Film and Line Tension Effects on the Attachment of Particles to an Interface

I. Conditions for Mechanical Equilibrium of Fluid and Solid Particles at a Fluid Interface

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A general variational approach has been applied to derive the conditions for mechanical equilibrium of fluid and solid particles at an interface in the presence of an external field. It is shown that Young's equation for solid particles does not follow from force balance, which is due to the difference between the surface tension and the specific surface free energy of the solid. The correct definition of the contact angles in the presence of an external field is discussed.

1. INTRODUCTION

The interest in line tension kept increasing during the last decade. To a large extent it was stimulated by the role of the line tension in the occurrence of a number of processes of practical importance: heterogeneous nucleation (1, 2), flotation of ores (3), droplet coalescence in emulsions (4), microbial adhesion (5), etc. Line tension effects may prove important for other phenomena like membrane fusion, plasmapheresis, etc.

The foundations of the thermodynamic theory of systems with line tension were laid by Gibbs (6) and further developed by Buff and Saltsburg (7) and Boruvka and Neumann (8). The theory of the line tension for systems containing planar thin liquid films in contact with fluid phases was worked out in Refs. (9–11). Tarazona and Navascues (12) and Rusanov (13) considered the case when one of the bulk phases was solid (Rusanov accounted also for the deformation of the solid). Similarly to the surface tension of small drops, the line tension must depend on the radius of the (three phase) contact line (10) and more generally speaking—on the geometry of the system. This viewpoint was confirmed by the model calculations of the line tension for particular systems performed in Refs. (9, 13, 14–16).

All these theoretical developments as well as the plausible practical implications of the line tension effects called for direct experimental measurement. The line tension can in principle be measured by studying any phenomenon that is supposed to be affected by it, e.g., from the rate of heterogeneous nucleation (2). This approach requires, however, knowledge (and/or fitting) of several parameters. Therefore, in a way it is better to determine the line tension directly from the conditions for mechanical equilibrium of small particles at another interface. Pethica (17) was the first to introduce a line tension term in Young's equation and Lane (18) modified it for the case when the drop is formed in a conic pore. Torza and Mason (4) wrote the force balance equations (in the absence of gravity) for the attachment of two drops of different radii and Pujado

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and Scriven (19) formulated the general conditions for equilibrium of a bubble or drop pressed against another fluid interface by the gravity force.

As far as we are aware, the first attempt for measuring the line tension was undertaken by Langmuir (20) for a floating lense. However, he used the wrong force balance equation (19) and as pointed out by Princen (see (21), p. 61) the quantity he measured was not the Gibbs line tension.

In a series of papers Scheludko, Platikanov, and co-workers experimentally determined the line tension by investigating the attachment of a solid sphere (22, 23) to a liquid surface. In Refs. (23, 25) they used the shrinking bubble method of Princen and Mason (26) combined with the equilibrium conditions of Pujado and Scriven (19). These works will be discussed in more details in Part IV of the present series. For the time being we will only mention that the authors of Refs. (22–25) as opposed to Churaev *et al.* (15, 16), have neglected the dependence of the line tension on the radius of the contact line and when interpreting their data they have made use of some hypothesis in order to make up for the insufficiency of their experimental information. Besides, if the line tension of a bubble depends on the geometrical parameters of the system studied, the film tension may also depend on them, i.e., the latter may have no longer the same value as for an infinite planar film.

Therefore, we decided to undertake measurements of the film and line tension for gas bubbles attached to a liquid interface. We also used the shrinking bubble method of Princen and Mason (26). We tried to put forward a systematic approach, free of any hypothesis that could not be given firm theoretical or experimental justification. Toward this aim we had to resolve several auxiliary problems; we believe that some of them present independent interest and can prove useful in studying other phenomena.

In Section 2 of this paper (Part I of the present series) the conditions for equilibrium of a fluid particle are derived and in Section 3 the same is done for a solid particle. It is shown that the difference between these two systems resides in the fact that the solid/liquid surface free energy differs from the respective surface tension. Some problems connected with the correct definition of the contact angles are discussed in Section 4. In the Appendix the effect of the weight of the film on the conditions for equilibrium is discussed.

In Part II (Ref. (27)) we derive perturbational equations for the shape of the bubble and the external meniscus, necessary for the calculation of the slope angles of these surfaces at the contact line. Part III (Ref. (28)) is devoted to the theoretical foundation and the experimental realization of a differential–interferometric method for the determination of the radius of curvature of the bubble hat, i.e., of the film intervening between the bubble and the gas phase. The basic results from Parts I–III (necessary to perform the final calculations) are summarized and the experimental procedure is described in Part IV (Ref. (29)), where measured values of the film and line tension as functions of the system parameters are presented and discussed.

2. EQUILIBRIUM OF A FLUID PARTICLE AT A FLUID INTERFACE

The conditions for mechanical equilibrium in a capillary system in most cases can be easily derived on the grounds of simple intuitive force balance considerations. However, in more complicated cases this approach can lead (and has led sometimes) to erroneous conclusions. Therefore, we prefer to derive the conditions for mechanical equilibrium by means of the general method of Gibbs (6), which consists in the minimization of the appropriate thermodynamic potential of the system. This allowed us to shed some light on several somewhat obscure problems (see below), e.g., to reveal the fundamental difference between the conditions for equilibrium of a fluid and a solid particle.

Let us consider a fluid particle (bubble, drop, or lense—phase 1) attached to the in-

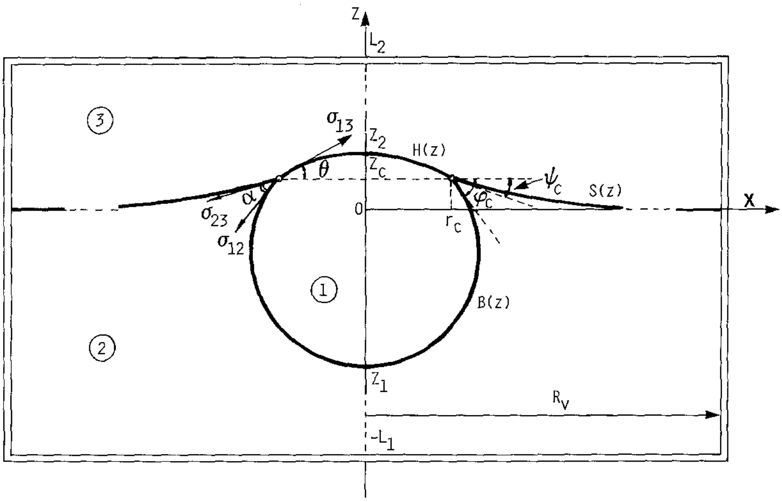

FIG. 1. A fluid particle (phase 1) at the interface between two other fluid phases 2 and 3. The system is enclosed in a rigid cylindrical vessel of radius R_v and height $L = L_1 + L_2$. $B(z)$, $H(z)$, and $S(z)$ are, respectively, the equations of the lower bubble surface, the hat of the bubble (the film), and the external meniscus, and σ_{12}, σ_{13}, and σ_{23} are the interfacial tensions. The three interfaces meet the plane $z = z_c$ at angles φ_c, θ, and ψ_c; r_c and z_c are the radius and elevation of the contact line above the horizontal liquid surface $z = 0$.

terface between two other fluid phases 2 and 3 (see Fig. 1). The whole system is enclosed in a rigid cylindrical vessel of radius R_v and height L $(=L_1 + L_2)$ and is under the action of an acceleration g (gravitational or inertial) directed opposite to the axis z. If one assumes that the interfacial tensions σ_{12}, σ_{13}, and σ_{23} and the line tension (the specific line free energy) κ do not depend on the acceleration the latter only makes the pressures p_i $(i = 1, 2, 3)$ in the bulk phases depended on z. In the case of nonzero gravity and negligible change of the densities ρ_i with z,

$$p_i = p_i^0 - \rho_i g z \qquad [1]$$

where p_i^0 is the reference pressure at $z = 0$. For the sake of brevity we will call sometimes the particle "bubble." (That is the case depicted in Fig. 1. Note that in this case the interface 1/3 must be a thin film, whose total tension, whenever necessary, will be denoted by γ. A thin film can be present even when phase 1 is liquid). The interface 1/2 will be called "bubble surface," the interface 1/3—"hat," and the interface 2/3—"surface." Correspondingly the equations of the generatrices of these interfaces will be denoted by $B(z)$, $H(z)$, and $S(z)$.

If one leaves out the temperature and chemical potential terms (they lead to the trivial condition for uniformity of the temperature and the chemical potentials throughout the system) the free energy $\mathcal{F}$ of the whole system will consist of a sum of three kinds of products[2]: pressure to volume, interfacial tension to surface area, and line tension to (three-phase-contact-line) length. By using standard geometrical considerations one can write then the expression for the free energy of the system as follows (the primes denote differentiation with respect to z):

$$\mathcal{F} = \pi \int_{z_1}^{z_c} \Phi_1 dz + \pi \int_0^{z_c} \Phi_2 dz + \pi \int_{z_c}^{z_2} \Phi_3 dz + \text{const} \qquad [2]$$

[2] An alternative approach, used in (30), is to assume that the bulk pressures are constant (equal to p_i^0) and to account for the acceleration by introducing potential energy terms. We will make use of this approach in the Appendix, to estimate the contribution of the thin film weight to the free energy and the force balance.

where

$$\Phi_1(z, B, B') = (p_2 - p_1)B^2 + 2\sigma_{12}B\sqrt{1 + B'^2} \quad [3]$$

$$\Phi_2(z, S, S') = (p_3 - p_2)S^2 + 2\sigma_{23}S\sqrt{1 + S'^2} \quad [4]$$

$$\Phi_3(z, H, H') = (p_3 - p_1)H^2 + 2\sigma_{13}H\sqrt{1 + H'^2} - 2\kappa H' \quad [5]$$

and the constant contains all terms that do not depend on B, S, and H.

Hence, the free energy turns out to be a functional of $B(z)$, $H(z)$, and $S(z)$ and their derivatives. According to the Gibbs' principle (6) the necessary condition for equilibrium of the system is $\delta^{(1)}\mathcal{F} = 0$ at constant R_v and L. If, however, the bubble radius is much smaller than R_v, i.e., if $R_v \rightarrow \infty$, the variation can be taken at constant L_1 and L_2. One of the conditions for extremum of the functional [2] is that each integrand in [2] Φ_i $(i = 1, 2, 3)$ must satisfy Euler's equation (see (31) Chap. 6, Sect. 3):

$$\frac{\partial \Phi_i}{\partial K_i} - \frac{d}{dz}\left(\frac{\partial \Phi_i}{\partial K_i'}\right) = 0 \quad [6]$$

where K_i $(i = 1, 2, 3)$ stands for B or S or H. This leads naturally to three Laplace's equations for the three interfaces (p_i in the equations below are the local values of the pressures in the respective phases at a given point at the interface):

$$D(B) = (p_2 - p_1)/\sigma_{12} \quad [7]$$

$$D(S) = (p_3 - p_2)/\sigma_{23} \quad [8]$$

$$D(H) = (p_3 - p_1)/\sigma_{13} \quad [9]$$

where

$$D(K_i) = \frac{K_i''}{(1 + K_i'^2)^{3/2}} - \frac{1}{K_i(1 + K_i'^2)^{1/2}}; \quad i = 1, 2, 3. \quad [10]$$

The solution of Eqs. [7]–[9] with the appropriate boundary conditions will give the equations of B, S, and H. This problem is investigated in great details in the excellent review of Princen (21).

The other necessary conditions for the extremum of the functional [2] will be obtained below by taking the variation of $\mathcal{F}$ with respect to the boundaries z_1, z_2, and z_c. Since however by definition

$$B(z_1) = 0; \quad \left.\frac{\partial z}{\partial B}\right|_{z=z_1} = 0;$$

$$H(z_2) = 0; \quad \left.\frac{\partial z}{\partial H}\right|_{z=z_2} = 0 \quad [11]$$

the variations with respect to z_1 and z_2 do not lead to new results.

When taking the variations with respect to z_c one must keep in mind that the point (z_c, r_c) is a point of intersection of the three curves, in other words, it must satisfy the conditions

$$B(z_c) = S(z_c) = H(z_c) = r_c$$

and

$$\delta B(z_c) = \delta S(z_c) = \delta H(z_c) = \delta r_c.$$

Besides, because of the fluidity of all interfaces the variations with respect to z_c and r_c are independent so that in order to have $\delta^{(1)}\mathcal{F} = 0$, the following equations must hold (see (31) Chap. 7, Sect. 2):

$$\left.\left(\Phi_1 + \Phi_2 - \Phi_3 - B'\frac{\partial \Phi_1}{\partial B'} - S'\frac{\partial \Phi_2}{\partial S'} + H'\frac{\partial \Phi_3}{\partial H'}\right)\right|_{z=z_c} = 0 \quad [12]$$

$$\left.\left(\frac{\partial \Phi_1}{\partial B'} + \frac{\partial \Phi_2}{\partial S'} - \frac{\partial \Phi_3}{\partial H'}\right)\right|_{z=z_c} = 0. \quad [13]$$

Let φ_c, ψ_c, and θ be the angles comprised between the positive axis z and the normals to the curves B, S, and H at $z = z_c$ (see Fig. 1), so that

$$B'(z_c) = -\text{ctg}\,\varphi_c, \quad S'(z_c) = -\text{ctg}\,\psi_c,$$
$$H'(z_c) = -\text{ctg}\,\theta. \quad [14]$$

Then Eqs. [12] and [13], along with [3]–[5] and [14] yield the sought equilibrium conditions

$$\sigma_{13}\sin\theta = \sigma_{12}\sin\varphi_c + \sigma_{23}\sin\psi_c \quad [15]$$

$$\sigma_{13}\cos\theta = \sigma_{12}\cos\varphi_c + \sigma_{23}\cos\psi_c - \frac{\kappa}{r_c}. \quad [16]$$

Note that all terms in [2], containing the pressures p_i and hence, the acceleration, have identically cancelled. Taking into account the definition of the angles φ_c, ψ_c, and θ one can write the system [15] and [16] in the equivalent vectorial form

$$\boldsymbol{\sigma}_{13} + \boldsymbol{\sigma}_\kappa + \boldsymbol{\sigma}_{12} + \boldsymbol{\sigma}_{23} = 0, \quad [17]$$

where the vector $\boldsymbol{\sigma}_\kappa(|\boldsymbol{\sigma}_\kappa| = \kappa/r_c)$ accounts for the line tension effect and is directed toward the center of curvature of the contact line, (see, e.g., (32) or (23)). Equations [15] and [16] were formulated in (19) using force balance considerations. In the absence of gravity (i.e., for $\psi_c = 0$) they were also used in (4) for two drops of different radii and in (33) for a lense at a fluid interface.

We will transform now the normal force balance Eq. [15] into an alternative form including explicitly the buoyancy and the mass forces. With that end in view we observe that (cf. also Eqs. [10] and [11])

$$r_c\sin\varphi_c = \int_{z_1}^{z_c} d\left(\frac{B}{\sqrt{1+B'^2}}\right) = -\int_{z_1}^{z_c} BB'D(B)dz, \quad [18]$$

and

$$r_c\sin\theta = \int_{z_2}^{z_c} d\left(\frac{H}{\sqrt{1+H'^2}}\right) = -\int_{z_2}^{z_c} HH'D(H)dz. \quad [19]$$

Then from Eqs. [7]–[9] and [15] one has

$$r_c\sigma_{23}\sin\psi_c = \int_{z_1}^{z_c} (p_2 - p_1)BB'dz + \int_{z_c}^{z_2} (p_3 - p_1)HH'dz = \int_{z_1}^{z_2} (\bar{p} - p_1)KK'dz \quad [20]$$

where

$$\bar{p}(z) = p_2\theta(z_c - z) + p_3\theta(z - z_c) \quad [21]$$

$$K(z) = B(z)\theta(z_c - z) + H(z)\theta(z - z_c) \quad [22]$$

and

$$\theta(z) = \begin{cases} 1 & \text{at} \quad z > 0, \\ 0 & \text{at} \quad z < 0, \end{cases} \quad [23]$$

is Heaviside's stepwise function.

The general definition of the buoyancy force $\mathbf{F}_b$ acting on the fluid particle (phase 1) is

$$\mathbf{F}_b = -\oint \bar{p}d\mathbf{s}, \quad [24]$$

where the integral is taken over the whole surface of phase 1 and the normal to the surface is oriented outward. Further, since the external force acceleration is acting along the z axis, one obtains the following expression for the magnitude, F_b, of the buoyancy force, which coincides with its z component:

$$F_b = (\mathbf{F}_b)_z = -\oint \bar{p}\mathbf{k}\cdot d\mathbf{s} = 2\pi\int_{z_1}^{z_2} \bar{p}KK'dz, \quad [25]$$

where $\mathbf{k}$ is the unit vector of the z axis. So [20] takes the form

$$2\pi\sigma_{23}r_c\sin\psi_c + F_m = F_b, \quad [26]$$

where

$$F_m = 2\pi\int_{z_1}^{z_2} p_1KK'dz \quad [27]$$

is the magnitude of the mass force acting on phase 1. Indeed, from the theorem of Gauss–Ostrogradsky one has

$$F_m = -\oint p_1\mathbf{k}\cdot d\mathbf{s} = -\int_{(V_b)} \mathrm{div}(p_1\mathbf{k})dV = -\int_{(V_b)} \frac{\partial p_1}{\partial z}dV \quad [28]$$

and from Eq. [1]

$$F_m = \rho_1 g V_b \quad [29]$$

where V_b is the particle volume.

The origin of the buoyancy force F_b and the way it must be calculated for capillary systems are clear from its definition, Eq. [25]. Yet, the literature abounds with erroneous calculations of F_b (some of them have been analyzed by Princen (21)), whence, we will transform [25] in a simpler form, similar to [29]. In the same way as [28] was derived, one can put [25] in the form

$$F_b = -\int_{(V_b)} \frac{\partial \bar{p}}{\partial z} dV. \qquad [30]$$

When differentiating [21] (see also [1]) one must keep in mind that $d\theta/dz = \delta(z)$, the δ function of Dirac. Using also the properties of the δ function (see, e.g., Sect. 21.9-2 of (34)), we obtain from [30]

$$F_b = \rho_2 g V_l + \rho_3 g V_u + [p_2(z_c) - p_3(z_c)]S_c \qquad [31]$$

where V_l and V_u are the volumes of the lower ($z < z_c$) and upper ($z > z_c$) parts of the bubble ($V_l + V_u = V_b$) and S_c is the area inside the contact line. From [1] $p_2(z_c) - p_3(z_c) = -(\rho_2 - \rho_3)gz_c$, so that

$$F_b = g[\rho_2 V_l + \rho_3 V_u \mp (\rho_2 - \rho_3)V_c] \qquad [32]$$

where V_c is the volume of the cylinder lying over the contact line and having a height $|z_c|$; the upper sign in [32] is for $z_c > 0$ (see Fig. 1) and lower one for $z_c < 0$ (see Fig. 2). Note that when deriving [32] we did not make any assumption regarding the shape or symmetry of the particle. Equations of the same kind were formulated (and used) by Princen (21), Nutt (35), Nikolov and Scheludko (36), and others without proof on the grounds of force considerations.

3. EQUILIBRIUM OF A SOLID PARTICLE AT A FLUID INTERFACE

The system under consideration represents an axisymmetric particle 1 of "length" l attached to a liquid interface (Fig. 2). Using the same considerations as in Section 2 one can write the free energy of the system as

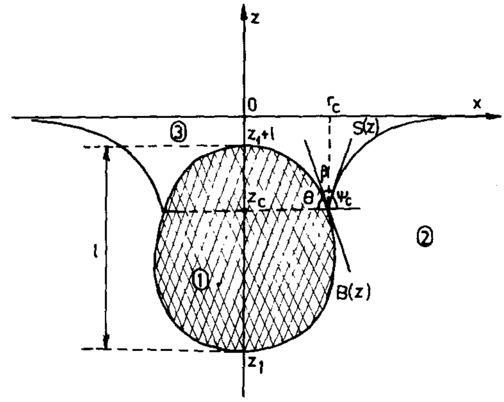

FIG. 2. A solid axisymmetric particle 1 of length l and equation of the generatrix $B(z)$ at the fluid interface $S(z)$ between the phases 2 and 3; r_c and z_c are the radius and the distance from the contact line to the horizontal liquid surface $z = 0$.

$$\mathcal{F} = \pi \int_{z_c}^{0} \Phi(z, S, S') + \pi F(z_c, z_1, r_c) + \text{const} \qquad [33]$$

where

$$\Phi(z, S, S') = (p_2 - p_3)S^2(z) + 2\sigma_{23} S(z)\sqrt{1 + S'^2} \qquad [34]$$

and

$$F(z_c, z_1, r_c) = \int_{z_1}^{z_c} dz[p_2 B^2(z) + 2\sigma_{12} B(z)\sqrt{1 + B'^2}] + \int_{z_c}^{z_1+l} [p_3 B^2(z) + 2\sigma_{13} B(z)\sqrt{1 + B'^2}]dz + 2\pi r_c \kappa + mg(z_m + z_1). \qquad [35]$$

Here σ_{12}, σ_{13}, and σ_{23} are the specific surface free energies of the respective interfaces. The last term in [35] is the potential energy of a particle of mass m, whose center lies at a distance z_m from z_1. To have full correspondence with Section 2, we have accounted in [35] for the line tension. We have done the whole derivation for an ideal solid. As shown by Rusanov (13) the energy of deformation of the solid also leads to an effect thermodynamically equivalent to a line tension term.

The variation of $\mathcal{F}$ at fixed boundary points will obviously lead to the Laplace's equation [8] for the equilibrium curve $S(z)$. The variations with respect to z_c, z_1, and r_c, however, are not independent, because whatever values z_c and z_1 acquire, the point (z_c, r_c) must lie on the curve $B(z)$, which describes the (constant) shape of the particle. Therefore, the variation δr_c can be expressed through δz_c and δz_1:

$$\delta r_c = \frac{\partial B}{\partial z}\bigg|_{z=z_c} \delta z_c + \frac{\partial B}{\partial z_1}\bigg|_{z=z_c} \delta z_1. \quad [36]$$

This is the transversality condition.

On the other hand, the variation of z_1 will move the particle up and down without affecting its shape. In other words B depends on z and z_1 only through the difference $z - z_1$, which means

$$\frac{\partial B}{\partial z_1} = -\frac{\partial B}{\partial z}. \quad [37]$$

Keeping in mind that $r_c = S(z_c)$, the condition $\delta^{(1)}\mathcal{F} = 0$ can be written in the form (cf. (31), Chap. 7, Sect. 2):

$$\left(-\Phi + S'\frac{\partial \Phi}{\partial S'}\right)_{z=z_c} \delta z_c - \left(\frac{\partial \Phi}{\partial S'}\right)_{z=z_c} \delta r_c + \frac{\partial F}{\partial z_c}\delta z_c + \frac{\partial F}{\partial z_1}\delta z_1 + \frac{\partial F}{\partial r_c}\delta r_c = 0.$$

By setting equal to zero the coefficients before the independent variations δz_c and δz_1 (see also [36] and [37]) we obtain the following two equations:

$$\left[\Phi + (B' - S')\frac{\partial \Phi}{\partial S'} - B'\frac{\partial F}{\partial r_c}\right]_{z=z_c} - \frac{\partial F}{\partial z_c} = 0, \quad [38]$$

$$\pi\left[B'\frac{\partial \Phi}{\partial S'} - B'\frac{\partial F}{\partial r_c}\right]_{z=z_c} + \pi\frac{\partial F}{\partial z_1} = 0. \quad [39]$$

By using the relationships

$$B'|_{z=z_c} = -\text{ctg}\,\theta,$$

$$S'|_{z=z_c} = \text{ctg}\,\psi_c, \quad [40]$$

and

$$\theta + \psi_c + \beta = \pi \quad [41]$$

from [38], along with [34] and [35], one can easily obtain

$$\sigma_{23}\cos\beta = \sigma_{12} - \sigma_{13} - \frac{\kappa}{r_c}\cos\theta. \quad [42]$$

When taking the derivative $\partial F/\partial z_1$ in [39] one must keep in mind that F depends on z_1 both through the limits of the integrals and through $B(z - z_1)$. In this way, by using also [37], [40], and [41], one obtains from [39]

$$F_{\text{m}} = F_{\text{b}} + \frac{2\pi r_c}{\sin\theta}(\sigma_{12} - \sigma_{13} + \sigma_{23}\cos\theta\cos\psi_c) - 2\pi\kappa\,\text{ctg}\,\theta \quad [43]$$

where

$$F_{\text{m}} = mg \quad [44]$$

and

$$F_{\text{b}} = 2\pi\int_{z_1}^{z_1+l} \bar{p}(z)BB'dz, \quad [45]$$

$\bar{p}$ being defined by [21]. If one eliminates $\sigma_{12} - \sigma_{13}$ by means of [42], Eq. [43] will yield

$$F_{\text{m}} = F_{\text{b}} + 2\pi r_c\sigma_{23}\sin\psi_c \quad [46]$$

which is analogous to [26]. Note that in this case the "surface force" is directed upward.

4. DISCUSSION

It was already pointed out in Section 2 that the conditions for equilibrium [15] and [16] are in some cases force balance equations (see [17]) and could have been derived much easier by simply taking the projections along the axis x and z of all forces acting on the contact line. The major advantage of the variational approach used in the present paper is its universality and physical transparency which in turn gives answers to several somewhat obscure questions.

One of them is connected with the number of independent equations of mechanical balance at the contact line. In the case of a fluid particle there are two independent equations [15] and [16], which can be combined to yield the vectorial Eq. [17]. The two equations [15] and [16] correspond to the two independent variations δr_c and δz_c of the coordinates of the boundary point (r_c, z_c) (see Fig. 1). However, in the case of a floating solid particle (see Fig. 2) the variations δr_c and δz_c are no longer independent, because the boundary point (r_c, z_c) can move along the particle surface only. So, there is one degree of freedom which results in the existence of only one condition for mechanical equilibrium at the contact line. Indeed, we obtained only one relationship between the σs and κ, Eq. [42]. Moreover, we found out that contrary to what "intuition" would suggest, no force balance can be written for the contact line on a solid particle. Therefore in spite of its resemblance to a force balance along the tangent to the solid surface it is *not* the result of compensation of forces. (Remarkably, with $\kappa = 0$, it has the same form as Young's equation for the equilibrium of a drop on a flat solid surface.) We believe that the reason for this fundamental difference between fluid and solid particles lies in the fact that surface tensions and specific surface free energies do not coincide for solid surfaces as they do for fluid surfaces (for detailed discussion of this difference see e.g., (6, 37, 38). The σs entering in the expressions for the system free energy (Eqs. [2] and [33]) are *specific surface free energies* but for the fluid surfaces they are equivalent to surface tensions, i.e., to forces (per unit length). That is why when *all* surfaces are fluid the variation of the free energy leads to a force balance. However, the solid/fluid specific surface free energies σ_{12} and σ_{13} in Section 3 cannot be looked at as forces and no force balance can be written for the contact line. The only forces acting on the particle are F_b, F_m, and the fluid/fluid surface tension σ_{23} and their balance leads to Eq. [46]. Incidentally, another important result of the variational procedure is that this equation, which is usually written on the grounds of intuitive considerations (and more specifically its surface tension term $2\pi r_c\sigma_{23}\sin\psi_c$) could have been derived here from first principles.

An important question, that was a matter of controversy in the literature (see e.g., (39–41)) is whether or not the contact angles depend on the gravity and/or other external fields. In order to analyze this problem let us introduce the contact angles

$$\alpha = \varphi_c - \psi_c \quad [47]$$

(between σ_{12} and σ_{23}) and

$$\beta = \pi - \theta + \psi_c \quad [48]$$

(between σ_{23} and σ_{13}). With these notations Eqs. [15] and [16] can be rewritten as

$$(\sigma_{13}\sin\beta - \sigma_{12}\sin\alpha)\cos\psi_c - (\sigma_{13}\cos\beta + \sigma_{12}\cos\alpha + \sigma_{23})\sin\psi_c = 0 \quad [49]$$

$$(\sigma_{13}\sin\beta - \sigma_{12}\sin\alpha)\sin\psi_c + (\sigma_{13}\cos\beta + \sigma_{12}\cos\alpha + \sigma_{23})\cos\psi_c = \frac{\kappa}{r_c}. \quad [50]$$

Since the matrix

$$\begin{pmatrix} \cos\psi_c & -\sin\psi_c \\ \sin\psi_c & \cos\psi_c \end{pmatrix}$$

corresponds to a rotation at angle ψ_c clockwise, if κ/r_c were zero the only result of the action of the external field would have been such a rotation of Neumann's triangle without any change of the angles α and β. Indeed, if one solves the system of [49] and [50] with $\kappa/r_c = 0$ (the respective angles are denoted by α_0 and β_0) one easily gets (19)

$$\cos\alpha_0 = \frac{\sigma_{13}^2 - \sigma_{12}^2 - \sigma_{23}^2}{2\sigma_{12}\sigma_{23}};$$

$$\cos\beta_0 = \frac{\sigma_{12}^2 - \sigma_{13}^2 - \sigma_{23}^2}{2\sigma_{13}\sigma_{23}}, \quad [51]$$

i.e., α_0 and β_0 do not depend on the field.

Note, however, that if some of the σs depend on the external field (this may be the case when a thin film intervenes between the phases 1 and 3) the contact angles may depend on it too. The angle θ (see Fig. 1) between σ_{13} and the plane of the three-phase contact line will however always depend on the external field, because it is *not* a real contact angle between two interfaces.

The situation will change if $\kappa/r_c \neq 0$. The solution of Eqs. [49] and [50] is

$$\sigma_{12}\sigma_{23}(\cos\alpha_\kappa - \cos\alpha) = \frac{\kappa}{r_c}[\sigma_{23}(1 - \cos\psi_c) + \sigma_{12}(\cos\alpha_\kappa - \cos(\alpha + \psi_c))], \quad [52]$$

$$\sigma_{13}\sigma_{23}(\cos\beta_\kappa - \cos\beta) = \frac{\kappa}{r_c}[\sigma_{23}(1 - \cos\psi_c) + \sigma_{13}(\cos\beta_\kappa - \cos(\beta - \psi_c))] \quad [53]$$

where

$$\cos\alpha_\kappa = \frac{\sigma_{13}^2 - \sigma_{12}^2 - (\sigma_{23} - \kappa/r_c)^2}{2\sigma_{12}(\sigma_{23} - \kappa/r_c)} \quad [54]$$

and

$$\cos\beta_\kappa = \frac{\sigma_{12}^2 - \sigma_{13}^2 - (\sigma_{23} - \kappa/r_c)^2}{2\sigma_{13}(\sigma_{23} - \kappa/r_c)} \quad [55]$$

are gravity independent quantities. Therefore, if $\kappa/r_c \neq 0$ the contact angles α and β will depend on the external field.

We must emphasize that the above conclusions about the behavior of the contact angles are valid only for the true, i.e., correctly defined, contact angles. Experimentally the contact angles are usually measured by determining with some optical method the shape of the interfaces at some distance from the contact line and then by *extrapolating* them until they intersect.

The first problem encountered when this procedure is carried out in practice is that the minimum distance from the contact line at which one can still obtain *experimental* information about the shape of the interfaces is limited by the microscope magnification (41). At the same time the deformation of the interfaces caused by the gravity is much larger close to the contact line then away from it (see Table V in Part II of this series). Therefore, if this effect is not properly taken into account one will determine only an apparent contact angle and its value will depend not only on the gravity but also on the optical method used.

The second problem is related to the so-called "transition region." As a matter of fact the *microscopic* contact angle between fluid interfaces should be zero, because in the transition region, where the interfaces meet each other, they should undergo a smooth transition from the one interface to the other (e.g., from B and S to H in Fig. 1). Although the width of the transition-region is most probably smaller (it was estimated to 1 μm in (9)) than the resolution of the optical methods if some of the experimental points happen to lie there this will again affect the extrapolation procedure and hence—the value of the *macroscopic* contact angle.

The only way to avoid these two errors is (i) to make sure that all experimental points used lie outside of the transition region and (ii) to carry out the extrapolation of the surface in such a way that its shape all the time satisfies Laplace's equation with the macroscopic value of the surface tension. (In the absence of external fields the second statement means that the extrapolation must be carried out at constant capillary pressure as suggested in (10).) Toward this aim in Part II we will present an asymptotic solution of the Laplace's equation for the system from Fig. 1 and in Part III it will be shown how the extrapolation must be carried out so that the contact line and angles can be properly defined.

The final point we want to discuss in this Section is the number of geometric parameters that must be measured for the determination of some unknown interfacial or line tensions. For a bubble at an interface one can assume $\sigma_{12} = \sigma_{23} = \sigma$ and γ must be substituted for σ_{13}. Then Eqs. [15] and [16] can be written in the form (cf. also Eq. [47])

$$\gamma\sin\theta = 2\sigma\sin\theta_0\cos\frac{\alpha}{2} \quad [56]$$

$$\gamma\cos\theta = 2\sigma\cos\theta_0\cos\frac{\alpha}{2} - \frac{\kappa}{r_c} \quad [57]$$

where

$$\theta_0 = \frac{1}{2}(\varphi_c + \psi_c). \quad [58]$$

The angles φ_c and ψ_c (and hence α and θ_0) can be calculated from the measured radii of the contact line r_c and of the bubble maximum cross section R (see Part III). To calculate θ one must also measure the radius of curvature R_f of the hat (see Part III). Then [56] allows the calculation of the film tension γ. An equation only for the line tension can be derived by eliminating γ between [56] and [57]. The result reads

$$\frac{\kappa}{r_c} = 2\sigma \cos\frac{\alpha}{2} \frac{\sin(\theta_0 - \theta)}{\sin\theta}. \qquad [59]$$

One observes that the line tension effect κ/r_c manifests itself through the difference between the angles θ and θ_0. Consequently, the assumption $\theta = \theta_0$ (or $\theta = \alpha/2$ in the absence of gravity) is according to [59] tantamount to setting $\kappa/r_c = 0$ and should not be used when line tension effects are being studied.

If γ is known, one can eliminate θ between [56] and [57] and obtain an equation allowing the calculation of κ from the measured values of r_c and R. The exact result is

$$\frac{1}{\cos(\alpha/2)}\left[1 - 4\frac{2\sigma}{\gamma}\frac{\kappa}{\gamma r_c}\cos\frac{\alpha}{2}\sin\varphi_c\sin\psi_c - \left(\frac{\kappa}{\gamma r_c}\right)^2 \sin^2\frac{\alpha}{2}\right]^{1/2} = \frac{2\sigma}{\gamma} - \frac{\kappa}{\gamma r_c}. \qquad [60]$$

An approximate form of this equation and its suitability for the calculation of the line tension will be discussed in Part IV.

5. CONCLUDING REMARKS

A general variational approach has been applied to derive the conditions for mechanical equilibrium of an axisymmetric little particle (fluid or solid) at a fluid interface in the presence of an external field. In the case of a fluid particle (Section 2) two conditions (Eqs. [15] and [16]), having the form of a force balance, for the equilibrium of the contact line are obtained. It is shown that the buoyancy force equation [26] follows from the vertical force balance equation [15] and the Laplace's equation. In the case of a solid particle (Section 3) there is only one relationship between the σs and the line tension κ at the contact line (Eq. [42]). The latter is not a result of a force balance. It is pointed out that the reason for this difference between fluid and solid particles is due to the fact that the specific surface free energies at a solid/fluid interface have no meaning as surface tensions.

It is demonstrated that the contact angles can depend on the external field only when a line tension effect is present. Some problems that may arise with the correct definition of the contact angles, when they are experimentally measured are discussed in Section 4.

When the conditions for equilibrium are used for the experimental measurement of some intensive parameters (surface or line tensions) the number of the geometric parameters that have to be measured will depend of course on the number of unknown parameters. It is shown that when a bubble is attached to a fluid interface the film and line tension can be determined only if three angles (θ, φ_c, and ψ_c on Fig. 1) are measured.

APPENDIX

On the Effect of the Film Weight on the Conditions for Mechanical Equilibrium

As we have already pointed out, when a thin film intervenes between the phases 1 and 3 (see Fig. 1) its tension γ must be substituted for σ_{13} in Eqs. [9], [15], and [16]. A problem that arises as this is how to account for the gravitational energy of the film. Indeed, although the film is very thin and light (of thickness $h < 100$ nm), its weight can still in principle lead to an additional deformation of the interface $H(z)$ and also affect the contact line force balance. We will estimate this effect by using the same approach as in (30). When the phases 1 and 3 are gases (in this case the effect must be the largest) the additional gravitational energy (with respect to the level z_c) equals

$$\rho^f g(z - z_c)hdA = 2\pi h\rho^f g \int_{z_c}^{z_2} (z - z_c)H(z)\sqrt{1 + H'^2}dz \qquad [61]$$

where $\rho^f \approx \rho_2$ is the average film density. This energy will lead only to the appearance of an additional term

$$2\tilde{p}(z - z_c)H\sqrt{1 + H'^2} \qquad [62]$$

($\tilde{p} = h\rho^f g$) in the righthand side of [5]. Carrying out the same calculations as in Section 2, one arrives at the following new conditions for equilibrium (instead of [9] and [17]):

$$\gamma(z)D(H) = (p_3 - p_1) - \tilde{p}\frac{H'}{\sqrt{1 + H'^2}} \quad [63]$$

$$\gamma_c + \sigma_{12} + \sigma_{23} + \sigma_\kappa = 0 \quad [64]$$

where $\gamma_c = \gamma(z_c)$ and

$$\gamma(z) = \gamma_c + \tilde{p}(z - z_c). \quad [65]$$

The film thickness, h, is usually 10–100 nm, so that $\tilde{p}$ does not exceed 10^{-3} N/m^2. Therefore, the term with $\tilde{p}$ in [63] can be of any importance only when $p_3 = p_1$. The quantity of interest in thin film studies is usually the difference $\tilde{\gamma} = 2\sigma - \gamma$. It can be measured with a precision of the order of 10^{-3} mN/m, so that the term $\tilde{p}(z - z_c)$ in [65] can become perceptible only when the difference $(z - z_c)$ in [65] is larger than 1 cm.

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