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NOTE

Three-Dimensional Convex Particles at Interfaces

The equilibrium position of a solid spherical particle at a liquid–liquid interface in the gravity free situation is usually derived by assuming that the liquid–liquid interface is flat and nonbendable. We show that this approach cannot be correctly generalized to the case of an arbitrary convex three-dimensional body.

1. INTRODUCTION

The problem of a small solid particle located at the interface between two fluids is of interest for a number of practical reasons, notably in froth flotation processes used in the extraction of minerals (1). In general one considers a solid body, 3, placed in a system of two liquids, 1 and 2, separated by an interface as shown in Fig. 1a. For simplicity the solid and the liquids are assumed to have the same density (the "gravity free" situation). Of importance here is the Young angle, θ_Y, defined by

$$\cos\theta_Y = \frac{\gamma_{13} - \gamma_{23}}{\gamma_{12}}, \qquad [1]$$

where γ_{ij} is the energy per unit area between phases i and j.

In order to find the equilibrium position(s) of the body it is usually assumed that the liquid interface is *flat* and *nonbendable* so that the interface may be treated as a plane. The case of a sphere was studied some time ago (2, 3), and this has recently been extended to a prism of arbitrary cross section (4). Provided the Young angle θ_Y exists, this analysis implies for the case of a sphere that the body sits between the interface, and moreover that the local angle θ_t between the plane tangent to the body on the contact line and the liquid–liquid interface always obeys $\theta_t = \theta_Y$ all along the contact line. This is also true for a prism—Young's equation is satisfied all along the contact line.

In this paper we demonstrate that this approach cannot be correctly generalized to the case of an arbitrary convex three-dimensional body. We do this by explicitly calculating (Section 2) the conditions under which the energy is a minimum using the assumption of a flat, nonbendable interface. This gives us three conditions which are of the form of integrals of a force and two torques around the contact line. These equations predict that in general the Young condition is not satisfied locally, but only in some global sense. In Section 3 we discuss the origin of this unphysical result.

2. CALCULATION

We first need to write down the free energy of the system and to differentiate it with respect to the degrees of freedom of the particle. It is easiest to think of the particle as fixed with respect to a coordinate system (x, y, z) and the liquid–liquid interface moving around in space so as to minimize the free energy. The liquid–liquid interface is assumed to be planar (see Section 1) and may be represented as

$$m_1 x + m_2 y + m_3 z = 1. \qquad [2]$$

There are only three coordinates needed to specify the configuration of the system and these are taken as the m_i's. The free energy of the system is

$$W = \gamma_{13} A_c + \gamma_{23}(A - A_c) - \gamma_{12} A_p, \qquad [3]$$

where $\mathbf{A}_c$ is the curved area of the surface lying in liquid 1, A is the total area of the curved surface, and A_p is the area of the plane intersected by the surface. The minimum energy conditions are just

$$\frac{\partial W}{\partial m_i} = 0 \quad i = 1, 2, 3. \qquad [4]$$

We choose our fixed xyz coordinate system so that the curve $\mathscr{C}_f$ formed by the intersection of the plane with the surface lies entirely on one side of the xy plane. This curve has some projection $\mathscr{C}_p$ onto the xy plane, which encloses some region $\mathscr{S}_p$ (see Fig. 1b). The area of the planar interface A_p, removed from the system by the presence of the particle, is then given by

$$A_p = \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}} \iint_{\mathscr{S}_p} dxdy, \qquad [5]$$

which is just the projected area multiplied by a function of the plane's orientation. The portion of the convex body lying in liquid 1 is represented by an equation $z = f(x, y)$ and its surface area is

$$A_c = \iint_{\mathscr{S}_p} dxdyB(x, y), \qquad [6]$$

where

$$B(x, y) = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2 + 1}. \qquad [7]$$

It is important to note that we do not actually need to find the areas A_p and A_c; only their derivatives with respect to $\mathbf{m} = (m_1, m_2, m_3)$ are required. To do this we write [6] as

$$A_c = \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx \int_{y_1(x,\mathbf{m})}^{y_2(x,\mathbf{m})} dyB(x, y), \qquad [8]$$

and [5] as

$$A_p = \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}} \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx[y_2(x, \mathbf{m}) - y_1(x, \mathbf{m})]. \qquad [9]$$

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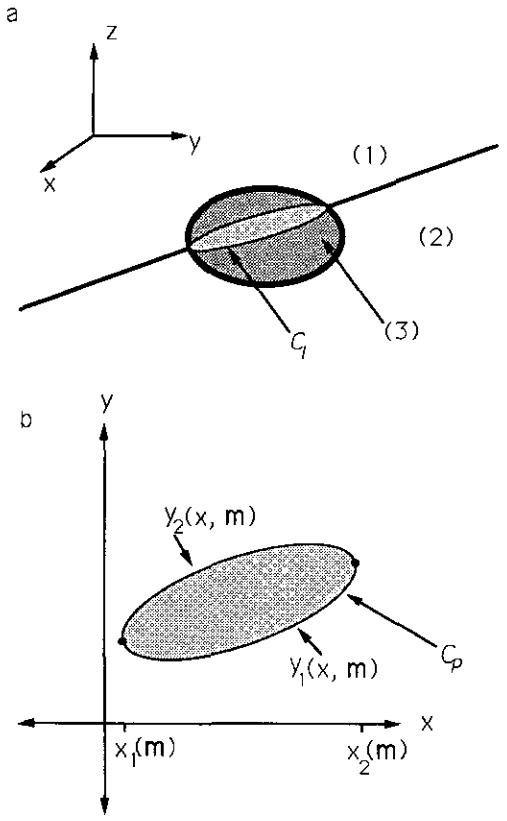

FIG. 1. (a) The coordinate system used in the calculation. (1) and (2) are liquids and (3) is the solid body. The curve $\mathcal{C}_J$ is formed by the intersection of the solid body and the liquid–liquid surface. (b) The projection $\mathcal{C}_P$ of the $\mathcal{C}_J$ onto the xy plane. The curve consists of two single-valued functions $y_1(x, \mathbf{m})$ and $y_2(x, \mathbf{m})$ with x varying between two $\mathbf{m}$-dependent limits, $x_1(\mathbf{m})$ and $x_2(\mathbf{m})$.

Here we have defined the curve $\mathcal{C}_P$ in the xy plane as being bounded by two single-valued functions $y_1(x, \mathbf{m})$ and $y_2(x, \mathbf{m})$, where $x \in [x_1(\mathbf{m}), x_2(\mathbf{m})]$ (see Fig. 1b).

The derivatives are now

$$\frac{\partial A_c}{\partial m_i} = \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx\left[\frac{\partial y_2(x, \mathbf{m})}{\partial m_i} B(x, y_2(x, \mathbf{m})) - \frac{\partial y_1(x, \mathbf{m})}{\partial m_i} B(x, y_1(x, \mathbf{m}))\right], \quad [10]$$

and

$$\frac{\partial A_p}{\partial m_i} = \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}} \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx\left[\frac{\partial y_2(x, \mathbf{m})}{\partial m_i} - \frac{\partial y_1(x, \mathbf{m})}{\partial m_i}\right] + \frac{1}{|m_3|}\left(\frac{m_i}{|\mathbf{m}|} - \frac{|\mathbf{m}|}{m_3}\delta_{i3}\right) \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx[y_2(x, \mathbf{m}) - y_1(x, \mathbf{m})], \quad [11]$$

where we have used the fact that $y_1(x_1(\mathbf{m}), \mathbf{m}) = y_2(x_1(\mathbf{m}), \mathbf{m})$ and $y_1(x_2(\mathbf{m}), \mathbf{m}) = y_2(x_2(\mathbf{m}), \mathbf{m})$. Equation [4] now becomes

$$\cos\theta_Y \frac{\partial A_c}{\partial \mathbf{m}} - \frac{\partial A_p}{\partial \mathbf{m}} = 0 \quad [12]$$

or, equivalently,

$$0 = \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx\left\{\frac{\partial y_2(x, \mathbf{m})}{\partial m_i}\left[\cos\theta_Y B(x, y_2(x, \mathbf{m})) - \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}}\right] + \frac{1}{|m_3|}\left(\frac{m_i}{|\mathbf{m}|} - \frac{|\mathbf{m}|}{m_3}\delta_{i3}\right) y_2(x, \mathbf{m}) - (y_2 \to y_1)\right\}. \quad [13]$$

We can simplify these equations somewhat by noting that $y_2(x, \mathbf{m})$ and $y_1(x, \mathbf{m})$ satisfy

$$f(x, y_i) = \frac{1}{m_3}(1 - m_1 x - m_2 y_i) \quad i = 1, 2. \quad [14]$$

i.e., the condition that the curve $\mathcal{C}_J$ is the intersection of the liquid plane and the convex body. This allows us to eliminate the derivatives with respect to $\mathbf{m}$ in [13]. If we define

$$H = \frac{[\cdots]|\mathbf{m}|}{m_3 \dfrac{\partial f}{\partial_y} + m_2}, \quad [15]$$

where $[\cdots]$ is the term in square brackets in [13], then the three equations [13] become

$$0 = \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx\left[-xH + \frac{m_1}{|m_3|} y_2(x, \mathbf{m}) - (y_2 \to y_1)\right] \quad [16]$$

$$0 = \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx\left[-y_2 H + \frac{m_2}{|m_3|} y_2(x, \mathbf{m}) - (y_2 \to y_1)\right] \quad [17]$$

$$0 = \int_{x_1(\mathbf{m})}^{x_2(\mathbf{m})} dx\left[-fH + \frac{1}{|m_3|}\left(m_3 - \frac{|\mathbf{m}|^2}{m_3}\right) y_2(x, \mathbf{m}) - (y_2 \to y_1)\right]. \quad [18]$$

These three equations determine an energy minimum value for $\mathbf{m}$ with respect to the initial reference frame. Now we are free to choose the xy plane in any way we want (by transforming coordinate systems), so we choose it to be the equilibrium liquid plane so that $m_1 = m_2 = 0$ and $m_3 = \infty$. The terms of the form constant y_2 (or y_1) in [16]–[18] then disappear. A linear combination of [16]–[18] yields

$$\int_{x_1}^{x_2} dx[H(x, y_1(x)) - H(x, y_2(x))] = 0. \quad [19]$$

Now H [15] can be written as

$$H = \frac{[\cos\theta_Y - \cos\theta_{txy}]}{\cos\theta_{cx}}, \quad [20]$$

where θ_{txy} is the angle made by the plane tangent to the convex body with the xy plane, and θ_{cx} is the angle made by the tangent to the curve $\mathcal{C}_J$ with the x axis. We note that $dx/\cos\theta_{cx} = ds$ is effectively the differential arc length of the curve $\mathcal{C}_J$ so that we may write [19] as

$$\int_{\mathcal{C}_J} ds[\cos\theta_Y - \cos\theta_t(s)] = 0. \quad [21]$$

In this equation θ_t is to be interpreted as the angle between the tangent to the surface and the liquid plane. One notes that this equation is a global

condition on θ_t and not a local one, and it is in some sense just an integral of the force around the loop.

Similarly, [16] and [17] give

$$\int_{\mathcal{C}_J} ds[\cos\theta_Y - \cos\theta_t(s)]x_J(s) = 0 \qquad [22]$$

and

$$\int_{\mathcal{C}_J} ds[\cos\theta_Y - \cos\theta_t(s)]y_J(s) = 0, \qquad [23]$$

where $(x_J(s), y_J(s))$ are the coordinates of the contact line in the liquid plane. These global equations are just moment equations. One can prove that Eqs. [21] to [23] are in general not sufficient to force Young's equation to be satisfied everywhere. To do so one can consider the example of an ellipsoid,

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1. \qquad [24]$$

One can attempt to find a position satisfying [21] to [23] by slicing the ellipsoid at various values of z, i.e., by planes parallel to the xy plane. The curve $\mathcal{C}_J$ formed is then an ellipse and it is clear that the monent equations [22]–[23] are automatically satisfied because for every given point (x, y) on the ellipse there is a point $(-x, -y)$ which has the same value of $\cos\theta_Y - \cos\theta_t$. We need to examine the force equation [21]. It is first clear that $\cos\theta_t$ is not a constant (except in the special case $a = b$). We can rewrite the force equation as

$$\cos\theta_Y = \langle\cos\theta_t\rangle, \qquad [25]$$

where $\langle\cdots\rangle$ is an average along the ellipse $\mathcal{C}_J$. It is clear that $\langle\cos\theta_t\rangle$ varies continuously between -1 and 1 as z varies between c and $-c$. Thus, given a particular Young angle θ_Y one can always find a position for the ellipsoid which satisfies [21] to [23] but which violates the Young equation locally.

3. DISCUSSION AND CONCLUSIONS

It was proved by Gauss (for a more recent discussion see (5)) that for a finite drop of fluid on a solid surface the Young condition is always satisfied along the contact line. Although our system is different from the one considered by Gauss we can still expect the Young condition to be obeyed everywhere along the contact line. In the previous section we have however derived less-stringent, global, equilibrium conditions, [21] to [23]. The resolution of this paradox arises from our assumption of an unbendable interface. This produces a number of false extrema in the free energy. These extrema are not true equilibrium positions because ordinary interfaces can distort and thus have many more degrees of freedom then suggested here (6). Our extrema are thus only extrema in the restricted space where the interface is flat. All real equilibrium solutions should satisfy Young's equation locally.

Perhaps a discussion of the previous cases of a sphere and a prism is in order. For these two cases equilibrium equations [21]–[23] are actually enough to force Young's equation to be satisfied everywhere, but this is only because of the high degree of symmetry of the solid particles under consideration.

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6. Even in equilibrium the interface can be curved. Indeed the liquid–liquid interface should just satisfy $1/R_1 + 1/R_2 = 0$ where R_1, R_2 are the two radii of curvature of the surface which is assumed to be flat far away from the particle.

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