The Actual Contact Angle on a Heterogeneous Rough Surface in Three Dimensions

ARTICLE *in* LANGMUIR · SEPTEMBER 1998

Impact Factor: 4.46 · DOI: 10.1021/la960723p

2 AUTHORS:

Gershon Wolansky
Technion - Israel Institute of Technology

Abraham Marmur
Technion - Israel Institute of Technology

The Actual Contact Angle on a Heterogeneous Rough Surface in Three Dimensions

Gershon Wolansky† and Abraham Marmur*,‡

Departments of Mathematics and Chemical Engineering, Technion—Israel Institute of Technology, 32000 Haifa, Israel

Received July 22, 1996. In Final Form: February 27, 1998

A general equation is presented for the actual contact angle on a solid surface in a three-dimensional setting. The solid surface may be rough or heterogeneous or both. The effects of the existence of line tension and its variation with the position of the contact line are also included. It is shown that when line tension can be ignored, the actual contact angle at each point on the solid surface always equals the intrinsic contact angle (which is given in this case by the Young equation). However, when line tension is significant, the actual contact angle deviates from the Young contact angle by a term proportional to the geodesic curvature of the contact line and a term depending on the directional derivative of the line tension. Various situations are presented and discussed. Of particular interest is the example of a drop on a sphere, for which it is shown that the actual contact angle equals the Young contact angle when the contact line coincides with the equator of the sphere.

1. Introduction

The contact angle concept is of fundamental importance in all solid−liquid−fluid interfacial phenomena, such as wetting of solid surfaces, capillary penetration into porous media, and flotation.[1−4] The contact angle that a liquid makes with an ideal (i.e., rigid, flat, chemically homogeneous, insoluble, and nonreactive) solid surface is termed the intrinsic contact angle (see Figure 1a). The first equation that was developed for the intrinsic contact angle is the well-known Young equation,[1] which reads:

$$\cos \theta_Y = \frac{\sigma_{sf} - \sigma_{sl}}{\sigma_{lf}} \quad (1)$$

where θ_Y is the Young contact angle (i.e., the intrinsic contact angle as calculated from the Young equation), and σ_{lf}, σ_{sl}, and σ_{sf} are the liquid−fluid, solid−liquid, and solid−fluid interfacial tensions, respectively.

The Young equation ignores the three-phase molecular interactions at the contact line between the solid, liquid, and fluid phases. Various solutions have been proposed to this problem,[5−16] the most popular of which seems to be the line tension approach. Line tension is the one-dimensional analog of surface tension in the sense that it accounts for the difference, per unit length of the contact line, between the actual energy of the three-phase system and its assumed energy, ignoring the three-phase interactions at the contact line. For an ideal solid surface (therefore an axisymmetric drop), the following equation was developed long ago for the intrinsic contact angle, θ_i,[6,7,11] based on a suggestion by Gibbs:[5]

$$\cos \theta_i = \cos \theta_Y - \frac{\tau}{R\sigma_{lf}} \quad (2)$$

where τ is the line tension and R is the radius of the contact line. In eq 2, the line tension is assumed constant.

Real solid surfaces are usually rough and chemically heterogeneous. On such surfaces, the actual contact angle (defined as the angle measured from the tangent to the surface of the solid at any given point on the contact line to the tangent to the liquid−fluid interface at this point, see Figure 1b) may vary from point to point. Moreover, if the solid surface is chemically heterogeneous, the local intrinsic contact angle (i.e., the contact angle that would characterize an ideal solid surface of the same chemical composition as the local composition of the real surface) varies from point to point. It is not a priori clear whether the actual contact angle at each point necessarily equals the intrinsic one.

For two-dimensional and axisymmetric systems with rough and heterogeneous solid surfaces, it has been known through many examples and has recently been formally shown[14] that the actual contact angle always equals the intrinsic one when line tension effects are negligible. However, when line tension effects are meaningful, the actual contact angle is different from the intrinsic one if the solid surface is rough.[16] In addition, it was pointed out that line tension cannot be constant; consequently, eq

* To whom correspondence should be addressed. Fax: 972-4-8293088. E-mail: marmur@tx.technion.ac.il.

† Department of Mathematics.

‡ Department of Chemical Engineering.

(1) Young, T. *Phil. Trans. Roy. Soc. (London)* **1805**, *95*, 65.
(2) Neumann, A.W. In *Wetting, Spreading and Adhesion*, Padday, J.F., Ed.; Academic: New York, 1978; p 3.
(3) Good, R.J. In *Surface and Colloid Science*, Good, R.J., Stromberg, R.R., Eds.; Plenum Press: New York, 1979; Vol. 11, p 1.
(4) Marmur, A. *Adv. Colloid Interface Sci.* **1983**, *19*, 75.
(5) Gibbs, J.W. *The Scientific Papers of J. Willard Gibbs*; Dover: New York, **1961**; Vol. 1, p 288.
(6) Veselovski, V.S.; Pertchov, V. N. *Zh. Fiz. Khim.* **1936**, *8*, 245.
(7) Pethica, B.A. *Rep. Prog. Appl. Chem.* **1961**, *46*, 14.
(8) Miller, C.A.; Ruckenstein, E. *J. Colloid Interface Sci.* **1974**, *48*, 368.
(9) Ruckenstein, E.; Lee, P.S. *Surface Sci.* **1975**, *52*, 298.
(10) Jameson, G. J.; del Cerro, M. C. G. *J. Chem. Soc. Faraday Trans. I* **1976**, *72*, 883.
(11) Pethica, B.A. *J. Colloid Interface Sci.* **1977**, *62*, 567.
(12) Marmur, A. *J. Colloid Interface Sci.* **1992**, *148*, 541.
(13) Marmur, A. *J. Adhesion Sci. Tech.* **1992**, *6*, 689.
(14) Marmur, A. *Adv. Colloid Interface Sci.* **1994**, *50*, 121.
(15) Marmur, A. *J. Colloid Interface Sci.* **1997**, *186*, 462.
(16) Marmur, A. *Colloids and Surfaces A* **1998**, *136*, 81.

S0743-7463(96)00723-8 CCC: $15.00
Published on Web 08/14/1998

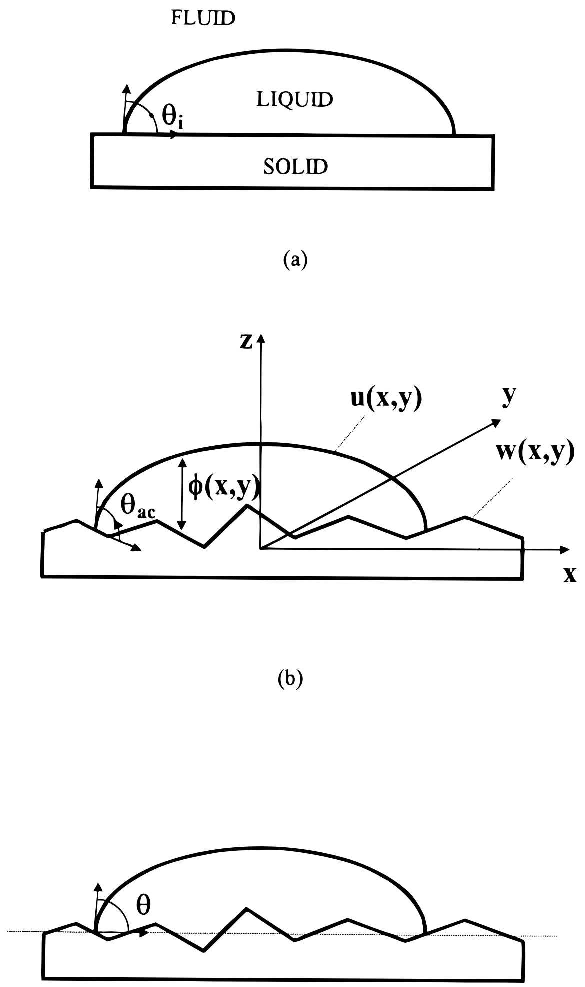

Figure 1. (a) The intrinsic contact angle; (b) the actual contact angle and the geometry of the system; (c) the apparent contact angle.

2 was modified to include the dependence of line tension on position:[15,16]

$$\cos\theta_{\mathrm{i}} = \cos\theta_{\mathrm{Y}} - \frac{\tau}{R\sigma_{\mathrm{lf}}} - \frac{1}{\sigma_{\mathrm{lf}}}\frac{\mathrm{d}\tau}{\mathrm{d}R} \qquad (3)$$

This dependence is due to the fact that line tension, which corrects for the three-phase interactions at the contact line, depends on the shape of the liquid−fluid interface. Such dependence makes the problem of calculating the contact angle, taking line tension into account, an integro-differential problem. To avoid such mathematical complexity, it was assumed that line tension depends on the position of the contact line.[15,16] In particular, considering the dependence of line tension on the position of the contact line becomes essential when heterogeneous surfaces are discussed.

The purpose of the present paper is to generalize the conclusions just presented, obtained for two-dimensional situations, to the three-dimensional case in which no symmetry is assumed. It will be shown that if line tension is significant, the actual contact angle is usually different from the intrinsic one given by eq 3, because it depends on the geometric properties of the solid surface. Previous attempts in this direction[4,17,18] did not consider roughness or line tension in a sufficiently general way.

(17) Johnson, R.E., Jr. *J. Phys. Chem.* **1959**, *63*, 1655.
(18) Boruvka, L.; Neumann, A.W. *J. Chem. Phys.* **1977**, *66*, 5464.

2. Theory

The system to be discussed includes a liquid drop on a rough and heterogeneous solid surface, both immersed in a fluid. It is assumed that the elevation of the solid surface is a graph of a smooth function $\{x, y, w(x,y)\}$, defined over the whole $\{x,y\}$ plane. The liquid−fluid interface is given by a graph of a function $\{x, y, u(x,y)\}$, and the set $\phi = u - w$ describes the thickness of the liquid at each point (see Figure 1b). The definitions of $w(x,y)$ and $u(x,y)$ as functions imply that there are unique values of w and u for each point $\{x,y\}$. This implication restricts to some extent the nature of the roughness of the solid surface and requires the apparent contact angles to be acute (the apparent contact angle is the angle measured from the direction parallel to the $\{x,y\}$ plane at any given point on the contact line to the tangent to the liquid−fluid interface at this point, see Figure 1c). These restrictions can be removed, but the mathematical details will be much more complicated. Therefore, the present discussion is based on the assumptions just presented, hoping that the physical conclusions hold for all apparent contact angles.

Even though the wetted surface occupies, in general, only a portion of the solid, it will be assumed for mathematical convenience, as will explained later, that the function u is virtually extended over the whole $\{x,y\}$ plane. Naturally, this assumption also holds for ϕ and does not limit the generality of the results. The wetted surface of the solid is then given by the surface $\Omega_\phi \equiv \{(x, y, w(x,y)); \phi(x,y) > 0\}$, and its projection over the $\{x,y\}$ plane is $\underline{\Omega}_\phi \equiv \{(x,y); (x, y, w(x,y)) \in \Omega_\phi\}$. The three-phase contact line, which is the boundary of Ω_ϕ, is denoted by $\Gamma_\phi \equiv \{(x, y, w(x,y)); \phi(x,y) = 0\}$. Its projection on the $\{x,y\}$ plane is $\underline{\Gamma}_\phi \equiv \{(x,y); (x, y, w(x,y)) \in \Gamma_\phi\}$.

Equilibrium of the system is achieved when the internal energy of the system and its environment is a minimum. This is expressed by three conditions: the thermal and chemical equilibrium conditions that imply uniformity of temperature and chemical potentials, and the mechanical equilibrium condition that determines the equilibrium shape of the liquid−fluid interface and the contact angles. The latter condition is achieved by minimizing the sum of energies associated with the interfaces, displacement of the liquid−fluid interface, and gravity.[19] The sum of these energies can be written as

$$G(\phi) = \int\int_{\underline{\Omega}_\phi} \mathbf{F}(\phi, \nabla\phi, x, y)\,\mathrm{d}x\,\mathrm{d}y + \int_{\Gamma_\phi} \tau(x,y)\,\mathrm{d}s \equiv G_{\mathrm{i}} + G_{\mathrm{c}} \qquad (4)$$

G is considered a function of ϕ, because it depends on the shape of the liquid−fluid interface, u ; therefore, through the substitution $u = \phi + w$, where w is a priori known, it depends on ϕ. The first integral in this equation, denoted G_{i}, stands for the energy associated with the interfaces of the system (assuming that the interfacial tensions are not affected by the presence of a third phase in the close vicinity of each interface at the contact line), the work done by displacing the liquid−fluid interface, and gravity. $\mathbf{F}$ can be easily generalized from the two-dimensional case of a volatile drop in the gravitational field[19] to be

$$\mathbf{F} \equiv (P_{\mathrm{f}} - P_{\mathrm{l}})(u - w) - \frac{1}{2}(u - w)^2\Delta\rho g + \sigma_{\mathrm{lf}}\sqrt{1 + |\nabla u|^2} + [\sigma_{\mathrm{sl}}(x,y) - \sigma_{\mathrm{sf}}(x,y)]r(x,y) \qquad (5)$$

(19) Marmur, A. *Langmuir* **1996**, *12*, 5704.

where P_f and P_l are the pressures in the fluid and liquid phases, respectively, $\Delta\rho$ is the (positive) density difference between the liquid and the fluid, g is the gravitational acceleration, ∇ is the horizontal gradient in the $\{x,y\}$ plane, and the roughness ratio, r, is given by

$$r(x,y) \equiv \sqrt{1 + |\nabla w|^2} \tag{6}$$

The second integral in eq 4, denoted G_c, accounts for the contribution of the line tension, τ, along the contact line, Γ_ϕ, for which s is the arc-length. It should be noticed that line tension is not assumed constant.

Dealing with eq 4 as written is inconvenient for two reasons. First, G depends on ϕ not only through $\mathbf{F}$ but also through the domain of integration Ω_ϕ. In addition, the two integrals have different domains of integration. Therefore, the two integrals in eq 4 will now be converted to integrals over the whole $\{x,y\}$ plane. For G_i this is easily achieved by introducing the step function $H(\phi) = 1$ if $\phi \geq 0$ and $H(\phi) = 0$ if $\phi < 0$, and writing:

$$G_i(\phi) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H(\phi)\mathbf{F}(\nabla\phi, x, y)\, dx\, dy \tag{7}$$

Writing G_c as an integral over the whole $\{x,y\}$ plane is somewhat more difficult. As proven in Appendix A, it turns out to be

$$G_c(\phi) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \tau(x,y)\sqrt{1 + \left|\frac{\nabla w \times \nabla\phi}{|\nabla\phi|}\right|^2} \times |\nabla\phi|\delta(\phi)\, dx\, dy \tag{8}$$

where $\delta(\phi)$ is the Dirac delta function. The expressions for G_i and G_c are now collected to write G as

$$G(\phi) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathsf{G}(\phi, \nabla\phi, x, y)\, dx\, dy \tag{9}$$

where

$$\mathsf{G}(\phi, \nabla\phi, x, y) = H(\phi)\mathbf{F}(\phi, \nabla\phi, x, y) + \tau(x, y)\sqrt{1 + \left|\frac{\nabla w \times \nabla\phi}{|\nabla\phi|}\right|^2}\, |\nabla\phi|\delta(\phi) \tag{10}$$

To formulate the equilibrium conditions, the necessary condition for the existence of an extremum in $G(\phi)$ has to be written, which is done by applying the Euler–Lagrange equation to G:

$$-\nabla\cdot\left[\frac{\partial \mathsf{G}}{\partial\nabla\phi}\right] + \frac{\partial \mathsf{G}}{\partial\phi} = 0 \tag{11}$$

Applying this equation to the first part of G in eq 10 yields

$$H\left[-\nabla\cdot\frac{\partial\mathbf{F}}{\partial\nabla\phi} + \frac{\partial\mathbf{F}}{\partial\phi}\right] + H'\left[\mathbf{F} - \nabla\phi\cdot\frac{\partial\mathbf{F}}{\partial\nabla\phi}\right] \tag{12}$$

Applying the Euler–Lagrange equation to the second part of G in eq 10 yields

$$-\nabla\cdot\left\{\tau(x,y)\delta(\phi)\frac{\nabla\phi + (\nabla\phi \times \nabla w) \times \nabla w}{\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2}}\right\} + \delta'(\phi)\tau(x,y)\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2} \tag{13}$$

Using the relationship $H' = \delta$ and substituting eqs 12 and 13 into eq 11, one obtains

$$H(\phi)\left[-\nabla\cdot\left(\frac{\partial\mathbf{F}}{\partial\nabla\phi}\right) + \frac{\partial\mathbf{F}}{\partial\phi}\right] + \delta(\phi)\left[-\tau(x,y)\nabla\cdot\left\{\frac{\nabla\phi + (\nabla\phi \times \nabla w) \times \nabla w}{\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2}}\right\} - \frac{\nabla\tau\cdot\nabla\phi + (\nabla\tau \times \nabla w)\cdot(\nabla w \times \nabla\phi)}{\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2}} + \mathbf{F} - \nabla\phi\cdot\frac{\partial\mathbf{F}}{\partial\nabla\phi}\right] = 0 \tag{14}$$

It is worthwhile to notice that eq 14 does not contain a term with $\delta'(\phi)$. This will be the case if τ is a function depending on x, y and $\nabla\phi/|\nabla\phi|$ (i.e., on the *orientation* of the contact line). If, however, τ depends nontrivially on $|\nabla\phi|$ (i.e., on the *inclination* of the interface) then eq 13 will contain a δ' term. The first part of eq 14 is meaningful only within the projection of the wetted surface on the $\{x,y\}$ plane, whereas the second part is meaningful only on the contact line. Therefore, the sum can be zero only if each part independently equals zero. The first part of eq 14 yields the equation for the liquid–fluid interface (the Young–Laplace equation), whereas the second part yields the boundary condition, namely, the equation for the contact angle:

$$-\tau(x,y)\nabla\cdot\left\{\frac{\nabla\phi + (\nabla\phi \times \nabla w) \times \nabla w}{\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2}}\right\} - \frac{\nabla\tau\cdot\nabla\phi + (\nabla\tau \times \nabla w)\cdot(\nabla w \times \nabla\phi)}{\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2}} + \mathbf{F} - \nabla\phi\cdot\frac{\partial\mathbf{F}}{\partial\nabla\phi} = 0 \tag{15}$$

The latter is the condition of interest in the present paper, because it has not been previously developed for the three-dimensional case.

Equation 15 needs now to be written in a more explicit form, which will relate the geometry to the material properties. First, it should be recognized that the first term in this equation is related to the geodesic curvature, which is given by

$$\chi(x,y) \equiv -\frac{1}{\sqrt{1 + |\nabla w|^2}}\nabla\cdot\left\{\frac{\nabla\phi + (\nabla\phi \times \nabla w) \times \nabla w}{\sqrt{|\nabla\phi|^2 + |\nabla\phi \times \nabla w|^2}}\right\} \tag{18}$$

where $\chi(x,y)$ is the geodesic curvature of the level curve $\phi(x,y)$ embedded on the surface $\{x, y, w(x,y)\}$ at the prescribed point $\{x,y\}$.

Next, using eq 5 for $\mathbf{F}$, the third and fourth terms of eq 15 become

$$\mathbf{F} - \nabla\phi\cdot\frac{\partial\mathbf{F}}{\partial\nabla\phi} = \sigma_{lf}\sqrt{1 + |\nabla u|^2} - \sigma_{lf}\frac{\nabla u\cdot\nabla\phi}{\sqrt{1 + |\nabla u|^2}} + [\sigma_{sl} - \sigma_{sf}]\sqrt{1 + |\nabla w|^2} \tag{17}$$

Thus, with the aid of eqs 16 and 17, eq 15 for the contact angle takes the form

$$\sigma_{\mathrm{lf}}\sqrt{1+|\nabla u|^2}-\sigma_{\mathrm{lf}}\frac{\nabla u\cdot\nabla\phi}{\sqrt{1+|\nabla u|^2}}+[\sigma_{\mathrm{sl}}-\sigma_{\mathrm{sf}}+\tau\chi]\sqrt{1+|\nabla w|^2}+\frac{\nabla\tau\cdot\nabla\phi+(\nabla\tau\times\nabla w)\cdot(\nabla w\times\nabla\phi)}{\sqrt{|\nabla\phi|^2+|\nabla\phi\times\nabla w|^2}}=0 \quad (18)$$

This equation can be rewritten as

$$\frac{1+|\nabla u|^2-\nabla u\cdot\nabla\phi}{\sqrt{1+|\nabla u|^2}\sqrt{1+|\nabla w|^2}}=\frac{\sigma_{\mathrm{sf}}-\sigma_{\mathrm{sl}}-\tau\chi}{\sigma_{\mathrm{lf}}}-\frac{\nabla\tau\cdot\nabla\phi+(\nabla\tau\times\nabla w)\cdot(\nabla w\times\nabla\phi)}{r\sigma_{\mathrm{lf}}\sqrt{|\nabla\phi|^2+|\nabla\phi\times\nabla w|^2}} \quad (19)$$

As shown in Appendix B, the left-hand side of eq 19 is simply the actual contact angle. Thus, the three-dimensional equation for the actual contact angle, under the above-stated assumptions, is

$$\cos\theta_{\mathrm{ac}}=\cos\theta_{\mathrm{Y}}-\frac{\tau\chi}{\sigma_{\mathrm{lf}}}-\frac{\nabla\tau\cdot\nabla\phi+(\nabla\tau\times\nabla w)\cdot(\nabla w\times\nabla\phi)}{r\sigma_{\mathrm{lf}}\sqrt{|\nabla\phi|^2+|\nabla\phi\times\nabla w|^2}} \quad (20)$$

The first two terms on the right-hand side of this equation are also included in an equation developed previously.[18]

3. Discussion

The first and immediate conclusion that can be drawn from eq 20 is that if the effect of line tension is negligible, the actual contact angle equals the Young contact angle. In other words, the shape of the liquid−fluid interface has to adjust itself in such a way that the actual contact angle at each point equals θ_{Y}. This conclusion has been intuitively believed to be true, based on discussions of two-dimensional and axisymmetric systems; however it has never been previously proven in a rigorous way for a heterogeneous and/or rough surface in three dimensions.

Nonetheless, ignoring line tension effects may not be possible for rough or heterogeneous surfaces, for which the scale of roughness or heterogeneity is of the order of magnitude of a few micrometers or less.[15,16] Therefore, the actual contact angle is usually different from the Young contact angle. Moreover, the additional interesting conclusion from eq 20 is that the actual contact angle may be different also from the intrinsic contact angle, which is given by eq 3. In the general case of a heterogeneous rough surface, for which there is no symmetry, it is clear that the local geodesic curvature is different from $1/R$ of the same drop had it been put on an ideal solid surface. In addition, eq 20 contains a term accounting for the variation of line tension across the surface in a much more complicated way then in eq 3. Thus, the difference between the local actual contact angle given by eq 20 and the intrinsic contact angle, given by eq 3 is self-evident.

However, it is useful to consider also a few specific cases. A relatively simple one is that of a flat surface ($w \equiv 0$). Then, the last term in eq 20 is

$$\frac{\nabla\tau\cdot\nabla\phi}{r\sigma_{\mathrm{lf}}|\nabla\phi|} \quad (21)$$

This term (disregarding the factor $r\sigma_{\mathrm{lf}}$) is the directional derivative of τ along the normal to the contact line in the $\{x,y\}$ plane. In addition,

$$\chi=\nabla\cdot\left(\frac{\nabla\phi}{|\nabla\phi|}\right) \quad (22)$$

which means that the geodesic curvature of a curve on a plane equals the curvature of this curve. If the solid surface is also chemically homogeneous, the drop must be axisymmetric. Then, the directional derivative of τ becomes $d\tau/dR$, the geodesic curvature becomes $1/R$, and eq 3 is recovered from the more general eq 20 (by definition, the intrinsic contact angle is the actual contact angle on an ideal surface, which must be flat and homogeneous).

If the (flat) solid surface is chemically heterogeneous, but in an axisymmetric way, the drop must also be axisymmetric. In this case, the equation for the contact angle appears to be the same as eq 3 for the intrinsic contact angle; however, the two angles are not the same because the value of $d\tau/dR$ in the heterogeneous case is different from that in the homogeneous case. If the (flat) solid surface is chemically heterogeneous without axial symmetry, the directional derivative of τ and the geodesic curvature vary from point to point along the contact line. Therefore, the local actual contact angle is different from the intrinsic contact angle of a drop of the same volume on an ideal solid surface of the same composition as the local composition of the real surface.

Another specific case of interest is that of a rough solid surface, which may be either homogeneous or heterogeneous, but characterized by axial symmetry (if the surface is chemically heterogeneous, the heterogeneity must also be axisymmetric). In this case both ϕ and w depend only on $x^2 + y^2$, therefore $\nabla w \times \nabla\phi = 0$. Consequently the last term in eq 20 is again given by eq 21, and

$$\chi=\frac{1}{\sqrt{1+|\nabla w|^2}}\nabla\cdot\left(\frac{\nabla\phi}{|\nabla\phi|}\right)=\frac{1}{rR} \quad (23)$$

Due to the axial symmetry, the contact line must be a circle; therefore, the directional derivative is $d\tau/dR$ and R is uniform along the contact line. Introducing this information into eq 20 one gets

$$\cos\theta_{\mathrm{ac}}=\cos\theta_{\mathrm{Y}}-\frac{1}{r\sigma_{\mathrm{lf}}}\left(\frac{\tau}{R}+\frac{d\tau}{dR}\right) \quad (24)$$

as previously developed for axisymmetric systems.[16] In this case, the actual contact angle is different from the intrinsic contact angle because the geodesic curvature of a contact line is different from the curvature of its projection on the $\{x,y\}$ plane, $1/R$. It is interesting to notice that this difference in curvatures for an axisymmetric system stems from the roughness and not from the chemical heterogeneity. To further clarify this point, a specific example is discussed next.

Consider an axisymmetric liquid droplet located on a flat solid surface, and a second one located on the bottom of a spherical smooth surface of radius R_s (see Figure 2).

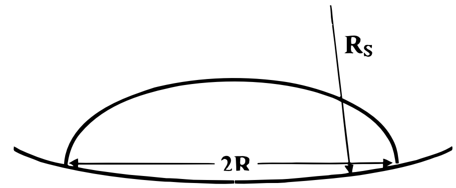

Figure 2. A drop on a spherical solid surface of radius R_s. The planar radius of the contact line is R.

The assumption of axial symmetry implies that the solid surfaces are either chemically homogeneous or heterogeneous in an axisymmetric way. The two drops are chosen to be such that the contact line of both is identical: a circle of radius R. In the first case (flat solid surface), the geodesic curvature of the contact line is given by $\chi_{\mathrm{flat}} = 1/R$. Hence, the actual contact angle is given by eq 3.

In the second case, the geodesic curvature of a circle of radius R embedded in a spherical shell of radius R_s needs to be calculated. Suppose that $w(x,y) = -\sqrt{R_s^2 - (x^2 + y^2)}$. Hence, by eq 23

$$\chi_{\mathrm{sphere}} = \frac{\sqrt{1 - (R/R_s)^2}}{R} \tag{25}$$

Thus,

$$\cos\theta_{\mathrm{ac}} = \cos\theta_{\mathrm{Y}} - \frac{\sqrt{1 - (R/R_s)^2}}{\sigma_{\mathrm{lf}}}\left(\frac{\tau}{R} + \frac{d\tau}{dR}\right) \tag{26}$$

Notice that if $R = R_s$, $\chi_{\mathrm{sphere}} = 0$ (a great circle on the sphere is a geodesic curve with zero geodesic curvature); hence, $\theta_{\mathrm{ac}} = \theta_{\mathrm{Y}}$ in this case. This result is an interesting example of the actual contact angle being equal to the Young contact angle due to a geometric circumstance, without being equal to the intrinsic contact angle.

4. Summary

The following conclusions can be drawn from eq 20 regarding the relationship between the actual, intrinsic, and Young contact angles along the contact line:

1. If line tension can be ignored, the actual contact angle on a heterogeneous and/or rough surface in three dimensions equals the intrinsic contact angle (which, in turn, equals the Young contact angle).

2. If line tension is significant and the solid surface is rough, the actual contact angle is different from the intrinsic contact angle. This generalizes the results obtained for axisymmetric systems[16] to the three-dimensional case. Under special circumstances (zero $1/r$) the actual contact angle may equal the Young contact angle.

3. If line tension is significant and the solid surface is heterogeneous, the actual contact angle is also different from the intrinsic contact angle. The effect of heterogeneity on the difference between the actual and intrinsic contact angles is partially due to a three-dimensional effect that could not have been elucidated by analyses of axisymmetric situations.

5. Appendix A

This appendix shows how the expression for G_c in eq 4, which is a line integral over the three-phase contact line, is transformed into the expression for G_c in eq 8, which is a surface integral over the whole $\{x,y\}$ plane. Because G_c in eq 4 is integrated along the contact line, Γ_ϕ, which is not necessarily in the $\{x,y\}$ plane, this integral needs first to be written as an integral over the projection of the contact line on the plane, $\bar{\Gamma}_\phi$. If s is the arc-length along the contact line (in the three-dimensional space), and ζ is the arc-length along the projection of the contact line on the two-dimensional $\{x,y\}$ plane, then it is well known that

$$ds = \sqrt{1 + \left|\frac{\nabla w \times \nabla\phi}{|\nabla\phi|}\right|^2}\, d\zeta \tag{27}$$

Hence

$$G_c(\phi) = \int_{\bar{\Gamma}_\phi} \tau\sqrt{1 + \left|\frac{\nabla w \times \nabla\phi}{|\nabla\phi|}\right|^2}\, d\zeta \tag{28}$$

Now, a line integral such as in eq 28 can be transformed into a surface integral by

$$\int_{\bar{\Gamma}_\phi} d\zeta = \int\int \delta(\phi)\, d\phi\, d\zeta \tag{29}$$

where $\delta(\phi)$ is the Dirac delta function, and (ϕ,ζ) serves as a new coordinate representation. The next step, then, is to transform the ϕ, ζ coordinates into the $\{x,y\}$ plane. The Jacobian of this transformation is given by

$$d\phi\, d\zeta = |\nabla\phi|\, dx\, dy \tag{30}$$

Combining eqs 28, 29, and 30, one gets

$$G_c(\phi) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \tau\sqrt{1 + \left|\frac{\nabla w \times \nabla\phi}{|\nabla\phi|}\right|^2}\, |\nabla\phi|\delta(\phi) dx\, dy \tag{31}$$

6. Appendix B

This appendix proves that the left-hand side of eq 19 is the actual contact angle. Let the vector $\vec{n}$ be defined as $\vec{n} = \nabla\phi/|\nabla\phi|$, that is, $|\nabla\phi| = \nabla\phi\cdot\vec{n}$ ($\vec{n}$ is a unit vector in the $\{x,y\}$ plane, which is perpendicular to the projection of the contact line on this plane, $\bar{\Gamma}_\phi$). Also, let the set ∂_n be the derivative in the direction of $\vec{n}$; that is, $\partial_n u = \nabla u\cdot\vec{n}$. Then $\nabla u\cdot\nabla\phi = (\partial_n u)^2 - (\partial_n u)(\partial_n w)$, and the left-hand side of eq 19 can be written as

$$\frac{1 + |\nabla u|^2 - \nabla u\cdot\nabla\phi}{\sqrt{1 + |\nabla u|^2}\sqrt{1 + |\nabla w|^2}} = \frac{1 + |\nabla u|^2 - (\partial_n u)^2 + (\partial_n u)(\partial_n w)}{\sqrt{1 + |\nabla u|^2}\sqrt{1 + |\nabla w|^2}} \tag{32}$$

It has to be shown now that this expression is equal to the actual contact angle, which from purely geometrical considerations can be written as

$$\cos\theta_{\mathrm{ac}} = \frac{\nabla^{(3)}\psi\cdot\nabla^{(3)}W}{|\nabla^{(3)}\psi||\nabla^{(3)}W|} \tag{33}$$

where $\psi(x,y,z) = z - u(x,y)$ and $W(x,y,z) = z - w(x,y)$, z is the coordinate in the direction perpendicular to the x,y plane, and $\nabla^{(3)}$ is the gradient of a function of three variables. Thus it needs to be proven that

$$\frac{1 + |\nabla u|^2 - (\partial_n \mathrm{u})^2 + (\partial_n \mathrm{u})(\partial_n w)}{\sqrt{1 + |\nabla u|^2}\sqrt{1 + |\nabla w|^2}} = \frac{\nabla^{(3)}\psi\cdot\nabla^{(3)}W}{|\nabla^{(3)}\psi||\nabla^{(3)}W|} \tag{34}$$

The proof will consist of demonstrating first that the denominators of the two sides of eq 34 are equal, and then that the numerators are equal. Let $\vec{t}$ be a unit vector in the $\{x,y\}$ plane tangent to the planar projection of the contact line, $\bar{\Gamma}_\phi$, and $\vec{z}$ be a unit normal to the $\{x,y\}$ plane. Then $\{\vec{t},\vec{n},\vec{z}\}$ form an orthonormal set in the three-dimensional space. Any function of the form $\psi(x,y,z) = z - u(x,y)$ satisfies:

$$\nabla^{(3)}\psi = \vec{z} - (\partial_t u)\vec{t} - (\partial_n u)\vec{n} \tag{35}$$

where $u(x,y)$ is a differentiable function, and $\partial_t u = \vec{t}\cdot\nabla u$ is the directional derivative along $\vec{t}$.

From the orthonormality of $\{\vec{z},\vec{n},\vec{t}\}$ and from eq 35 one obtains:

$$|\nabla^{(3)}\psi| = (1 + |\partial_n u|^2 + |\partial_t u|^2)^{1/2} \tag{36}$$

Also, the horizontal gradient of u is written as:

$$\nabla u = (\partial_n u)\vec{n} + (\partial_t u)\vec{t} \tag{37}$$

from which one gets that

$$|\nabla u|^2 = |\partial_n u|^2 + |\partial_t u|^2 \tag{38}$$

Thus,

$$|\nabla^{(3)}\psi| = \sqrt{1 + |\nabla u|^2} \tag{39}$$

Applying eq 39 also for W it becomes clear that the denominators of the two sides of eq 34 are identical.

To prove that the numerators are identical as well, the following steps are taken. Using eq 38, the numerator of left-hand side of eq 34 takes the form

$$1 + |\partial_t u|^2 + (\partial_n w)(\partial_n u) \tag{40}$$

Now, $u = w$ on the contact line Γ_ϕ; hence, $\partial_t u = \partial_t w$ and eq 40 can be rewritten as

$$1 + (\partial_t u)(\partial_t w) + (\partial_n w)(\partial_n u) = [\vec{z} - (\partial_n u)\vec{n} - (\partial_t u)\vec{t}]\cdot [\vec{z} - (\partial_n w)\vec{n} - (\partial_t w)\vec{t}] = \nabla^{(3)}\psi\cdot\nabla^{(3)}W \tag{41}$$

The first equality is proven by performing the product and the second equality by eq 35. Thus, the numerators of the two sides of eq 34 are identical as well.

LA960723P