Tip-Surface Capillary Interactions

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The capillary adhesion force between the tip of a particle and a flat surface is calculated by numerical solution of the equations which are developed as well as by an approximate analytical equation which is suggested. Results are presented for spherical, paraboloidal, and conical tips. They are compared with the classical approximate equation for the capillary adhesion force between a sphere and a flat surface, which predicts that the force is independent of the position of the liquid-fluid interface. The present analysis shows that the situations for which the classical equation can be used are rather limited. For quantitative analysis of experimental data, such as the measurement of thin film profiles using atomic force microscopy, accurate knowledge of the geometry of the tip of the particle and numerical solution of the equations are usually required.

Introduction

The interaction of particles with solid surfaces is of importance in many scientific and industrial fields.[1] Recently,[2,3] this subject has regained attention due to the novel usage of the atomic force microscope (AFM) for studying thin lubricant films. Understanding the interaction between the tip of the AFM and a liquid film is essential for the interpretation of measurements of film profiles. The interaction of the tip of a particle with a surface may stem from a few mechanisms,[4] the most important of which are the intermolecular force, capillary force, and interfacial tension force. The latter two become relevant whenever the tip and the surface are in contact with both a liquid and a fluid (i.e. vapor or a second immiscible liquid). The term "capillary force" refers to the force due to the pressure difference across the curved liquid-fluid interface in the capillary space between the tip and the surface. The term "interfacial tension force" implies the force by which the liquid-fluid interface directly pulls the solid surface at the contact line.

In the present paper, attention is focused on the calculation of the capillary force. A very simple approximate equation has been used to describe the force of capillary adhesion due to a liquid bridge between a rigid spherical particle and a flat and rigid solid surface, which are immersed in a fluid[1,5]

$$F_0 = 4\pi R\sigma \cos\theta \qquad (1)$$

where R is the radius of the particle, σ is the liquid-fluid interfacial tension, and θ is the contact angle. The assumptions underlying this equation are the following: the radii of the solid-liquid-fluid contact lines (see Figure 1) are very small compared with R; the radii of the two contact lines are equal; the distance between the particle surface and the flat surface is very small compared with the radius of the contact line; and the effect of the curvature of the liquid-fluid interface which is measured at the horizontal plane is negligible.

Equation 1 predicts that the capillary adhesion force is independent of the position of the solid-liquid-fluid contact line. For obvious reasons, this feature may be extremely useful in interpreting experimental data. However, the validity of the assumptions underlying eq 1 and the possibility of applying this equation to nonspherical tips have not been sufficiently tested; therefore the use of this equation to interpret experimental data may be questionable. The goals of this paper are to present general (though somewhat approximate) equations for calculating the capillary interaction between the tip of a particle and a flat solid surface, and discuss the conditions under which eq 1 may or may not be used. Special emphasis is put on the effect of the tip geometry, which is shown to have a major role in determining the capillary adhesion force.

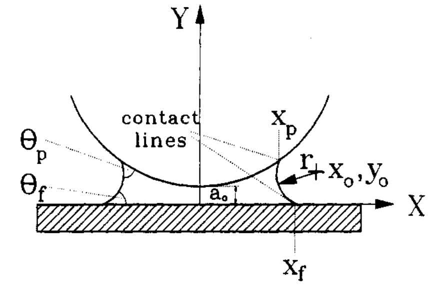

Figure 1. System under study: a tip near a flat surface.

Theory

The system under study is shown in Figure 1. The tip is assumed rigid and axisymmetric; its cross section is described by a function $Y = Y_p(X)$, where X is the local radial distance from the axis of symmetry. The flat and rigid solid surface is described by $Y = 0$. The liquid contacts the tip at a horizontal circle, the radius of which is x_p, and the contact angle is θ_p. The liquid contacts the flat surface at a circle, the radius of which is x_f, and the contact angle is θ_f. The problem is to calculate the radius of curvature of the liquid-fluid interface, in order to calculate the pressure difference across it, and subsequently the force of capillary adhesion. The equations to be developed below may be easily extended to particle-particle interaction. However, the case of tip-surface interaction is sufficient to demonstrate the essential points. In most practical situations the tips are sufficiently small to justify the neglect of gravity.

The calculation of the exact shape of the liquid-fluid interface is rather tedious, and usually requires numerical

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integration, e.g. ref 6. It was shown,[7] however, that describing the cross-section of the liquid–fluid interface by a circle is a very good approximation. Therefore, the contact points of the liquid–fluid interface with the cross sections of the tip and the flat surface, respectively, obey the following relationships

$$(y_p - y_0)^2 + (x_p - x_0)^2 = r^2 \tag{2}$$

and

$$y_0^2 + (x_f - x_0)^2 = r^2 \tag{3}$$

where y_p is the vertical coordinate of the contract line with the tip, (x_0, y_0) is the center of the circle describing the cross section of the liquid-fluid interface, and r is its radius.

The parameters defining the system, for a given tip and surface, are x_f, θ_p, and θ_f. In order to solve eqs 1 and 2, additional equations are required. One is the condition that the contact points of the liquid with the tip are necessarily described by the equation expressing the tip geometry

$$y_p = Y_p(x_p) \tag{4}$$

The other equations are the conditions that the circle describing the liquid–fluid interface forms the correct contact angles with the tip and the flat surface, respectively

$$-\frac{x_p - x_0}{y_p - y_0} = \frac{y_p'(x_p) + \tan\theta_p}{1 - y_p'(x_p)\tan\theta_p} \tag{5}$$

and

$$\frac{x_f - x_0}{y_0} = -\tan\theta_f \tag{6}$$

The left-hand sides of the last two equations give the slopes of the tangents to the liquid–fluid interface at the contact lines with the tip and the flat surface, in terms of the coordinates of the contact points. The right-hand sides give the same slopes in terms of the contact angles and the inclination of the solid surfaces.

In general, the system of eqs 2–6 needs to be solved in order to determine the radius of the circle. However, since this solution may require numerical procedures, it is worthwhile to develop an approximate analytical solution, which will enable simple evaluation of r. From eqs 3 and 6, the expression for the radius of the circle is

$$r = \frac{y_0}{\cos\theta_f} \tag{7}$$

From eqs 2, 6, and 7, the equation for y_0 is

$$y_0 = \frac{1}{2}\frac{y_p^2 + (x - x_f)^2}{y_p + (x - x_f)\tan\theta_f} \tag{8}$$

In this equation x_p is still unknown, but if the assumption of $x_p \approx x_f$ is made, then

$$y_0 \approx \frac{y_p(x_f)}{2} \tag{9}$$

leading to

$$r \approx \frac{y_p(x_f)}{2\cos\theta_f} \tag{10}$$

This approximation will be termed "the symmetric case", since it is based on the assumption that the liquid–fluid interface is symmetrically oriented with respect to the plane $y = y_0$.

Once the radius of the circle is known, either from an exact solution of the equations or from the approximate eq 10, the pressure difference can be calculated using the Young–Laplace equation

$$\Delta P = \sigma\left(\frac{1}{x_f} - \frac{1}{r}\right) \tag{11}$$

In this equation, x_f approximates the radius of curvature in the horizontal plane and $-r$ approximates the radius of curvature in the vertical plane going through the axis of symmetry. The force of adhesion due to the capillary interaction can be approximately calculated by

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

The negative sign in this equation assures, for reasons of convenience, that the value of the force is in most cases positive.

Results and Discussion

Results will be presented and discussed for three tip geometries: a sphere, a paraboloid, and a cone. In the latter two cases, the axis of symmetry is perpendicular to the flat surface, and the apex is closest to it. For the sphere, the point closest to the flat surface will be referred to as the "apex". The calculations can be easily performed for any other geometry, but these three choices seem sufficient to elucidate the main points which need to be discussed. First, the "symmetric" case will be presented, since it offers analytical formulas which enable immediate insight. Then, it will be compared with the numerical solutions of the full set of equations. In all calculations it is assumed that $\theta_f = \theta_p$. This assumption does not affect the conclusions drawn from this study.

The Symmetric Case ($x \equiv x_p \approx x_f$). For spherical tips, eq 4 reads

$$y_p/R = a_0/R + 1 - (1 - (x/R)^2)^{1/2} \tag{13}$$

where a_0 is the distance of the apex from the flat surface and R is the radius of the sphere. Inserting this equation into eqs 10–12, and normalizing the result with respect to the force predicted by eq 1, the dimensionless capillary adhesion force for a spherical tip is given by

$$\frac{F_s}{F_0} = \frac{1}{2}\frac{(x/R)^2}{a_0/R + 1 - (1 - (x/R)^2)^{1/2}} - \frac{x/R}{4\cos\theta_f} \tag{14}$$

For $x/R \ll 1$, i.e. for a liquid–fluid interface which is very close to the apex, eq 13 turns into a parabola:

$$y_p/R = a_0/R + \frac{1}{2}(x/R)^2 \tag{15}$$

For this case, eq 14 is simplified to

$$\frac{F_s^*}{F_0} = \frac{(x/R)^2}{2a_0/R + (x/R)^2} - \frac{x/R}{4\cos\theta_f} \tag{16}$$

Equation 16, in addition to being an approximation for the dimensionless capillary adhesion force near the apex of a spherical tip ($x/R \ll 1$), is generally valid for a paraboloid described by eq 15.

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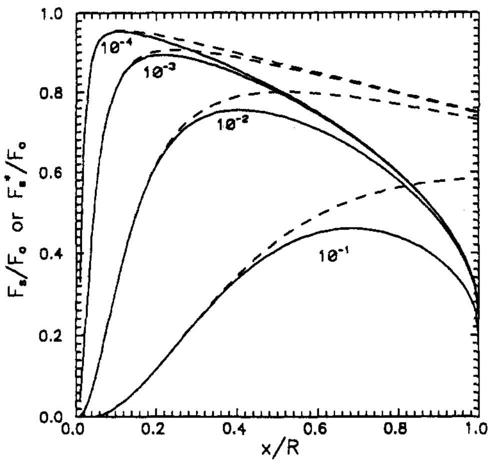

Figure 2. Dimensionless capillary adhesion force for a spherical (solid curves) and a paraboloidal (dashed curves) tip, calculated under the symmetric case approximation. The numbers indicate the dimensionless distance of the apex from the flat surface.

By use of eq 16, the conditions under which the classical eq 1 may hold can be emphasized: the assumption of symmetry ($x_p = x_f$), $x/R \ll 1$, $a_0/R \ll x/R$, and ignoring the curvature ($1/x$). The extent of deviation from the capillary adhesion force predicted by eq 1 is shown in Figure 2. The full curves in this figure show the results for a spherical tip, as calculated from eq 14, and the dashed curves are the results for a paraboloid, as calculated from eq 16. The different pairs of curves are labeled by numbers, which indicate the values of a_0/R. All the curves in this figure are calculated for $\theta_f = 0$. The most prominent conclusion which can be made based on Figure 2 is that *the force of adhesion is in most cases far from the value predicted by eq 1*.

With the aid of Figure 2 it can be concluded that all the factors which were varied in the calculations, i.e. the distance of the apex from the surface, the geometry of the tip, and the radial distance, contribute to the deviation from eq 1. First, the distance from the apex is seen to have a major effect on the capillary adhesion force. When a_0/R approaches zero, the dimensionless capillary adhesion force increases toward unity, namely the capillary adhesion force approaches the value predicted by eq 1. Actually, as seen from eq 16, the independence of the capillary adhesion force on the radial distance, which is the most prominent feature of eq 1, can be materialized only if a_0/R is negligible. The physical reason behind this independence, when it is pertinent, is that the pressure difference is proportional to x^{-2}; therefore the product of the pressure difference and the contact area is a constant.

The second factor is the tip geometry. Close to the apex, the difference between the capillary adhesion force acting on a sphere and on a paraboloid is negligible. However, as a_0/R decreases, and as the radical distance from the apex increases, this deviation becomes more appreciable. The third factor which affects the capillary adhesion force is the radial distance from the apex. This effect is seen in Figure 2 to be very pronounced, in marked contrast to the prediction of eq 1. Close to the axis of symmetry ($x = 0$), the force of capillary adhesion goes to zero. Then, the dimensionless capillary adhesion force goes through a maximum, the value of which strongly depends on a_0/R. This dependence on x/R is partly due to the effect of the area of contact, πx^2, and partly to the effect of the curvature, $1/x$, which is not accounted for in eq 1.

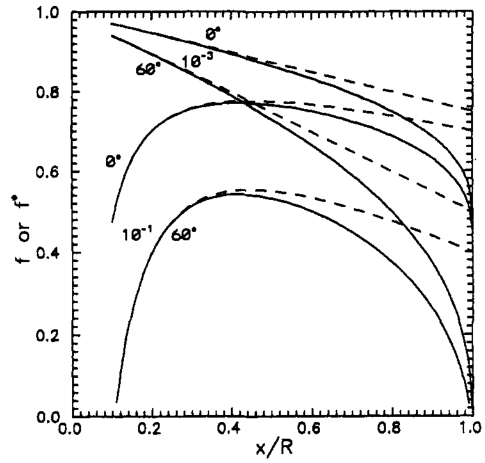

Figure 3. Effect of the curvature in the horizontal plane as shown by the ratios defined in eq 17 for a spherical tip (solid curves) and in eq 18 for a paraboloidal tip (dashed curves), under the symmetric case approximation. The powers of 10 indicate the dimensionless distance of the apex from the flat surface, and the other numbers indicate the contact angle.

Figure 3 assists in differentiating between these two contributions by showing the ratio of the capillary adhesion force as given by eq 14 or 16 to the capillary adhesion force which would have been predicted if the contribution of the curvature $1/x$ had been ignored. This ratio is given for a sphere by

$$f \equiv \left[\frac{(x/R)^2}{a_0/R + 1 - (1 - (x/R)^2)^{1/2}} - \frac{x/R}{2\cos\theta_f}\right] \Big/ \left[\frac{(x/R)^2}{a_0/R + 1 - (1 - (x/R)^2)^{1/2}}\right] \quad (17)$$

and for a paraboloid by

$$f^* \equiv \left[\frac{(x/R)^2}{2a_0/R + (x/R)^2} - \frac{x/R}{4\cos\theta_f}\right] \Big/ \left[\frac{(x/R)^2}{2a_0/R + (x/R)^2}\right] \quad (18)$$

Figure 3 shows calculations for two values of a_0/R and for two contact angles. The full curves show f and the dashed curves show f^*. It is clear that omission of the term containing the curvature $1/x$ leads to serious errors at large distances from the apex. For high values of a_0/R this error can be very appreciable also at relatively low radial distances. The magnitude of the error depends also on the contact angle: the higher the contact angle, the higher the error. *This effect of the contact angle on the dimensionless capillary adhesion force is mathematically linked with the effect of the curvature* $1/x$, as shown in eqs 14 and 16.

The dependence of the capillary adhesion force on the geometry of the tip is more pronounced when a cone is considered. In this case, under no circumstances is eq 1 expected to hold, since the pressure difference is not proportional to x^{-2}. The cross section of the specific cone to be studied here, for which the height above the apex equals the radius at this height, is given by

$$y_p R = a_0/R + x/R \quad (19)$$

This cone is chosen to enable convenient comparison with the spherical tip of radius R, the equator of which coincides with the circumference of the base of the cone when their apexes coincide. The dimensionless capillary adhesion force for such a cone (normalized as before to the force predicted by eq 1) is

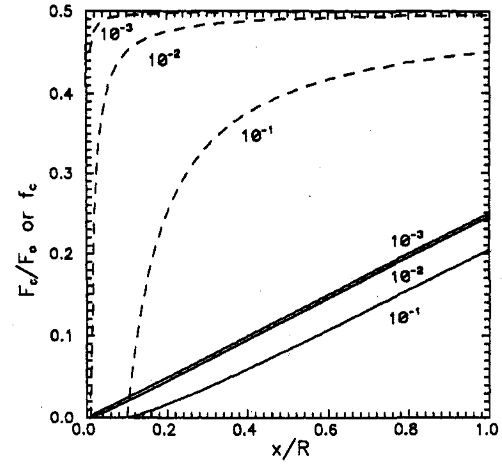

Figure 4. Dimensionless capillary adhesion force for a conical tip (solid curves) and the effect of the curvature in the horizontal plane as demonstrated by the ratio defined by eq 21 (dashed curves), under the symmetric case approximation. The numbers indicate the dimensionless distance of the apex from the flat surface.

$$\frac{F_c}{F_0} = \frac{(x/R)^2}{2(a_0/R + x/R)} - \frac{x/R}{4\cos\theta_f} \tag{20}$$

Figure 4 shows in full curves the dimensionless capillary adhesion force for this cone, as calculated from eq 20 for zero contact angle. When the apex of the cone is very close to the flat surface, the capillary adhesion force depends linearly on the radial distance from the apex. As the value of a_0/R increases, this dependence deviates from being linear, however not too much. It is very clear that eq 1 does not hold in this case at all.

The dashed curves in Figure 4 show the effect of the curvature $1/x$. This is done by presenting the ratio f_c of the capillary adhesion force given by eq 20 to that which would have been calculated if the effect of the curvature $1/x$ had been ignored

$$f_c \equiv \left[\frac{(x/R)^2}{2(a_0/R + x/R)} - \frac{x/R}{4\cos\theta_f}\right] \Big/ \left[\frac{(x/R)^2}{2(a_0/R + x/R)}\right] \tag{21}$$

As seen in Figure 4, the neglect of this curvature leads to a major error, of at least a factor of 2, and usually much more.

Numerical Solution of the Equations. The symmetric case has been presented above in detail, since it is amenable to analytical solution. However, it is important to test the validity of the assumption of "symmetry." For this purpose, the set of equations 2–6 was numerically solved. The comparison is presented in Figures 5–7, in terms of the ratio of the numerically calculated radius of the circle describing the cross section of the liquid–vapor interface (eq 7) to the value calculated under the assumption of "summetry" (eq 10)

$$f_r = \frac{2y_0}{y_p(x_f)} \tag{22}$$

This ratio was chosen for presentation rather than the capillary adhesion force itself, since it directly pertains to the essence of the symmetric case approximation. Figures 5, 6, and 7 show data for a sphere, a paraboloid, and a cone, respectively. The solid curves are for $a_0/R = 10^{-1}$, and the dashed curves are for $a_0/R = 10^{-4}$. All calculations were done for three values of the contact angle, which are indicated in the figures.

Two general conclusions can be drawn from these figures for all three tip shapes. First, the symmetric case approximation is better justified the smaller the contact angle. This is understandable, since high contact angles further enhance the distortion of symmetry which is caused by the inclination of the tip surface. The second conclusion is, that the effect of the distance of the apex from the flat surface on the validity of the symmetric case approximation is minor.

There are two additional conclusions to be drawn which, however, do depend on the shape of the tip. Figures 5 and

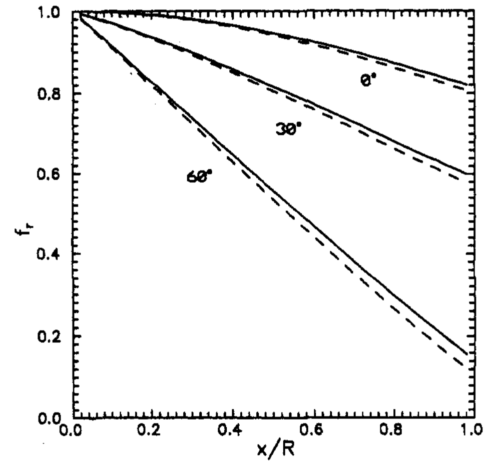

Figure 5. A test of the analytical symmetric case approximation for a spherical tip: the ratio of the numerically calculated radius of the circle describing the cross section of the liquid–vapor interface to the value calculated under the symmetric case approximation (see eq 22; solid curves, $a_0/R = 10^{-1}$; dashed curves, $a_0/R = 10^{-4}$. The numbers indicate the contact angle.

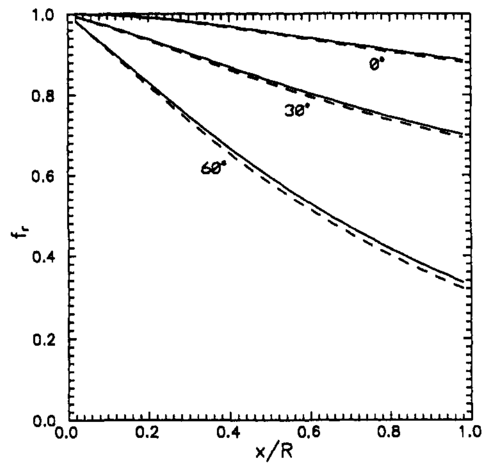

Figure 6. The same as Figure 5, for a paraboloidal tip.

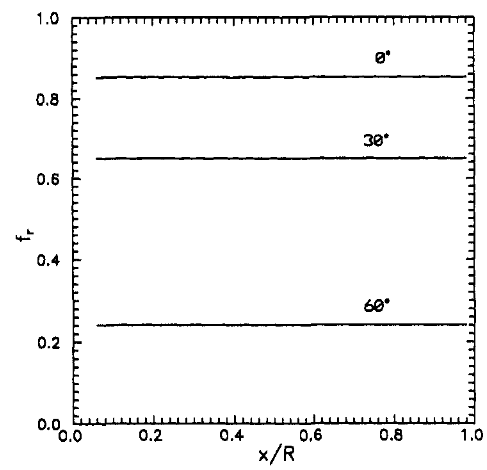

Figure 7. The same as Figure 5, for a conical tip.

6 show that the symmetric case approximation for the sphere and the paraboloid becomes better the closer one gets to the apex. Also, for zero contact angle, the symmetric case is quite accurate up to distances of about $0.4R$. In contrast, Figure 7 demonstrates, that for a conical tip f_r is constant with the radical distances, and the symmetric case is never very accurate.

Summary and Conclusions

Equations for the capillary force acting between a rigid tip and a rigid flat surface were developed. Since these equations have to be numerically solved, an analytical approximate solution was suggested. The predictions of these equations were compared with those of the classical equation for the capillary adhesion force between a particle and a flat surface, eq 1. The question of the validity of eq 1 is of significant practical importance, since it predicts the capillary adhesion force to be independent of the position of the three-phase contact line. It can be generally concluded that eq 1 is valid only under rather restricted conditions. The present analytical approximation is very useful in understanding qualitative trends; however, it is not always sufficiently accurate. The main specific conclusions which can be drawn from this study are summarized as follows:

1. The geometry of the tip has a major effect on the capillary adhesion force, on the validity of eq 1, and on the validity of the symmetric case approximation.

2. The distance of the apex from the flat surface also has a major effect on the capillary adhesion force and on the validity of eq 1. However, it does not appreciably affect the accuracy of the symmetric case approximation.

3. The curvature in the horizontal plane, $(1/x)$, the effect of which was neglected in the development of eq 1, has an important contribution to the capillary adhesion force.

4. The contact angle affects the dimensionless capillary adhesion force, due to its involvement in the term containing the curvature $1/x$. This effect is on top of the major influence which the contact angle has on the capillary adhesion force itself.

5. In most cases, for accurate evaluation of the capillary adhesion force, the full system of equations should be numerically solved. However, the analytical approximation is still usually far better than eq 1.