

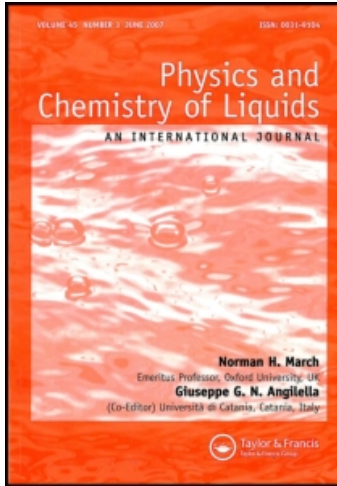
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General Equations for the Equilibrium Shape of a Fluid Interface and for Its Angle of Contact with a Solid

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The classical equations of Young-Laplace (equilibrium shape of a fluid interface in a uniform gravitational field) and Young (angle of contact of the fluid interface with a solid) are generalized to take into account: (i) the presence of externally applied fields of any type; (ii) the variation of the interfacial tensions from point to point; (iii) the variation of the fluid interfacial tension with its orientation in space.

The general equations are deduced simultaneously by a variational method, which allows the determination of the minimum Helmholtz energy configuration of a system comprising the two fluids and the solid. An axially symmetric geometry is assumed.

The equations so derived clarify the difficulties that have been found in the application of the classical equations—particularly Young's equation—to actual systems. Both equations, in their general form, contain terms that may be interpreted as representing the interaction between the three interfaces near their line of contact, and such an interaction cannot be ignored in actual systems.

1 INTRODUCTION

The equilibrium shape of the interface between two fluids (i.e., liquid-liquid or liquid-vapour) in a uniform gravitational field g can be determined from the Young-Laplace equation¹⁻³. This equation establishes that the difference in hydrostatic pressure between two points, at the same height, one in each fluid, is balanced by the pressure difference across the interface, the latter being given by $\gamma(1/R_1 + 1/R_2)$, where R_1 , R_2 are the principal radii of curvature of the interface at any point and γ is the interfacial tension.

For an axially symmetric geometry, with the interface intersecting the axis of symmetry (z -axis) at a point O , it is convenient to place the origin at O and choose z pointing to the centre of curvature at O . If x denotes the distance to the z -axis (i.e., x is the usual cylindrical coordinate), the interface is defined by $x = f(z)$ and Young-Laplace's equation takes the form:

$$\gamma(1 + f'^2)^{-3/2} \left(-f'' + \frac{1 + f'^2}{f} \right) = \frac{2\gamma}{R} + \Delta\rho g^* z. \quad (1)$$

Here $\Delta\rho = \rho_i - \rho_e$, where ρ_i and ρ_e , respectively, are the densities of the fluids in the "inner" and "outer" sides of the interface, "inner" meaning the side of the centre of curvature at O ; g^* is the z -component of \mathbf{g} (i.e., $g^* = \pm g$); and R ($R > 0$) is the radius of curvature at the apex O of the interface. Equation (1) can also be deduced by a thermodynamic argument, imposing a minimum Helmholtz energy to a system comprising the two fluids and their interface.⁴

In general, the two fluids and their interface contact a solid, and boundary conditions for $f(z)$ have to be introduced at the line of contact of the three interfaces (the fluid interface and the two solid-fluid interfaces). It is, of course, assumed that Eq. 1 is applicable, with the same value of γ , up to that line. In addition to boundary conditions of a geometrical nature, it is generally agreed that the angle of contact of the fluid interface with the solid surface has a fixed value, which can be determined from the three interfacial tensions by Young's equation^{1,3}

$$\cos \theta_i = \frac{\gamma_e - \gamma_i}{\gamma}. \quad (2)$$

Here γ_e , γ_i are the interfacial tensions for the solid-fluid i and solid-fluid e interfaces and the angle of contact θ_i is defined as the angle between the fluid interface and the solid-fluid i interface ($\theta_e = \pi - \theta_i$).

The derivation of Eq. 2 is somewhat controversial. In elementary texts it is derived from the equilibrium of force components parallel to the solid surface, identifying the interfacial tensions with forces (per unit length) parallel to the interfaces and acting perpendicularly to the line of contact. This identification is objectionable in the case of the solid-fluid interfaces, where a distinction has to be made between surface tension (essentially a surface energy) and surface stresses.⁵ Also, no equilibrium of such "forces" is obtained when the components normal to the solid surface are considered. More refined deductions of Young's equation are based on thermodynamic arguments,⁶⁻⁸ but they consider particular geometries (e.g., a planar solid surface) and do not take into account possible effects of externally applied

fields. It is by no means obvious that the angle of contact should be independent of \mathbf{g} , to mention only gravitational fields.

In addition to these difficulties, there is the problem, recently raised by various authors,⁹⁻¹² that the interfacial tensions may be altered or perturbed near the line of contact, due to the interaction of the various interfaces, and it is not clear what should be the form of Young's equation when these effects are taken into account. Furthermore, in such a situation the two equations (Young-Laplace and Young) can no longer be treated and derived as independent equations, as they classically are, since γ cannot be regarded as independent of position in (and of) the interface, as implicit in the Young-Laplace equation.

In this paper we derive simultaneously the equation for the fluid interface profile and that for the angle of contact, in a very general situation, and, at the same time, we clarify the points raised above in connection with the applicability and derivation of the usual form of those equations (Eqs. 1 and 2). The question of the possible effect of external fields on the angle of contact is also discussed.

A general axially symmetric geometry is considered, with a solid surface of any shape. The only restriction is that we assume that the fluid interface intersects the axis of symmetry; this restriction could be avoided, but it considerably simplifies the mathematical solution of the problem (see Appendix). The derivation takes into account the presence of conservative fields of any type, which may affect both the bulk and interfacial free energy of the fluids. Finally, it is assumed that the solid-fluid interfacial tensions may change with position, so as to simulate a non-homogeneous solid, and that the fluid interface tension may change both with position and with the orientation of the interface in space. The case where γ also varies with curvature cannot be treated by the mathematical technique used in this paper.

The method to be used is essentially a thermodynamical one, in that we minimize the Helmholtz energy of a system comprising the three interfaces. For such a general situation, as the one we shall deal with, relatively complex methods of variational calculus are required. The problem turns out to be a particular, though complicated, form of the so-called isoperimetric problem, known as Mayer's problem with a variable end-point, the solution of which is discussed in detail in Ref. 13.

2 FORMULATION OF THE PROBLEM

Let us consider a closed system (see Figure 1) at a given temperature, with axial symmetry, formed by a solid and two immiscible fluids and their interfaces. The two fluids are essentially treated as incompressible.

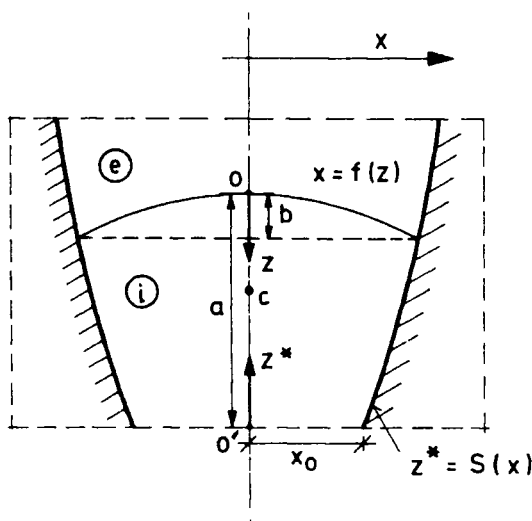


FIGURE 1. Diagram of the system to be analysed. The two fluids are denoted by i and e ; their interface is defined by $x = f(z)$. The solid surface has a profile $z^* = S(x)$. The z -axis is directed to the center of curvature C at the apex O of the fluid interface; z^* is antiparallel to z .

The fluid interface intersects the axis of symmetry (z -axis) at a point O , and z is directed to the centre of curvature C of the interface at O . We call fluid i the one in the side of C and fluid e the other.

The shape of the solid surface is given and is defined by

$$z^* = S(x) \quad (3)$$

with the axes x , z^* fixed to the solid. We choose z^* antiparallel to z , as in Figure 1. The (conservative) external fields give rise to potential energies P_i and P_e per unit volume of fluids i and e . Both P_i and P_e depend on position relative to a "fixed" referential, i.e., they depend on x , z^* . The interfacial tensions will be denoted by γ , γ_i and γ_e . γ may vary with position in and orientation of the interface, due to the external fields, and γ_i , γ_e may vary with position in the interface, if, for example, the solid is not homogeneous.

The system is defined by a fixed boundary and includes given volumes of the two fluids and a fixed extension of the solid surface. The boundary can be placed anywhere provided it includes the entire fluid interface. The equilibrium configuration under these conditions is the one that minimizes the Helmholtz energy of the system. The energy terms that have to be taken into account are the interfacial energy terms, A_s , and the bulk potential energy, A_p .

Alternatively, one may consider that the value of the pressure is fixed somewhere in one of the fluids (e.g., where that fluid meets the boundary of the system). If, within the region that comprises the fluid interface, we neglect

the variation of density due to the variation of pressure from point to point, we can determine, from the value of that pressure, the volume occupied by each fluid, independently of the position of the interface. This case, where both fluids are regarded as incompressible relative to pressure variations within the region of the interface, is then equivalent to the previous one, as far as the thermodynamical criterion of equilibrium is concerned.

It is then required to minimize $A = A_s + A_p$ for a given volume of fluid i , for example. Note that since the boundary of the system is fixed, V_e is determined by V_i .

We denote by a the distance between the origins of the axis z and z^* (Figure 1), so that

$$z^* = a - z. \quad (4)$$

Let

$$x = f(z) \quad (5)$$

be the equation of the fluid interface profile. It would be possible, though not so convenient, to take x as the independent variable. The point where the profile meets the solid has a coordinate $z = b$ (Figure 1). Then

$$a = b + S(f(b)). \quad (6)$$

We introduce

$$\begin{aligned} P &= P_i - P_e \\ \Gamma &= \gamma_i - \gamma_e. \end{aligned} \quad (7)$$

We then have

$$\begin{aligned} \gamma &= \gamma(f(z); a - z; f'(z)) \\ \Gamma &= \Gamma(x) \\ P &= P(x; a - z). \end{aligned} \quad (8)$$

As $f(z)$ and/or b vary, the Helmholtz energy $A = A_s + A_p$ varies. The energy terms that may, in fact, vary, can be written as follows (η, ξ denote auxiliary variables which replace x, z respectively; i.e., $S = S(\eta)$; $\Gamma = \Gamma(\eta)$; $f = f(\xi)$; $P = P(\eta; a - \xi)$; $\gamma = \gamma(f(\xi); a - \xi; f'(\xi))$):

$$A_s = \int_0^b 2\pi\gamma f(1 + f'^2)^{1/2} d\xi + \int_{x_0}^{f(b)} 2\pi\eta\Gamma(1 + S'^2)^{1/2} d\eta \quad (9)$$

$$A_p = \int_0^{f(b)} 2\pi\eta d\eta \int_b^{a-S(\eta)} P d\xi + \int_0^b d\xi \int_{x_0}^{f(\xi)} 2\pi\eta P d\eta. \quad (10)$$

In these equations x_0 is the value of x at the point of intersection of the solid-fluid i interface with the boundary of the system (Figure 1). It should be made clear that the γ 's in Eq. 9 are the surface tensions and not the specific surface Helmholtz energies. The two quantities only coincide when no adsorption occurs (6).

The volume of fluid i is

$$V_i = \int_0^b \pi f^2 d\xi + \int_{x_0}^{f(b)} \pi \eta^2 S' d\eta. \quad (11)$$

Strictly, these expressions apply if $S'(x) \geq 0$ and $f'(z) \geq 0$ everywhere. To take into account all possibilities, one would have to decompose some of the integrals above into as many integrals of the same type (but with inverted or different limits) as the regions where $S'(x)$ and $f'(z)$ have a given (\pm) sign. These complications do not alter the final equations, and will not be treated explicitly.

Therefore, the problem to be solved can be formulated in the following way. Given the functions S , Γ , γ , P (see Eqs. 3 and 8) and the volume V_i (Eq. 11), find the function $x = f(z)$ and the value b , for which $A = A_s + A_p$ (Eqs. 9 and 10) is a minimum. The value of a is then determined from Eq. 6.

This is a problem in variational calculus. Its solution can be obtained by a method due to Mayer,¹³ but not for a general dependence of γ and P on their arguments. The difficulty is the presence of the unknown parameter a in the argument of these functions. However, the difficulty can be avoided if we take for γ and P the polynomial forms:

$$\begin{aligned} \gamma &= \sum_{n=0}^N \gamma_n (a - z)^n \\ P &= \sum_{n=0}^N P_n (a - z)^n \end{aligned} \quad (12)$$

with $\gamma_n = \gamma_n(x; f'(z))$ and $P_n = P_n(x)$. Some of the γ_n , P_n may be identically zero (N can be taken the same in the two expressions); in particular, P_0 can always be taken equal to zero. The form [12] is in general a reasonable approximation since almost any physically relevant γ or P can be written in that form.

The details of the solution are indicated in the Appendix. In the following section we present and discuss the main equations derived in the Appendix, and in the final section we give examples of application of each of these equations.

3 FUNDAMENTAL EQUATIONS

The main equations obtained in the solution of the problem formulated in the previous section are as follows (for details of the solution see the Appendix).

3a Equation of the Fluid Surface

The differential equation that determines the fluid interface profile is Eq. A23 of the Appendix:

$$\begin{aligned} \frac{d}{dz} \left[ff'(1+f'^2)^{-1/2}\gamma + f(1+f'^2)^{1/2} \frac{\partial\gamma}{\partial f'} \right] \\ = (1+f'^2)^{1/2} \left(\gamma + f \frac{\partial\gamma}{\partial f} \right) + fP - kf \end{aligned} \quad (13)$$

where k is a constant and all the functions and their derivatives are taken at a point $x = f(z)$; z of the interface (for example, $P = P(f(z); a - z)$; $\partial\gamma/\partial f = (\partial\gamma/\partial x)_{x=f(z)}$). This equation may be written in the form:

$$\begin{aligned} \frac{d}{dz} \left[f(1+f'^2)^{-1/2}\gamma - ff'(1+f'^2)^{1/2} \frac{\partial\gamma}{\partial f'} \right] \\ = f(1+f'^2)^{1/2} \frac{\partial\gamma}{\partial z} - ff'P + kff'. \end{aligned} \quad (14)$$

The constant k can be related to the curvature at the origin:†

$$k = \frac{2\gamma(o)}{R} - \left(\frac{\partial\gamma}{\partial z} \right)_o + P(o) \quad (15)$$

where R is the radius of curvature at the origin and (o) means "at the origin."

If x (instead of z) is chosen as the independent variable, the profile $z = g(x)$ is obtained from:

$$\frac{d}{dx} \left[xg'(1+g'^2)^{-1/2}\gamma + x(1+g'^2)^{1/2} \frac{\partial\gamma}{\partial g'} \right] = x(1+g'^2)^{1/2} \frac{\partial\gamma}{\partial g} - xP + kx \quad (16)$$

These equations are to be regarded as a generalization of the Young-Laplace equation to cases where any external fields are applied and the interfacial tension changes from point to point and with inclination.

Note that the solid-fluid interfacial tensions do not appear in the equations. The same can be said about the shape of the solid. This does not mean, however, that the solid may not have an indirect effect on the equilibrium shape, since it may affect the value of γ in its neighbourhood.

(†) The average curvature λ , at any point is given by

$$2\lambda = \frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{ff'} \frac{d}{dz} [f(1+f'^2)^{-1/2}] = (1+f'^2)^{-3/2} \left(-f'' + \frac{1+f'^2}{f} \right)$$

The particular form of γ and P that was assumed (Eq. 12) does not figure explicitly in the final equations 13, 14, 15, which suggests that these equations are valid for any γ and P . Finally, the restriction that the fluid interface should intersect the symmetry axis, although convenient in the derivation, is likely to be physically irrelevant, so that the equation should also apply to cases where this condition is not met (e.g., in liquid bridges). The restriction could in fact be avoided by using the arc length s along the profile as the independent variable, but the formalism would be greatly complicated. In such cases, for example, in liquid bridges, the origin of the axes is conveniently placed at one of the solid surfaces and directed to other; fluid i is then the one that "wets" the z -axis in the region $z \gtrsim 0$.

For $\gamma = \text{constant}$, the equation of the profile takes the form

$$\gamma(1 + f'^2)^{-3/2} \left(-f'' + \frac{1 + f'^2}{f} \right) = -P + k \quad (17)$$

which, for $P = -\Delta\rho \cdot g^* \cdot z$, is identical to Eq. 1. In general, Eq. 17 can be written in the form

$$\Delta p + P = k = \text{constant} \quad (18)$$

where Δp is the pressure difference across the interface. The average curvature λ of the interface changes from point to point in such a way that the variation in $\Delta p = 2\lambda\gamma$ is equal to the change in P (P is the difference between the potential energies per unit volume of the two fluids at the same point). In particular, the interface can only be an equipotential of the external field if that equipotential is a surface of constant curvature.

3b Equation for the angle of contact

This is Eq. A25 of the Appendix, which can be written in the simpler form A28:

$$\gamma_e - \gamma_i = \gamma \cos \theta_i - \sin \theta_i \frac{\partial \gamma}{\partial \sin \alpha} \quad (z = b). \quad (19)$$

θ_i is the angle of contact of fluid i with the solid; α determines the orientation (or inclination) of the interface in space (Figure 2) and is defined by $\alpha = \text{ctg}^{-1} f'$. The values of the γ 's and of $\partial\gamma/\partial \sin \alpha$ are taken at the point where the three interfaces meet.

The angle of contact is independent of geometry and of any external fields that change the bulk energy of the fluids. When γ is independent of inclination, Eq. 19 reduces to the form of Young's equation (Eq. 2), although the γ 's may vary from point to point.

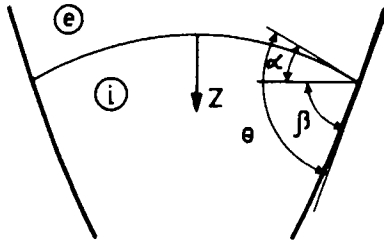


FIGURE 2 Definition of angles that enter in the equations of the angle of contact. α defines the orientation in space of the fluid interface and θ is the angle of contact for fluid i .

It may be possible that an applied field changes the values of the γ 's as compared to their values in the absence of that field. Equation 19 is also valid in such cases, provided the appropriate values of the γ 's are introduced in the equation. In general, then, there may be an effect of the applied fields in the angle of contact. This will certainly be the case of an electric field applied to charged interfaces (see Section 4c). However, gravitational and centrifugal fields (of the type to be considered in Section 4) will probably have little or no effect on the equilibrium structure and charge distribution at an interface and do not consequently alter the angle of contact.¹²

It is interesting to note that Eq. 19 can still be obtained from an equilibrium of forces parallel to the solid surface, if in addition to the interfacial tensions we include, among the forces, a "torque," i.e., a force $\partial\gamma/\partial \sin \alpha$ acting along the normal to the fluid interface, as shown in Figure 3. Note that the "torque" is $\partial\gamma/\partial \sin \alpha = (1/\cos \alpha)\partial\gamma/\partial \alpha$ and not $\partial\gamma/\partial \alpha$ as generally believed.¹⁴

If the solid surface is planar, as in Figure 4, we may take $a = b$, and the functions γ and P , of the type defined in Eqs. 8 or 12, can be thought of as

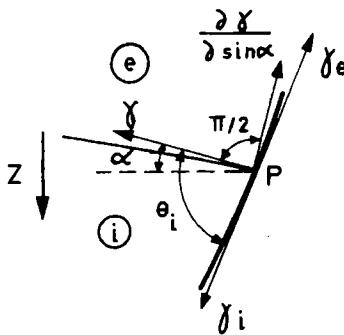


FIGURE 3 Diagram showing "the forces" that enter in the equation for the angle of contact. The γ 's act parallel to the respective interfaces, while $\partial\gamma/\partial \sin \alpha$ acts along the normal to the fluid interface.

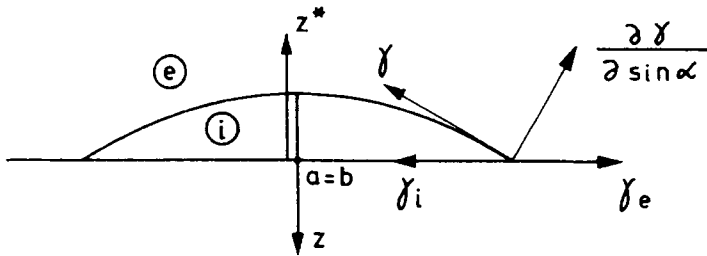


FIGURE 4 The equilibrium configuration of a fluid interface in contact with a planar surface. The value of γ may depend on the distance to the solid surface.

describing the short range interaction with the solid surface, since this interaction will depend on the distance to that surface. The angle of contact, as given by Eq. 19, may then deviate significantly from the one calculated by Young's equation using the unperturbed values of the interfacial tensions (i.e., the values far from the line of contact), even if the effect of inclination is not taken into account.

In general, and even in the absence of any other effects, it is therefore necessary to distinguish between a microscopic angle of contact, calculated from Eq. 19, and a macroscopic angle of contact, which can be obtained from Young's equation (Eq. 2) with the unperturbed values of the interfacial tensions. It has been argued, Ref. (11), that the latter angle is the one that is macroscopically measurable. In this context it would then be illuminating to calculate the fluid interface profile up to macroscopic distances to the solid, assuming a particular short range interaction with the solid, in order to see if the macroscopic angle of contact (in the sense of asymptotic) coincides with the one obtained with the unperturbed values of the γ 's.

3c Overall relations

The last fundamental equation is Eq. A26 of the Appendix:

$$\begin{aligned} \gamma f(1+f'^2)^{-1/2} - f f'(1+f'^2)^{1/2} \frac{\partial \gamma}{\partial f'} - \frac{k}{2} f^2 - \int_0^b f(1+f'^2)^{1/2} \frac{\partial \gamma}{\partial \xi} d\xi \\ + \int_0^{f(b)} \eta P(\eta, b) d\eta - \int_0^b d\xi \int_0^{f(\xi)} \eta \frac{\partial P}{\partial \xi} d\eta = 0 \quad (z = b) \quad (20) \end{aligned}$$

where the first three terms are calculated at the point of contact.

This equation can, in fact, be derived directly from Eq. 14 of the fluid interface profile. If this last equation is integrated between $z = 0$ and $z = b$,

we obtain, since $f(0) = 0$, $1/f'(0) = 0$:

$$\gamma f(1 + f'^2)^{-1/2} - ff'(1 + f'^2)^{1/2} \frac{\partial \gamma}{\partial f'} - \frac{k}{2} f^2 - \int_0^b f(1 + f'^2)^{1/2} \frac{\partial \gamma}{\partial \xi} d\xi + \int_0^b ff'P d\xi = 0 \quad (21)$$

which is equivalent to Eq. 20. This can be seen by integrating by parts the last integral in Eq. 20.

These equations establish a useful relation between various geometrical parameters of the fluid interface (i.e., R , b , $f(b)$, $f'(b)$), the surface tension and the applied potential. An example will be given in Section 4b.

Equations similar to Eqs. 20 and 21 can be obtained for any value of z (instead of b). Such equations, for a variable z , are integro-differential equations equivalent to the differential equation of the profile (Eq. 13 and 14), but they include the boundary condition at the origin.

4 APPLICATIONS

In this section we apply the general equations of the previous section to three simple problems and at the same time discuss some important aspects of the applicability of those equations.

4a Rotating fluids

Consider two rotating fluids (constant angular speed, ω), at rest relative to the solid surface (Figure 5). The axis of rotation is an axis of symmetry of this

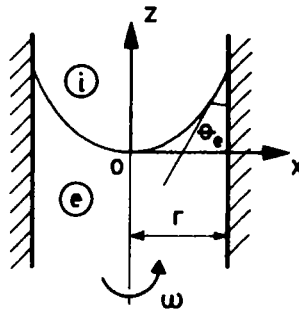


FIGURE 5 Two fluids i and e in a cylindrical container. The system is in rigid body rotation with constant angular speed ω .

surface. We shall neglect gravity. Then

$$P = P_i - P_e = -\frac{\omega^2}{2}(\rho_i - \rho_e)x^2 = \mu x^2 \quad (22)$$

where ρ_i and ρ_e are the densities of the fluids in the side i (the side of the centre of curvature at the apex) and in the side e , respectively. This corresponds to associating a pseudo-potential to the centrifugal force, the value of which, per unit volume, is $(-\omega^2 \rho x^2/2)$.

For $\gamma = \text{constant}$, Eq. 16 gives for the profile $z = g(x)$

$$\frac{d}{dx} \left[\frac{xg'}{(1+g'^2)^{1/2}} \right] = \frac{2}{R}x - \frac{\mu}{\gamma}x^3. \quad (23)$$

$R(R > 0)$ is, as usual, the radius of curvature at the apex. This equation was used by Princen *et al.*¹⁵ to calculate the shape of a rotating drop surrounded by a fluid of higher density. Integrating Eq. 23 once, we obtain, introducing the conditions at the apex

$$\frac{g'}{(1+g'^2)^{1/2}} = \alpha x - \beta x^3 \quad (24)$$

where

$$\begin{aligned} \alpha &= 1/R \\ \beta &= \frac{\mu}{4\gamma} = \frac{\rho_e - \rho_i}{8\gamma} \omega^2 \end{aligned} \quad (25)$$

Eq. 24 can be integrated again to obtain $z = g(x)$. We shall only discuss the types of shapes that can be obtained, and to simplify we assume that the solid surface is cylindrical, of radius r . Then the boundary condition is (from Eq. 24)

$$\cos \theta_e = \alpha r - \beta r^3 \quad (26)$$

where θ_e is the angle of contact of fluid e with the solid. We assume, as discussed previously, that this angle is independent of ω ; in particular, it is the same as for the fluid at absolute rest. There may be additional stationary points in the profile, that is, points for which $g' = 0$. These are defined by $x^2 = \alpha/\beta$ (from Eq. 24) and can only occur if $0 < \alpha/\beta \leq r^2$. Using Eq. 26 this is equivalent to

$$-1 < \frac{\cos \theta_e}{\beta r^3} \leq 0. \quad (27)$$

If two fluids 1, 2 of densities ρ_1, ρ_2 , such that $\Delta\rho = \rho_1 - \rho_2 > 0$ (e.g., fluid 1 is a liquid, fluid 2 is a vapour), are to be placed in the sides i and e , the following possibilities should be distinguished.

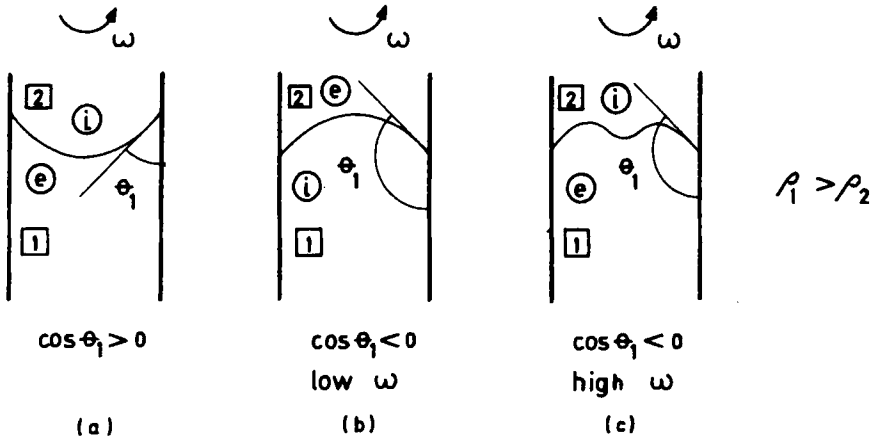


FIGURE 6 Possible shapes for the interface between two rotating fluids in a cylindrical container. For $\theta_1 > \pi/2$ (with $\rho_1 > \rho_2$) the interface develops a "concavity" at high angular speeds.

a) fluid 1 has an acute angle of contact with the solid ($\cos \theta_1 > 0$); the configuration of the interface is of the type shown schematically in Figure 6a.

b) fluid 1 has an obtuse angle of contact with the solid ($\cos \theta_1 < 0$); now two configurations may occur, one for low ω , as in Figure 6b, and another for high ω , as in Figure 6c. The threshold between these two configurations occurs for (see Eq. 27)

$$\omega^2 = \frac{8\gamma |\cos \theta_1|}{r^3 \Delta\rho}. \quad (28)$$

For this value of ω , the radius of curvature R is infinite.

The previous analysis is based on the assumption that the angle of contact is independent of ω , i.e., of the intensity of the applied field. This assumption, which, as previously discussed, is probably correct, could then be tested experimentally by studying the shapes of rotating fluid interfaces as a function of the field intensity (i.e., of ω), a possibility which is remote in the case of gravitational fields.

4b. Relation between dimensions in sessile and pendant drops

We apply Eq. 20 to a liquid-vapour interface ($\Delta\rho = \rho_l - \rho_v$) in contact with a planar horizontal solid surface, in a uniform gravitational field of intensity g . In this case $P = \pm \Delta\rho \cdot g \cdot z$, where the sign + applies to a sessile drop and the sign - to a pendant drop (Figure 7). With $f(b) = d$, the

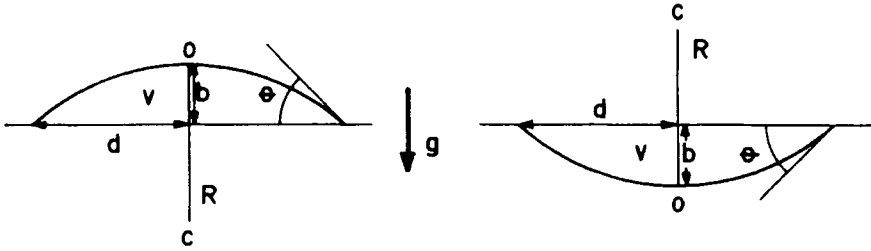


FIGURE 7 The geometrical parameters, d , b , R , V and θ that enter in Eq. 29 deduced for sessile and pendant drops.

integrals in Eq. 20 give

$$\int_0^{f(b)} \eta P(\eta, b) d\eta = \pm \frac{1}{2} \Delta\rho \cdot g \cdot b \cdot d^2$$

$$\int_0^b d\xi \int_0^{f(\xi)} \eta \frac{\partial P}{\partial \xi} d\eta = \pm \Delta\rho \cdot g \int_0^b \frac{f^2}{2} d\xi.$$

The last integral is $V/2\pi$, where V is the volume of the liquid drop. If θ is the contact angle of the liquid, then

$$(1 + f'^2(b))^{-1/2} = \sin \theta.$$

Inserting in Eq. 20 (with $\gamma = \text{constant}$), we finally obtain

$$\gamma \sin \theta \pm \frac{1}{2} \Delta\rho g b d \mp \frac{1}{2\pi} \Delta\rho g \frac{V}{d} + \frac{d\gamma}{R} = 0. \tag{29}$$

The top signs apply to a sessile drop. All quantities in Eq. 29 are positive.

Similar relations can be obtained for a non-planar solid surface (e.g., liquid menisci) and are very useful in discussions of capillarity phenomena.

4 Shape and contact angle of drop with a surface double layer in a uniform electric field

If a permanent double layer of momentum \mathbf{p} (with $p = \text{constant}$) is present at the fluid interface, the appropriate expression for γ , when a uniform electric field \mathbf{E} is applied in the direction of the z -axis, (Figure 8), is

$$\gamma = \gamma_0 - \mathbf{p} \cdot \mathbf{E} \tag{30}$$

where γ_0 is the interfacial tension in the absence of \mathbf{E} . We treat two ideal simple cases; no other fields are considered.

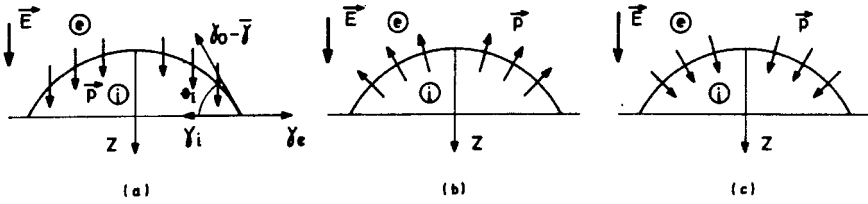


FIGURE 8 A fluid interface containing an electric double layer of momentum \mathbf{p} of various orientations. The applied electric field \mathbf{E} is parallel to the symmetry axis. The horizontal line represents the solid surface.

a) The dipoles are oriented parallel to the applied field (Figure 8a). Then

$$\gamma = \gamma_0 - \bar{\gamma}; \quad \bar{\gamma} = pE \quad (31)$$

In this case γ is a constant, and the equilibrium shape is spherical. The angle of contact, θ_i , of the liquid in the drop (fluid i) is

$$\cos \theta_i = \frac{\gamma_e - \gamma_i}{\gamma_0 - \bar{\gamma}} \quad (32)$$

where γ_e, γ_i are the interfacial tensions for the solid-fluid interfaces.

b) The dipoles are oriented perpendicular to the fluid interface (Fig. 8b, 8c). Then

$$\gamma = \gamma_0 - \bar{\gamma} \cos \delta; \quad \bar{\gamma} = pE \quad (33)$$

where

$$\cos \delta = \pm f'(1 + f'^2)^{-1/2}. \quad (34)$$

The $+$ sign applies to the situation of Figure 8b and the $-$ sign to that of Fig. 8c. In this case γ depends on the inclination of the interface, and

$$\frac{\partial \gamma}{\partial f'} = \mp \bar{\gamma} (1 + f'^2)^{-3/2}. \quad (35)$$

Inserting in Eq. 14, we again obtain a surface of constant curvature, i.e., a spherical drop.

For the angle of contact we obtain from Eq. 19 (or, preferably, from Eq. A25)

$$\cos \theta_i = \frac{\gamma_e - \gamma_i \mp \bar{\gamma}}{\gamma_0}. \quad (36)$$

In Figure 9 we indicate the profiles of drops of a given volume, in contact with a planar solid surface, perpendicular to \mathbf{E} . The angles θ_i were calculated from Eqs. 32 and 36 for $\gamma_e - \gamma_i = 2\gamma = \gamma_0/2\gamma_0$. It was assumed that $(\gamma_e - \gamma_i)/\gamma_0$ is not affected by the field.

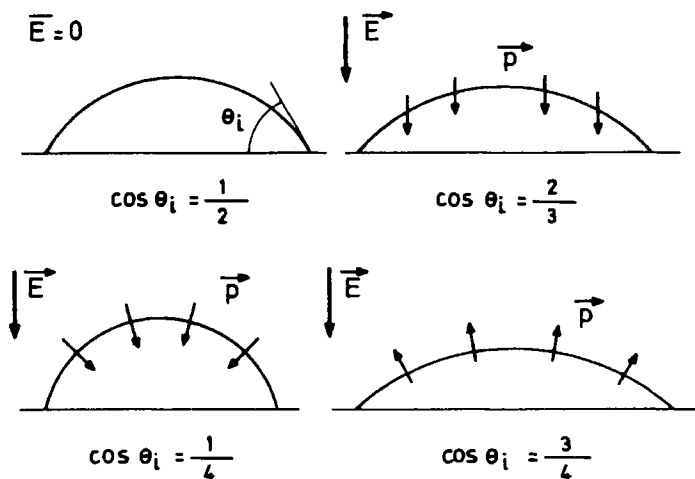


FIGURE 9 Calculated shapes of a drop of a given volume in an electric field \mathbf{E} . The profile is always circular, but the angle of contact changes with the orientation of the dipoles in the interface. The momentum \mathbf{p} and the field \mathbf{E} have the same magnitude in all cases.

These results deserve some comments. When dipolar molecules are adsorbed at the interfaces, effects of this type should be present, since the dipoles at the fluid interface will interact, at least near the line of contact, with the electric field created by adsorbed molecules at the solid surface. This example shows once more that if such interactions are taken into account, large deviations are to be expected in the value of the (microscopic) contact angle as compared to its unperturbed (macroscopic) value obtained from Young's equation.

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Appendix

We follow closely the procedure and notation used in reference 13 to solve the isoperimetric problem enunciated in Section 2.

It is required to find the function $x = f(z)$ such that, for a particular but unknown value b of z , the Helmholtz energy $A = A_s + A_p$ (see Eqs. 9 and 10) is a minimum:

$$\begin{aligned} \frac{A}{2\pi} = & \int_0^b \gamma f(1 + f'^2)^{1/2} d\xi + \int_{x_0}^{f(b)} \Gamma \eta(1 + S'^2)^{1/2} d\eta \\ & + \int_0^{f(b)} \eta d\eta \int_b^{a-S(\eta)} P d\xi + \int_0^b d\xi \int_{x_0}^{f(\xi)} \eta P d\eta \end{aligned} \quad (\text{A1})$$

with (cf. Eq. 6)

$$a = b + S(f(b)) \quad (\text{A2})$$

subject to the condition (cf. Eq. 11)

$$\frac{V_i}{\pi} = \int_0^b f^2 d\xi + \int_{x_0}^{f(b)} \eta^2 S' d\eta = \text{constant}. \quad (\text{A3})$$

S , Γ , γ , P are given functions of their arguments (Eq. 3 and 8), γ and P being of the form defined in Eq. 12. That is, in the various integrals of (A1) and (A2), we have

$$S = S(\eta); \quad \Gamma = \Gamma(\eta) \quad (\text{A4})$$

and

$$\begin{aligned} \gamma &= \sum_{n=0}^N \gamma_n (a - \xi)^n; & \gamma_n &= \gamma_n(f(\xi); f'(\xi)) \\ P &= \sum_{n=0}^N P_n (a - \xi)^n; & P_n &= P_n(\eta). \end{aligned} \quad (\text{A5})$$

In this and following expressions a dash means derivation with respect to the argument of a function.

We first introduce the expressions (A5) in (A1) and simplify the integrals containing P . Next we define the following functions of the variable z :

$$f_0(z) = \sum_{n=0}^N f_{n0}(z) + \int_{x_0}^{f(z)} \Gamma \eta (1 + S'^2)^{1/2} d\eta + \sum_{n=0}^N \int_0^{f(z)} \frac{\eta P_n}{n+1} [S^{n+1}(f(z)) - S^{n+1}(\eta)] d\eta \quad (A6)$$

$$f_{ni} = \frac{n!}{(n-i)!} \left[\int_0^z f(1 + f'^2)^{1/2} \gamma_n(a - \xi)^{n-i} d\xi + \int_0^z (a - \xi)^{n-i} d\xi \int_{x_0}^{f(\xi)} \eta P_n d\eta \right] \quad (n = 0, \dots, N; i \leq N) \quad (A7)$$

$$f_n^*(z) = \int_0^{f(z)} \eta P_n d\eta \quad (n = 0, \dots, N) \quad (A8)$$

$$f_1(z) = \frac{1}{2} \int_0^z f^2 d\xi + \frac{1}{2} \int_{x_0}^{f(z)} \eta^2 S' d\eta \quad (A9)$$

with

$$a(z) = z + S(f(z)). \quad (A10)$$

We note that for $z = 0$ all these functions, and also $f(z)$, equal zero; and $f_0(b) = A/2\pi, f_1(b) = V_i/2\pi$.

We now calculate the z -derivatives of the functions (A6) to (A9), and introduce additional functions ϕ associated with each of those functions

$$\begin{aligned} \phi_0 &= f'_0 - \sum_{n=0}^N f'_{n0} - \Gamma f f'(1 + S'^2)^{1/2} - S' f' \sum_{n=0}^N S^n f_n^* \\ \phi_1 &= f'_1 - \frac{f^2}{2} - \frac{f^2 f' S'}{2} \quad (A11) \\ \phi_{ni} &= f'_{ni} - \frac{n!}{(n-i)!} S^{n-i} [f(1 + f'^2)^{1/2} \gamma_n + f_n^*] - (1 + S' f') f_{n,i+1} \\ \phi_n^* &= f_n^{*'} - f f' P_n \end{aligned}$$

Each of the ϕ 's is the difference between a f' and the calculated derivative of f , and is therefore identically zero. In Eqs. A11 all the functions depend on z ; for example $\Gamma = \Gamma(f(z)); S = S(f(z)); S' = S'(f(z)); \gamma_n = \gamma_n(f(z); f'(z)); P_n = P_n(f(z)),$ etc.

Finally we introduce the following functions of z :

$$\begin{aligned}\psi_0 &= f_0 \\ \psi_1 &= f_1 - \frac{V_i}{2\pi}\end{aligned}\tag{A12}$$

The problem can now be reformulated as follows. The vectorial function $\vec{f}(z) = \{f, f_0, f_1, f_{ni}, f_n^*\}$, which we designate briefly by $\vec{f}(z) = \{f_k\}$, satisfies the "initial" condition

$$f_k(0) = 0\tag{A13}$$

and the binding conditions (\dagger) (Eqs. A11):

$$\phi_k(z) = 0\tag{A14}$$

with

$$a(z) = z + S(f(z)).\tag{A15}$$

It is required to find the vectorial function $\vec{f}(z)$ such that, for a particular $z = b$,

$$\begin{aligned}\psi_0 &\text{ is a minimum} \\ \psi_1 &= 0\end{aligned}\quad (z = b)\tag{A16}$$

The solution of this problem (isoperimetric problem) can be found by Mayer's method, in the following way:

1) Take

$$h = \lambda_0 \phi_0 + \lambda_1 \phi_1 + \sum_{n,i} \lambda_{ni} \phi_{ni} + \sum_n \lambda_n^* \phi_n^*\tag{A17}$$

where $\vec{\lambda} = \{\lambda_0, \lambda_1, \lambda_{ni}, \lambda_n^*\} = \{\lambda_k\}$ is a vectorial function of z , to be determined. We denote by $h_{f_k}, h_{f'_k}$ the partial derivatives of h with respect to f_k, f'_k . Then the solution $\vec{f}(z)$ of the problem satisfies Mayer's equations:

$$h_{f_k} = \frac{d}{dz} h_{f'_k}.\tag{A18}$$

2) In addition, for $z = b$, the functions have to satisfy the following "transversability" conditions

$$v_0 \psi_{0z} + v_1 \psi_{1z} = \sum_{\text{all } f_k} h_{f'_k} \cdot f'_k \quad (z = b)\tag{A19}$$

$$v_0 \psi_{0f_k} + v_1 \psi_{1f_k} = h_{f_k} \quad (z = b) \text{ for each } f_k\tag{A20}$$

\dagger The method cannot be applied if the ϕ_k contain non-solvable integrals involving f_i, f'_i . This is why the general form of γ, P (Eq. 8) cannot be treated.

where ψ_{0z}, ψ_{0f_k} , etc. are partial derivatives in order to z, f_k etc., and $\bar{v} = \{v_0, v_1\}$ is a constant vector.

We shall omit the details of the calculations. The solution for λ_k is obtained from Eqs. (A18), with the help of Eqs. (A20).

$$\begin{aligned} \lambda_0, \lambda_1 &= \text{constant} \\ \lambda_{ni} &= \frac{\lambda_0}{i!} [a(b) - z - S(f(z))] \\ \lambda_n^* &= \frac{\lambda_0}{n+1} \{[a(b) - z]^{n+1} - S^{n+1}(f(z))\}. \end{aligned} \tag{A21}$$

Also

$$\begin{aligned} v_0 &= \lambda_0 \\ v_1 &= \lambda_1. \end{aligned} \tag{A22}$$

Equation A18, for $f_k = f$, gives upon introduction of the λ_k and simplification

$$\begin{aligned} \frac{d}{dz} \left[ff'(1 + f'^2)^{-1/2} \gamma + f(1 + f'^2)^{1/2} \frac{\partial \gamma}{\partial f'} \right] \\ = \gamma(1 + f'^2)^{1/2} + f(1 + f'^2)^{1/2} \frac{\partial \gamma}{\partial f} + fP - kf \end{aligned} \tag{A23}$$

where

$$k = -\frac{\lambda_1}{\lambda_0} = \text{constant}. \tag{A24}$$

All the functions are calculated at a point $x = f(z); z$. For example: $P = P(f(z); a - z); \gamma = \gamma(f(z); a - z; f'(z))$. Note that no vestiges of the particular forms of γ and P used in the derivation (Eq. A5) appear in (A23).

Finally, the transversability conditions (A19) and (A20) for $f_k = f$ can be combined to obtain two more equations. The first, obtained by eliminating the potential energy terms, is

$$\begin{aligned} \frac{1}{1 + S'f'} [(1 + f'^2)^{1/2} \gamma + f'(1 + S'^2)^{1/2} \Gamma] \\ = \frac{1}{S'} \left[f'(1 + f'^2)^{-1/2} \gamma + (1 + f'^2)^{1/2} \frac{\partial \gamma}{\partial f'} + (1 + S'^2)^{1/2} \Gamma \right]. \end{aligned} \tag{A25}$$

The second relation is obtained by eliminating Γ :

$$f(1 + f'^2)^{-1/2}\gamma - ff'(1 + f'^2)^{1/2} \frac{\partial\gamma}{\partial f'} - \frac{k}{2}f^2 - \int_0^b f(1 + f'^2)^{1/2} \frac{\partial\gamma}{\partial\xi} d\xi \\ + \int_0^{f(b)} \eta P(\eta, b) d\eta - \int_0^b d\xi \int_0^{f(\xi)} \eta \frac{\partial P}{\partial\xi} d\eta = 0 \quad (z = b). \quad (\text{A26})$$

Equation (A25) can be transformed by introducing the angles α , β and $\theta = \alpha + \beta$ defined in Figure 2. Since

$$\text{tg } \alpha = 1/f'; \quad \text{tg } \beta = S'$$

we obtain

$$-\Gamma = \gamma_e - \gamma_i = \gamma \cos \theta + \sin \theta (1 + f'^2) \frac{\partial\gamma}{\partial f'} \quad (z = b) \quad (\text{A27})$$

or

$$\gamma_e - \gamma_i = \gamma \cos \theta - \sin \theta \frac{\partial\gamma}{\partial \sin \alpha} \quad (z = b). \quad (\text{A28})$$