Theoretical Study on the Capillary Force between an Atomic Force Microscope Tip and a Nanoparticle *

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Considering that capillary force is one of the most important forces between nanoparticles and atomic force microscope (AFM) tips in ambient atmosphere, we develop an analytic approach on the capillary force between an AFM tip and a nanoparticle. The results show that the capillary forces are considerably affected by the geometry of the AFM tip, the humidity of the environment, the vertical distance between the AFM tip and the nanoparticle, as well as the contact angles of the meniscus with an AFM tip and a nanoparticle. It is found that the sharper the AFM tip, the smaller the capillary force. The analyses and results are expected to be helpful for the quantitative imaging and manipulating of nanoparticles by AFMs.

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Properties of nanoparticles have attracted much attention because of their importance and widespread applications in nanoscience and nanotechnology.[1−7] It has been found that gold nanoparticles are widely utilized in a variety of ultrasensitive biosensor strategies,[2−4] and can enhance the efficiency[5] and the specificity of the amplification of the polymerase chain reaction (PCR).[6] The strong toxicity that silver exhibits in a wide range of microorganisms is well known, and silver nanoparticles have recently been shown to be a promising antimicrobial material.[7] It is believed that these physiochemical and medical applications of the nanoparticles are due to the particular behaviour of particles on the nanoscale, which is usually very different from the bulk ones.

Atomic force microscope (AFM) is one of the most important scanning probe microscopes that allow both imaging and manipulating nanoparticles.[8−15] Recently, it becomes popular to manipulate particles with length scale from several tens to several hundreds of nanometres such as polymers, biological molecules and metal nanoparticles, by AFM at ambient conditions.[8−15] When imaging and manipulating a nanoparticle in air, the ambient humidity usually leads to the formation of capillary meniscus between AFM tip and nanoparticles.[11]

There have been numerical theoretical analyses to explore the capillary forces between two macrospherical particles[16−18] and an AFM tip with a flat surfaces.[19−22] Israelachvili[16] has developed an expression for calculating the capillary force between two macrospherical particles. In the derivation of the capillary force equation, he assumed that the radii of the solid–liquid–vapour contact lines are very small compared with the radii of the two macrospherical particles (see, for example, Fig. 1 and the text in the following, this assumption corresponds to $x_t, x_p \ll R_1$ or R_2, where x_t and x_p are the radii of the solid–liquid–vapour contact lines). It is clear that those approximations are not satisfied when the particles are on nanoscales, where the radii of the solid–liquid–vapour contact lines are usually comparable to the radii of the particles. For a similar reason, the nanoparticle cannot be approximated by a flat surface in an environment where the humidity is not very small. Therefore, it is imperative to study systematically the capillary force between an AFM tip and nanoparticles.

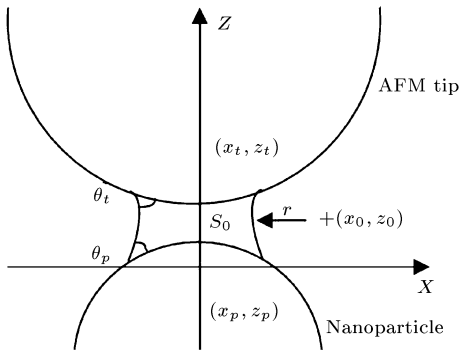


Fig. 1. A schematic representation of the side view of a capillary meniscus formed between an AFM tip and a nanoparticle separated by a distance S_0. The coordinates of the contact points of the capillary meniscus formed with the AFM tip and the nanoparticle are (x_t, z_t) and (x_p, z_p). The contact angles formed by the capillary meniscus with the AFM tip and the nanoparticle are θ_t and θ_p, respectively.

In this Letter, we report a theoretical study of the capillary force between an AFM tip and a nanoparticle. The effects of three major factors, including the vertical distance between an AFM tip and a spherical nanoparticle, the radial distance of the liquid–vapour interface of the meniscus and the contact angles of water meniscus formed with an AFM tip and the

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nanoparticles on the capillary force, are analysed in detail. We also discuss the cases that AFM tips have the different shapes (sphere, parabola, cone), and the results show that a sharp tip would always lead to a small capillary force.

The side view of the capillary meniscus between an AFM tip and a nanoparticle is shown in Fig. 1. The tip is assumed to be rigid and axisymmetric and its cross section is described by a function $Z = Z_t(X)$, where X denotes the local radial distance of the liquid–vapour interface of the meniscus from the Z axis. In this study, the geometries of the AFM tips are not restricted to spheres. The nanoparticle is assumed to be a sphere with a radius R_2 and its cross section is depicted by a function $Z = Z_p(X)$. The vertical distance between the tip and the nanoparticle, named as the vertical distance, is denoted by S_0. The liquid contacts the tip and the nanoparticle at a horizontal circle with contact angles θ_t and θ_p, respectively. The coordinates of the contact points in the side view are (x_t, z_t) and (x_p, z_p), separately. For convenience, the radius of the horizontal circle is called the radial distance. The radius of curvature of the liquid–vapour interface is crucial to calculate the pressure difference, and the subsequent capillary force. The calculation of the exact shape of the liquid–vapour interface is rather tedious, and usually requires numerical integration.[23] However, it has been shown that the description of the cross section of the liquid–vapour interface by a circle is a good approximation.[24] Thus, in this study, the contact points of the liquid–vapour interface with the cross sections of the tip and the nanoparticle (x_t, z_t) and (x_p, z_p) is assumed to obey the circle equations

$$(z_t - z_0)^2 + (x_t - x_0)^2 = r^2, \tag{1}$$

$$z_0^2 + (x_p - x_0)^2 = r^2, \tag{2}$$

where z_t is the vertical coordinate of the contact line with the tip, (x_0, z_0) denotes the centre of the circle describing the cross section of the liquid–vapour interface, and r is the radius of this circle. In order to solve Eqs. (1) and (2), additional equations are required. One condition is that the contact points of the liquid with the tip and the nanoparticle are necessarily described by the equation expressing the tip geometry and the nanoparticle,

$$z_t = Z_t(X_t), \tag{3}$$

$$z_p = Z_p(X_p) \equiv 0, \tag{4}$$

where $z_p \equiv 0$ because z_p is always on the X axis. The other equations describe the conditions that the circle describing the liquid–vapour interface forms the correct contact angles with the tip and the nanoparticle, respectively,

$$-\frac{x_t - x_0}{z_t - z_0} = \frac{z_t'(x_t) + \tan(\theta_t)}{1 - z_t'(x_t) \cdot \tan(\theta_t)}, \tag{5}$$

$$\frac{x_0 - x_p}{z_0} = \frac{z_p'(x_p) + \tan(\theta_p)}{1 - z_p'(x_p) \cdot \tan(\theta_p)}, \tag{6}$$

where $z_p'(x_p)$ denotes the tangent of the nanoparticle at x. The left-hand sides of Eqs. (5) and (6) give the slopes of the tangent to the liquid–vapour interface at the contact lines with the tip and the nanoparticle, in terms of the coordinates of the contact points. The right sides give the same slopes in terms of the corresponding contact angles and the inclinations of the solid surfaces. For convenience, let

$$w_t = \frac{z_t'(x_t) + \tan(\theta_t)}{1 - z_t'(x_t) \cdot \tan(\theta_t)},$$

$$w_p = \frac{z_p'(x_p) + \tan(\theta_p)}{1 - z_p'(x_p) \cdot \tan(\theta_p)},$$

then Eqs. (5) and (6) can be rewritten as

$$-\frac{x_t - x_0}{z_t - z_0} = w_t, \tag{7}$$

and

$$\frac{x_0 - x_p}{z_0} = w_p. \tag{8}$$

From Eqs. (2) and (8), the expression for the radius of the circle is

$$r = z_0\sqrt{1 + w_p^2}. \tag{9}$$

From Eqs. (1), (7) and (9), the expression of z_0 can be written as

$$z_0 = \frac{-z_t(1 + w_t^2) + z_t\sqrt{(1 + w_t^2)(1 + w_p^2)}}{(w_p^2 - w_t^2)}. \tag{10}$$

where we assume $x_t = x_p = x$. This assumption has been widely used in the theoretical analysis of the capillary force.[19,20] The pressure difference can be calculated using the Young–Laplace equation[16]

$$\Delta P = \gamma_l\Big(\frac{1}{x} - \frac{1}{\gamma}\Big). \tag{11}$$

Here positive and negative values of ΔP correspond to repulsive and attractive forces on the tip, respectively. The capillary force can be approximately calculated by[16]

$$F = -\pi x^2 \Delta P, \tag{12}$$

where the negative sign in this equation ensures that the value of the force is positive in most cases for the attraction. Thus the capillary force is derived from Eqs. (8)–(10),

$$F = -\pi\gamma_l x + \pi\gamma_l x^2 \cdot \frac{w_p^2 - w_t^2}{z_t[(1 + w_p^2)\sqrt{1 + w_t^2} - (1 + w_t^2)\sqrt{1 + w_p^2}]}. \tag{13}$$

When the radius of the nanoparticle $R_2 \to \infty$, corresponding to the case of the capillary force of an AFM tip with a flat plane, under the assumption $\theta_t = \theta_p = \theta$, Eq. (13) is reduced to

$$F = -\pi\gamma_l x + 2\pi\gamma_l x^2 \cos\theta / z_t. \tag{14}$$

This equation is identical to that presented by Marmur.[19]

Now we discuss the cases with various geometries of the AFM tips: a sphere, a parabola, and a cone. For a spherical tip with radius R_1, the contact point of the liquid–vapour interface with the tip fulfils the relationship

$$z_t = R_2 - \sqrt{R_2^2 - x^2} + S_0 + R_1 - \sqrt{R_1^2 - x^2}. \quad (15)$$

For a paraboloidal tip with the focus of this paraboloidal equation $R_1/2$, the contact points satisfy the equation

$$z_t = R_2 - \sqrt{R_2^2 - x^2} + S_0 + \frac{1}{2}\frac{x^2}{R_1}. \quad (16)$$

This equation is also a good approximation of a spherical tip with the condition $x \ll R_1$. For a conical tip to be studied, the cross section is simply given by

$$z_t = R_2 - \sqrt{R_2^2 - x^2} + S_0 + x, \quad (17)$$

where the height of the conical tip is chosen to be equal with the radius. Thus the tangent at x for the spherical, paraboloidal and conical tips are $z_t'(x) = x/\sqrt{R_1^2 - x^2}$, $z_t'(x) = x/R_1$ and $z_t'(x) = 1$, respectively. In the following, we discuss the effects of four factors x, S_0, θ_t and θ_p, on the capillary force for these three geometrical tips.

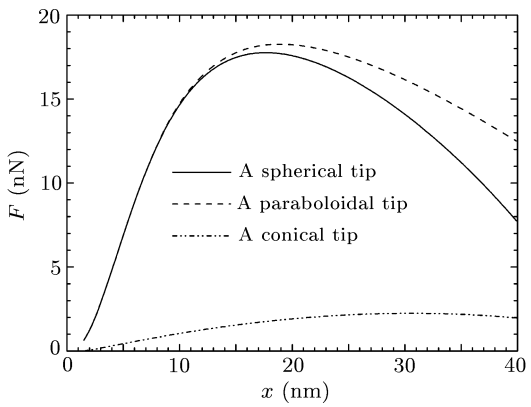


Fig. 2. Capillary forces between a nanoparticle and three kinds of tips: spherical (solid), paraboloidal (dashed) and conical (dot-dot-dashed) tips, vs the radial distance x.

When the humidity increases, the volume of the capillary bridge increases correspondingly, leading to a larger value of x for a fixed vertical distance S_0. Figure 2 shows the capillary forces for three geometrical tips, i.e. spherical, paraboloidal and conical tips with a nanoparticle, as a function of the radial distance x. The radii of the tip and the nanoparticle are selected as $R_1 = 50.0\,\mathrm{nm}$ and $R_2 = 80.0\,\mathrm{nm}$, respectively.[11,15] All the curves in this figure are calculated at $\gamma_l = 72\,\mathrm{mN/m^2}$, $\theta_t = 30°$, $\theta_p = 0°$ and $S_0 = 1.0\,\mathrm{nm}$.

From Fig. 2, it is easily found that the capillary forces for all the three kinds of tips increase first, reach their maxima and then decrease with the increase of x. This result is similar to that reported in Ref. [25] for the capillary forces between a spherical nanoparticle and a flat surface. It is emphasized that the capillary force does not increases monotonically with respect to the humility. There is a critical value of the humidity, above which the capillary force decreases as the humility increases. Numerically, we denote the critical values of the radial distance for three cases are 17.6 nm, 18.9 nm and 30.6 nm, respectively. The capillary forces for the spherical and the paraboloidal tips are almost identical before $x = 13.0\,\mathrm{nm}$. However, after this point the capillary force of a paraboloidal tip is larger than that of a spherical one and this deviation becomes more distinct as x increases. However, in the case of a conical tip, the situation is very different. The maximum of the capillary force of the conical tip is 0.7 nN and only about 5% of that for the other two tips. Consequently, the capillary force considerably depends on the tip geometry and the radial distance.

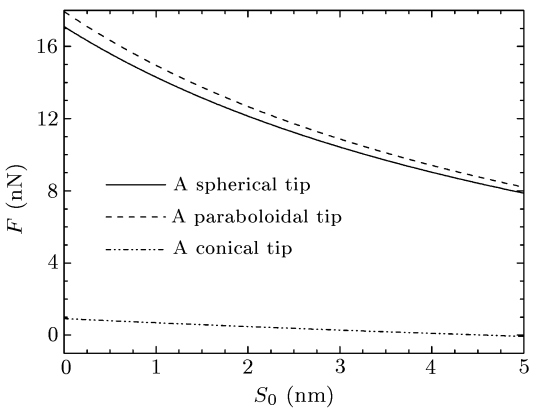


Fig. 3. Capillary forces between a nanoparticle and tips with different geometries: spherical (solid), paraboloidal (dashed) and conical (dot-dot-dashed) tips, vs the vertical distance S_0.

Figure 3 displays the capillary forces between three geometrical tips and a nanoparticle, as a function of the vertical distance S_0. In the calculation, the radial distance $x = 20.0\,\mathrm{nm}$ and other parameters are the same as those in Fig. 2. We can find that a small vertical distance induces a large capillary force. The closer the distance between the AFM tip and the nanoparticle, the larger the value of the capillary force. Similarly to Fig. 2, the role of the tip geometry is also obvious. The capillary force of the paraboloidal tip is the largest, while for the conical tip it is the smallest.

The contact angle usually reflects the wetting condition of a solid surface by a liquid. Figure 4 displays the effect of the different contact angles of the tip and a nanoparticle on the capillary forces for the three geometrical tips. All the curves are calculated at $S_0 = 1.0\,\mathrm{nm}$. We can find that the contact angles of a tip and a nanoparticle have an explicit impact on the capillary force. Compared to the case of $\theta_t = \theta_p = 0°$, the capillary force for $\theta_t = 0°$, $\theta_p = 30°$ is smaller at small radial distance, whereas it is large at large radial

distance. The capillary forces for $\theta_t = 30°$, $\theta_p = 0°$ is always smaller than those for the cases of $\theta_t = 0°$, $\theta_p = 30°$ and $\theta_t = \theta_p = 0°$.

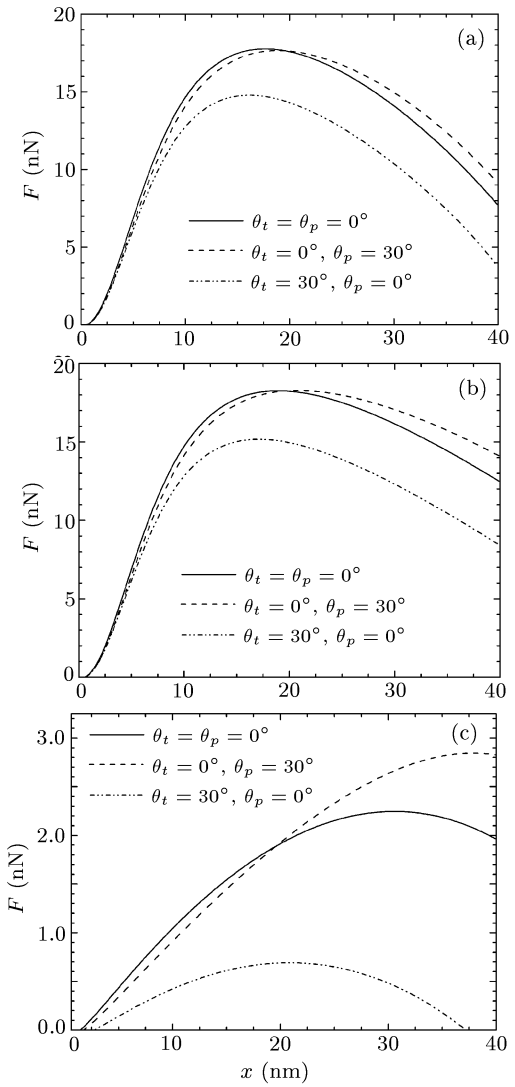


Fig. 4. Capillary forces between a nanoparticle and tips with different geometries: spherical (a), paraboloidal (b) and conical (c) tips for different contact angles of the tips and the nanoparticle, vs the radial distance x.

In summary, we have systematically analysed the interactions between an AFM tip and a nanoparticle and have developed an explicit equation for the capillary force. The results for some typical cases show that the shape of a tip, the humidity, the vertical distance and the contact angles of a tip and the nanoparticle all have significant effects on the capillary forces. Our study should be helpful to a quantitative measurement of the forces by AFM and useful to the understanding of the interactions between two particles on the nanoscale. It should be noted that the interactions between an AFM tip and nanoparticles are usually very complex. For example, when the humidity is very small so that the capillary force may be comparable and smaller than van der Waals force, van der Waals should be included in the analysis of the interactions between an AFM tip and a nanoparticle. However, when the humidity is large, van der Waals forces are usually negligible (i.e., when the nanoparticles are made by gold and with a radius of 80 nm and a silicon AFM tip is used, van der Walls is negligible if the radial distance of the solid–liquid–vapour contact line is larger than 5 nm). The case for a low humidity environment will be discussed elsewhere.

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