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 non-bendable. We show that this approach cannot be correctly generalized to the case of an arbitrary convex three-dimensional body.

\[ m_1x + m_2y + m_3z = 1. \]  

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

\[ W = \gamma_{13}A_{c} + \gamma_{23}(A - A_{c}) \gamma_{12}A_{p}, \]  

where \( A_{c} \) 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

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

We choose our fixed \( xyz \) coordinate system so that the curve \( \theta_y \) formed by the intersection of the plane with the surface lies entirely on one side of the \( xy \) plane. This curve has some projection \( \theta_y \) onto the \( xy \) plane, which encloses some region \( \delta_{\theta} \) (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

\[ A_{p} = \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}} \int \int dx dy, \]  

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

\[ A_{c} = \int \int_{\delta_{\theta}} dxdyB(x, y), \]  

where

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

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 \( m = (m_1, m_2, m_3) \) are required. To do this we write [6] as

\[ A_{c} = \int_{\delta_{\theta}(m)} \int_{\delta_{\theta}(m)} dxdyB(x, y), \]  

and [5] as

\[ A_{p} = \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}} \int_{\delta_{\theta}(m)} dy \int_{\delta_{\theta}(m)} \left[ r_{2}(y, m) - y_{1}(x, m) \right]. \]
NOTE

or, equivalently,

\[ 0 = \int_{J_{\lambda}^{\mu}} dx \left[ \frac{\partial y_3(x, m)}{\partial m_1} \left( \cos \theta_x B(x, y_2(x, m)) - \frac{m_1^2 + m_2^2 + m_3^2}{m_3^2} \right) \right. \]

\[ + \frac{1}{m_3} \left( \frac{m_1}{|m|} - \frac{|m|}{m_3} \delta_{3} \right) y_2(x, m) - (y_2 \rightarrow y_1) \left. \right] \quad [13] \]

We can simplify these equations somewhat by noting that \( y_3(x, m) \) and \( y_1(x, m) \) 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 \( \mathcal{C}_S \) is the intersection of the liquid plane and the convex body. This allows us to eliminate the derivatives with respect to \( m \) in [13]. If we define

\[ H = \frac{[\cdots]}{m_1 \frac{\partial f}{\partial x} + m_2}, \quad [15] \]

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

\[ 0 = \int_{J_{\lambda}^{\mu}} dx \left[ -x H + \frac{m_1}{|m_3^2|} y_2(x, m) - (y_2 \rightarrow y_1) \right] \quad [16] \]

\[ 0 = \int_{J_{\lambda}^{\mu}} dx \left[ -y_2 H + \frac{m_2}{|m_3^2|} y_2(x, m) - (y_2 \rightarrow y_1) \right] \quad [17] \]

\[ 0 = \int_{J_{\lambda}^{\mu}} dx \left[ -f H + \frac{1}{m_3} \left( m_1 - \frac{|m|}{m_3} \right) y_2(x, m) - (y_2 \rightarrow y_1) \right] \quad [18] \]

These three equations determine an energy minimum value for \( m \) 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

\[ \int_{\mathcal{C}_S} dx [H(x, y_1(x)) - H(x, y_2(x))] = 0. \quad [19] \]

Now \( H [15] \) can be written as

\[ H = \frac{[\cos \theta_y - \cos \theta_{xy}]}{\cos \theta_x}, \quad [20] \]

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

\[ \int_{\mathcal{C}_S} ds [\cos \theta_y - \cos \theta_{xy}] = 0. \quad [21] \]

In this equation \( \theta_y \) 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

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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 \( \mathcal{C}_S \) is formed by the intersection of the solid body and the liquid–liquid surface. (b) The projection \( \mathcal{C}_p \) of the \( \mathcal{C}_S \) onto the \( xy \) plane. The curve consists of two single-valued functions \( y_1(x, m) \) and \( y_2(x, m) \) with \( x \) varying between two \( m \)-dependent limits, \( x_1(m) \) and \( x_2(m) \).

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

The derivatives are now

\[ \frac{\partial A_e}{\partial m_1} = \int_{J_{\lambda}^{\mu}} dx \left[ \frac{\partial y_3(x, m)}{\partial m_1} B(x, y_2(x, m)) - \frac{\partial y_1(x, m)}{\partial m_1} B(x, y_1(x, m)) \right], \quad [10] \]

and

\[ \frac{\partial A_p}{\partial m_1} = \sqrt{\frac{m_1^2 + m_2^2 + m_3^2}{m_3^2}} \int_{J_{\lambda}^{\mu}} dx \left[ \frac{\partial y_3(x, m)}{\partial m_1} - \frac{\partial y_1(x, m)}{\partial m_1} \right] \]

\[ + \frac{1}{m_3} \left( \frac{m_1}{|m|} - \frac{|m|}{m_3} \delta_{3} \right) \int_{J_{\lambda}^{\mu}} dx \left( y_2(x, m) - y_1(x, m) \right), \quad [11] \]

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

\[ \cos \theta_y \frac{\partial A_e}{\partial m} - \frac{\partial A_p}{\partial m} = 0 \quad [12] \]
condition on \( \theta \), 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

\[
\int_{C_x} ds [\cos \theta_y - \cos \theta_i(s)] y(s) = 0 \tag{22}
\]

and

\[
\int_{C_x} ds [\cos \theta_y - \cos \theta_i(s)] x(s) = 0, \tag{23}
\]

where \((x(s), y(s))\) 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,

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

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 \( C_x \) formed in this way is an ellipse and it is clear that the moment 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 \( \cos \theta_y - \cos \theta_i \). We need to examine the force equation [21]. It is first clear that \( \cos \theta_i \) is not a constant (except in the special case \( a = b \)). We can rewrite the force equation as

\[
\cos \theta_y = \langle \cos \theta_i \rangle, \tag{25}
\]

where \( \langle \cdots \rangle \) is an average along the ellipse \( C_x \). It is clear that \( \langle \cos \theta_i \rangle \) varies continuously between \(-1\) and \( 1 \) as \( z \) varies between \( c \) and \(-c \). Thus, given a particular Young angle \( \theta_y \) 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 inter-

face. 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 than 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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### REFERENCES

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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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