Stability of a Flat Gas−Liquid Interface Containing Nonidentical Spheres to Gas Transport: Toward an Explanation of Particle Stabilization of Gas Bubbles

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It is shown that a flat interface between a soluble gas and a liquid that contains an arbitrary number of partially wetting nonidentical spheres is linearly stable to slight perturbations caused by fluctuations in the gas volume. Stability is proved by showing that the rate of change of the volume of the gas with curvature of the interface is positive in the neighborhood of the equilibrium state of zero interface curvature. Physically, the volume fluctuations induce fluctuations in the curvature of the interface that would naturally lead to dissolution of gas into the liquid in the case of positive curvature and entry of gas into the bubble in the case of negative curvature, either of which restores equilibrium. This result may possibly explain the unusual long-term stability of gas bubbles covered by colloidal particles in the recent experiments of Du et al. (Du, Z.; Bilbao-Montoya, M. P.; Binks, B. P.; Dickinson, E.; Ettelaie, R.; Murray, B. S. *Langmuir* **2003**, *19*, 3106).

Introduction

It was found by Du et al.[1] that the dissolution of isolated air bubbles in water can be arrested by the use of partially hydrophobic colloidal silica particles suspended in the liquid. The bubbles are introduced into water that is exposed to air across a flat gas−liquid interface. The water, therefore, is presumably saturated with the components of air at the prevailing temperature and pressure. Normally, the pressure inside the bubble should be larger than that in the air because of the effect of surface tension. This larger pressure leads to a larger concentration of dissolved air at the bubble−water interface than that prevailing in the bulk liquid (strictly speaking, one should consider each component of air separately, but for convenience we lump them together). As a result, the air diffuses away from the interface, and the bubble shrinks. In the experiments of Du et al.[1] the colloidal particles were found to adsorb at the interface, and under the right conditions, the air bubbles were found to remain nearly constant in size over a period of several days, in contrast to bubbles stabilized by protein foam stabilizers, which disappeared in 1−2 h. The authors do not offer an explanation of the mechanism of this long-term stabilization. Based on additional experiments, Dickinson et al.[2] suggested that the observed stability is likely caused by the formation of a continuous network of particles on the bubble surface (as well as in the bulk); however, even if the spheres are packed as closely as possible, unless they are deformed, contact among these spheres will only occur at points, and the transport of gas can occur freely over the small gas−liquid interfacial area that is still present.

Interestingly, Kam and Rossen[3] considered a two-dimensional problem of a gas bubble coated by solids ("armored") and showed that the interface between the particles can assume zero or negative curvature. If the curvature of the interface not covered by the particles in the experiments of Du et al.[1] is indeed zero, then the dissolved air concentration at the interface would be the same as that prevailing in the bulk liquid, and there would be no tendency for the air to leave or enter the bubble. Of course, to verify whether the interface of zero curvature is in stable equilibrium, one must inquire whether a small fluctuation in the system would lead to growth or dissolution of the bubble, destroying this equilibrium. For example, it is possible to arrange for a gas bubble to be in equilibrium with respect to gas transport in a liquid that contains dissolved gas, but this state of equilibrium is unstable, as we discuss below.

For the sake of simplicity, we assume a static system and neglect the role of hydrostatic variations of pressure in this discussion. In an isothermal static system in mechanical and electrochemical equilibrium, the Young−Laplace equation can be written as

$$p_g = p_l + 2\gamma\kappa \qquad (1)$$

where p_g is the pressure within the bubble, p_l is the pressure in the surrounding liquid, γ is the surface tension at the gas−liquid interface, and κ is the mean curvature of the interface, assumed constant. The term "curvature" is commonly used to designate the quantity 2κ. Our sign convention for curvature is such that $\nabla\cdot\mathbf{N} = 2\kappa$, where $\mathbf{N}$ is the unit normal to the interface pointing into the liquid. For example, κ would be positive and equal to $1/a$ for a spherical gas bubble of radius a. Now, consider a bubble of radius a placed in a supersaturated liquid. The liquid is at a pressure p_l, but it contains a dissolved gas concentration that corresponds to the equilibrium value

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(1) Du, Z.; Bilbao-Montoya, M. P.; Binks, B. P.; Dickinson, E.; Ettelaie, R.; Murray, B. S. *Langmuir* **2003**, *19*, 3106.
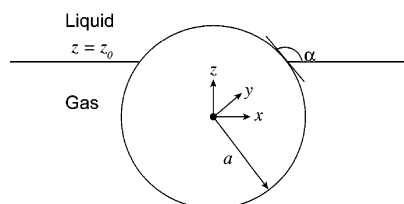(2) Dickinson, E.; Ettelaie, R.; Kostakis, T.; Murray, B. S. *Langmuir* **2004**, *20*, 8517.

(3) Kam, S. I.; Rossen, W. R. *J. Colloid Interface Sci.* **1999**, *213*, 329.

attained across a flat interface at a pressure $p_l + 2\gamma/a$. With this specific choice of supersaturation, the dissolved gas concentration would be the same in the liquid at the bubble surface as that in the bulk. Hence, there would be no tendency for transport of gas between the gas bubble and the liquid, and one can regard this as a state of equilibrium with respect to gas transport across the interface. But, if the radius of the bubble decreases slightly, the pressure inside the bubble would increase slightly, leading to a larger dissolved gas concentration at the interface. This change will lead to transport of gas away from the interface, which depletes the gas in the bubble and thereby leads to continuing decrease in bubble size. Likewise, a slight increase in the bubble radius would lead to a decrease in the dissolved gas concentration at the interface, which drives transport of gas toward and into the bubble. As a result, the bubble would grow indefinitely. Therefore, the equilibrium state for a pure gas bubble in a liquid is unstable to the transport of gas across the interface.

Larsen[4] has considered an arbitrary pocket of gas surrounded by liquid and solid boundaries in equilibrium with the liquid and obtained a condition for this equilibrium state to be linearly stable to small perturbations in the gas volume using a kinetic approach. He assumes the curvature of the gas−liquid interface to be constant and the ideal gas law to be applicable to the gas and uses Henry's law to describe the relationship between the pressure in the bubble and the dissolved gas concentration in the liquid at the interface. Larsen[4] shows that if the volume of the gas is V and the curvature of the gas−liquid interface is κ, the equilibrium state is stable when $dV/d\kappa > 0$.[4,5] The same condition also can be obtained independently from the thermodynamic stability criterion given in equation (549) of Gibbs.[5] In the case of an isolated gas bubble in equilibrium with the surrounding liquid considered in the previous paragraph, the rate of change of gas volume with curvature is negative, and the equilibrium state is unstable in that situation. Instead, consider a gas pocket at equilibrium with the surrounding liquid for which a slight increase in curvature accompanies a slight increase in volume. If the pressure in the liquid is held constant, from eq 1 we see that the increased curvature will cause a slight increase in the pressure in the pocket, leading to an increase in the dissolved gas concentration at the interface. This will cause gas to leave the pocket, restoring the original equilibrium. In a like manner, a slight decrease in curvature, accompanied by a concomitant decrease in gas volume, will lead to gas entering the pocket, once again restoring equilibrium. Thus, a positive value of $dV/d\kappa$ confers stability on the gas pocket.

We prove in the present work that when a gas−liquid interface contains particles that are partially wetted by the liquid and is flat in its equilibrium state, this state is linearly stable to small perturbations in the volume of the gas, suggesting that this may be one possible reason for the observed stability of the air bubbles in the experiments of Du et al.[1] Even though those experiments were performed on spherical gas bubbles with significant curvature, in the limit when the particles are small compared with the radius of the bubble, one can envision the gas−liquid interface in their experiments as being approximated by the present model system. Our approach is based on demonstrating that the rate of change of the

(4) Larsen, R. J.; Ph.D. Dissertation in preparation, Harvard University, Cambridge, MA.

(5) *The Scientific Papers of J. Willard Gibbs. Vol. I. Thermodynamics, Chapter III. On the Equilibrium of Heterogeneous Substances*; Longmans: London, 1906.

Figure 1. Sketch of a reference sphere at the interface, showing the coordinate system and other symbols used in the analysis.

volume of gas with respect to curvature at the equilibrium state is positive.

Numerical results were obtained by Hilden and Trumble[6] in a related problem. These authors used Surface Evolver software and calculated the pressure required for the penetration of a liquid into an array of identical close-packed spheres on a hexagonal lattice as a function of the radius of the spheres, surface tension, contact angle, and volume. The pressure difference between the liquid and the vapor across the interface is proportional to the interface curvature. From the numerical results of Hilden and Trumble,[6] it is possible to infer that the derivative of the volume of the gas with respect to the curvature as seen from the gas side, when the curvature is zero, is always positive regardless of the value of the contact angle. Hilden and Trumble also present results for the case when the spheres are slightly separated and placed on a hexagonal lattice, and the same inference can be drawn from those results. We prove analytically in the present work that this is a general result, applicable to a situation in which nonidentical spheres are placed at arbitrary locations on a planar gas−liquid interface.

Analysis

Consider a collection of partially wetted nonidentical spheres present at a planar gas−liquid interface so that the contact angle α made by the liquid on their surface lies between 0 and 180°. This contact angle can be different for each sphere but must be a constant on the surface of a given sphere. The system is bounded by a cylindrical container of arbitrary cross-section, and for the purpose of this analysis we assume the contact angle with the container to be 90°. Later, we comment on this restriction and how it can be relaxed. The spheres are not assumed to be arranged in any regular pattern, nor does any detailed pattern influence the final result. We neglect hydrostatic effects in this treatment. This is a good assumption over small length scales in a gravitational field (i.e., distances smaller than the capillary length) and over substantial length scales in a reduced gravity environment, such as that prevailing aboard orbiting spacecraft or outer space probes. The interface will be flat in the absence of the spheres so that the pressures in the gas and liquid will be the same, neglecting hydrostatic effects. If the liquid is saturated with the gas at the prevailing pressure, the concentration of dissolved gas at the interface will be the same as that in the bulk liquid. Thus, the system is in equilibrium in the absence of the spheres.

When the spheres are introduced at the interface, it is possible to find an equilibrium situation wherein the interface is flat in the region not covered by the spheres. Figure 1 shows rectangular Cartesian coordinates (x, y, z) measured from an origin located at the center of a reference sphere of radius a, with z directed normal to the flat interface and measured toward the liquid side of the

(6) Hilden, J. L.; Trumble, K. P. *J. Colloid Interface Sci.* **2003**, *267*, 463.

interface and (x, y) measured laterally on a plane parallel to the flat interface. Referring to Figure 1, the equilibrium interface will be located at $z = z_0 = -a \cos \alpha$, where α is the contact angle. When $\alpha > 90°$, $z_0 > 0$, and likewise, when $\alpha < 90°$, $z_0 < 0$. The location of the interface everywhere will remain the same with respect to the chosen origin, but for a sphere of a different radius and a different contact angle, the relative location with respect to its center will change. In general, the location of the interface with respect to a similar rectangular Cartesian coordinate system with the center of sphere i as the origin will be given by $z = z_0 = -a_i \cos \alpha_i$ where a_i is the radius of sphere i, and α_i is the contact angle. Note that purely for convenience, we have located the gas below the liquid in the figure. The actual orientation is irrelevant because gravitational effects are neglected in the model.

In the following development, we scale all distances by a reference length, which is chosen as the radius of a reference sphere, a. Therefore the volume of the gas is scaled by a^3, and curvature is scaled by $1/a$. For convenience, after being mentioned at first occurrence, the prefix "scaled" will be mostly omitted, but implied where appropriate.

The curvature of the equilibrium interface is zero. Now, we consider a slight perturbation in the scaled volume of the gas V, which leads to a perturbation in the curvature of the interface from the equilibrium value of zero everywhere. Because the pressure is assumed spatially uniform in both phases, this perturbation of the curvature will be constant. We label the scaled curvature ϵ. The question to be answered is whether $[dV/d\epsilon]_{\epsilon=0}$ is positive or negative. If it is positive, then a slight increase in volume leads to a slight positive curvature of the interface, leading to higher dissolved gas concentration at the interface, and efflux of gas out of the volume so that the volume returns to its original value. Likewise, a slight decrease in volume leads to a negative curvature and an influx of gas into the volume. Thus, the gas volume would be linearly stable to slight perturbations provided $[dV/d\epsilon]_{\epsilon=0} > 0$. We now proceed to prove this to be the case.

Let the perturbed gas−liquid interface be given by

$$z = z_0 + h(x,y;\epsilon) \tag{2}$$

where, because scaled variables are being used, $z_0 = -\cos \alpha$. To avoid clutter in the subsequent development, the parametric dependence on ϵ will not be displayed explicitly as in eq 2. At equilibrium, the function $h(x,y)$ must satisfy[7]

$$\frac{1}{A^3}[(1 + h_y{}^2)h_{xx} + (1 + h_x{}^2)h_{yy} - 2h_x h_y h_{xy}] = -\epsilon \tag{3}$$

where

$$A = \sqrt{1 + h_x{}^2 + h_y{}^2} \tag{4}$$

and h_x stands for $\partial h/\partial x$, with similar notation applying to the entire equation. The perturbation in gas volume can, in general, be accompanied by a perturbation in the location of the contact line. At the perturbed contact line on the surface of the sphere, the contact angle must still be specified as α. This fact provides the boundary condition that must be satisfied at the surface of each sphere (using the contact angle pertaining to that sphere). At the container wall, the contact angle is specified as 90°.

(7) Finn, R. *Equilibrium Capillary Surfaces*; Springer-Verlag: New York, 1986.
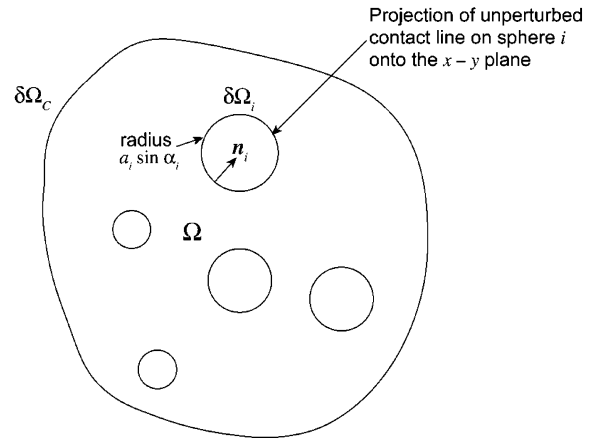
Figure 2. The domain on which the function $h(x, y)$ is defined and a representative sample of its boundary.

For small curvatures ϵ, we can expand the solution of eq 3 as

$$h = \epsilon h_0(x, y) + O(\epsilon^2) \tag{5}$$

When eq 5 is substituted into eq 4 and the result is ordered, we obtain

$$A = 1 + \frac{1}{2}\epsilon^2(h_{0x}{}^2 + h_{0y}{}^2) + O(\epsilon^3) \tag{6}$$

so that

$$\frac{1}{A^3} = 1 - \frac{3}{2}\epsilon^2(h_{0x}{}^2 + h_{0y}{}^2) + O(\epsilon^3) \tag{7}$$

Substitution of eq 5 in eq 3 and use of eq 7 yields

$$\left[1 - \frac{3}{2}\epsilon^2(h_{0x}{}^2 + h_{0y}{}^2) + O(\epsilon^3)\right][\epsilon(h_{0xx} + h_{0yy}) + O(\epsilon^2)] = -\epsilon \tag{8}$$

Therefore, at leading order in ϵ, we obtain

$$\nabla^2 h_0 = -1 \tag{9}$$

where ∇^2 is the two-dimensional scaled Laplacian operator. The domain on which the function $h_0(x, y)$ and higher order functions in the expansion envisioned in eq 5 are defined is termed Ω. As shown in Figure 2, Ω is the portion of the $x−y$ plane enclosed by the container, from which the areas of the circles corresponding to the projection on the $x−y$ plane of the unperturbed contact lines on the surfaces of the spheres are excluded. The boundary of this domain, $\delta\Omega$, comprises the footprint of the container wall, $\delta\Omega_C$, and the circles $\delta\Omega_i$ corresponding to each of the spheres noted above. We define a unit outward normal on the circle corresponding to sphere i as $\mathbf{n}_i$. Note that $\mathbf{n}_i$ points into the circle by definition.

The scaled volume of the gas is given by

$$V = V_0 + \int_\Omega h(x,y) \, dA \tag{10}$$

where the integration is carried out over the area occupied by the domain Ω. The constant V_0 in the right side of eq 10 represents the scaled baseline volume of the gas when

the interface is unperturbed. Substituting the expansion from eq 5 into eq 10 yields

$$V = V_0 + \epsilon \int_\Omega h_0(x,y) \, dA + O(\epsilon^2) \tag{11}$$

As noted earlier, linear stability of the interface to gas transport across it requires that $[dV/d\epsilon]_{\epsilon=0} > 0$. Therefore, the condition for stability reduces to

$$\int_\Omega h_0(x,y) \, dA > 0 \tag{12}$$

We prove that eq 12 holds in the current problem by invoking a two-dimensional version of Green's theorem.[8] For an arbitrary function $\phi(x, y)$ defined on the domain Ω bounded by the curve $\delta\Omega$,

$$\int_\Omega [\phi\nabla^2\phi + (\nabla\phi)\cdot(\nabla\phi)] \, dA = \oint_{\delta\Omega} \phi\mathbf{n}\cdot\nabla\phi \, ds \tag{13}$$

where ds is a line element on $\delta\Omega$, and $\mathbf{n}$ is the unit outward normal to $\delta\Omega$. If we substitute $\phi = h_0$ and use eq 9, we obtain

$$\int_\Omega h_0(x,y) \, dx \, dy =$$
$$\int_\Omega [(\nabla h_0)\cdot(\nabla h_0)] \, dA - \oint_{\delta\Omega} h_0\mathbf{n}\cdot\nabla h_0 \, ds \tag{14}$$

The first integral in the right side is always positive because $\nabla h_0 \neq \mathbf{0}$ identically in the domain. If we can establish that on the boundary $\delta\Omega$ either $h_0\mathbf{n}\cdot\nabla h_0$ is zero or negative, it follows that the requirement for stability given in eq 12 will be satisfied.
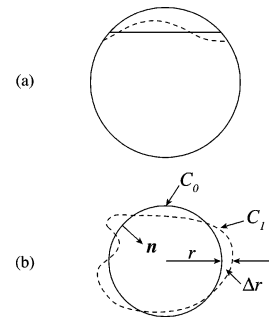
On the portion of the domain boundary corresponding to the footprint of the container wall $\delta\Omega_C$, the contact angle is prescribed to be 90°. This requires the normal to the perturbed interface to be orthogonal to the normal to the container wall along the contact line on the container wall. Because the normal to the container wall is parallel to the $x-y$ plane, it follows that the normal to the perturbed interface must be orthogonal to that plane. If we write the equation for the interface shape in the vicinity of the container wall as

$$f(x,y,z) = z - C - h(x,y) = 0 \tag{15}$$

where C is an arbitrary constant, the normal to the interface (pointing into the gas) can be obtained by evaluating $-\nabla f/|\nabla f|$. Therefore, it can be seen that $\nabla h = \mathbf{0}$ on the contact line with the container wall, and it follows that $h_0\mathbf{n}\cdot\nabla h_0 = 0$ on $\delta\Omega_C$. Moreover, it can be shown that h_0 and $\mathbf{n}\cdot\nabla h_0$ are of opposite sign on the circular boundaries $\delta\Omega_i$ corresponding to the projection of the unperturbed contact line on each sphere. The detailed proof of this fact for the reference sphere is somewhat laborious and is provided in the Appendix. Thus, we conclude that the gas−liquid interface in the present problem is linearly stable to the transport of gas across the interface.

Concluding Remarks

In developing the proof here, we had to assume that the system is bounded by a container wall at which the contact angle is set at 90°. The container can be eliminated if the system is extended to infinity, and the spheres only cover a finite segment of the interface, because the interface will be flat at the equivalent domain boundary $\delta\Omega_C$. It is

(8) Hildebrand, F. B. *Advanced Calculus for Applications*; Prentice Hall: Englewood Cliffs, NJ, 1976.

Figure 3. The equilibrium (solid) and perturbed (dashed) contact lines on the surface of the reference sphere; (a) front view, (b) projection on the $x-y$ plane showing the curves C_0 and C_1, the normal $\mathbf{n}$ to C_0, and the radial distances r and Δr used in the analysis in the Appendix; an arbitrary perturbation is chosen for illustration.

likely that the result proved here can be extended to objects other than spheres, so long as the surface curvature is qualitatively similar. The proof given in the Appendix hinges on the fact that a slight elevation of the contact line from the equilibrium state will require that the surface slope upward to preserve the contact angle boundary condition (and likewise, a slight depression requires the surface to slope downward). This behavior at the solid surface happens naturally for a spherical particle for any contact angle α such that $0 < \alpha < 180°$. Objects such as ellipsoids, arranged with a symmetry axis normal to the equilibrium interface, would yield the same response, whereas hourglass-shaped objects would not.

Other directions in which this work can be extended include the consideration of the stability of an interface that is not flat, but has zero curvature, as is likely the case corresponding to the experiments that motivated this study, namely, a gas bubble covered by particles. On a global level, a bubble can appear spherical, but if the origin of the stability of the bubble is correctly represented by the present analysis, the interface would be deformed by the particles such that the curvature is zero everywhere. Of course, it would require a minimum number of particles of a certain size on a given bubble surface to produce this condition; the establishment of this number for a specified particle-to-bubble size ratio should be a useful exercise in itself.

Appendix

The objective of this Appendix is to show that the signs of h_0 and $\mathbf{n}\cdot\nabla h_0$ are opposite on every circular boundary $\delta\Omega_i$ corresponding to the projection onto the $x-y$ plane of the unperturbed contact line on the surface of sphere i. The analysis uses a reference sphere of radius a with contact angle α, for convenience, and the rectangular Cartesian coordinate system identified in Figure 1. Scaled variables are used, as indicated in the main body of this work.

In Figure 3a, the equilibrium contact line and a perturbed contact line on the reference sphere are displayed. The corresponding projections of these two contact lines are shown in Figure 3b, along with some symbols that are used in the analysis in this Appendix.

Because the perturbation in the position of the contact line is permitted to be arbitrary, albeit small, we must establish the location of the perturbed contact line by satisfying the equations for the surface of the sphere and the perturbed gas−liquid interface simultaneously. The contact angle is the angle between the normals to these two surfaces (chosen in suitable directions) at the contact line, which comprises the loci of the points of intersection. The projection of the perturbed contact line onto the $x−y$ plane is the boundary of the perturbed domain, which will depend on ϵ. The baseline boundary that corresponds to a flat interface is a circle of scaled radius $\sin \alpha$, where α is the contact angle. It is on this circular boundary that the relationship between the signs of h_0 and $\mathbf{n}\cdot\nabla h_0$ needs to be established when using eq 14 to prove stability.

We can write the equation for the surface of the sphere, using scaled coordinates, as

$$f_1(x,y,z) = x^2 + y^2 + z^2 - 1 = 0 \qquad (A1)$$

The unit outward normal to this surface $\mathbf{n}_1$ is given by $\nabla f_1/|\nabla f_1|$ and can be shown to be the scaled position vector.

$$\mathbf{n}_1 = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \qquad (A2)$$

In eq A2, $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ represent the usual triad of orthogonal unit vectors in the coordinate directions (x, y, z). The gas−liquid interface can be described by

$$f_2(x,y,z) = z - z_0 - h(x,y) = 0 \qquad (A3)$$

Here $z_0 = -\cos \alpha$ is the initial scaled height of the flat gas−liquid interface in the base state. Acute contact angles imply a base state below the origin, and obtuse contact angles lead to a base state above the origin.

We can find the unit normal to the gas−liquid interface $\mathbf{n}_2$ pointing into the gas by determining $\nabla f_2/|\nabla f_2|$ and inverting the sign.

$$\mathbf{n}_2 = \frac{1}{\sqrt{1 + h_x^2 + h_y^2}}(\mathbf{i}h_x + \mathbf{j}h_y - \mathbf{k}) \qquad (A4)$$

The orientations of $\mathbf{n}_1$ and $\mathbf{n}_2$ have been chosen such that $\mathbf{n}_1\cdot\mathbf{n}_2 = \cos \alpha$, which leads to the following relationship at the intersection of the two surfaces.

$$xh_x + yh_y - z = \cos \alpha\sqrt{1 + h_x^2 + h_y^2} \qquad (A5)$$

Substituting for z from eq A3 and expanding the right side using the fact that $(h_x^2 + h_y^2) \ll 1$ leads to

$$xh_x + yh_y - h = \frac{\cos \alpha}{2}\Big[h_x^2 + h_y^2 - \frac{1}{4}(h_x^2 + h_y^2)^2 + ...\Big] \qquad (A6)$$

along the contact line.

Because eqs A1 and A3 must both be satisfied at the contact line, we can eliminate z between them to write

$$x^2 + y^2 - \sin^2 \alpha - 2h \cos \alpha + h^2 = 0 \qquad (A7)$$

a relationship that applies to the (x,y) coordinates of every point on the contact line; because z has been eliminated, it is also the projection of the perturbed contact line onto the $x−y$ plane. The function $h(x, y)$ appearing in eq A7

must be evaluated at this projected boundary. This curve is labeled C_1 in Figure 3b. The circular boundary of the unperturbed domain, assigned the label C_0 in Figure 3b, is given by

$$x^2 + y^2 - \sin^2 \alpha = 0 \qquad (A8)$$

The outward normal to curve C_0 (as seen from the domain Ω) is

$$\mathbf{n} = -\frac{1}{\sin \alpha}(\mathbf{i}x + \mathbf{j}y) \qquad (A9)$$

The next task is to use eq A6, which is obtained from the contact angle boundary condition at the perturbed contact line, to obtain the desired result on the circle C_0. To do this, we shall write Taylor series expansions of functions about points on the circle C_0. Each point on this circle is mapped into a corresponding point on the boundary curve C_1 by a radial line drawn from the origin on the $x−y$ plane. The scaled radial distance from the origin to any point on the circle C_0 is $r = \sin \alpha$. Let the distance between the two curves along this radial line be Δr so that the scaled radial distance from the origin to a point on C_1 is $r + \Delta r$. On C_1,

$$x^2 + y^2 = (\sin \alpha + \Delta r)^2 = \sin^2 \alpha + 2h \cos \alpha - h^2 \quad (A10)$$

when use is made of eq A7. This quadratic equation for Δr can be solved to obtain two solutions, only one of which is admissible. It is

$$\Delta r = \sin \alpha\left(-1 + \sqrt{1 + 2h\frac{\cos \alpha}{\sin^2 \alpha}}\right) \qquad (A11)$$

The right side of eq A11 can be expanded by making use of the fact that $h \ll 1$. This yields the following result.

$$\Delta r = h \cot \alpha - \frac{h^2}{4}\frac{\cos^2 \alpha}{\sin^3 \alpha} + ... \qquad (A12)$$

As noted earlier, the function $h(x, y)$ in the result for Δr must be evaluated on C_1.

Equation A6 applies on C_1, and we must now transform it to apply to functions evaluated on C_0. Expanding the function $h(x, y)$ in a Taylor series about a point on C_0, the value at the corresponding point on C_1 on a radial line drawn from the origin is given by

$$[h]_{C_1} = [h]_{C_0} - \Delta r[\nabla h]_{C_0}\cdot\mathbf{n} + ... \qquad (A13)$$

Upon working this out, we obtain

$$[h]_{C_1} = [h]_{C_0} + [h]_{C_1}\frac{\cos \alpha}{\sin^2 \alpha}[xh_x + yh_y]_{C_0} + ... \qquad (A14)$$

where higher order terms are not explicitly displayed, because they are not needed.

In a like manner, the following result can be written.

$$[xh_x + yh_y]_{C_1} = [xh_x + yh_y]_{C_0} + [h]_{C_1}\frac{\cos \alpha}{\sin^2 \alpha}[xh_x + \\ yh_y + x^2h_{xx} + y^2h_{yy} + 2xyh_{xy}]_{C_0} + ... \quad (A15)$$

Using the results from eqs A14 and A15 in eq A6, we obtain

$$[xh_x + yh_y - h]_{C_0} = -[h]_{C_1}\frac{\cos\alpha}{\sin^2\alpha}[x^2h_{xx} + y^2h_{yy} +$$

$$2xyh_{xy}]_{C_0} + \frac{\cos\alpha}{2}\left[h_x^2 + h_y^2 - \frac{1}{4}(h_x^2 + h_y^2)^2 + ...\right]_{C_1} +$$

$$... \ (\text{A16})$$

Now, substitute the expansion for $h(x, y)$ given in eq 5 to obtain

$$\epsilon[xh_{0x} + yh_{0y} - h_0]_{C_0} = O(\epsilon^2) \qquad (\text{A17})$$

Therefore, in the limit as $\epsilon \rightarrow 0$, eq A17 reduces to

$$[xh_{0x} + yh_{0y} - h_0]_{C_0} = 0 \qquad (\text{A18})$$

From eq A9,

$$[\mathbf{n}\cdot\nabla h_0]_{C_0} = -\frac{1}{\sin\alpha}[xh_{0x} + yh_{0y}]_{C_0} \qquad (\text{A19})$$

Hence, we find that

$$\mathbf{n}\cdot[\nabla h_0]_{C_0} = -\frac{1}{\sin\alpha}[h_0]_{C_0} \qquad (\text{A20})$$

Because $\sin\alpha > 0$ for $0 < \alpha < 180°$, the desired result is proved.