} = \left( \frac{\partial W}{\partial \theta_1} + \frac{\partial W}{\partial \theta_2} + \frac{\partial W}{\partial z_1} \right) = \gamma_{ls} \left( \frac{\partial V_l}{\partial \theta_1} + \frac{\partial V_l}{\partial \theta_2} + \frac{\partial V_l}{\partial z_1} \right)$$

$$\frac{\partial V_l}{\partial \theta_1} = \frac{\partial V_l}{\partial \theta_2} + \frac{\partial V_l}{\partial z_1} + \frac{\partial V_l}{\partial \phi} = 0$$

$$\frac{\partial \phi}{\partial D}$$

is calculated based on the condition:

$$\frac{\partial V_l}{\partial \theta_1} = \frac{\partial V_l}{\partial \theta_2} + \frac{\partial V_l}{\partial z_1} + \frac{\partial V_l}{\partial \phi} = 0$$

Where:

$$\frac{\partial r}{\partial D} = \frac{1}{\cos (\phi + \theta_1) + \cos \theta_2} \left( R \sin (\phi + \theta_1) \cos (\phi + \theta_1) + \sin (\phi + \theta_1) \left( R(1 - \cos \phi) + D \right) \frac{\partial \phi}{\partial D} \right)$$
The capillary force can be calculated by substituting $\frac{\partial \phi}{\partial D}$ in (26).

**CAPILLARY FORCE BETWEEN A TRUNCATED CONE TIP AND A SOLID PLANE**

Most AFM tip images show that the end of the tip is not actually sphere or conical shape \([5, 7]\). Usually two models are employed for AFM tips; these are two-sphere and truncated cone models. In this section we will derive the capillary force between the truncated conical AFM tip and substrate. In the next section, we present the two-sphere model. Figure 4 shows the model for truncated cone tip and the solid plane linked by a water meniscus.

In this figure, the radius of sphere is depicted by $R$, $\phi_{\text{max}}$ is the half of the opening angle of the spherical part, $b$ is the radius of the circle of the water meniscus wetting the truncated cone, $\alpha$ is the cone half angle and $D$ is the distance between tip and substrate. For $b < R \sin \phi_{\text{max}}$ the liquid bridge is formed between the spherical end of the tip and substrate. In this case, all formulas and derivations are identical with the case of spherical tip in section 4. For $b \geq R \sin \phi_{\text{max}}$ the liquid bridge is formed on the cone boundary. In this case, $r$ and $l$ the radii curvature of the liquid bridge is described by:

$$r = \frac{b - R \sin \phi_{\text{max}} + D + R(1 - \cos \phi_{\text{max}})}{\sin(\alpha - \theta_0) + \cos \theta_2}, \quad l = b - r(1 - \cos(\alpha - \theta_0))$$

(32)

The respective coordinates of points 1 and 2 in Fig. 2 are:

$$x_1 = r + 1 - \sin \theta_0, \quad x_2 = b$$

(33)

And

$$z_1 = 0, z_2 = \sin(\alpha - \theta_0) + r \sin \theta_2$$

(34)

Thus, the volume $V_1$ becomes:

$$V_1 = \pi x_2 \left( (r + 1)^2 + r^2 \right) - \frac{\pi}{3} \left( r^3 \sin^3(\alpha - \theta_0) + r^3 \cos^3 \theta_2 \right)$$

$$- \pi r^2 \left( \cos(\alpha - \theta_0) \sin(\alpha - \theta_0) + \sin^{-1}(\sin(\alpha - \theta_0)) + \sin \theta_2 \cos \theta_2 - \sin^{-1}(-\cos \theta_2) \right)$$

$$- \frac{\pi}{3} R^3 \left( 1 - \cos \phi_{\text{max}} \right) \left( 1 + \sin^2 \phi_{\text{max}} \cos \phi_{\text{max}} - \cos \phi_{\text{max}} \right) - \frac{\pi}{3} h \left( R \sin \phi_{\text{max}} \right)^2 + b^2 + b R \sin \phi_{\text{max}}$$

(35)

Where

$$h = \frac{b - R \sin \phi_{\text{max}}}{\tan \alpha}$$

The area is given by:

$$A = 2 \pi x_2 (r + 1) - \pi \left( \sin(\alpha - \theta_0) \cos(\alpha - \theta_0) + \sin^{-1}(\sin(\alpha - \theta_0)) + \sin \theta_2 \cos \theta_2 - \sin^{-1}(-\cos \theta_2) \right)$$

$$- \pi \left( (b + R \sin \phi_{\text{max}}) \left( b - R \sin \phi_{\text{max}} \right)^2 + h^2 + b^2 + R^2 \sin^2 \phi_{\text{max}} + R^2 \left( 1 - \cos \phi_{\text{max}} \right) \cos \theta_2 \right)$$

$$- \pi \left( R^2 \left( 1 - \cos \phi_{\text{max}} \right) \right) \cos \theta_2 - \pi \alpha_2 \cos \theta_2$$

(36)
To calculate the capillary force, we need to take the derivative of the energy with respect to the distance. So:

$$F = -\frac{\partial W}{\partial D}$$  

(37)

Therefore:

$$F = \left( \frac{\partial W}{\partial r} \frac{\partial r}{\partial D} + \frac{\partial W}{\partial l} \frac{\partial l}{\partial D} + \frac{\partial W}{\partial z_1} \frac{\partial z_1}{\partial D} + \frac{\partial W}{\partial h} \frac{\partial h}{\partial D} + \frac{\partial W}{\partial b} \frac{\partial b}{\partial D} \right) = \gamma_b \left( \frac{\partial A}{\partial r} \frac{\partial r}{\partial D} + \frac{\partial A}{\partial l} \frac{\partial l}{\partial D} + \frac{\partial A}{\partial z_1} \frac{\partial z_1}{\partial D} + \frac{\partial A}{\partial h} \frac{\partial h}{\partial D} + \frac{\partial A}{\partial b} \frac{\partial b}{\partial D} \right)$$  

(38)

$\partial b/\partial D$ is calculated based on the condition:

$$\frac{\partial V_i}{\partial D} = \frac{\partial V_i}{\partial r} \frac{\partial r}{\partial D} + \frac{\partial V_i}{\partial l} \frac{\partial l}{\partial D} + \frac{\partial V_i}{\partial z_1} \frac{\partial z_1}{\partial D} + \frac{\partial V_i}{\partial h} \frac{\partial h}{\partial D} + \frac{\partial V_i}{\partial b} \frac{\partial b}{\partial D} = 0$$  

(39)

Where:

$$\frac{\partial r}{\partial D} = \frac{1}{\sin(\alpha - \theta_1)} + \frac{1}{\tan(\alpha) \left( \sin(\alpha - \theta_1) \right)}$$  

(40)

$$\frac{\partial l}{\partial D} = \frac{\partial b}{\partial D} \left( 1 - \cos(\alpha - \theta_1) \right)$$  

(41)

$$\frac{\partial z_1}{\partial D} = \left( \sin(\alpha - \theta_1) + \sin \theta_2 \right) \frac{\partial r}{\partial D}$$  

(42)

$$\frac{\partial x_1}{\partial D} = \frac{\partial l}{\partial D} + \frac{\partial r}{\partial D} \left( 1 - \sin \theta_2 \right)$$  

(43)

The capillary force may be calculated by substituting $\partial b/\partial D$ obtained from (39) in (38).

**CAPILLARY FORCE BETWEEN A TWO-SPHERE TIP AND A SOLID PLANE**

The model geometry for the analysis of a sphere tip and a planar substrate is shown in Fig. 5. In this figure, the radius of spheres are depicted by $R_1$, $R_2$, $\alpha_1$ is the maximum of the half opening angle for the partial sphere 1 and $\alpha_2$ is the minimum half opening angle for sphere 2, $b$ is the circle radius for the water meniscus wetting the sphere tip and $D$ is the distance between the tip and substrate.

For $b < R_1 \sin \alpha_1 = R_2 \sin \alpha_2$, the liquid bridge is formed between the first spherical end of the tip and substrate ($R_1$). For this case, procedure is identical to the case of sphere tip in section 4.

For $b \geq R_1 \sin \alpha_1 = R_2 \sin \alpha_2$, the liquid bridge is formed on the sphere 2 boundary. In this case, $r$ and $l$ the radii curvature for the liquid bridge are given by:

$$r = \frac{R_\omega \left( \cos \alpha_2 - \cos \phi_2 \right) + D + R_2 (1 - \cos \alpha_2)}{\cos \phi_2 + \cos \theta_2}$$

$$l = r \sin (\theta_1 + \phi_2) + R_2 \sin \phi_2 - r$$  

(44)

The volume of the liquid bridge $V_i$ is obtained by (7), but the coordinates for contact points 1 and 2 are:

$$x_1 = r + l - r \sin \theta_1, x_2 = b = R_2 \sin \phi_2$$  

And

$$z_1 = 0, z_2 = r \cos (\theta_1 + \phi_2) + r \cos \theta_2$$

(45)

(46)

So, the volume becomes:
The area used in the Eq (47) is:

\[ A = 2\pi z (r+1) - \pi^2 \left( \cos(\theta_1 + \phi_1) \sin(\theta_1 + \phi_1) + \sin^{-1}(\cos(\theta_1 + \phi_1)) + \sin(\theta_1 \cos(\theta_1 + \phi_1)) \right) \]

where \( h_1 = R_z (1 - \cos \theta_1) \). Again, to calculate the capillary force, we need to take the derivative of the energy with respect to the distance. Thus:

\[ F = \frac{\partial W}{\partial D} = \left( \frac{\partial W}{\partial r} \frac{\partial r}{\partial D} + \frac{\partial W}{\partial l} \frac{\partial l}{\partial D} + \frac{\partial W}{\partial z} \frac{\partial z}{\partial D} + \frac{\partial W}{\partial x} \frac{\partial x}{\partial D} + \frac{\partial W}{\partial y} \frac{\partial y}{\partial D} + \frac{\partial W}{\partial D} \right) = \gamma_{lv} \left( \frac{\partial A}{\partial r} \frac{\partial r}{\partial D} + \frac{\partial A}{\partial l} \frac{\partial l}{\partial D} + \frac{\partial A}{\partial z} \frac{\partial z}{\partial D} + \frac{\partial A}{\partial x} \frac{\partial x}{\partial D} + \frac{\partial A}{\partial y} \frac{\partial y}{\partial D} + \frac{\partial A}{\partial D} \right) \]

(49)

\( \frac{\partial \phi}{\partial D} \) is calculated using the condition:

\[ \frac{\partial V_1}{\partial D} + \frac{\partial V_1}{\partial r} \frac{\partial r}{\partial D} + \frac{\partial V_1}{\partial l} \frac{\partial l}{\partial D} + \frac{\partial V_1}{\partial z} \frac{\partial z}{\partial D} + \frac{\partial V_1}{\partial x} \frac{\partial x}{\partial D} + \frac{\partial V_1}{\partial y} \frac{\partial y}{\partial D} + \frac{\partial V_1}{\partial h} \frac{\partial h}{\partial D} = 0 \]

(50)

where:

\[ \frac{\partial r}{\partial D} = \frac{1}{\cos(\phi_2 + \theta_1) + \cos \theta_2} + \frac{R_z \sin \phi_1 \left( \cos(\phi_2 + \theta_1) + \cos \theta_1 \right) + \sin(\phi_2 + \theta_1) \left( R_z \cos \alpha_1 - \cos \phi_2 \right) + D + R_z (1 - \cos \alpha_1)}{\left( \cos(\phi_2 + \theta_1) + \cos \theta_2 \right)^2} \]

(51)

\[ \frac{\partial l}{\partial D} = \left( \cos(\phi_2 + \theta_1) + \cos \theta_1 \right) \frac{\partial \phi_1}{\partial D} + \frac{\partial r}{\partial D} \left( \sin(\phi_2 + \theta_1) - 1 \right) \]

(52)

\[ \frac{\partial z_2}{\partial D} = \left( \cos(\phi_2 + \theta_1) + \cos \theta_1 \right) \frac{\partial r}{\partial D} - \sin(\phi_2 + \theta_1) \frac{\partial \phi_1}{\partial D} \]

(53)

\[ \frac{\partial x_1}{\partial D} = \frac{\partial l}{\partial D} + \frac{\partial r}{\partial D} \left( 1 - \sin \theta_2 \right) \]

(54)

\[ \frac{\partial x_2}{\partial D} = R_z \cos \phi_1 \frac{\partial \phi_1}{\partial D} \]

(55)

\[ \frac{\partial h_1}{\partial D} = R_z \sin \phi_1 \frac{\partial \phi_1}{\partial D} \]

(56)

Substituting \( \frac{\partial \phi}{\partial D} \) in (49), the capillary force is calculated.

**NUMERICAL RESULTS AND DISCUSSION**

**Conical tip and substrate:** Figure 6 shows the relation between the AFM tip and substrate distance and capillary force. As expected, by increasing the distance, the capillary force is reduced. Also, decreasing the radius of the circle of the wet adhesion on the cone tip decreases the magnitude of capillary force.

The hydrophobicity and hydrophilicity of the particles is determined by the contact angle. In Fig. 7 the capillary force is calculated based on the contact angle. In this test, the wetting circle radius is fixed and the tip/substrate distance is decreased. As shown in Fig. 7, decreasing both the contact angles and the distance leads to an increase in the capillary force. This means that the capillary force for hydrophilic particles is greater than that for hydrophobic particles.

To study the influence of contact angles on the humidity dependence of the capillary force, we consider two cases, the symmetric interface and the asymmetric interface. Figure 8 (a) and (b) show the capillary force for these two cases. It is observed that decreasing the contact angle leads to an increase in the meniscus force. Increasing humidity, strongly affects the capillary force, in this case the capillary force is increased.

**Spherical tip and substrate:** The dependence of capillary force on the AFM tip and substrate distance for the spherical tip geometry is shown in Fig. 9. As expected, with the increasing the AFM tip-substrate distance the capillary force is reduced. Also, decreasing
Fig. 6: The capillary force as a function of the distance between tip and substrate

Fig. 7: The capillary force as a function of the contact angles

Fig. 8: The capillary force versus humidity with different contact angles a) symmetric case b) asymmetric case

Fig. 9: The capillary force as a function of the distance between tip and substrate

Fig. 10: The capillary force versus humidity for a) several gap distance between tip and substrate b) several tip radii

The sphere tip radius leads to a reduction in capillary force. Figure 10 shows the dependence of capillary force on the humidity. In this case, the effects of several parameters are considered. In Fig. 10 (a), the gap between tip and the substrate is decreased. This leads to an increase in the capillary force. In Fig. 10 (b), the distance is fixed, but the sphere radius is changed. The larger radii lead to the larger capillary forces. In Fig. 11 we show the effects of sphere tip angle, tip-substrate distance and contact angles on the capillary force for the case where geometry is asymmetric. From this
Fig. 11: The capillary force versus humidity for different contact angles, different filling angle and different gap distance. In the figure, we conclude that decreasing the contact angle between substrate and liquid leads to an increase in the capillary force. Also, the effect of tip substrate distance is depicted in Fig. 11. In Fig. 11 (a), there is 0.5 (nm) gap between AFM tip and substrate, while in Fig. 11 (b) the AFM tip and substrate are in contact. As shown, in Fig. 11 (b), increasing the humidity leads to the decrease in capillary force, while in Fig. 11 (b), this behavior is different.

A comparison between Fig. 8 and 11 reveals that the capillary force behavior for spherical tip model versus relative humidity is different than that for the conical tip model. As shown, in the conical tip model, increase the humidity, leads to increase in the capillary force, but in the spherical tip model, depending on the gap distance, the capillary force has different behavior versus the relative humidity. For example, by comparing Fig. 10 and 11 one can see that when D = 0, increasing the humidity, decreases the capillary force. In contrast, when there is a gap between tip and substrate, capillary force versus relative humidity shows different characteristics. In the region of low and medium humidity, increasing the humidity leads to a significant increase in the meniscus force. On the other hand, when the relative humidity approaches unity, capillary force is decreased.

Fig. 12: The capillary force versus humidity for a) smooth transition when tip/substrate distance is taken as varying parameter, b) non-smooth transition when contact angle is taken as varying parameter.

**Truncated Conical tip and substrate:** Here, we consider two situations. Smooth ((α + φ_max) = π/2) and non-smooth ((α + φ_max) ≠ π/2) transitions between the spherical and conical parts. In Fig. 12 (a) the smooth transition is considered and the relation between capillary force and relative humidity is illustrated while the tip/substrate distance is taken as parameter. In the non-transition case, as illustrated, the capillary force first increases as humidity is increased, then in the vicinity of the transition region, the capillary force is decreased and finally when the wet boundary approaches the conical part, the capillary force is increased strongly. The difference between smooth and non-smooth transition from spherical part to the conical part is quite obvious from this figure.

Similar to the spherical tip shape, the different behavior of capillary force with gap distance is depicted in Fig. 12a. This is related to spherical end of the truncated cone tip model. In this case, when the humidity is increased, wet boundary approaches the conical part of the tip. Similar to the conical tip model, increasing the humidity, leads to the significant increase of the capillary force.
Fig. 13: The capillary force versus humidity for a) different tip/substrate distance, b) different contact angles

Fig. 14: The simulation of the experimental measurement in [7] with the presented model and comparison with the calculated model in [7] (---)

Fig. 15: Results of [7]

**Two-sphere tip and substrate:** Figure 13 depicts the dependence of the capillary force on the humidity for the case of the two-sphere-model. It is seen that, when the wet circle boundary is located on the first sphere, the capillary force increases with the humidity. However, when the transition occurs between the two spheres, the capillary force decreases as the humidity is increased. Decrease in the contact angles and the gap between tip and substrate, lead to an increase in the capillary force.
COMPARISON WITH EXPERIMENTAL MEASUREMENTS

In this section, the validity and effectiveness of the proposed approach described in previous section is examined. For this purpose, the two sphere model of AFM tip shape is considered and adhesion force versus humidity curve is reproduced and compared with experimental measurement [7]. The results of the proposed model and regenerated model of [7], are shown in Fig. 14. The parameters of experimental measurement given in [7] were used for the simulation. As can be seen, the results of the proposed method show a good match with the experimental measurement.

CONCLUSION

Considering several AFM tip shapes and flat substrates, the capillary adhesion forces were calculated based on the energy method. These models were based on the circular interface in a radial cross section. The advantage of the presented approach is that the equations are solved analytically. They do not employ simplifying approximations considered in the earlier analytical approaches. In addition, by considering the analytical energy method, we analyzed both the symmetric and asymmetric cases for the meniscus geometry. To the best of our knowledge, this is the first time such treatment is reported for AFM tip shapes. Different AFM tip shapes, show different behaviors of capillary force versus relative humidity. For the cone tip shape, when humidity increases, capillary force is increased. Behavior in spherical tip model depends on the tip-substrate distance. When the distance is zero, capillary force is decreased while the humidity is increased. But, when there exists a gap between tip and substrate, capillary force show two types of behavior when humidity is changed. In the low and medium humidity, increasing the humidity leads to an increase in capillary force. In contrast, in the high humidity environment, increasing the humidity leads to a reduction of capillary force for spherical tip shape. The behavior of truncated cone tip model may be viewed as the combination of two previous tip shapes. An important point regarding capillary force behavior versus to humidity, for truncated cone tip, is the transition between its spherical and conical parts. Using the two-sphere tip model, we see that the size of the spheres has significant effect on the capillary force versus humidity curve. However, each of spheres in two sphere model has similar behavior with the spherical tip shape in the capillary force versus humidity curves. Our model can predict available measurement data within experimental accuracy.

REFERENCES


