J. Fluid Mech. (1973), *vol.* 59, *part* 4, *pp.* 753–767
Printed in Great Britain

The stability of pendent liquid drops. Part 1. Drops formed in a narrow gap

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(Received 28 September 1972 and in revised form 22 February 1973)

We consider a drop of liquid hanging from a horizontal support and sandwiched between two vertical plates separated by a very narrow gap. Equilibrium profiles of such 'two-dimensional' drops were calculated by Neumann (1894) for the case when the angle of contact between the liquid and the horizontal support is zero. This paper gives the equilibrium profiles for other contact angles and the criterion for their stability. Neumann showed that, as the drop height increases, its cross-sectional area increases until a maximum is reached. Thereafter, as the height increases, the equilibrium area decreases. This behaviour is shown to be typical of all contact angles. When the maximum area is reached, the total energy is a minimum. It is shown that the drops are stable as long as the height and the area increase together.

1. Introduction

The growth of a drop of liquid hanging from a support was studied by a number of workers in the early years of the century and many of their findings have been summarized by Bakker (1928). Besides its practical application in the measurement of surface tension, the subject was also of interest because of the mathematical problem of the calculation of the shape of the drop. This is determined by the equilibrium of the forces due to the weight of the liquid, the pressure and the surface tension. As the drop grows in size, its weight eventually cannot be balanced by surface tension forces. One aim of the early work was to calculate the maximum equilibrium volume attainable before the drop breaks and liquid falls. However, the impossibility of balancing the forces is not the only conceivable cause of the breaking of the drop, which could happen as a result of the equilibrium becoming unstable. This possibility has been largely ignored, but recently Padday (1971) and Padday & Pitt (1973) have examined this question. They used purely numerical methods, which, although informative in many ways, nevertheless cannot fully reveal the behaviour of the perturbed drop. It therefore seemed appropriate to attempt a theoretical analysis of the equilibrium and stability of hanging drops.

As a particular example, we may consider the condensation of water to form drops on a ceiling. In order that a stable drop may contain a given volume of water, there are two distinct theoretical requirements. First, it must be possible to find a physically realizable drop shape which satisfies the conditions of equilibrium. The second requirement concerns the change in the the total energy of the

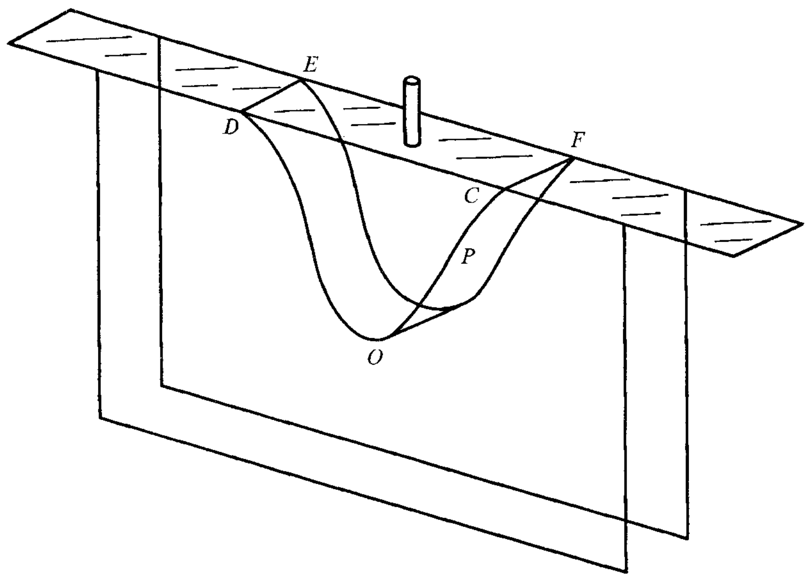

FIGURE 1. The two-dimensional drop. The thickness DE is greatly exaggerated.

drop when its equilibrium is slightly disturbed. If the disturbance increases the total energy, we may expect the drop to return to the equilibrium from which it has departed, since it represents a state of lower energy. If this disturbance decreases the total energy, such a return will no longer occur and the drop will be unstable.

For hanging drops (which are axially symmetric) the analysis immediately poses a severe difficulty, because the solutions of the basic equations of equilibrium cannot be expressed in terms of known functions. For this reason it appeared prudent to make a preliminary study of a simpler example, for which the equilibrium drop profiles can be expressed in known functions and which can also be realized experimentally. The features revealed in this case are in fact helpful in understanding the behaviour of axially symmetric drops, which will be described in a later paper.

We shall consider a 'two-dimensional' drop which hangs below a horizontal surface with which it maintains a given contact angle, and which is sandwiched between two vertical parallel glass plates which are very close to each other (see figure 1, in which the separation of the plates is greatly exaggerated). Since the separation is very small the profile of the meniscus across the gap between the walls will generally be very close to a circular arc, of constant curvature, which will not affect the profile in the vertical plane; indeed if the angle of contact of the liquid and the vertical wall is exactly 90°, the meniscus will be a cylindrical surface through $DOPC$. We shall study the behaviour of such a meniscus assuming that the gap is so narrow that the surface cannot be disturbed along the direction perpendicular to the vertical plane. We suppose that the liquid is introduced through a narrow tube which is closed when a given volume has been inserted below the support. The first problem is to find the equilibrium profiles and the volume they contain, which is equivalent to finding

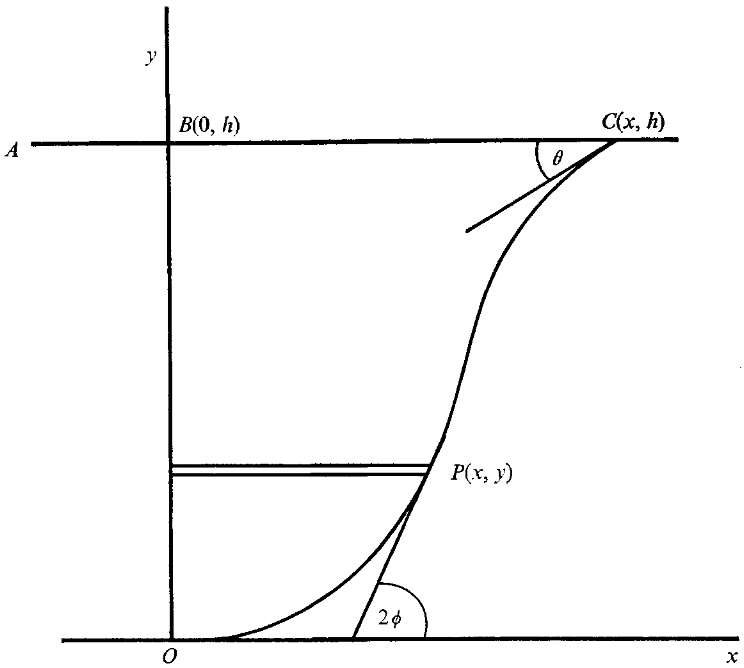

FIGURE 2. The co-ordinate system.

their cross-sectional area. The next problem is to determine whether these equilibria are stable. We shall consider disturbances of the two-dimensional drop which are analogous to those likely to be experienced by a drop hanging from a ceiling, that is, the volume will be held constant, but the profile of the drop and its length in contact with the horizontal support *DC* will be varied.

The equilibrium shapes of two-dimensional drops essentially of this kind were studied by Neumann (1894) for liquids having a zero contact angle with the horizontal support. He showed that their cross-section grows to a maximum beyond which no equilibria exist, and below which for a given area there are two possible profiles. He appeared to regard both profiles as being stable. Wangerin in a note added to Neumann's article contradicted this. Unfortunately it has not been possible to discover whether Wangerin published his work. Bakker (1928) refers only to Neumann and Wangerin and since that time no further work appears to have been done to clarify the situation.

In this paper the problem will be examined by the methods of the calculus of variations, which permit a unified approach to the determination of the equilibrium and its stability. The vanishing of the first variation of the total energy gives rise to the equations for equilibrium, and the criteria for stability are derived from the second variation.

2. The equilibrium profiles

In order to carry out the variational treatment we need an expression for the total energy of the drop. Figure 2 shows the vertical cross-section of half of the drop hanging from the horizontal support ABC, and introduces a convenient co-ordinate system. If we calculate the energy per unit length of surface in the z direction in figure 2, then for half of the drop an element of length ds (in the x, y plane) at P contributes $\gamma\, ds$, where γ is the surface tension. The horizontal element of liquid at P contributes potential energy, which we shall reckon relative to the level ABC; thus the contribution is $-(h-y)\,xg\rho\, dy$, where h is the height OB of the drop, g is the acceleration due to gravity and ρ is the liquid density. The interface between the liquid and the support also contributes to the energy an amount proportional to the length BC which we may write as bx_0, where b is a constant. Thus if the total energy of the whole drop per unit length in the z direction is $2E$, we have

$$E = \int_0^h \left[\gamma \frac{ds}{dy} - x(h-y)\, g\rho\right] dy + bx_0.$$

If $2A$ is the total area of the cross-section of the drop, then

$$A = \int_0^h x\, dy.$$

For a given value of A, the value of E will depend on the shape $x(y)$ of the drop. The equilibrium profile will be that which minimizes E, subject to the condition that A is constant. Applying the standard methods of the calculus of variations, we obtain the well-known equations relating hydrostatic pressure, surface tension and the curvature of the surface, and find that the profile of the drop must cut the y axis at right angles at O, and that we also must have

$$b = -\gamma \cos\theta,$$

where θ is the angle of contact shown in figure 2. In addition, it follows that there cannot be corners in the profile and that the Weierstrass condition for a strong minimum is satisfied by the integrand in the definition of E. This formal approach of course merely reproduces the results usually derived directly by simple physical arguments.

It will be convenient to use dimensionless variables, choosing $(\gamma/\rho g)^{\frac{1}{2}}$ as the unit of length and defining κ as the height of the drop and 2λ as the length of the drop in contact with the support, i.e.

$$\kappa = h(\gamma/\rho g)^{-\frac{1}{2}}, \quad \lambda = x_0(\gamma/\rho g)^{-\frac{1}{2}}.$$

Corresponding to the energy E and the area A we shall introduce dimensionless quantities E_0 and α defined by

$$E_0 = E\gamma^{-\frac{3}{2}}(\rho g)^{\frac{1}{2}}, \quad \alpha = A\rho g/\gamma.$$

Differentiation will be indicated by a suffix, e.g. $x_y \equiv dx/dy$. With these definitions the basic equations can be written as

$$E_0 = -\alpha\kappa + \int_0^\kappa [(1+x_y^2)^{\frac{1}{2}} + xy]\, dy - \lambda\cos\theta, \tag{1}$$

$$\alpha = \int_0^\kappa x\, dy, \tag{2}$$

and according to the rules of variational calculus we require that the first variation of $E_0 - \mu\alpha$, where μ is an arbitrary multiplier, must vanish. The Euler–Lagrange equation immediately gives the familiar result

$$y - \mu = d[x_y(1+x_y^2)^{-\frac{1}{2}}]/dy$$
$$= x_{yy}(1+x_y^2)^{-\frac{3}{2}}. \tag{3}$$

In the usual derivation of (3) by considering the pressures, the left-hand side corresponds to the hydrostatic pressure and the right-hand side to the pressure due to the surface tension and the curvature. From (3) it will be seen that μ is the magnitude of the curvature of the profile of the drop at the apex O, where y is zero. Also, when y is equal to μ, the profile has an inflexion point.

Equation (3) may be integrated immediately with the result

$$\tfrac{1}{2}y^2 - \mu y + 1 = x_y(1+x_y^2)^{-\frac{1}{2}}, \tag{4}$$

where we have used the condition that when y is zero x_y is infinite. We now put

$$u = \mu y - \tfrac{1}{2}y^2, \tag{5}$$

so that
$$x_y^2 = (1-u)^2/u(2-u). \tag{6}$$

This shows that
$$0 \leqslant u \leqslant 2. \tag{7}$$

Since y is necessarily positive, it follows from (5) that

$$0 \leqslant \mu. \tag{8}$$

If we put
$$u = 2\sin^2\phi \tag{9}$$

equation (7) is automatically satisfied and we find

$$x_y = \cot 2\phi, \tag{10}$$

and thus $\tan 2\phi$ is the gradient of the curve at P (see figure 2). At C, x_y is equal to $\cot\theta$, so that there ϕ is equal to $\frac{1}{2}\theta$. From (5)

$$y = \mu - (\mu^2 - 4\sin^2\phi)^{\frac{1}{2}}, \tag{11}$$

so that, when ϕ is zero y is zero. From (10) and (11) we obtain

$$x = 2\int_0^\phi \cos 2\phi(\mu^2 - 4\sin^2\phi)^{-\frac{1}{2}}\,d\phi, \tag{12}$$

which may be expressed in terms of elliptic integrals of the first and second kinds:

$$x = \mu^{-1}(2-\mu^2)\,F\,(2\mu^{-1}, \phi) + \mu E(2\mu^{-1}, \phi). \tag{13}$$

Provided μ is greater than 2, the value of ϕ varies between zero and $\frac{1}{2}\theta$, which corresponds to its value at the point C. From (11) we see that y is never equal to μ, and hence the profile does not have a point of inflexion. However, if μ is less than 2, equation (13) is transformed by standard methods into

$$x = 2E(\tfrac{1}{2}\mu, \psi) - F(\tfrac{1}{2}\mu, \psi), \tag{14}$$

where
$$\sin\psi = 2\mu^{-1}\sin\phi. \tag{15}$$

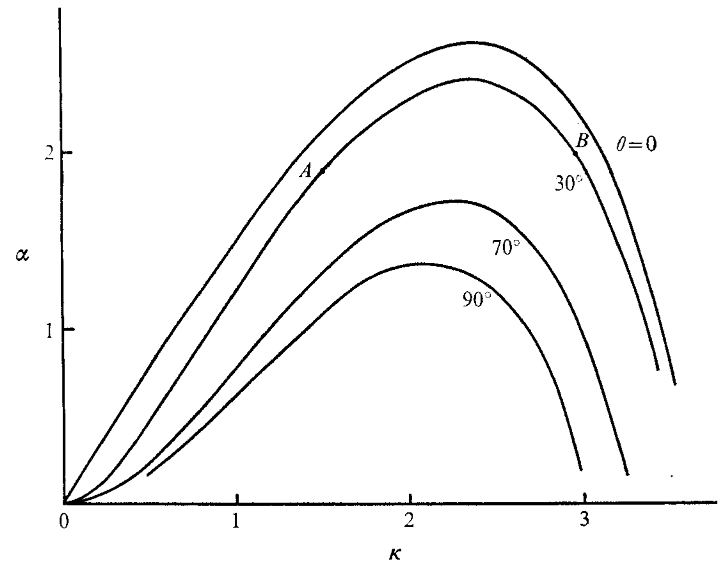

FIGURE 3. Area α as a function of height κ.

The maximum possible value of ϕ is therefore $\sin^{-1}(\frac{1}{2}\mu)$, when from (11) we see that y is equal to μ, i.e. the inflexion point has been reached. To obtain the rest of the profile, we note that (5) also has a solution

$$y = \mu + (\mu^2 - 4\sin^2\phi)^{\frac{1}{2}}, \tag{16}$$

which corresponds to the part of the curve beyond the inflexion point $y = \mu$ up to the point C, where ϕ is equal to $\frac{1}{2}\theta$.

After straightforward manipulation we find in this region

$$x = 4E(\tfrac{1}{2}\mu) - 2K(\tfrac{1}{2}\mu) - 2E(\tfrac{1}{2}\mu, \psi) + F(\tfrac{1}{2}\mu, \psi), \tag{17}$$

where $E(\frac{1}{2}\mu)$ and $K(\frac{1}{2}\mu)$ are the complete elliptic integrals.

The cross-sectional area may be obtained by multiplying (3) by x_y and integrating. With the condition that x_y is infinite when y is zero we obtain

$$-\mu x + xy - \int_0^y x\,dy = -(1+x_y^2)^{-\frac{1}{2}}, \tag{18}$$

and if y is put equal to κ we find

$$\alpha - \kappa\lambda + \mu\lambda - \sin\theta = 0. \tag{19}$$

For a particular choice of θ and μ, if μ exceeds 2 we calculate κ and λ from (11) and (13) respectively, with ϕ equal to $\frac{1}{2}\theta$. If μ is less than 2, equations (16) and (17) are used. The area of the cross-section is then calculated from (19).

In figure 3 values of α have been plotted as a function of κ for different angles of contact. As Neumann showed for zero contact angle, there is a maximum in the possible values α may attain. Below this maximum two profiles exist having for the same area α two different heights κ. As an example, the profiles are shown in figure 4 for a contact angle of 30° corresponding to the points A and B in

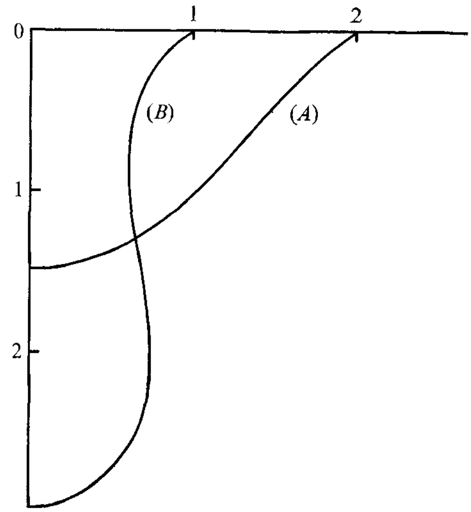

FIGURE 4. Two profiles of equal area.

figure 3. It will also be seen that, if we have an equilibrium shape, then by drawing the horizontal surface from which the drop hangs at a different level we automatically obtain an equilibrium solution for a different area and contact angle.

From figure 3 we see that, as liquid is added to the drop, the height κ increases until the maximum cross-sectional area is reached. Addition of more liquid would then result in a situation for which no equilibrium is possible, and so liquid would certainly separate from the drop. However, if the maximum cross-section were exactly attained and liquid were withdrawn, the figure shows that it is possible for the drop height κ to continue to increase, since points such as B represent an equilibrium. Obviously in practice this region would be very difficult to enter, since a slight excess of liquid above the maximum would cause the drop to break, while an amount less than the maximum would make it impossible to reach points like B by removal of liquid.

When we know the equilibrium profile of the drop, we can evaluate its energy by means of (1). It is interesting that the energy is at a minimum when α has its maximum value. This can be shown as follows. The profile x is a function of both y and the parameter μ, and likewise for a given contact angle κ and λ depend on μ. If we differentiate (1) with respect to μ, we finally obtain

$$dE_0/d\mu = (\mu-\kappa)\, d\alpha/d\mu. \tag{20}$$

(In the derivation of this expression we have used the result

$$\int_0^\kappa x_y\,(1+x_y^2)^{-\frac{1}{2}}\frac{\partial x_y}{\partial \mu}\,dy = \left[x_y\,(1+x_y^2)^{-\frac{1}{2}}\frac{\partial x}{\partial \mu}\right]_0^\kappa - \int_0^\kappa (y-\mu)\,\frac{\partial x}{\partial \mu}\,dy, \tag{21}$$

which is obtained by integrating by parts and using (3). Evaluation of the limits by means of Taylor series and the subsequent use of (19) then gives (20) after straightforward algebra.) Since for drops with very small volumes the profile does not at first have an inflexion point (unless the contact angle is zero) initially μ exceeds κ and therefore E_0 and α increase together. Eventually μ is less than κ

and the profiles possess an inflexion point, and hence as α increases E_0 decreases. When α attains its maximum, E_0 therefore passes through a minimum.

The dimensionless factor $\mu-\kappa$ occurring in (20) corresponds to the pressure in the liquid at the horizontal support. Thus (20) has a simple physical interpretation: the change in energy dE_0 is equal to the change in volume $d\alpha$ multiplied by the pressure in the liquid at the level of the support.

One further property of the equilibrium solution will be derived here for use later. From (4), when y is put equal to κ, we find

$$\tfrac{1}{2}\kappa^2-\mu\kappa+1 = \cos\theta, \tag{22}$$

and so by differentiation

$$(\kappa-\mu)\,d\kappa/d\mu-\kappa = 0. \tag{23}$$

3. Stability

The stability of the equilibrium of the drops can be investigated by examining the change in energy when a small perturbation is made. In accordance with our assumption that the volume in the drop is fixed, the perturbations must be such as to leave the volume unchanged, but both the height of the drop and its length in contact with the support may be altered.

We therefore determine the change δE_0 in the energy when small changes $\delta\kappa$ and $\delta\lambda$ are made in κ and λ. We suppose that the equilibrium profile $x(y)$ is replaced by $x+\epsilon s(y)$, and that ϵ, $\delta\kappa$ and $\delta\lambda$ are all of the same order of magnitude. If we put

$$F(y,x,x_y) = (1+x_y^2)^{\frac{1}{2}}+xy, \tag{24}$$

then from (1) we find

$$\delta E_0+\delta\lambda\cos\theta+\alpha\delta\kappa = \int_0^{\kappa+\delta\kappa} F(y,x+\epsilon s,x_y+\epsilon s_y)\,dy-\int_0^{\kappa} F(y,x,x_y)\,dy. \tag{25}$$

The condition for constant volume is

$$\int_0^{\kappa} x\,dy = \int_0^{\kappa+\delta\kappa}(x+\epsilon s)\,dy. \tag{26}$$

We shall suppose that the perturbation $s(y)$ vanishes for values of y in the range $(0, y_0)$, that is, the profile is undisturbed in a region close to the apex (see figure 5). Later the consequences of allowing y_0 to tend to zero will be examined. Thus, the condition (26) becomes

$$0 = \lambda\delta\kappa+\tfrac{1}{2}\delta\kappa^2\cot\theta+\epsilon\int_{y_0}^{\kappa} s\,dy+O(\epsilon^3), \tag{27}$$

and we have

$$\epsilon s(y_0) = 0 \tag{28}$$

and

$$\lambda+\delta\lambda = x(\kappa+\delta\kappa)+\epsilon s(\kappa+\delta\kappa), \tag{29}$$

which is equivalent to

$$\epsilon s(\kappa) = \delta\lambda-\delta\kappa\cot\theta+O(\epsilon^2). \tag{30}$$

We also need the expansions of the profile $x(y)$ near C and O, which are

$$\kappa-y = (\lambda-x)\tan\theta+O(\lambda-x)^2, \tag{31}$$

$$x = (2y/\mu)^{\frac{1}{2}}+O(y^{\frac{3}{2}}). \tag{32}$$

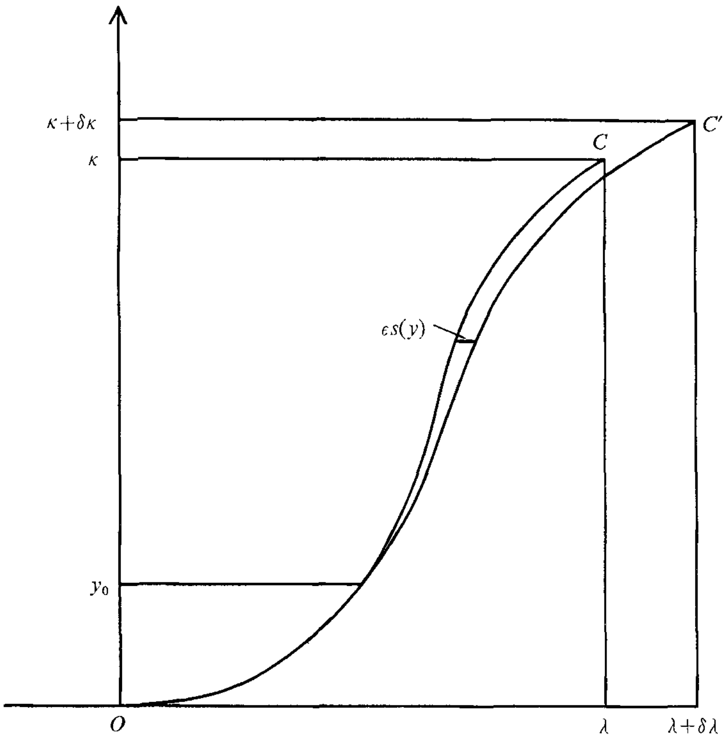

FIGURE 5. The variation of the profile.

The value of δE_0 can now be evaluated from (25) as far as terms $O(\epsilon^2)$. In simplifying the expressions obtained, we use the equilibrium condition given by (3), the value of α from (19) and the condition in (27). After lengthy algebra, we obtain

$$\delta E_0 = \tfrac{1}{2}[\lambda-(\kappa-\mu)\cot\theta]\,\delta\kappa^2+(\kappa-\mu)\,\delta\lambda\,\delta\kappa+\tfrac{1}{2}\epsilon^2\int_{y_0}^{\kappa} s_y^2(1+x_y^2)^{-\frac{3}{2}}\,dy+O(\epsilon^3). \quad (33)$$

We have now to examine the dependence of δE_0 on the perturbation. If δE_0 is always positive, the equilibrium will be stable, but if by a suitable choice of $\delta\lambda$, $\delta\kappa$ and $\epsilon s(y)$ the value of δE_0 can be made negative, the equilibrium will be unstable. The perturbation $s(y)$ has to satisfy the conditions (27), (28) and (30), but is otherwise arbitrary. If we choose $s(y)$ so that the integral in (33) is as small as possible (given particular values $\delta\lambda$ and $\delta\kappa$) we shall have made δE_0 as small as possible. If this minimum value is never negative, no matter what $\delta\lambda$ and $\delta\kappa$ may be, the equilibrium will be stable.

It is therefore necessary to find the minimum value of the integral in (33), subject to the condition (27). This again is an isoperimetric variational problem, and accordingly we consider the first variation of

$$J=\int_0^{\kappa}[s_y^2(1+x_y^2)^{-\frac{3}{2}}+2ps]\,dy, \quad (34)$$

where $2p$ is an arbitrary multiplier. The Euler–Lagrange equation for the vanishing of the first variation is

$$d[s_y(1+x_y^2)^{-\frac{3}{2}}]/dy = p, \quad (35)$$

which is the Jacobi accessory equation for the variational treatment of the energy. A solution to this equation can always be found by differentiation of the equilibrium equation (3), from which we obtain

$$\frac{d}{dy}\left[\frac{\partial x_y}{\partial \mu}(1+x_y^2)^{-\frac{3}{2}}\right] = -1, \tag{36}$$

and also

$$\frac{d}{dy}\left[\frac{dx_y}{dy}(1+x_y^2)^{-\frac{3}{2}}\right] = 1. \tag{37}$$

It is therefore obvious that the general solution of (35) can be written as

$$s = lx_y + (l-p)\,\partial x/\partial\mu + m, \tag{38}$$

where l, m and p are constants. Equation (28) then requires

$$0 = lx_y(y_0) + (l-p)\,(\partial x/\partial\mu)_{y_0} + m \tag{39}$$

and if terms $O(\epsilon)$ are omitted (30) and (27) give respectively

$$\epsilon^{-1}(\delta\lambda - \delta\kappa\cot\theta) = l\cot\theta + (l-p)\,(\partial x/\partial\mu)_\kappa + m, \tag{40}$$

$$-\epsilon^{-1}\lambda\,\delta\kappa = l(\lambda - x_0) + (l-p)\int_{y_0}^{\kappa}\frac{\partial x}{\partial\mu}dy + m(\kappa - y_0). \tag{41}$$

The value of the integral in (33) can be evaluated by integrating by parts and the use of (35). We find

$$\begin{aligned}\epsilon\int_{y_0}^{\kappa} s_y^2(1+x_y^2)^{-\frac{3}{2}}\,dy &= \epsilon\left[ss_y(1+x_y^2)^{-\frac{3}{2}}\right]_{y_0}^{\kappa} - \epsilon p\int_{y_0}^{\kappa} s\,dy \\ &= (\delta\lambda - \delta\kappa\cot\theta)\,(p\kappa - l\mu) + p\lambda\,\delta\kappa,\end{aligned} \tag{42}$$

where the value of x_{yy} from (3) and $\partial x_y/\partial\mu$ obtained from (4) have been inserted.

Equations (39), (40) and (41) can be solved to give l, m and p in terms of $\delta\lambda$ and $\delta\kappa$. These values may be inserted in (42) and finally from (33) the value of δE_0 can be found. The result is obviously of the form

$$\delta E_0 = a\delta\lambda^2 + b\,\delta\lambda\,\delta\kappa + c\,\delta\kappa^2, \tag{43}$$

and (if a is positive) δE_0 will always be positive provided

$$4ac \geqslant b^2, \tag{44}$$

which serves as the criterion for stability.

Since the algebra involved in simplifying this inequality is so complicated, a brief outline of the steps has been placed in the appendix. It is shown that (44) finally reduces to the condition

$$0 \leqslant \left\{\frac{d\alpha}{d\kappa}[x + (\mu - y)\,x_y] + (\kappa - \mu)\left[x_y\int_0^y \frac{\partial x}{\partial\mu} - x\frac{\partial x}{\partial\kappa}\right]\right\}_{y=y_0}. \tag{45}$$

We shall later consider the behaviour of this result when y_0 tends to zero. If we had chosen y_0 equal to zero initially, then since x_y tends to infinity as y_0 tends to zero, and s must be zero there, it follows from the expression (38) that l and m would have to be zero. The expression for s would then simply be $-p\,\partial x/\partial\mu$.

This contains only one adjustable constant, but two conditions, namely (30) and (27), have to be satisfied. This can only be achieved if there is a particular relation between $\delta\lambda$ and $\delta\kappa$. Equation (30) gives

$$\delta\lambda - \delta\kappa \cot\theta = -\epsilon p(\partial x/\partial\mu)_\kappa + O(\epsilon^2), \tag{46}$$

and (27) gives

$$\lambda\, \delta\kappa = \epsilon p \int_0^\kappa \frac{\partial x}{\partial\mu} dy + O(\epsilon^2). \tag{47}$$

By differentiation of (2) we find

$$\int_0^\kappa \frac{\partial x}{\partial\mu} dy = \frac{d\alpha}{d\mu} - \lambda \frac{d\kappa}{d\mu}. \tag{48}$$

Hence by eliminating p from (46) and (47) we find

$$\frac{\delta\lambda}{\delta\kappa} = \left(\frac{d\alpha}{d\mu}\cot\theta - \lambda\frac{d\lambda}{d\mu}\right)\left(\frac{d\alpha}{d\mu} - \lambda\frac{d\kappa}{d\mu}\right)^{-1} + O(\epsilon). \tag{49}$$

We can now evaluate δE_0 in (33), using (42) (with l and m zero), the value of p from (46) and the value of $\delta\lambda/\delta\kappa$. The final result is

$$\delta E_0/\delta\kappa^2 = \frac{d\alpha}{d\kappa}(\mu - \kappa)\left(\frac{d\alpha}{d\kappa} - \lambda\right)^{-2} \frac{d}{d\kappa}(\lambda^2 - 2\alpha\cot\theta). \tag{50}$$

4. Discussion

The stability criterion (45) has been deduced from the requirement that the change in total energy is positive when the shape of the drop is distorted by a small perturbation which extends over the surface between the height y_0 and the point of support, where y is equal to κ. Any naturally occurring perturbation must in fact extend over the whole surface, and so we must examine the behaviour of the criterion as y_0 approaches zero.

Let us first examine the inequality (45) when y_0 tends to κ. Use of the expression (32) and equation (48) shows that in this limit the criterion reduces to the condition

$$0 \leqslant \lambda^2\mu, \tag{51}$$

which is always true.

If we now allow y_0 to approach zero, where x_y is infinite, and evaluate the terms in (45) by means of (32), we find

$$0 \leqslant \mu(d\alpha/d\kappa)\, x_y + O(y_0^{\frac{1}{2}}). \tag{52}$$

It follows that, if $d\alpha/d\kappa$ is negative, as y_0 approaches zero the inequality is not satisfied. (The occurrence of the factor x_y, which is infinite at the origin, arises from the cancellation of factors in the manipulation of the condition (44), as explained in the appendix. We are only interested in the sign of the term in (52).) Hence, when the cross-section α of the drop in equilibrium decreases with increasing height κ, the drop is unstable. When α increases with κ, the drop is stable.

It is of interest to examine the behaviour of (50), which is deduced by assuming at the outset that the perturbation extends over the whole surface. It can be shown by a rather lengthy argument which we omit that, in this expression, the

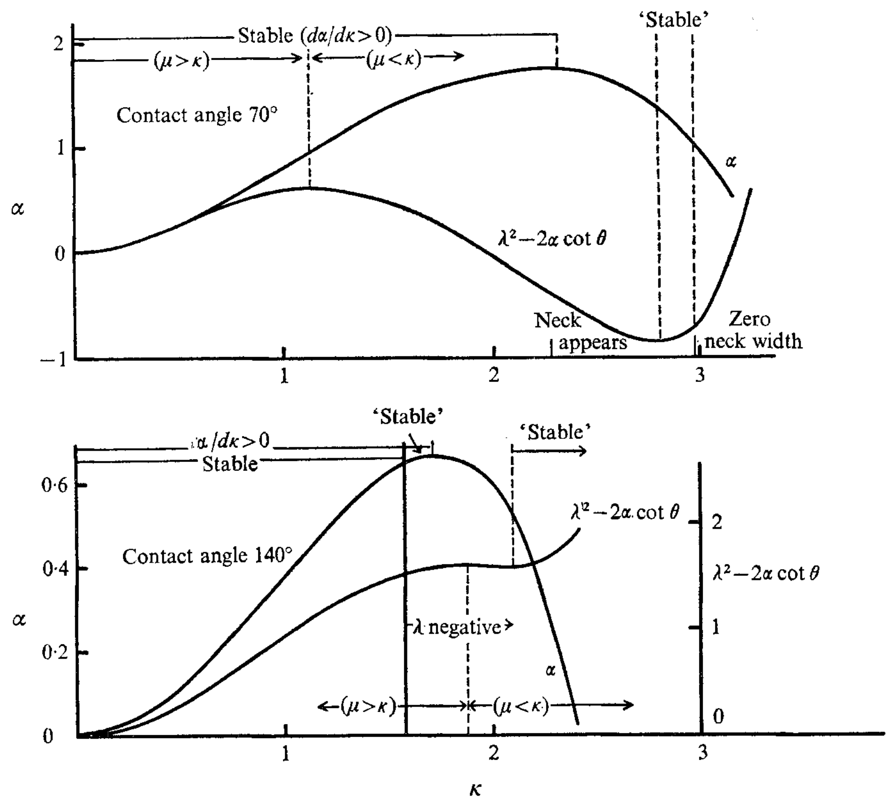

FIGURE 6. The stability criterion according to (50), showing spurious regions of stability when $d\alpha/d\kappa$ is negative.

right-hand side is always positive whenever $d\alpha/d\kappa$ is positive. Thus the result here agrees with that obtained from the limiting process applied to (45). However, a difference appears when $d\alpha/d\kappa$ is negative. It is indeed true that, as $d\alpha/d\kappa$ passes from positive to negative values, δE_0 in (50) changes from positive to negative, but for some regions where $d\alpha/d\kappa$ is negative, δE_0 in equation (50) may be positive. This is illustrated in figure 6 for contact angles of 70° and 140°. Examination of the gradients of the curves and the expression (50) reveals a region where δE_0 is positive although $d\alpha/d\kappa$ is negative. This result arises because equation (50) corresponds to a particular value of the ratio $\delta\lambda/\delta\kappa$, and is not a correct description of the conditions when the perturbation is entirely arbitrary and $\delta\lambda$ and $\delta\kappa$ can take any values whatever.

Figure 6 also illustrates another feature of the results. It will be seen that, for a contact angle of 140°, the value of λ becomes negative before the maximum theoretical cross-section is reached. This obviously corresponds to physically impossible conditions, and the drops must fall when λ becomes zero. Up to this stage the drops are stable, since $d\alpha/d\kappa$ is positive.

The outcome of the analysis is therefore the conclusion that, whenever the volume of the drop increases with increasing height, the equilibria are stable. Those equilibria in the region where the volume decreases with increasing height are unstable. These results are in agreement with the assertion made by Wangerin in his comments on Neumann's work. An interesting feature of the problem is the need to approach the perturbed state by allowing a perturbation limited to a part of the surface to extend over the whole surface, rather than assume this at the outset.

I am grateful for helpful discussions with Mr Marriage of these Laboratories, for the stimulus provided by the numerical investigations which Dr Padday and his colleagues have completed, and for the comments of a referee on the presentation of this work.

Appendix

We have to solve (39), (40) and (41) for l, m and p. We define

$$L = \int_{y_0}^{\kappa} \frac{\partial x_y}{\partial \mu} dy, \quad L_1 = \int_{y_0}^{\kappa} (\kappa - y) \frac{\partial x_y}{\partial \mu} dy, \tag{A 1), (A 2}$$

$$M = \int_{y_0}^{\kappa} x_{yy}\, dy, \quad M_1 = \int_{y_0}^{\kappa} (\kappa - y)\, x_{yy}\, dy, \tag{A 3), (A 4}$$

and put

$$D = \begin{vmatrix} x_y(y_0) & (\partial x/\partial \mu)_{y_0} & 1 \\ \cot\theta & (\partial x/\partial \mu)_{\kappa} & 1 \\ \lambda - x_0 & \int_{y_0}^{\kappa} \frac{\partial x}{\partial \mu} dy & \kappa - y_0 \end{vmatrix}$$

$$= ML_1 - M_1 L. \tag{A 5}$$

From (39), (40) and (41) we find

$$\epsilon l D = (\delta\lambda - \delta\kappa \cot\theta)\, L_1 + \lambda\, \delta\kappa L, \tag{A 6}$$

$$\epsilon p D = (\delta\lambda - \delta\kappa \cot\theta)\,(L_1 + M_1) + \lambda\, \delta\kappa (L + M). \tag{A 7}$$

From (42) we therefore obtain

$$\epsilon^2 D \int_{y_0}^{\kappa} s_y^2 (1 + x_y^2)^{-\frac{3}{2}}\, dy = A_0(\delta\lambda - \delta\kappa \cot\theta)^2 + B_0 \lambda\, \delta\kappa (\delta\lambda - \delta\kappa \cot\theta) + C_0 \lambda^2 \delta\kappa^2, \tag{A 8}$$

where

$$A_0 = (\kappa - \mu)\, L_1 + \kappa M_1, \tag{A 9}$$

$$B_0 = (\kappa - \mu)\, L + \kappa M + L_1 + M_1, \tag{A 10}$$

$$C_0 = L + M. \tag{A 11}$$

This result is substituted in (33) and we obtain

$$2\delta E_0 = A_1 \delta\lambda^2 + B_1 \delta\lambda\, \delta\kappa + C_1 \delta\kappa^2, \tag{A 12}$$

where

$$A_1 = A_0 D^{-1}, \tag{A 13}$$

$$B_1 = [\lambda B_0 + 2D(\kappa - \mu) - 2A_0 \cot\theta]\, D^{-1}, \tag{A 14}$$

$$C_1 = [\lambda D - (\kappa - \mu)\, D \cot\theta + A_0 \cot^2\theta - \lambda\, B_0 \cot\theta + \lambda^2 C_0]\, D^{-1}. \tag{A 15}$$

We have now to consider the signs of A_0 and D. From (3) we have

$$x_{yy} = (y - \mu)\,(1 + x_y^2)^{\frac{3}{2}}, \tag{A 16}$$

and from (4) we derive

$$\partial x_y/\partial \mu = -y(1+x_y^2)^{\frac{3}{2}}. \tag{A 17}$$

Then, from the definitions in (A 9), (A 2) and (A 4)

$$A_0 = -\mu\int_{y_0}^{\kappa} (\kappa - y)^2 (1+x_y^2)^{\frac{3}{2}}\, dy, \tag{A 18}$$

which is negative. The sign of D may be found as follows. Put

$$r_n = \int_{y_0}^{\kappa} y^n (1+x_y^2)^{\frac{3}{2}}\, dy. \tag{A 19}$$

Then from the definitions and the expression (A 5) we find

$$D = -\mu(r_2 r_0 - r_1^2). \tag{A 20}$$

Since

$$\int_{y_0}^{\kappa} (y+\nu)^2 (1+x_y^2)^{\frac{3}{2}}\, dy = r_2 + 2\nu r_1 + \nu^2 r_0$$

is always positive, it follows that

$$r_0 r_2 \geqslant r_1^2,$$

and hence D is negative. Thus, A_1 in (A 13) is positive.

The expression (A 12) for δE_0 will therefore always be positive provided

$$4A_1 C_1 \geqslant B_1^2. \tag{A 21}$$

In manipulating this expression, reference to (A 13), (A 14) and (A 15) shows that on the left-hand side there is a term $4\lambda^2 A_0 C_0 D^{-1}$ and on the right-hand side a term $\lambda^2 B_0^2$. Now from the expressions (A 16) and (A 17) we find that

$$L_1 + M_1 = (\kappa - \mu) L + \kappa M, \tag{A 22}$$

and so from (A 10) we may write

$$B_0^2 = 4[(\kappa-\mu) L + \kappa M][L_1 + M_1]. \tag{A 23}$$

With this result, we then find

$$4A_0 C_0 - B_0^2 = -4\mu D, \tag{A 24}$$

and when this is used in (A 21) we find that, after cancellation of common terms appearing on both sides of the inequality, we can divide throughout by D. Since this is negative, the sense of the inequality is changed after the division, and we obtain

$$\mu\lambda^2 + \lambda B_0(\kappa-\mu) - [\lambda + (\kappa-\mu)\cot\theta] A_0 + D(\kappa-\mu)^2 \geqslant 0. \tag{A 25}$$

When the expressions for L, L_1 etc. are integrated and inserted in A_0, B_0 and D, after straightforward manipulation we obtain (45), when (23) is used.

It should be noted that the common factor D^{-2} has been cancelled on both sides of (A 21). If this were retained, then both sides of (A 25) would be divided by $|D|$. As y_0 tends to zero, $|D|$ is $O(x_y)$, and the resulting leading term in the inequality would remain finite, other terms being $O(x_y^{-1})$. However, we are only interested in the sign, so that (A 25) is sufficient for our purposes.

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