

Conditions for Stable Attachment of Fluid Particles to Solid Surfaces

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Received November 15, 1995. In Final Form: August 23, 1996[⊗]

Recently Eriksson and Ljunggren (*Langmuir* 1995, 11, 2325) established theoretically that in some cases the Young contact angle equation corresponds to a maximum of the energy of the system (that is an unstable equilibrium) rather than to a minimum. In fact, these authors have found out an apparent paradox in the classical field of interfacial thermodynamics. Indeed, it is known from the experiment that bubbles or droplets attached to smooth solid surfaces *tend* to form an equilibrium contact angle, θ , whereas it is shown in ref 1 that under some conditions the fluid particles should *avoid* formation of an equilibrium contact angle because of an unstable equilibrium. Below we extend the analysis of Eriksson and Ljunggren to demonstrate that the conditions for the stability of particle attachment are different depending on whether the fluid particle contains an independent component, i.e. a component whose chemical potential is independent from those of the components in the surrounding medium. The results show that the equilibrium contact angle corresponds to an *unstable* equilibrium only when (i) $90^\circ < \theta < 180^\circ$ and (ii) the independent component is missing. In all other cases the equilibrium contact angle corresponds to the *stable* configuration of the attached fluid particle. These conclusions can be important not only for the specific problem about the bridging cavities as an explanation of the hydrophobic surface force but also for the whole broad field of wetting and spreading.

1. Introduction

There has been a recent discussion about the possible role of bubble nucleation between two hydrophobic surfaces as they approach each other.² It is expected that a spontaneous capillary condensation of a vapor or gaseous bridge between two surfaces would pull the surfaces together with a strong force due to a resolved surface tension component and a negative Laplace pressure within the bridging cavity.³ Ducker et al.⁴ found out additional experimental evidence in favor of this hypothesis and estimated the resulting hydrophobic surface force. However, Eriksson and Ljunggren¹ pointed out that these cavities are not mechanically stable between perfect hydrophobic surfaces. In particular, these authors demonstrated that the Young equation for the contact angle of a gas bubble attached to a hydrophobic solid surface corresponds to a *maximum* of the grand thermodynamic potential, i.e. to an *unstable* equilibrium. Note that in the conventional theory of nucleation the critical nucleus is supposed to be *mechanically* stable though it is unstable with respect to the *chemical (diffusion)* equilibrium.^{5,6} Therefore, the existence of *mechanically* stable bridging cavities is a prerequisite for a possible cavity nucleation and growth in the gap between two hydrophobic surfaces.

As known,⁷ there are three basic necessary conditions for the full thermodynamic equilibrium of a system: (i) *thermal* equilibrium (no heat flow), (ii) *mechanical* equilibrium (no convective flow), and (iii) *chemical or diffusion* equilibrium (no diffusive transport of components). Below

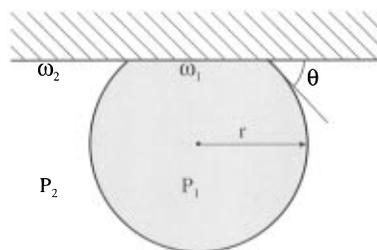


Figure 1. Sketch of a fluid particle attached to a solid surface. P_1 and P_2 are the pressures inside and outside the particle; r and θ are its curvature radius and contact angle.

we assume that *thermal* equilibrium is present. We will focus our attention on the conditions for *mechanical* equilibrium and stability. In particular, we investigate under which conditions the Young equation corresponds to a stable or unstable equilibrium. It turns out that these conditions can be different depending on whether an independent component is present or not present within the fluid particle.

As mentioned in the abstract, we call an independent component a component contained in the fluid particle whose chemical potential is thermodynamically independent from those of the components in the surrounding medium. For example, it can be a component insoluble in the surrounding medium. In the case when all components within the fluid particle are soluble in the medium, it is also possible to have independent components if the system is out of *diffusive* equilibrium. Indeed, if a slow process of diffusion across the phase boundary is present, the transported component inside the fluid particle can be treated as an independent component in so far as its chemical potential is different from that in the surrounding fluid phase. Since usually the mechanical equilibrium is established much faster than the diffusive one, we may investigate the equilibrium shape of the attached fluid particle irrespective of the lack of a diffusive equilibrium.

For the sake of simplicity we will consider the attachment of a bubble or droplet to a flat plate (negligible gravity effects; Figure 1). The same system is investigated in the

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1996.

(1) Eriksson, J. C.; Ljunggren, S. *Langmuir* 1995, 11, 2325.

(2) Craig, V. S. J.; Ninham, B. W.; Pashley, R. M. *J. Phys. Chem.* 1993, 97, 10192.

(3) Christenson, H. K.; Fang, J.; Israelachvili, J. N. *Phys. Rev. B* 1989, 39, 11750.

(4) Ducker, W. A.; Xu, Z.; Israelachvili, J. N. *Langmuir* 1994, 10, 3279.

(5) Shchukin, E. D.; Pertsov, A. V.; Amelina, E. A. *Colloid Chemistry*; Moscow University Press: Moscow, 1982 (in Russian).

(6) Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley: New York, 1976.

(7) Kirkwood, J. G.; Oppenheim, I. *Chemical Thermodynamics*; McGraw-Hill: New York, 1961.

article by Eriksson and Ljunggren¹ (eqs 26–29). The approach can be further extended to describe bridging cavities.

2. Basic Equations

The variation of the grand thermodynamic potential of the system reads

$$\delta\Omega = -\Delta p\delta V + \gamma\delta A_l + \Delta\gamma\delta A_s - \sum_{i=1}^k N_i\delta\mu_i \quad (1)$$

where $\Delta p = P_1 - P_2$ (Figure 1) is the capillary pressure, γ and A_l are the surface tension and the area of the liquid/gas interface, A_s is the area of the solid/gas interface, $\Delta\gamma = \omega_1 - \omega_2$ is the difference between the surface densities of the grand potential for the solid/fluid 1 and solid/fluid 2 interfaces, V is the volume of the attached particle of fluid 1, and N_i and μ_i denote the number of molecules and the chemical potential of the i -th component ($1 \leq i \leq k$).

Let us denote

$$x = \cos \theta \quad (2)$$

Then some geometrical considerations yield

$$V = \frac{\pi}{3}r^3(2 + 3x - x^3) = \frac{\pi}{3}r^3(1 + x)^2(2 - x) \quad (3)$$

$$A_l = 2\pi r^2(1 + x); \quad A_s = \pi r^2(1 - x^2) \quad (4)$$

where r is the curvature radius of the fluid interface. Further we consider a process taking place at $\delta\mu_i = 0$ ($i = 1, \dots, k$). Then we substitute eqs 3 and 4 into eq 1 and in the resulting expression set the coefficients multiplying the independent variations, δr and δx , equal to zero to derive

$$\left(\frac{\partial\Omega}{\partial r}\right)_x = \pi r(1 + x)[- \Delta p r(1 + x)(2 - x) + 4\gamma + 2\Delta\gamma(1 - x)] = 0 \quad (5)$$

$$\left(\frac{\partial\Omega}{\partial x}\right)_r = \pi r^2[- \Delta p r(1 - x^2) + 2\gamma - 2\Delta\gamma x] = 0 \quad (6)$$

Finally, from eqs 5 and 6 one derives

$$\Delta p = 2\gamma/r \quad (\text{Laplace}) \quad (7)$$

$$\gamma x = \Delta\gamma \quad (\text{Young}) \quad (8)$$

In this way we establish that both the Laplace and Young equations correspond to a local extremum of Ω , i.e. to the *equilibrium* position of the attached fluid particle at the solid substrate (Figure 1). Our purpose below is to investigate under which conditions this equilibrium position is *stable* (Ω is minimum) or *unstable* (Ω is maximum).

3. Particle Attachment at Fixed Chemical Potentials

Let us first imagine a process which takes place at fixed chemical potentials of *all* components. Such a process can happen if all components present in the bubble/droplet are soluble in the surrounding outer liquid phase, and in addition, the process should be slow enough for the diffusion equilibrium between the inner and outer fluid phases to be permanently present. Because of the Gibbs–Duhem equation, one has $\Delta p = \Delta p(\mu_1, \dots, \mu_k)$, i.e. Δp is constant during an isothermal process at fixed chemical potentials. The same is true for γ and $\Delta\gamma$. For such a

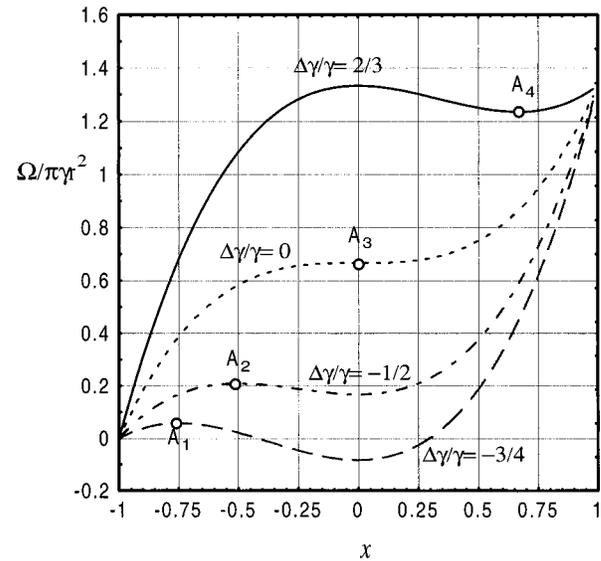


Figure 2. Plot of $\tilde{\Omega}/\pi\gamma r^2$ vs x for various values of $\Delta\gamma/\gamma$ for a process of particle attachment at fixed chemical potentials, see eq 11; A_1, \dots, A_4 denote the points at which the Young equation (eq 8) is satisfied.

process eq 1 can be explicitly integrated to yield

$$\Omega = -\Delta p V + \gamma A_l + \Delta\gamma A_s \quad (9)$$

Note also that fixed Δp and γ means fixed r because of the Laplace equation: $r = 2\gamma/\Delta p$.

When the fluid particle is a bubble of pure vapors of the surrounding liquid, then r can be determined as a solution of the equation

$$p_\infty \exp\left(-\frac{2\gamma v_1}{rkT}\right) = p_{\text{out}} + \frac{2\gamma}{r} \quad (10)$$

stemming from the Gibbs–Thomson⁸ and Laplace equations; here p_∞ is the equilibrium vapor pressure for $r \rightarrow \infty$ (flat interface), p_{out} is the pressure in the liquid phase surrounding the particle; v_1 is the volume per molecule in the latter liquid phase, k is the Boltzmann constant, and T is the temperature. Note that eq 10 has a solution for r only if $p_{\text{out}} \leq p_\infty$.

Following Eriksson and Ljunggren,¹ we substitute eqs 3, 4, and 7 into eq 9 to derive

$$\frac{\Omega}{\pi\gamma r^2} = \frac{2}{3}(1 + x^3) + \frac{\Delta\gamma}{\gamma}(1 - x^2) \quad (11)$$

$$\frac{1}{\pi\gamma r^2} \left(\frac{\partial\Omega}{\partial x}\right)_r = 2x \left(x - \frac{\Delta\gamma}{\gamma}\right); \quad \frac{1}{\pi\gamma r^2} \left(\frac{\partial^2\Omega}{\partial x^2}\right)_r = 4x - 2\frac{\Delta\gamma}{\gamma} \quad (12)$$

Equation 11 is visualized in Figure 2. Equation 12 shows that the grand potential Ω has two extrema: at $x = 0$ and at $x = \Delta\gamma/\gamma$. Moreover, (i) for $\Delta\gamma/\gamma > 0$, Ω has a maximum at $x = 0$ and a minimum at $x = \Delta\gamma/\gamma$; (ii) for $\Delta\gamma/\gamma < 0$, Ω has a minimum at $x = 0$ and a maximum at $x = \Delta\gamma/\gamma$; (iii) for $\Delta\gamma/\gamma = 0$, the two extrema merge into an inflection point at $x = 0$.

Next, we discuss the physical importance of these extrema of Ω . In particular, we have to establish which of the two extrema (that at $x = 0$ or that at $x = \Delta\gamma/\gamma$), or both of them, corresponds to the physical condition for the mechanical equilibrium of the system. With this end

(8) Ono, S.; Kondo, S. In *Handbuch der Physik*; Flügge, S., Ed.; Springer: Berlin, 1960; Vol. 10.

in view, we first bring eq 11 in the following alternative form:

$$\frac{\Omega}{\gamma\pi r^2} = \frac{2}{3}[1 + \text{sgn}(x)(1-y)^{3/2}] + \frac{\Delta\gamma}{\gamma}y; \quad y \equiv \frac{A_s}{\pi r^2} = 1 - x^2 \quad (11a)$$

where $\text{sgn}(x)$ denotes the sign of x . Then the condition for the extremum of the grand potential can be expressed in the form

$$\left(\frac{\partial\Omega}{\partial x}\right)_r = \left(\frac{\partial\Omega}{\partial y}\right)_r \left(\frac{dy}{dx}\right) = 0 \quad (13)$$

There are two sufficient conditions for eq 13 to be satisfied:

$$\frac{1}{\pi r^2} \left(\frac{\partial\Omega}{\partial y}\right)_r = -\gamma x + \Delta\gamma = 0 \quad (14)$$

and

$$\frac{dy}{dx} = -2x = 0 \quad (15)$$

On the other hand, there is only *one* mechanical degree of freedom of a circular contact line on a *solid* surface: the variation of the radius of the circumference. According to the variational calculus, the number of the equations derived by energy minimization is equal to the number of the independent variations.⁹ Consequently, there can be only *one* equation expressing the condition of mechanical equilibrium at the contact line. Therefore, only one of eqs 14 and 15 could express the condition for the mechanical equilibrium. This is eq 14, which gives exactly the Young equation, which expresses the condition for the mechanical equilibrium, as can be rigorously proven by means of variational calculus (see ref 9, eq 1.46).

The other sufficient condition, eq 15, simply expresses the fact that at constant radius, r , the parameter y (and the contact area, $A_s = \pi r^2 y$) is maximum for $x = 0$; this is a geometrical relation rather than a condition for the mechanical equilibrium.

Hence, in agreement with Eriksson and Ljunggren,¹ we conclude the following:

For $\Delta\gamma/\gamma > 0$ there is a stable position of the attached particle determined by the Young equation, eq 8, with an *acute* contact angle, $0 < \theta < 90^\circ$, cf. Figure 1.

For $\Delta\gamma/\gamma \leq 0$ there is no stable position of the attached particle corresponding to the mechanical equilibrium in so far as the Young equation, eq 14, does not correspond to a minimum of the grand potential Ω . This is a nontrivial conclusion. Indeed, all configurations of attached fluid particles with *obtuse* contact angles cannot be stable. Note that this conclusion holds only for fluid particles which do not contain an independent component.

4. Attachment of a Particle Containing an Independent Component

Second, let us imagine another process with a bubble/droplet containing (at least) one component which is insoluble in the outer fluid. For example, this can be an oil droplet or a nucleus of a bubble which is out of diffusion equilibrium with the surrounding liquid. Such a nucleus can grow or diminish due to the diffusion of gas (different from the liquid vapors) dissolved in the liquid. Such a "nonequilibrium" bubble is a typical object of the theory

of nucleation. Of course, we suppose that mechanical equilibrium is present but diffusion (chemical) equilibrium is absent. According to Gibbs,¹⁰ in the absence of chemical equilibrium the gas inside a bubble and the gas dissolved in the surrounding liquid can be treated as two different components. Let the gas inside the bubble be component 1. We will call component 1 the "independent" component because its chemical potential is independent from the chemical potentials in the outer phase. Instead of eq 1 we will use the expression

$$\delta\tilde{\Omega} = -\Delta p\delta V + \gamma\delta A_1 + \Delta\gamma\delta A_s + \mu_1\delta N_1 - \sum_{i=2}^k N_i\delta\mu_i \quad (16)$$

where $\tilde{\Omega} = \Omega + \mu_1 N_1$. The integration of eq 16 for $\delta N_1 = 0$ and $\delta\mu_i = 0$ ($2 \leq i \leq k$) leads to

$$\tilde{\Omega} = \int (-\Delta p\delta V + \gamma\delta A_1 + \Delta\gamma\delta A_s) \quad (17)$$

In contrast to the previous case, now Δp varies along the process and the first term in the parentheses cannot be directly integrated to yield $-\Delta pV$.

4.1. Case of the Liquid Droplet. To simplify the treatment, we assume a process at constant V , γ , and $\Delta\gamma$ (the condition $\delta V = 0$ is appropriate for a liquid drop). Then eq 17 can be integrated to yield

$$\tilde{\Omega} = \gamma A_1 + \Delta\gamma A_s \quad (18)$$

Substituting eq 4 into eq 18, one obtains

$$\tilde{\Omega} = 2\pi\gamma r^2(1+x) + \pi\Delta\gamma r^2(1-x^2) \quad (19)$$

Since $\delta V = 0$ (i.e. $V = \text{constant}$), x and r are not independent parameters. By using eq 3, we eliminate r from eq 19:

$$\frac{\tilde{\Omega}}{\pi\gamma r_0^2} = \left(\frac{4}{2-x}\right)^{2/3} (1+x)^{-1/3} \left[2 + \frac{\Delta\gamma}{\gamma}(1-x)\right] \quad (20)$$

where r_0 is the radius of the nondeformed spherical droplet of the same volume V . The differentiation of eq 20 along with eq 3 yields

$$\left(\frac{\partial\tilde{\Omega}}{\partial x}\right)_V = \frac{2\pi r^2}{2-x} (\gamma x - \Delta\gamma) \quad (21)$$

One sees that the Young equation, $\gamma x - \Delta\gamma = 0$, corresponds to the extremum of $\tilde{\Omega}$. Moreover, one easily derives

$$\left(\frac{\partial^2\tilde{\Omega}}{\partial x^2}\right)_V \Big|_{x=\Delta\gamma/\gamma} = \frac{2\pi\gamma r^2}{2-x} > 0 \quad (22)$$

that is, the extremum is minimum. In other words, the Young equation corresponds to a stable equilibrium for every value of the contact angle ($-1 < x < 1$) in the case of liquid droplets. Equation 20 is visualized in Figure 3 for the same values of $\Delta\gamma/\gamma$ as in Figure 2. One sees that for all curves with $-1 < \Delta\gamma/\gamma < 1$ there is a minimum determined by the Young equation (eq 8). The divergence of $\tilde{\Omega}$ at $x \rightarrow -1$ is due to the fact that for $x \rightarrow -1$ the droplet is flattened against the wall at constant volume and consequently its surface energy becomes infinite. Note also that for $\Delta\gamma/\gamma \rightarrow 1$ the minimum is rather shallow and corresponds to a weak attachment.

(9) Finn, R. *Equilibrium Capillary Surfaces*; Springer Verlag: New York, 1986.

(10) Gibbs, J. W. *The Scientific Papers of J. W. Gibbs*; Dover: New York, 1961; Vol. 1.

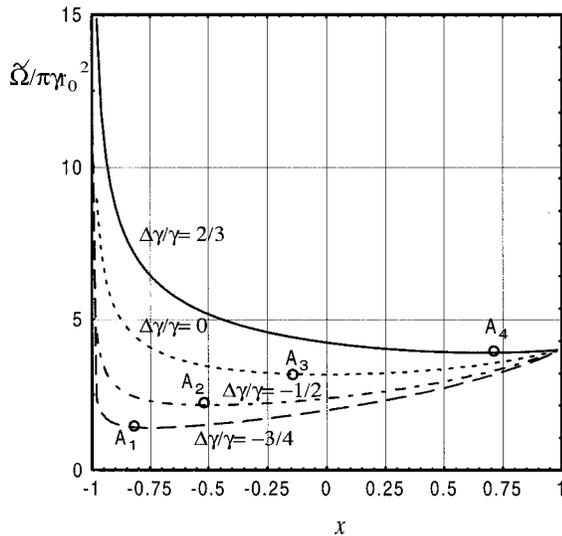


Figure 3. Plot of $\tilde{\Omega}/\pi\gamma r_0^2$ vs x for various values of $\Delta\gamma/\gamma$ for a process of attachment of a liquid droplet, see eq 20; A_1, \dots, A_4 denote the points at which the Young equation (eq 8) is satisfied.

4.2. Case of the Gas Bubble. We assume that we know the thermal equation of state of the gas in the bubble:

$$V = V(\Delta p) \quad (23)$$

Equations 3, 7, and 23 imply that there is only one independent variation on the right-hand side of eq 17. Let us choose the independent variable to be x . Then $r = r(x)$ and

$$\frac{d\tilde{\Omega}}{dx} = \left(\frac{\partial\tilde{\Omega}}{\partial x}\right)_r + \left(\frac{\partial\tilde{\Omega}}{\partial r}\right)_x \frac{dr}{dx} \quad (24)$$

In view of eqs 5–7 one can derive

$$\left(\frac{\partial\tilde{\Omega}}{\partial r}\right)_x = 2\pi r(1-x^2)(\Delta\gamma - \gamma x) \quad (25)$$

$$\left(\frac{\partial\tilde{\Omega}}{\partial x}\right)_r = 2\pi r^2 x(\gamma x - \Delta\gamma) \quad (26)$$

The combination of eqs 24–26 yields

$$\frac{d\tilde{\Omega}}{dx} = 2\pi r(\Delta\gamma - \gamma x) \left[(1-x^2) \frac{dr}{dx} - rx \right] = (\Delta\gamma - \gamma x) \frac{dA_s}{dx} \quad (27)$$

see eq 4. One sees that the Young equation (eq 8) is again a condition for equilibrium, i.e. extremal $\tilde{\Omega}$. To check whether the equilibrium is stable or unstable, we calculate the derivative

$$\frac{d^2\tilde{\Omega}}{dx^2} = -\gamma \frac{dA_s}{dx} \quad (x = \Delta\gamma/\gamma) \quad (28)$$

From eq 4 one obtains

$$-\frac{dA_s}{dx} = 2\pi r \left[rx - (1-x^2) \frac{dr}{dx} \right] \quad (29)$$

If dr/dx were zero, eq 28 would reduce to the result of Eriksson and Ljunggren.¹ However, in the present case $dr/dx \neq 0$; our aim below is to estimate this derivative.

For an ideal gas one can write

$$pV = (N_1 + N_2)kT; \quad p = p_{\text{out}} + \frac{2\gamma}{r} \quad (30)$$

where p is the pressure inside the bubble and N_1 and N_2 are the numbers of molecules of the gas and the liquid vapor, respectively. Note that we consider the case $N_1 = \text{constant}$, that is that the mechanical equilibrium is established much faster than the diffusion equilibrium with respect to component 1. On the other hand, $N_2 = N_2(V)$, but fortunately, $N_2/N_1 \ll 1$ at temperatures lower enough than the boiling temperature of the liquid. Thus for the saturated vapors of water in air one has

$$N_2/N_1 \leq 0.07 \quad \text{for } T \leq 40^\circ\text{C}$$

For the smallest bubble radii, $r < 10$ nm, the equilibrium vapor pressure is even lower because of the curvature effect, as predicted by the Gibbs–Thomson equation.⁸ Therefore we can neglect N_2 in eq 30 to derive

$$\frac{\partial V}{\partial p} = -\frac{V}{p} \quad (31)$$

Further, with the help of eqs 7 and 31 we obtain

$$\frac{dV}{dx} = \frac{\partial V}{\partial p} \frac{dp}{dr} \frac{dr}{dx} = \frac{2\gamma V}{pr^2} \frac{dr}{dx} \quad (32)$$

On the other hand, from eq 3 one derives

$$\frac{dV}{dx} = 3\frac{V}{r} \frac{dr}{dx} + \pi r^3(1-x^2) \quad (33)$$

Combining eqs 32 and 33, we get

$$-\frac{dr}{dx} = \frac{3r(1-x)}{2q(1+x)(2-x)} \quad (34)$$

where

$$q = \frac{3}{2} - \frac{\gamma}{pr} \quad (35)$$

Note that q is a quantity of bounded variation:

$$1 \leq q \leq \frac{3}{2} \quad (36)$$

The lower limit, $q = 1$, corresponds to $r \rightarrow 0$, cf. eq 30; the upper limit, $q = 3/2$, corresponds to $p_{\text{out}} \rightarrow \infty$ at finite r . The substitution of eq 34 into eq 29 yields

$$-\frac{dA_s}{dx} = 2\pi r \left[rx + \frac{3r(1-x)^2}{2q(2-x)} \right] \geq \frac{2\pi r^2}{2-x} \quad (37)$$

At the last step we exchanged q with its upper limit, $3/2$. Finally, combining eqs 37 and 28, we obtain

$$\frac{d^2\tilde{\Omega}}{dx^2} \geq \frac{2\pi\gamma r^2}{2-x} > 0 \quad (38)$$

that is, the Young equation again corresponds to the stable equilibrium. It is curious to note that eq 38 is very similar to eq 22 despite the quite different ways of their derivation.

5. Concluding Remarks

In summary, the Young equation always expresses a necessary condition for the mechanical *equilibrium* of a fluid particle attached to a solid surface. This equilibrium

is *stable* always when an independent component is *present* within the fluid particle. If the independent component is *absent*, the Young equation corresponds to a *stable* or *unstable* equilibrium depending on whether the contact angle θ is *acute* ($\Delta\gamma/\gamma > 0$) or *obtuse* ($\Delta\gamma/\gamma < 0$).

The latter conclusions, applied to the nucleation of bubbles at a solid surface, imply the following. A nucleus (except the critical one) is always out of diffusive equilibrium with the surrounding phase. Then the gas in a bubble nucleus can be treated as an independent component, as was discussed in the Introduction. Consequently, we may draw the curious conclusion that the configuration of such an attached bubble nucleus is *mechanically stable* (see eq 38), due to the fact that the nucleus is out of *diffusive* equilibrium.

The role of the hydrophobic surface can be (at least) to decrease the work of nucleation (formation of the critical nucleus): as shown in ref 5

$$w_{\text{het}} = w_{\text{hom}} f(\theta); \quad f(\theta) = \frac{1}{4}(1 + \cos \vartheta)^2(2 - \cos \theta) \quad (39)$$

where w_{hom} and w_{het} are the works of homogeneous and heterogeneous nucleation and $f(\theta)$ is a factor accounting

for the shape of the attached fluid particle (Figure 1). Note that $f(\theta)$ monotonically decreases with the increase of θ (i.e. with the increase of the solid surface hydrophobicity in the case of bubbles).

Finally we note that the existence of a *negative* line tension (neglected in the above considerations) in all cases leads to the appearance of a local minimum in the Ω vs x curves (corresponding to a stable attachment) in close vicinity to the point $x = 1$. Variational derivation of the Young equation with line tension can be found in ref 11; see also ref 12.

At a subsequent step this analysis can be extended to bridging cavities.

Acknowledgment. The author is indebted to Prof. J. C. Eriksson, Dr. Stig Ljunggren, and Prof. J.N. Israelachvili for stimulating discussions as well as to Mr. V. Paunov for the figure preparation.

LA9510386

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