NOTES

Equilibrium of a Spherical Particle at a Curved Liquid/Liquid Interface

We consider the equilibrium position of a solid spherical particle at a curved liquid/liquid interface. Our analysis is based on the total free energy of the system. It is shown in particular that (i) the contact angle at the three-phase line obeys the Young equation, and (ii) the particle is never ejected out of the droplet, whatever the curvature of the interface. We then study the equilibrium position of a "Janus bead," that is, a spherical particle with hemispheres of different surface energy.

The equilibrium position of solid particles at fluid/fluid interfaces is of considerable relevance in a wide range of technological processes: flotation of ores, stabilization of emulsions, etc. As a result, much work has been devoted to the study of solid–liquid–liquid systems (1–5).

In the gravity-free situation, a spherical particle 1 will be located at a planar liquid 2/liquid 3 interface if (1)

$$\left|\frac{\gamma_{13}-\gamma_{12}}{\gamma_{23}}\right| < 1, \qquad [1]$$

where γ_{12}, γ_{13}, and γ_{23} are the interfacial tensions characterizing the system. If the above inequality is not fulfilled, the particle remains entirely in one of the two liquids. Condition [1] simply expresses the existence of the angle θ, defined by the well-known Young equation

$$\cos\theta = \frac{\gamma_{13}-\gamma_{12}}{\gamma_{23}}. \qquad [2]$$

In this note we analyze how criterion [1] might be modified when the interface is no longer planar but *curved*. More precisely, we consider the equilibrium position of a spherical particle 1 at the interface between a droplet 2 and a continuous phase 3 (6). We investigate in particular the possibility of the solid particle being ejected out of the droplet.

The physical situation is represented in Fig. 1a and is fully determined by the radius of the drop R and the angles β and β' which locate the three-phase line. The interfacial tensions are supposed to verify condition [1].

A purely geometric relation between R, β, and β' is

$$R\sin\beta = r_0\sin\beta', \qquad [3]$$

where r_0 is the radius of the solid particle.

A second relation is obtained from the volume conservation of the liquid 2:

$$R^3 = \frac{4R_0^3 + r_0^3(2-3\cos\beta'+\cos^3\beta')}{2+3\cos\beta-\cos^3\beta} \qquad [4]$$

(R_0 being the radius of the liquid droplet 2 when the particle remains entirely in liquid 3).

Combining Eqs. [3] and [4], we get a relation between the angles β and β':

$$\frac{\epsilon^3\sin^3\beta'}{4+\epsilon^3(2-3\cos\beta'+\cos^3\beta')} = \frac{\sin^3\beta}{2+3\cos\beta-\cos^3\beta}, \qquad [5]$$

where $\epsilon = r_0/R_0$.

The total free energy E of the system is

$$E = 2\pi r_0^2\gamma_{13}(1+\cos\beta') + 2\pi r_0^2\gamma_{12}(1-\cos\beta') + 2\pi R^2\gamma_{23}(1+\cos\beta). \qquad [6]$$

By introducing the angle θ (Eq. [2]) and using Eqs. [3] and [6], we are led to

$$\frac{E}{2\pi r_0^2\gamma_{23}} = \left(\frac{\gamma_{12}+\gamma_{13}}{\gamma_{23}}\right) + \cos\theta\cos\beta' + \frac{\sin^2\beta'}{1-\cos\beta}. \qquad [7]$$

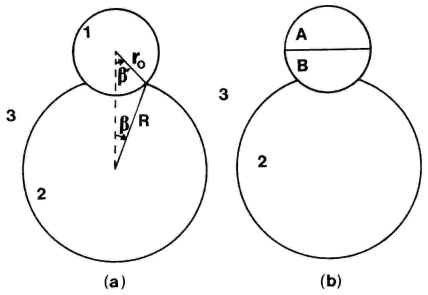

FIG. 1. (a) A solid particle 1 of radius r_0 is trapped at the interface of a liquid droplet 2 and a continuous liquid phase 3. (b) Same situation for a Janus bead. Each hemisphere of the bead is characterized by a surface energy defining two Young contact angles (see text).

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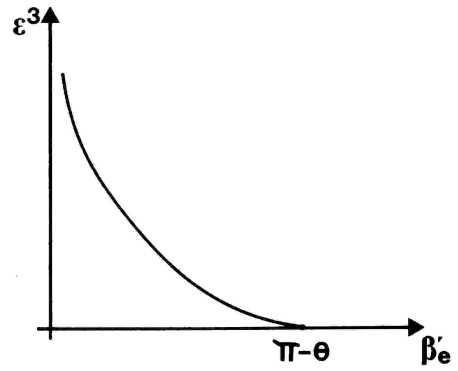

FIG. 2. Plot of $\epsilon^3 = (R_0/r_0)^3$ versus β'_e, the equilibrium value of β'.

Note that since β is related to β' by Eq. [5], the free energy [7] depends only on the single variable β'. Differentiating Eq. [7] with respect to β' (r_0 and R_0 being fixed) yields

$$\frac{1}{2\pi r_0^2 \gamma_{23}} \frac{dE}{d\beta'} = -\sin\beta'(1 - \cos\beta) \times (\cos\theta + \cos(\beta + \beta')). \quad [8]$$

At equilibrium, the free energy [7] must be minimal; thus

$$\beta_e + \beta'_e = \pi - \theta, \quad [9]$$

where the subscript e stands for equilibrium. We thus check that the contact angle $\pi - \beta'_e - \beta_e$ between the tangents of surfaces 12 and 23 at the three-phase line obeys the Young equation [2], as expected.

Replacing β_e by $\pi - \theta - \beta'_e$ in Eq. [5], one obtains

$$\epsilon^3 = \frac{4\sin^3(\theta + \beta'_e)}{(2 - 3\cos(\theta + \beta'_e) + \cos^3(\theta + \beta'_e))\sin^3\beta'_e - (2 - 3\cos\beta'_e + \cos^3\beta'_e)\sin^3(\theta + \beta'_e)}. \quad [10]$$

Figure 2 represents the variation of β'_e with ϵ^3: for each ϵ, there exists a value β'_e which minimizes the free energy.

We therefore conclude that if the interfacial tensions satisfy condition [1], the particle remains located at the liquid/liquid interface, *whatever the radius of curvature of the droplet.*

We now consider the case of a "Janus bead," that is, a solid spherical particle with two different hemispheres (see Fig. 1b). Such beads have been successfully prepared by Casagrande and co-workers and are currently under study (7). The A hemisphere (resp. the B hemisphere) is characterized by a Young angle θ_A (resp. θ_B) ($\cos\theta_A = (\gamma_{A3} - \gamma_{A2})/\gamma_{23}$ and $\cos\theta_B = (\gamma_{B3} - \gamma_{B2})/\gamma_{23}$). We set $\theta_B < \theta_A$.

The free energy of the system is now given by

$$\frac{E}{2\pi r_0^2 \gamma_{23}} = \frac{\gamma_{A3} + \gamma_{B2}}{\gamma_{23}} + \cos\theta_i \cos\beta' + \frac{\sin^2\beta'}{1 - \cos\beta}, \quad [11]$$

with $\theta_i = \theta_B$ for $\beta' < \pi/2$ and $\theta_i = \theta_A$ for $\beta' > \pi/2$.

Using the previous results relative to a homogeneous bead, we obtain the equilibrium position that minimizes the free energy [11].

Two regimes of interest may be distinguished:

(a) $\theta_B < \pi/2 < \theta$. The variation of the angle β'_e with the ratio $\epsilon = r_0/R_0$ is shown in Fig. 3a (solid line). The dashed lines represent the variation of β'_e for homogeneous

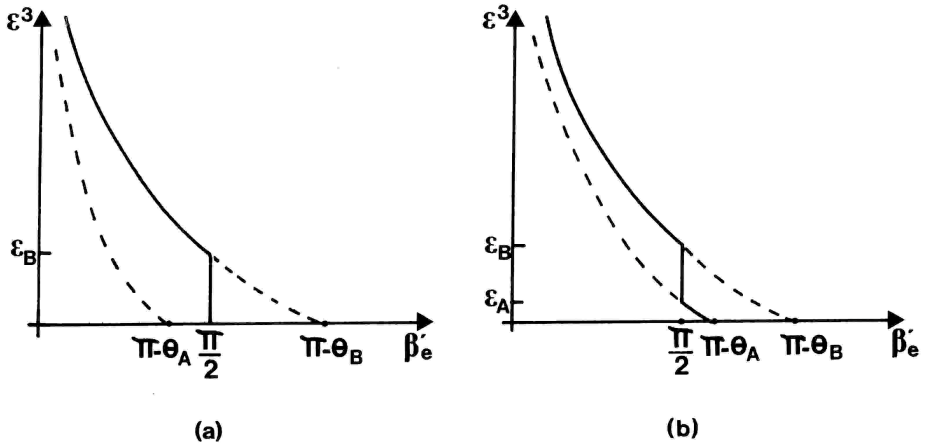

FIG. 3. Plot of $\epsilon^3 = (R_0/r_0)^3$ versus β'_e for a Janus bead (solid lines). The dashed lines are from homogeneous beads. (a) $\theta_B < \pi/2 < \theta_A$; (b) $\theta_B < \theta_A < \pi/2$.

A and B beads. For $\epsilon > \epsilon_B$, β'_e is given by the B branch, while for $\epsilon < \epsilon_B$, the three-phase line is pinned at the boundary between the two hemispheres ($\beta'_e = \pi/2$).

(b) $\theta_B < \theta_A < \pi/2$. The variations of β'_e with ϵ are represented in Fig. 3b. β'_e is given by the B branch for $\epsilon > \epsilon_B$ and by the A branch for $\epsilon < \epsilon_A$. For $\epsilon_A < \epsilon < \epsilon_B$, β'_e is locked to $\pi/2$. Physically, if we increase the droplet radius R_0, the three-phase line first creeps on the B hemisphere up to a critical value ϵ_B. The line is thereafter pinned at the boundary between the two hemispheres ($\beta'_e = \pi/2$) up to the critical value ϵ_A. For $\epsilon < \epsilon_A$, the line creeps on the A hemisphere, up to the final value $\beta'_e = \pi - \theta_A$ obtained for $\epsilon = 0$.

We have thus shown analytically that in both cases (a) and (b) the pinning situation is achieved for $\pi/2 - \theta_a < \beta_e < \pi/2 - \theta_B$. Note that in this pinning regime, the Young equation cannot be used since the contact line is then a four-phase line. Our results could be of interest for the study of other heterogeneous surfaces.

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REFERENCES

1. Von Reinders, W., *Kolloid-Z.* **13,** 235 (1913).
2. Princen, H. M., *in* "Surface and Colloid Science" (E. Matijevic, Ed.), Vol. 2, Interscience, New York.
3. Rapacchietta, A. V., and Neumann, A. W., *J. Colloid Interface Sci.* **59,** 555 (1977).
4. Menon, V. B., and Wasan, D. T., *Separation Sci. Technol.* **19,** 555 (1984).
5. Gelot, A., Friesen, W., and Hamza, H. A., *Colloids Surf.* **12,** 271 (1984).
6. This problem was first considered by M. T. Jacques, J. D. Henry, and A. D. Hovarongkura, *AICHEJ* **25**(1), 160 (1979).
7. Casagrande, C., and Veyssié, M., *C. R. Acad. Sci. Paris* **306**(II), 1423 (1988); Raphaël, E., *C. R. Acad. Sci. Paris* **307**(II), 9 (1988); Casagrande, C., Fabre, P., Raphaël, E., and Veyssié, M. *Europhys. Lett.* **9,** 251 (1989).

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