J. Fluid Mech. (1974), *vol.* 63, *part* 3, *pp.* 487–508
Printed in Great Britain

The stability of pendent liquid drops. Part 2. Axial symmetry

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(Received 8 June 1973)

In a drop of liquid which hangs below a horizontal support or at the end of a tube, the forces due to surface tension, pressure and gravity are in equilibrium. Amongst the many possible equilibrium shapes of the drop, only those which are stable occur naturally. The calculus of variations has been used to determine theoretically the stable equilibria, by calculating the energy change when the liquid in equilibrium experiences axially symmetrical perturbations under physically realistic constraints. If the energy change can be made negative, the drop is unstable. With this criterion, stable equilibria have been identified through which the naturally growing drops evolve until they reach a maximum volume, when they become unstable. These results are illustrated by calculations relating to typical experimental conditions.

1. Introduction

A drop of water hanging from a tap and drops of condensation on a ceiling are familiar phenomena which illustrate the balancing of forces due to surface tension, pressure and gravity. Measurements of drop shape have often been used as a means of determining surface tension, and for this reason considerable effort has been devoted in the past to the calculation of drop profiles by numerical integration of the equations determining the equilibrium. Bakker (1928) has summarized many of the results and discussed their practical application. Recently, Padday (1971) has made available extensive tables giving the equilibrium profiles of many axially symmetrical menisci, including those of pendent drops.

Amongst the earlier work that of Lohnstein (1906*a*, *b*, 1907) is particularly important. He showed that, for a drop hanging below a horizontal support which it wets, the area of contact cannot exceed a certain value. He also studied drops hanging from the end of a tube and showed that their maximum volumes depend on the radius of the tube. His aim was primarily to enable more accurate values of surface tension to be derived from experiment, and he introduced a hypothesis which enabled him to find the weight of liquid which fell from the drop when its limiting volume was exceeded.

All of this work was exclusively concerned with the determination of equilibrium shapes and the question of their stability was ignored. It is however not clear *a priori* whether the maximum drop volumes predicted by Lohnstein can be achieved in practice, or whether instability occurs at an earlier stage. An investigation of this possibility has recently been undertaken by Padday & Pitt (1973), using numerical methods. Unfortunately this approach requires an arbitrary assumption about the nature of the perturbation with respect to which stability is to be calculated. There remains doubt whether stability has been proved for other possible perturbations having the same symmetry.

To avoid this difficulty an analytical method is necessary and we shall present here a study of the stability of axially symmetrical pendent drops, using the calculus of variations. This method was used in an earlier publication (Pitts 1973, referred to subsequently as I) examining the stability of 'two-dimensional' drops, where the equilibrium profiles can be expressed in known functions. In contrast, axially symmetrical drop profiles cannot be expressed in closed form, and the stability problem is more troublesome. However, some easily interpreted results are nevertheless obtainable.

We shall consider three situations. First, we shall determine the stability of a drop hanging from a ceiling. The volume of liquid will be supposed fixed, but the area of contact and the height and shape of the drop can be perturbed. On simple physical grounds we expect the equilibrium volumes to be less than some limiting value (as Lohnstein showed by his calculations) and we shall investigate the stability of all the equilibria. The second problem is the stability of a drop of fixed volume hanging from a tube, where perturbations can only alter the drop height and shape. The third problem, whose equilibrium was studied by Lohnstein, relates to liquid held in a drop at the end of a tube by means of a suitable constant pressure applied to the liquid in the tube. Here perturbations occur at constant pressure and both the volume and the profile of the drop can change.

It will be assumed that the perturbations are axially symmetrical. In §2 the variational method will be outlined and subsequent sections will be based on this account.

2. A drop hanging from a horizontal support

2.1. *Equilibrium and stability*

We imagine a horizontal plane below which a drop of liquid hangs. The origin of co-ordinates is taken at the apex of the drop, with the x axis horizontal and the y axis vertically upwards (see figure 1). The support is the plane $y = h$. We require an expression for the energy of the drop. We consider an elementary slice of thickness dy and radius $x(y)$. If ds is the length of the profile of the drop intercepted by the slice, surface tension contributes energy $2\pi\gamma x\, ds$, where γ is the surface tension. If we reckon potential energy with reference to the horizontal support, the elementary slice will have lost potential energy equal to $\rho g \pi x^2 (h-y)\, dy$. Finally, there will be a contribution due to the interfacial energy of the liquid and the support. If x_0 is the radius of the liquid–support interface, the interfacial energy can be written as $\pi b x_0^2$, where b is a constant characterizing the liquid and the material of the support. Thus the total energy is

$$E = \int_0^h \left[2\pi\gamma x \frac{ds}{dy} - \pi\rho g (h-y)\, x^2 \right] dy + \pi b x_0^2,$$

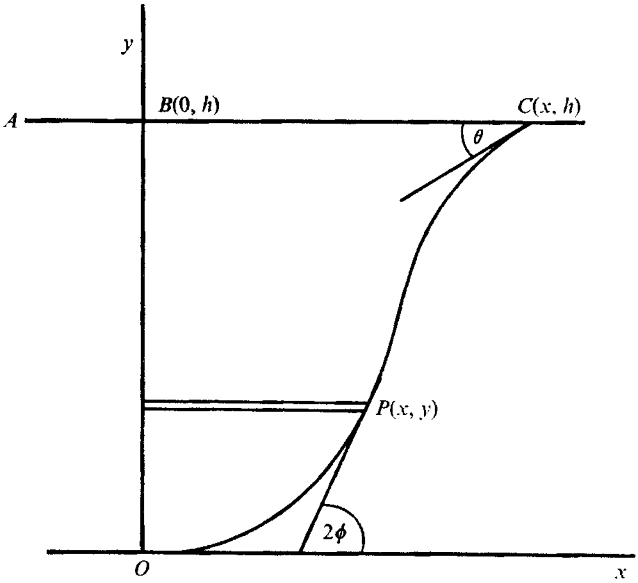

FIGURE 1. The co-ordinate system.

and the volume V of the drop is

$$V = \pi \int_0^h x^2 dy.$$

The equilibrium shape of the drop is obtained by finding the profile $x(y)$ which minimizes E while keeping V constant. This is a typical isoperimetric problem in the calculus of variations and we can immediately use the standard results. The Euler–Lagrange equation (for the vanishing of the first variation) yields the well-known equations relating hydrostatic pressure, surface tension and the curvature of the surface. Also, the end-point conditions show that the profile of the drop must cut the y axis at the origin at right angles, and at the support the relation

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

where θ is the angle of contact (see figure 1), must hold. Further, the profile cannot have any corners. These results can of course be derived more directly by simple physical arguments.

We shall now rewrite the basic equations, using dimensionless variables. Taking $(\gamma/\rho g)^{\frac{1}{2}}$ as the unit of length we define κ and λ by the equations

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

Corresponding to the energy and the volume we introduce dimensionless quantities E_0 and v defined by the equations

$$E_0 = E\rho g/\pi\gamma^2, \quad v = V(\rho g)^{\frac{3}{2}}/\pi\gamma^{\frac{3}{2}}.$$

If we use a suffix to denote differentiation (e.g. $x_y \equiv dx/dy$) the equations are

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

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

Equilibrium is determined by the vanishing of the first variation of $E_0 - \mu v$, where μ is an arbitrary multiplier. The Euler–Lagrange equation is

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

This may be rearranged in two familiar forms

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

and

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

From (3*b*) we see that μ is the sum of the curvatures at the origin and is necessarily positive for a pendent drop. At the point C in figure 1 we must have

$$x_y(\kappa) = \cot\theta. \tag{4}$$

Near the origin

$$x = 2y^{\frac{1}{2}}\mu^{-\frac{1}{2}} + O(y^{\frac{3}{2}}), \tag{5}$$

and near C

$$x = \lambda + (y-\kappa)\cot\theta + \tfrac{1}{2}(y-\kappa)^2[\lambda(\kappa-\mu)+\sin\theta]\,\lambda^{-1}\sin^{-3}\theta + O(y-\kappa)^3. \tag{6}$$

Here the value of $x_{yy}(\kappa)$ has been evaluated from (3*b*).

By integration of (3*c*) over the range 0 to κ, after integrating by parts and using (4) we find

$$v = \lambda^2(\kappa-\mu) + 2\lambda\sin\theta, \tag{7}$$

i.e. the weight is balanced by the forces due to pressure and surface tension at the interface. This result is the only integral of (3) which can be obtained in closed form. Extensive numerical tables of solutions have been made available by Padday (1971). Here we shall only remark that when μ is given, that is, the curvature at the origin is prescribed, numerical integration gives x as a function of y. The height κ is then determined by (4), which likewise determines λ. Hence from (7) the value of v can be found. The quantities κ, λ and v for the equilibrium drop can be regarded as dependent on the parameter μ.

We can differentiate E_0 in (1) with respect to μ, and after integration by parts, the use of (3) and evaluation of the limits by means of (5) and (6) we finally obtain

$$dE_0/d\mu = (\mu-\kappa)\,dv/d\mu, \tag{8}$$

a result which exactly corresponds to that in I. In (8), $\mu-\kappa$ is the sum of the curvatures at the horizontal support and so is proportional to the pressure in the liquid. The result (8) therefore expresses the change in energy as the product of the volume change and the pressure at which the element of volume must be introduced at the reference level. We note that, when the equilibrium volume has a maximum, the energy passes through a turning point; in fact since μ is then less than κ, E_0 passes through a minimum.

In order to investigate the stability of the equilibria described by the solutions of (3) we need the change δE_0 in the energy caused by perturbation of the drop. We suppose first of all that small changes $\delta\lambda$ and $\delta\kappa$ are made in λ and κ, and that the profile of the drop is unchanged from the apex up to a height y_0 (which will later be made to approach zero), and therefore the profile is $x(y)+\epsilon s(y)$. (See

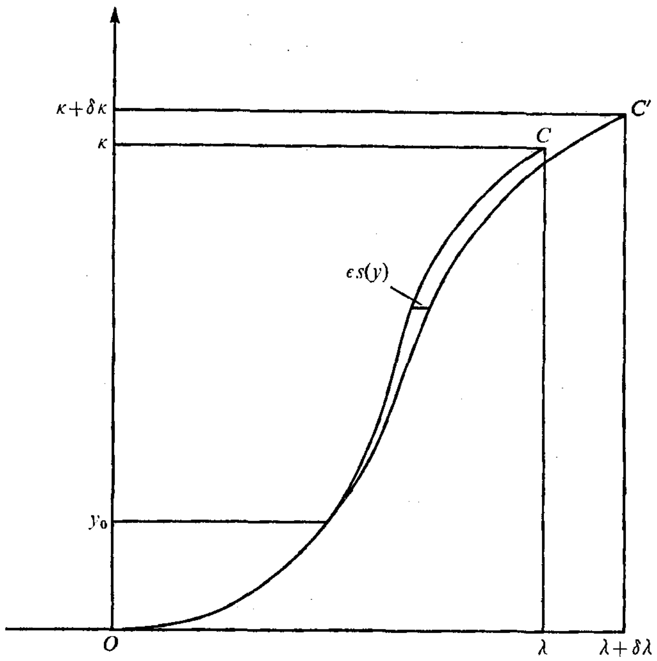

FIGURE 2. The variation of the profile.

figure 2.) Here $x(y)$ is the equilibrium profile and $\epsilon s(y)$ is the perturbation, ϵ being of the same magnitude as $\delta\lambda$ and $\delta\kappa$. The changed values of x, λ and κ are substituted in (1) to give the new value $E_0 + \delta E_0$. By subtraction δE_0 is obtained, the evaluation being continued as far as terms $O(\epsilon^2)$. The procedure is similar to that described in I. From geometry, we have

$$\epsilon s(y_0) = 0 \tag{9}$$

and

$$x(\kappa+\delta\kappa) + \epsilon s(\kappa+\delta\kappa) = \lambda + \delta\lambda. \tag{10}$$

The condition for constant volume is

$$\int_0^{\kappa} x^2\,dy = \int_0^{\kappa+\delta\kappa} (x+\epsilon s)^2\,dy. \tag{11}$$

After extensive manipulation and use of (3), (5) and (6) we obtain

$$\begin{aligned}\delta E_0 = &-\delta\lambda^2\cos\theta + 2\delta\lambda\,\delta\kappa[\lambda(\kappa-\mu)+\operatorname{cosec}\theta] \\ &+\tfrac{1}{2}\delta\kappa^2[\lambda^2 - 2\operatorname{cosec}\theta\cot\theta - 2\lambda(\kappa-\mu)\cot\theta] \\ &+\epsilon^2\int_{y_0}^{\kappa+\delta\kappa}[s^2(y-\mu) + 2ss_y x_y(1+x_y^2)^{-\frac{1}{2}} + xs_y^2(1+x_y^2)^{-\frac{3}{2}}]\,dy.\end{aligned} \tag{12}$$

(All first-order terms cancel, because of the equilibrium equations.) This expression for δE_0 evidently depends upon the function $s(y)$, which apart from satisfying (9)–(11) is otherwise arbitrary. If we choose $s(y)$ so that the integral in (12) is minimized for the given values of $\delta\lambda$ and $\delta\kappa$, we shall obtain the least possible value of δE_0. If this is always positive, no matter what $\delta\lambda$ and $\delta\kappa$, the equilibrium will be stable for this type of perturbation.

We therefore have to determine s to minimize the integral, subject to the condition (11), which may be written as

$$-\int_{\kappa}^{\kappa+\delta\kappa} x^2\,dy = 2\epsilon\int_{y_0}^{\kappa+\delta\kappa} xs\,dy + \epsilon^2\int_{y_0}^{\kappa+\delta\kappa} s^2\,dy. \tag{13}$$

This is again an isoperimetric variational problem. Following the standard method, we multiply (13) by an arbitrary multiplier (written as ϵa_1 for convenience) and add it to the integral in (12). We therefore seek the unconditional minimum of

$$J = \epsilon^2\int_{y_0}^{\kappa} [s^2(y-\mu) + 2a_1 sx + 2ss_y x_y(1+x_y^2)^{-\frac{1}{2}} + xs_y^2(1+x_y^2)^{-\frac{3}{2}}]\,dy. \tag{14}$$

The Euler–Lagrange equation is

$$s(y-\mu) + a_1 x + s_y x_y(1+x_y^2)^{-\frac{1}{2}} = d[sx_y(1+x_y^2)^{-\frac{1}{2}} + xs_y(1+x_y^2)^{-\frac{3}{2}}]/dy. \tag{15}$$

If we put

$$f = x(1+x_y^2)^{-\frac{3}{2}} \tag{16}$$

and use (3b) we find that (15) may be written as

$$d(fs_y)/dy + sx^{-1}(1+x_y^2)^{-\frac{1}{2}} = a_1 x. \tag{17}$$

This is the Jacobi accessory equation for our variational problem.

By integration by parts and use of (15) we find

$$\int_{y_0}^{\kappa} s_y\,[sx_y(1+x_y^2)^{-\frac{1}{2}} + xs_y(1+x_y^2)^{-\frac{3}{2}}]\,dy$$
$$= [s^2x_y(1+x_y^2)^{-\frac{1}{2}} + xss_y(1+x_y^2)^{-\frac{3}{2}}]_{y_0}^{\kappa} - \int_{y_0}^{\kappa} s[s_y x_y(1+x_y^2)^{-\frac{1}{2}} + s(y-\mu) + a_1 x]\,dy. \tag{18}$$

Hence we derive

$$\begin{aligned}\delta E_0 = {} & -\delta\lambda^2\cos\theta + 2\delta\lambda\,\delta\kappa[\lambda(\kappa-\mu) + \operatorname{cosec}\theta] \\ & + \tfrac{1}{2}\delta\kappa^2[\lambda^2 - 2\operatorname{cosec}\theta\cot\theta - 2\lambda(\kappa-\mu)\cot\theta] \\ & + \epsilon^2[s^2(\kappa)\cos\theta + \lambda s(\kappa)\,s_y(\kappa)\sin^3\theta] - \epsilon^2 a_1\int_{y_0}^{\kappa} xs\,dy. \end{aligned} \tag{19}$$

From (10) we can find $\epsilon s(\kappa)$ and from (13) the term in a_1 can be evaluated. Substitution then gives

$$\begin{aligned}\delta E_0 = {} & 2\delta\lambda\,\delta\kappa[\lambda(\kappa-\mu) + \sin\theta] + \tfrac{1}{2}\delta\kappa^2[\lambda^2 - 2\cos\theta - 2\lambda(\kappa-\mu)\cot\theta] \\ & + \epsilon s_y(\kappa)\,(\delta\lambda - \delta\kappa\cot\theta)\,\lambda\sin^3\theta + \tfrac{1}{2}\epsilon a_1\lambda^2\,\delta\kappa. \end{aligned} \tag{20}$$

We now have to obtain an $s(y)$ which satisfies (15). If we differentiate the equilibrium equation (3a) with respect to y, there results

$$x_y(y-\mu) + x + x_y x_{yy}(1+x_y^2)^{-\frac{1}{2}} = d[x_y^2(1+x_y^2)^{-\frac{1}{2}} + xx_{yy}(1+x_y^2)^{-\frac{3}{2}}]/dy. \tag{21}$$

Differentiation of (3a) with respect to μ gives

$$\frac{\partial x}{\partial\mu}(y-\mu) - x + x_y\frac{\partial x_y}{\partial\mu}(1+x_y^2)^{-\frac{1}{2}} = \frac{d}{dy}\left[x_y\frac{\partial x}{\partial\mu}(1+x_y^2)^{-\frac{1}{2}} + x\frac{\partial x_y}{\partial\mu}(1+x_y^2)^{-\frac{3}{2}}\right]. \tag{22}$$

By comparison with (15) we see that a particular solution is

$$s(y) = -a_1 \partial x/\partial\mu.$$

To this must be added the solutions of the homogeneous equation (i.e. equation (15) with a_1 equal to zero). By adding (21) and (22) we see that

$$r(y) = x_y + \partial x/\partial\mu \tag{23}$$

is one solution of the homogeneous equation. Standard methods show that the other solution $t(y)$ is given by

$$t(y) = -r\int_c^y (fr^2)^{-1}\,du, \tag{24}$$

where c is a constant. The general expression for s is therefore

$$s = -a_1\,\partial x/\partial\mu + a_2 r + a_3 t, \tag{25}$$

where a_1, a_2 and a_3 are constants. These are determined by the conditions (9), (10) and (13), whence we obtain

$$0 = -\epsilon a_1(\partial x/\partial\mu)_{y_0} + \epsilon a_2 r(y_0) + \epsilon a_3 t(y_0), \tag{26}$$

$$\delta\lambda - \delta\kappa\cot\theta = -\epsilon a_1(\partial x/\partial\mu)_\kappa + \epsilon a_2 r(\kappa) + \epsilon a_3 t(\kappa), \tag{27}$$

$$-\tfrac{1}{2}\lambda^2\delta\kappa = -\epsilon a_1\int_{y_0}^{\kappa} x\frac{\partial x}{\partial\mu}dy + \epsilon a_2\int_{y_0}^{\kappa} xr\,dy + \epsilon a_3\int_{y_0}^{\kappa} xt\,dy. \tag{28}$$

It is possible to manipulate these equations in a way analogous to that in I. In spite of considerable simplification, the result is too complicated to be very informative until we allow y_0 to tend to zero so that the perturbation extends over the entire surface of the drop. We shall therefore evaluate the constants bearing in mind that y_0 will be made to go to zero.

Near the origin, we see from (5) that

$$r = O(y^{-\frac{1}{2}}\mu^{-\frac{1}{2}}), \tag{29}$$

and hence

$$t = O(-y^{-\frac{1}{2}}\ln y). \tag{30}$$

Thus as y_0 tends to zero

$$(rt^{-1})_{y_0} \to 0. \tag{31}$$

If we divide (26) throughout by $t(y_0)$ and let y_0 tend to zero, we find

$$a_3 = O(rt^{-1})_{y_0} \to 0. \tag{32}$$

We may then solve equations (27) and (28) for a_1 and a_2. In simplifying the result, we use the definition in (23) and evaluate derivatives at κ from (6). Also, from (2) we have

$$\frac{dv}{d\mu} = \lambda^2\frac{d\kappa}{d\mu} + 2\int_0^{\kappa} x\frac{\partial x}{\partial\mu}dy. \tag{33}$$

If we put

$$N = 3v\cot\theta - \lambda^3, \tag{34}$$

we find

$$\epsilon a_1 \frac{dN}{d\mu} = 3\left(\frac{dv}{d\mu} - \lambda^2 \frac{d\kappa}{d\mu} + \lambda^2\right)\delta\lambda - \frac{dN}{d\mu}\delta\kappa, \tag{35}$$

$$\epsilon a_2 \frac{dN}{d\mu} = 3\left(\frac{dv}{d\mu} - \lambda^2 \frac{d\kappa}{d\mu}\right)\delta\lambda - \frac{dN}{d\mu}\delta\kappa. \tag{36}$$

With these results we obtain

$$\epsilon s_y(\kappa) = \left(3\frac{dv}{d\mu}\delta\lambda - \frac{dN}{d\mu}\delta\kappa\right)[\lambda(\kappa-\mu)+\sin\theta]\left(\lambda\sin^3\theta\frac{dN}{d\mu}\right)^{-1}. \tag{37}$$

The expression for δE_0 in (20) can now be evaluated. After much algebra, and using the value of $dv/d\mu$ found by differentiating (7), we obtain

$$\delta E_0 = 3\,\delta\lambda^2[\lambda(\kappa-\mu)+\sin\theta]\frac{dv}{d\mu}\left(\frac{dN}{d\mu}\right)^{-1}. \tag{38}$$

It will be noticed that there are no terms in $\delta\lambda\,\delta\kappa$ or $\delta\kappa^2$.

This result has been obtained by allowing y_0 to tend to zero. If we had assumed at the outset that y_0 was zero, then in order that $s(y_0)$ remained finite, we would have been obliged to have had a_2 and a_3 both zero. To satisfy (27) and (28) it would then have been necessary to assume that a_1 and also $\delta\lambda/\delta\kappa$ had particular values. With these values, the calculation of δE_0 again yields (38), a result we shall discuss in § 2.2.

In the foregoing it has been assumed that $\delta\lambda$ and $\delta\kappa$ do not both vanish. We have now to investigate the possibility that the perturbation takes place with fixed end points, so that both $\delta\lambda$ and $\delta\kappa$ are zero. We return to the expression (12) for δE_0, and suppose that the perturbation $s(y)$ is zero when $0 \leqslant y \leqslant y_0$ and also when $y_1 \leqslant y \leqslant \kappa$. Since $\delta\lambda$ and $\delta\kappa$ are now zero, we find

$$\delta E_0 = \epsilon^2 \int_{y_0}^{y_1} [s^2(y-\mu) + 2ss_y x_y(1+x_y^2)^{-\frac{1}{2}} + xs_y^2(1+x_y^2)^{-\frac{3}{2}}]\,dy. \tag{39}$$

The condition for constant volume from (13) is now

$$0 = 2\epsilon\int_{y_0}^{y_1} xs\,dy + \epsilon^2\int_{y_0}^{y_1} s^2\,dy. \tag{40}$$

We may add a multiple ϵa_1 of (40) to (39) and after an integration by parts obtain

$$\delta E_0 = \epsilon^2 \int_{y_0}^{y_1} s\left\{s(y-\mu) + a_1 x + ss_y x_y(1+x_y^2)^{-\frac{1}{2}} - \frac{d}{dy}[sx_y(1+x_y^2)^{-\frac{1}{2}} + xs_y(1+x_y^2)^{-\frac{3}{2}}]\right\}dy + [s^2 x_y(1+x_y^2)^{-\frac{1}{2}} + xss_y(1+x_y^2)^{-\frac{3}{2}}]_{y_2}^{y_1}. \tag{41}$$

Since $s(y_0)$ and $s(y_1)$ are both zero, we can evidently reduce δE_0 to zero provided that $s(y)$ satisfies the Jacobi equation (15). In this case, the energy change is $O(\epsilon^3)$, which can be made positive or negative, so that the equilibrium is unstable.

The solution of the Jacobi equation is given by (25) and the conditions corresponding to (26)–(28) are now

$$0 = -a_1(\partial x/\partial \mu)_{y_0} + a_2 r(y_0) + a_3 t(y_0), \tag{42}$$

$$0 = -a_1(\partial x/\partial \mu)_{y_1} + a_2 r(y_1) + a_3 t(y_1), \tag{43}$$

$$0 = -a_1\int_{y_0}^{y_1} x\frac{\partial x}{\partial \mu}dy + a_2\int_{y_0}^{y_1} xr\,dy + a_3\int_{y_0}^{y_1} xt\,dy. \tag{44}$$

In order that non-zero solutions for a_1, a_2 and a_3 may exist, the determinant of these equations must vanish. Expansion of the determinant gives

$$0 = \left(\frac{\partial x}{\partial \mu}\right)_{y_0}\left[t(y_1)\int_{y_0}^{y_1} xr\,dy - r(y_1)\int_{y_0}^{y_1} xt\,dy\right] + r(y_0)\left[\left(\frac{\partial x}{\partial \mu}\right)_{y_1}\int_{y_0}^{y_1} xt\,dy - t(y_1)\int_{y_0}^{y_1} x\frac{\partial x}{\partial \mu}dy\right] + t(y_0)\left[r(y_1)\int_{y_0}^{y_1} x\frac{\partial x}{\partial \mu}dy - \left(\frac{\partial x}{\partial \mu}\right)_{y_1}\int_{y_0}^{y_1} xr\,dy\right]. \tag{45}$$

Since $t(y_0)$ is $O(y_0^{-\frac{1}{2}}\ln y_0)$ and $r(y_0)$ is $O(y_0^{-\frac{1}{2}})$ as y_0 tends to zero, it may be shown that if (45) is to hold as y_0 tends to zero it is necessary and sufficient that the coefficient of $t(y_0)$ is zero, that is

$$M(y_1) = 0, \tag{46}$$

where

$$M(y) = r\int_0^y x\frac{\partial x}{\partial \mu}dy - \frac{\partial x}{\partial \mu}\int_0^y xr\,dy. \tag{47}$$

Now r satisfies the equation

$$d(fr_y)/dy + rx^{-1}(1+x_y^2)^{-\frac{1}{2}} = 0, \tag{48}$$

and from (22) we have

$$\frac{d}{dy}\left(f\frac{\partial x_y}{\partial \mu}\right) + \frac{\partial x}{\partial \mu}x^{-1}(1+x_y^2)^{-\frac{1}{2}} = -x. \tag{49}$$

If we multiply this equation by r, subtract it from (48) multiplied by $\partial x/\partial \mu$ and integrate we find

$$\int_0^y xr\,dy = f\left(\frac{\partial x}{\partial \mu}r_y - r\frac{\partial x_y}{\partial \mu}\right). \tag{50}$$

(The behaviour of r as y tends to zero shows that the constant of integration is zero.) From the definition in (47) we find

$$M = y^{\frac{3}{2}}\mu^{-\frac{5}{2}} + O(y^{\frac{5}{2}}) \tag{51}$$

and

$$rM_y - r_yM = \left(r_y\frac{\partial x}{\partial \mu} - r\frac{\partial x_y}{\partial \mu}\right)\int_0^y xr\,dy = f^{-1}\left(\int_0^y xr\,dy\right)^2. \tag{52}$$

From these results it follows that the zeros of M and r alternate. Thus M is initially zero and is certainly positive as long as the value of y does not exceed the first zero of r. M changes from positive to negative at a value of y between the first and second zeros of r.

From the definitions we find

$$M(\kappa) = \frac{1}{2}\left(\frac{dv}{d\mu}\cot\theta - \lambda^2\frac{d\lambda}{d\mu}\right)$$

$$= \tfrac{1}{6}\,dN/d\mu. \tag{53}$$

Hence, if $dN/d\mu$ is negative, it follows that, at some point in the range $(0, \kappa)$, M has passed through zero, and so the determinant can be made equal to zero and hence the drop is unstable.

2.2. *Discussion and numerical results*

These results may first of all be compared with those derived in I for the 'two-dimensional' drop. In that case, there is no requirement corresponding to (46) because the two-dimensional drop is always stable when the end points are fixed. This is immediately obvious because the integral for δE_0 corresponding to (39) has an integrand which is essentially positive. When the end points can move, it was shown in I that the condition $\delta E_0 > 0$ led to two different results depending whether it was assumed that y_0 was allowed to tend to zero, or whether it was taken as zero from the outset. In the latter circumstances, the analysis showed that geometrical conditions could only be satisfied by a particular ratio $\delta\lambda/\delta\kappa$, which implied an unrealistic limitation on the possible perturbations. Hence the stability criterion for the two-dimensional drop was deduced by using the limiting process. In the present problem, on the other hand, the analysis in §2.1 shows that, for the axially symmetrical drop, only one result is obtained (namely equation (38)) irrespective of the assumption about y_0. Also, it is interesting to note that (38) is exactly analogous to the result in I which arises by taking y_0 equal to zero initially. This behaviour is related to the fact noted earlier that terms in $\delta\lambda\,\delta\kappa$ and $\delta\kappa^2$ vanish in the result for δE_0. Such terms are present in I and the condition $\delta E_0 > 0$ imposes further requirements which have no counterpart in §2.1.

In the absence of analytical solutions of the equilibrium equations we shall use numerical results to illustrate the implications of (38) and (46). A brief account of the numerical method is placed in the appendix. The method used by Mills (1953) and Stauffer (1965) has been extended to obtain improved accuracy with little extra computing. (Padday (1971) used a geometrical method due to Kelvin, which is less convenient.) Results are calculated by choosing a particular value of θ and taking a set of values of μ. The integration of (3*b*) continues until (4) is satisfied, when the values of κ and λ are obtained. From (7) and (34) values of v and N are then found.

Equation (38) is expressed in terms of derivatives with respect to μ, the curvature at the apex. We could also express δE_0 in terms of dN/dv. However, neither

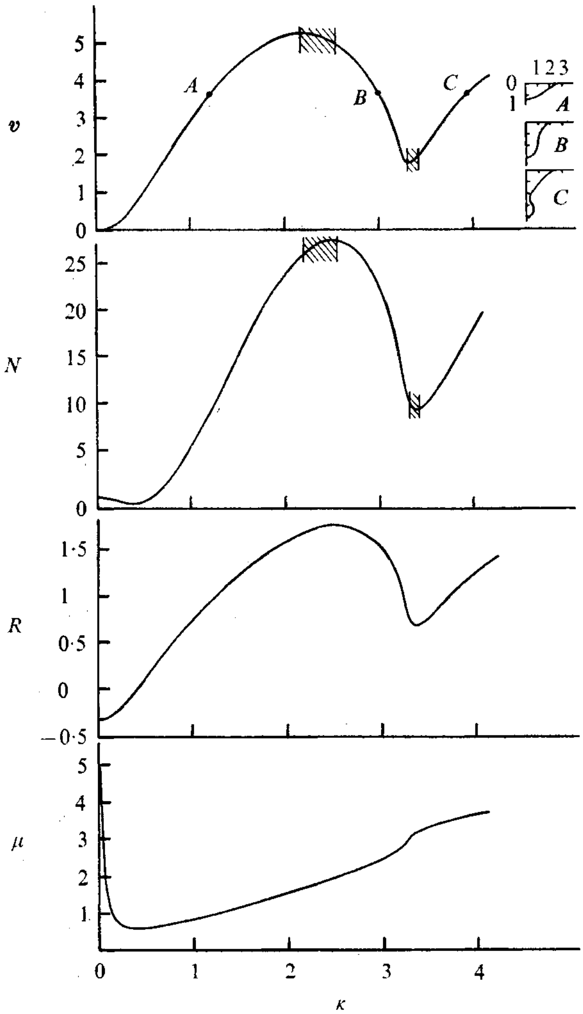

FIGURE 3. Calculated values of v, N, R and μ as functions of κ, for a drop hanging from a ceiling (contact angle 20°). Regions with $\delta E_0 < 0$ according to (38) are shown as hatched areas.

μ nor v is an easily visualized variable, and we shall choose instead the drop height κ as the independent variable. If we put

$$R = \lambda(\kappa - \mu) + \sin\theta, \tag{54}$$

equation (38) may evidently be written as

$$\delta E_0 = 3\,\delta\lambda^2 R \frac{dv}{d\kappa}\left(\frac{dN}{d\kappa}\right)^{-1}. \tag{55}$$

In figure 3 values of v, N, R and μ are shown as functions of κ for a contact angle of 20°. (For a contact angle of 5°, the qualitative features are the same.) It will be seen that initially R, $dN/d\kappa$ and $d\mu/d\kappa$ are all negative, and more detailed plots show that R, $dN/d\kappa$ and $d\mu/d\kappa$ are all zero for the same value of κ. This is a general result which can be demonstrated as follows. By differentiation of (6) we find

$$\left(\frac{\partial x}{\partial \mu}\right)_\kappa \frac{\partial \mu}{\partial \kappa} = \frac{d\lambda}{d\kappa} - \cot\theta, \tag{56}$$

and by differentiation of (4)

$$\left(\frac{\partial x_y}{\partial y}\right)_\kappa + \left(\frac{\partial x_y}{\partial \mu}\right)\frac{\partial \mu}{\partial \kappa} = 0. \tag{57}$$

When $d\mu/d\kappa$ is zero, providing that its coefficients in the preceding equations are finite, we see that

$$d\lambda/d\kappa = \cot\theta \tag{58}$$

and

$$x_{yy}(\kappa) = R\lambda^{-1}\sin^{-3}\theta = 0. \tag{59}$$

Combining these results we see that when $d\mu/d\kappa$ is zero

$$dN/d\kappa = 0. \tag{60}$$

Reference to figure 3 and equation (55) shows that, as v increases from zero with increasing κ, δE_0 is positive until v passes its maximum value, at which E_0 passes through a minimum as shown by (8). (The same result holds for a 5° contact angle.) As the height continues to increase, and the equilibrium volumes decrease, v passes through a minimum and then increases again. The regions in which δE_0 is negative according to (55) have been indicated in the figure. Outside these regions, at points such as A, B and C, whose profiles are shown, δE_0 is positive and the criterion (55) for stability is satisfied. However, we see that for drops such as B the value of $dN/d\kappa$ is negative, and so also is $dN/d\mu$. Hence, M has passed through zero, and according to the argument in §2.1 the drop is unstable. For drops such as C, $dN/d\mu$ has again become positive, which means that M has passed through two zeros and the drop is unstable.

Figure 3 therefore shows that for this contact angle the drop is stable with respect to axially symmetrical perturbations provided that $dv/d\kappa$ is positive since throughout this region $R\,dN/d\kappa$ is positive. A similar result holds for a contact angle of 5°.

A striking change occurs in the appearance of the results for a contact angle of 50°, and those for 70° are qualitatively similar. From figure 4 we see that, as v increases from zero, the drop first has a lens-like shape (e.g. at A). An inflexion point then appears in the profile as the volume and height increase (e.g. at B) and eventually v reaches a maximum. Thereafter v decreases and at first κ increases, but eventually reaches a maximum, and then both v and κ decrease together. The profiles of the drops corresponding to the points A, B, C, D and E are illustrated. Consideration of the curves for N and R also shows that according to (55) δE_0 is negative in the regions shown. At C, $dN/d\kappa$ changes sign, and for points between C and P (corresponding to the maximum value of κ) $dN/d\kappa$ is negative while $d\mu/d\kappa$ is positive. At P, $d\mu/d\kappa$ changes sign, becoming negative while $dN/d\kappa$ is positive. Thus, for all drops corresponding to points on the curve containing EDP up to C, $dN/d\mu$ is negative, and so they are unstable. It therefore follows from figure 4 that the growing drops are stable as long as $dv/d\kappa$ is positive.

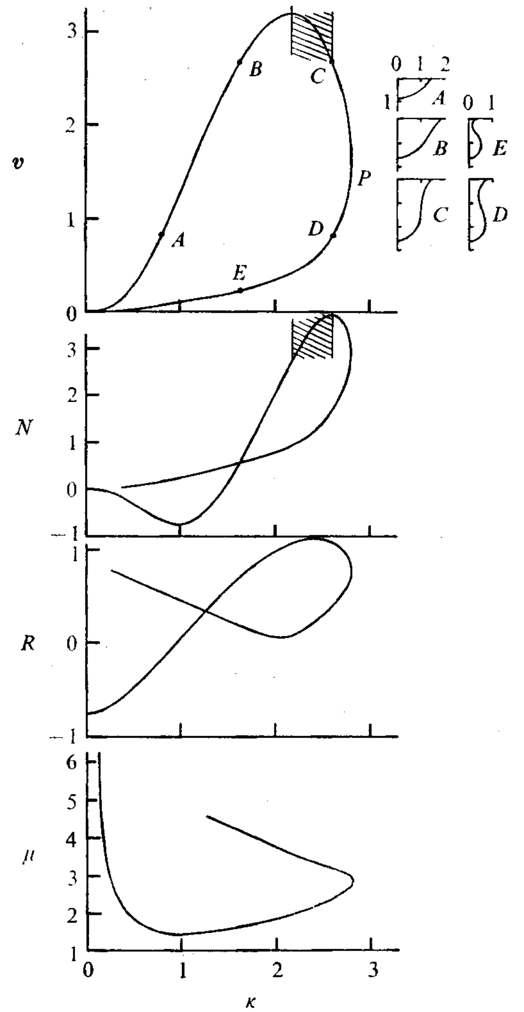

FIGURE 4. Calculated values of v, N, R and μ as functions of κ for a drop hanging from a ceiling (contact angle 50°). Regions with $\delta E_0 < 0$ according to (38) are shown as hatched areas.

The general result of the investigation is that for the contact angles considered the pendent drop grows in volume and height through a sequence of stable equilibria until it reaches its maximum volume. If more liquid is added, no equilibrium is possible, but if liquid is removed there exist equilibria having greater drop heights, which are unstable.

In conclusion, we recall that we have considered only axially symmetrical perturbations which extend over the whole surface of the drop. Other possible types of perturbation would require separate investigation. We have also assumed that the angle of contact is strictly constant. This is often untrue in practice; the angle of contact for a liquid whose area of contact with a solid is increasing may differ substantially from that when the area of the interface is diminishing. The remarkable change in the appearance of the v, κ plots shown in figures 3 and 4 is a noteworthy feature of the equilibrium solutions. More detailed calculations for angles of contact in the range 35°–45° show the very complex behaviour of the v, κ plot in the vicinity of the minimum of v in figure 3.

3. A drop hanging from a tube: constant volume

We imagine a vertical tube having a plunger below which liquid fills the tube and hangs in a drop from its end. When the position of the plunger is fixed, the volume of liquid in the drop is constant. We therefore have to consider the variation of the equilibrium shape of the drop keeping the volume constant, and a large part of the analysis in §2 can be used. When we reckon potential energy relative to the bottom of the tube, the energy is given by (1) without the term $\lambda^2 \cos\theta$. The radius λ of the tube is constant, so that the boundary condition in (4) is replaced by

$$x(\kappa) = \lambda. \tag{61}$$

The angle θ in (4) is no longer a constant, but varies with the volume of the drop. The calculation of the variation of the energy follows exactly the same course as before, but now λ is constant. The expression for δE_0 is given by (12) with $\delta\lambda$ equal to zero. The Jacobi accessory equation is again (17), whose solution has to satisfy conditions (9) and (10) (with $\delta\lambda$ zero) and the constant-volume condition (11). Equations (26)–(28) again apply and as before we find that a_3 must be zero. When $\delta\lambda$ is zero we find from (27) and (28) that

$$\epsilon a_1 = \epsilon a_2 = -\delta\kappa, \tag{62}$$

and hence

$$\epsilon s_y(\kappa) = -\delta\kappa[\lambda(\kappa-\mu)+\sin\theta]\,\lambda^{-1}\sin^{-3}\theta. \tag{63}$$

In this expression, terms in $\partial x_y/\partial\mu$ (which would involve $\partial\theta/\partial\mu$) cancel by virtue of (62). Substituting these results in (20) we find

$$\delta E_0 = 0, \tag{64}$$

that is, δE_0 depends on powers of ϵ greater than the second. (This result is obtained from (38) when $\delta\lambda$ is zero, but the problem requires more careful analysis because θ in the present example is no longer constant. Nevertheless, the disappearance of the terms in $\partial x_y/\partial\mu$ in s_y leads to agreement between (64) and (38) when $\delta\lambda$ is zero.)

Since the drop is in equilibrium, it follows that the coefficient of ϵ^3 in δE_0 must vanish, and δE_0 must depend on ϵ^4. This behaviour is quantitatively quite different from that of the drop on a ceiling discussed in §2. For a given small value of $\delta\kappa$ the energy change for a drop hanging on a tube at constant volume is smaller by two orders of $\delta\kappa$ than the change for the drop hanging from a ceiling. We shall not evaluate δE_0 further, but instead examine a different problem.

4. A drop hanging from a tube: constant pressure

4.1. *Equilibrium and stability*

Again we consider a drop hanging from a vertical tube, but we suppose that its equilibrium volume is controlled by the pressure in the liquid at the mouth of the tube. This pressure is kept constant while the drop is perturbed, and we now have to consider changes in volume.

If p_0 is the pressure at the mouth of the tube and potential energy is reckoned relative to the end of the tube, the energy is

$$E = \int_0^h \left\{2\pi\gamma x \frac{ds}{dy} - \pi x^2[p_0 + \rho g(h-y)]\right\} dy.$$

With the same dimensionless variables as in § 2, and writing

$$\omega = p_0(\gamma\rho g)^{-\frac{1}{2}}, \quad \mu = \kappa + \omega, \tag{65), (66}$$

we find

$$E_0 = \int_0^\kappa [2x(1+x_y^2)^{\frac{1}{2}} + x^2(y-\mu)]\, dy \tag{67}$$

and

$$v = \int_0^\kappa x^2\, dy. \tag{68}$$

The boundary condition is

$$x(\kappa) = \lambda, \tag{69}$$

and we shall define the (variable) angle θ by

$$x_y(\kappa) = \cot\theta$$

[equation (4)].

This is a simpler variational problem than those previously considered, since we are seeking an unconditional minimum of E_0. The Euler–Lagrange equation gives the already-familiar result in (3*a*). We now calculate the second variation of E_0. As before $x(y)$ is replaced by $x+\epsilon s$ and we suppose that $s(y)$ is zero for $0 \leqslant y \leqslant y_0$. We find

$$\begin{aligned}\delta E_0 = {} & -\delta\kappa\,\delta v + \tfrac{1}{2}\delta\kappa^2[\lambda^2 - 2\operatorname{cosec}\theta\cot\theta - 2\lambda(\kappa-\mu)\cot\theta] \\ & + \epsilon^2\int_{y_0}^\kappa [s^2(y-\mu) + 2ss_y x_y(1+x_y^2)^{-\frac{1}{2}} + xs_y^2(1+x_y^2)^{-\frac{3}{2}}]\, dy.\end{aligned} \tag{70}$$

Here

$$\begin{aligned}\delta v &= -\int_0^\kappa x^2\, dy + \int_0^{\kappa+\delta\kappa} (x+\epsilon s)^2\, dy \\ &= \lambda^2\delta\kappa + 2\epsilon\int_{y_0}^\kappa xs\, dy + O(\epsilon^2).\end{aligned} \tag{71}$$

The analysis follows a similar path to that in § 2. In the absence of the constant-volume condition, the Jacobi equation is now

$$s(y-\mu) + s_y x_y(1+x_y^2)^{-\frac{1}{2}} = d[sx_y(1+x_y^2)^{-\frac{1}{2}} + xs_y(1+x_y^2)^{-\frac{3}{2}}]/dy, \tag{72}$$

which corresponds to (17) with a_1 equal to zero. To obtain the solutions, we regard ω as the parameter of the solutions of the equilibrium equation (3a). Differentiation then shows that a solution of (72) is

$$r = \partial x/\partial \omega + (1 + d\kappa/d\omega)\, x_y. \tag{73}$$

The other solution is given by (24). The expression for s is therefore

$$s = a_2 r + a_3 t. \tag{74}$$

Evaluation of the integral in (70) then gives

$$\delta E_0 = -\delta\kappa\,\delta v + \tfrac{1}{2}\delta\kappa^2[\lambda^2 - \cos\theta - \lambda(\kappa-\mu)\cot\theta] - \epsilon\lambda\cot\theta\sin^3\theta\, s_y(\kappa)\,\delta\kappa. \tag{75}$$

There are only two conditions which s must satisfy, namely the geometrical conditions (9) and (10) with $\delta\lambda$ equal to zero. These give respectively

$$0 = \epsilon a_2 r(y_0) + \epsilon a_3 t(y_0), \tag{76}$$

$$-\delta\kappa\cot\theta = \epsilon a_2 r(\kappa) + \epsilon a_3 t(\kappa). \tag{77}$$

Taking the limit when y_0 tends to zero, (76) shows that a_3 is $O(rt^{-1})$, which tends to zero. With this result and the definition of r, we find

$$r(\kappa) = \cot\theta,$$

$$\epsilon s_y(\kappa) = -\delta\kappa[\lambda(\kappa-\mu) + \sin\theta]\,\lambda^{-1}\sin^{-3}\theta + \delta\kappa\,\operatorname{cosec}^2\theta\, d\theta/d\omega, \tag{78}$$

and so

$$\delta E_0 = -\delta\kappa\,\delta v + \tfrac{1}{2}\delta\kappa^2[\lambda^2 - 2\lambda\cos\theta\, d\theta/d\omega]. \tag{79}$$

Substituting the value of s in (71) we find

$$\begin{aligned}\delta v &= -\delta\kappa\left[\lambda^2\frac{d\kappa}{d\omega} + 2\int_0^\kappa x\frac{\partial x}{d\omega}dy\right]\\ &= -\delta\kappa\, dv/d\omega,\end{aligned} \tag{80}$$

from (68). By differentiating the result in (7) we also have

$$dv/d\omega = -\lambda^2 + 2\lambda\cos\theta\, d\theta/d\omega, \tag{81}$$

and so finally

$$\delta E_0 = \tfrac{1}{2}(dv/d\omega)\,\delta\kappa^2. \tag{82}$$

We have now to consider the possibility that the end points are both fixed. As in §2.1 we suppose that the perturbation is zero for values of y in the ranges $(0, y_0)$ and (y_1, κ) and we shall later allow y_0 to tend to zero. With this assumption, (70) gives

$$\delta E_0 = \epsilon^2\int_{y_0}^{y_1}[s^2(y-\mu) + 2ss_y x_y(1+x_y^2)^{-\frac{1}{2}} + xs_y(1+x_y^2)^{-\frac{3}{2}}]\,dy \tag{83}$$

and the conditions for s, corresponding to (76) and (77), are

$$0 = a_2 r(y_0) + a_3 t(y_0), \tag{84}$$

$$0 = a_2 r(y_1) + a_3 t(y_1). \tag{85}$$

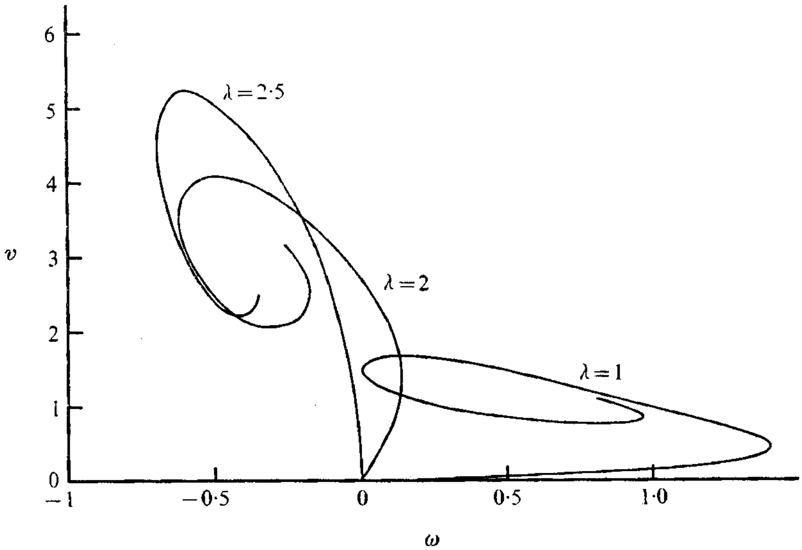

FIGURE 5. Calculated values of v for a drop hanging from a tube as a function of ω (proportional to the pressure in the liquid at the mouth of the tube). Results for three different radii λ are shown.

The arguments used in §2.1 can now be applied, and we see that δE_0 can be reduced to zero provided that (84) and (85) are satisfied. For these equations to have a non-zero solution for a_2 and a_3 we must evidently have

$$r(y_0)/t(y_0) = r(y_1)/t(y_1). \tag{86}$$

Hence, as y_0 tends to zero and the left-hand side of this equation tends to zero, we must have

$$r(y_1) = 0. \tag{87}$$

It follows that if r has a zero in the range $(0, \kappa)$ we can reduce δE_0 to terms of order ϵ^3, and we therefore have instability. We note that by integrating (48) we find

$$fr_y = -\int_0^y rx^{-\frac{1}{2}}(1+x_y^2)^{-\frac{1}{2}}\,dy, \tag{88}$$

and hence r_y is certainly negative throughout the range from the origin in which r is positive.

4.2. *Discussion and numerical results*

We shall first consider the implications of (82). Since ω is proportional to p_0, the pressure at the mouth of the tube, δE_0 is positive whenever the volume of the drop and the pressure increase or decrease together, and it appears that the drop is then stable. (We shall see later by considering (87) that this is not always true.) If the pressure decreases when v increases, it is obvious that the drop is unstable, since the small increase in v would cause more liquid to be sucked into the drop. Three examples have been calculated to illustrate this result, with $\lambda = 1, 2$ and $2{\cdot}5$. For water $(\gamma/\rho g)^{\frac{1}{2}}$ is about 0·26 cm, so that these values correspond to radii of 0·26, 0·52 and 0·65 cm approximately. Figure 5 shows the variation of v as a function of ω, and it will be seen that each curve has a number of regions in which $dv/d\omega$ is positive. For $\lambda = 1$ and 2, as v increases from zero $dv/d\omega$ is at first positive, and reverses sign at a value of v much less than the maximum theoretical equilibrium volume. On the other hand, when $\lambda = 2·5$, the initial value of $dv/d\omega$ is negative, so that the growing drop is unstable from the outset.

Before examining the other condition for stability related to (87), it is of interest to determine the smallest value of λ for which the drop is unstable from the beginning. We therefore have to find the smallest value of λ for which $dv/d\omega$ is initially negative. We consider a shallow drop in which the gradient of y with respect to x is small. If we rewrite the equilibrium equation (3a) in terms of y_x and neglect y_x^2 compared with unity, we obtain

$$xy_{xx} + y_x + x(y - \mu) = 0. \tag{89}$$

The solution of this equation which is finite at the origin is

$$y = \mu[1 - J_0(x)], \tag{90}$$

where $J_0(x)$ is the Bessel function of order zero. Condition (69) then gives

$$\kappa = \mu[1 - J_0(\lambda)], \tag{91}$$

and hence from (66)

$$\omega = \mu J_0(\lambda). \tag{92}$$

From the properties of Bessel functions we readily find

$$v = \mu\lambda^2 J_2(\lambda), \tag{93}$$

and hence

$$dv/d\omega = \lambda^2 J_2(\lambda)\,[J_0(\lambda)]^{-1}. \tag{94}$$

This result shows that when λ just exceeds the first zero of J_0 (which is 2·40483) $dv/d\omega$ is negative since $J_2(\lambda)$ is then positive. It follows that it is impossible to form stable drops under constant pressure if the radius of the tube exceeds 2·40483 in dimensionless units, which for water corresponds to a radius of about 0·625 cm. (Numerical integration of the equilibrium equation indicates that $dv/d\omega$ changes sign at a radius close to 2·4047.)

We have now to consider the further requirement for stability, namely that $r(y)$ should not possess a zero within the range $(0, \kappa)$. The definition (73) shows that for small values of y, for which x_y is very large and positive, if $1 + d\kappa/d\omega$ is positive r will be positive. If then r does not vanish in the range $(0, \kappa)$ equation (88) shows that r_y is negative throughout the range, and so the least value of r will occur when y is equal to κ. Since $r(\kappa)$ is equal to $\cot\theta$, if θ does not exceed $\frac{1}{2}\pi$ and is positive, then r will be positive in the range $(0, \kappa)$ and it will not be possible to satisfy (87), so that the drop will be stable relative to this type of perturbation. The calculations show that in fact $0 < \theta < \frac{1}{2}\pi$ and so we have only to examine the sign of $1 + d\kappa/d\omega$. If this is negative, for small values of y the value of r is very large and negative, but $\cot\theta$ is positive. It follows that $r(y)$ must have passed through zero, and hence the drop is not stable.

In figure 6, κ is shown as a function of ω for the three examples illustrated in

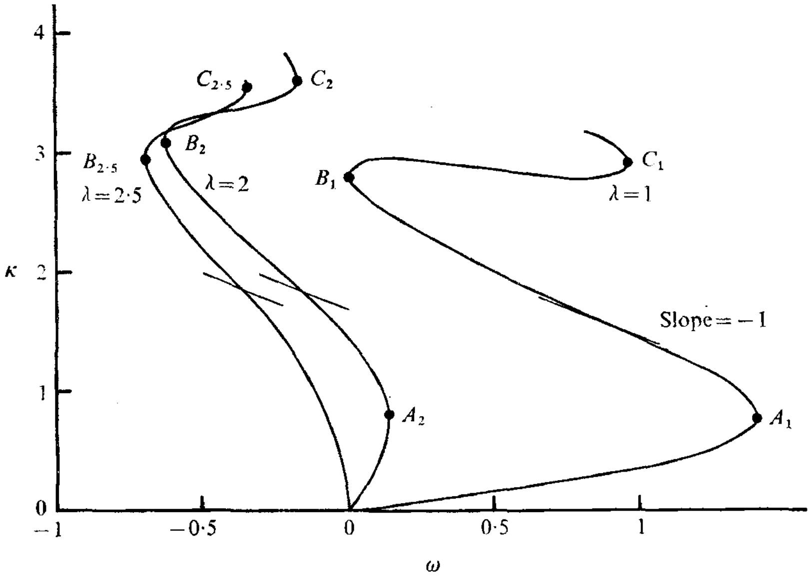

FIGURE 6. Calculated values of κ as a function of ω, corresponding to the results in figure 5.

figure 5. For the curves with $\lambda = 1$ and 2, as v increases from zero $d\kappa/d\omega$ is positive, becoming infinite at A_1 and A_2, where the value of ω is also that for which $dv/d\omega$ becomes infinite (see figure 5). From the preceding arguments it follows that, throughout the region from the origin to A_1 or A_2, δE_0 is certainly positive and the drop is stable. As has already been remarked, when $\lambda = 2{\cdot}5$ there is no corresponding region of the curve.

In the next region of the curve, that is A_1B_1 or A_2B_2, $d\kappa/d\omega$ is less than -1, as can be seen by comparing this gradient (indicated on figure 6) with that of the curve. Also, for the curve $\lambda = 2{\cdot}5$, the gradient of $d\kappa/d\omega$ is less than -1 in the region between the origin and $B_{2\cdot5}$. In all these regions it is therefore possible to satisfy (87) and so the drop is unstable. (Reference to figure 5 shows that, in part of these regions on the corresponding curves in the vicinity of B_1, B_2 and $B_{2\cdot5}$, $dv/d\omega$ is positive and (82) considered alone would indicate that the drops were stable.)

It follows that the profiles which correspond to points in figure 6 on the curves beyond A_1 and A_2 possess at least one zero of $r(y)$. All profiles corresponding to $\lambda = 2{\cdot}5$ include a zero. Thus the only stable drops are those corresponding to the regions OA_1 and OA_2.

5. Concluding remarks

The foregoing examples have the common feature that stable drops are those for which the volume and drop height increase together. The analysis has, however, revealed that this criterion is not the sole requirement. It is interesting that the disrupting axially symmetrical perturbations may be either those which change the end points of the drop profiles or those which do not, depending on circumstances. For the example of a drop of liquid of fixed volume hanging from the end of a tube, a full analysis would require a fourth-order perturbation treatment. Another noteworthy result is that stable drops on a tube can only be formed under constant pressure in the liquid if the radius is less than a certain critical value.

The results illustrate the complexity of the criteria for the stability of axially symmetrical pendent drops, which greatly exceeds that for 'two-dimensional' drops.

The stimulus to undertake this investigation arose in part from the numerical work of Dr Padday and his colleagues of the Research Division, Kodak Limited, and I am also grateful to Mr A. Marriage of the same Division for his constant interest and for many discussions which helped to clarify the meaning of the somewhat complicated analytical results.

Appendix

Most of the earlier work on the numerical integration of the equilibrium equations (3) used intrinsic variables of the curve, which are particularly convenient. For this reason, and to facilitate comparison with published calculations, we shall transform (3). We introduce a parameter β defined by

$$\beta = -4/\mu^2, \tag{A 1}$$

and define a length b by the equation

$$b^2 = -\beta\gamma/\rho g. \tag{A 2}$$

We replace the dimensionless variables of § 2 *et seq.* by new dimensionless variables ξ and η, given by

$$\xi = x(-\beta)^{-\frac{1}{2}}, \quad \eta = y(-\beta)^{-\frac{1}{2}}. \qquad \text{(A 3), (A 4)}$$

If l is the length along the profile of the drop from the apex, we put

$$s = l/b, \tag{A 5}$$

and put $\tan\phi$ equal to the gradient of the curve, so that

$$\xi_\eta = \cot\phi. \tag{A 6}$$

Hence

$$\xi = \int_0^s \cos\phi\, ds, \tag{A 7}$$

$$\eta = \int_0^s \sin\phi\, ds, \tag{A 8}$$

and equations (3) have the standard form (cf. Stauffer 1965)

$$\frac{d\phi}{ds} + \frac{\sin\phi}{\xi} = 2 + \beta\eta. \tag{A 9}$$

From this equation, we find by differentiation

$$\frac{d^2\phi}{ds^2}-\frac{\cos\phi}{\xi}\left(\frac{\sin\phi}{\xi}-\frac{d\phi}{ds}\right)=\beta\sin\phi. \tag{A 10}$$

The integration of (A 9) then proceeds as follows. We choose a small increment σ in the variable s. Suppose that, when s has the value s_0, ϕ is equal to ϕ_0 and ξ and η have the values ξ_0 and η_0. The values corresponding to $s+\sigma$ are then found from (A 7) and (A 8), and are

$$\xi_1=\xi_0+\sigma\cos\phi_0-\tfrac{1}{2}\sigma^2\phi_0'\sin\phi_0+O(\sigma^3), \tag{A 11}$$

$$\eta_1=\eta_0+\sigma\sin\phi_0+\tfrac{1}{2}\sigma^2\phi_0'\cos\phi_0+O(\sigma^3), \tag{A 12}$$

where the prime denotes d/ds. We may calculate the new value ϕ_1 at $s+\sigma$ from the Taylor series

$$\phi_1=\phi_0+\sigma\phi_0'+\tfrac{1}{2}\sigma^2\phi_0''+O(\sigma^3). \tag{A 13}$$

The derivatives of ϕ_1 are found from (A 9) and (A 10); hence

$$\phi_1'=-\xi_1^{-1}\sin\phi_1+2+\beta\eta_1, \tag{A 14}$$

$$\phi_1''=\xi_1^{-1}\cos\phi_1(\xi_1^{-1}\sin\phi_1-\phi_1')+\beta\sin\phi_1. \tag{A 15}$$

In the numerical work terms $O(\sigma^3)$ are neglected. The cycle of equations (A 11)–(A 15) is repeated with the values of ϕ_1 and ϕ_1' replacing ϕ_0 and ϕ_0' in (A 11) and (A 12), and ξ_1 and η_1 replacing ξ_0 and η_0; new values ξ_2 and η_2 are then calculated. Similar substitution in (A 13)–(A 15) competes the cycle.

Previous workers, for instance Mills (1953) and Stauffer (1965), omit terms in σ^2, but these are so easily calculated that they are worth retaining to take advantage of the increased accuracy. A value of σ of 0·001 is convenient. The calculation starts with the initial values

$$\phi=0,\quad \phi'=1,\quad \phi''=0.$$

The integration proceeds with a chosen value of β until ϕ is equal to θ, the angle of contact, or until ξ reaches a value which corresponds to the radius of the tube. A simple linear interpolation procedure determines these end points with sufficient accuracy. The integration is then continued to find other possible profiles which satisfy the boundary conditions for the given β.

The numerical results were checked against several sets of published values. As a further check, β was put equal to zero, in which case the solution is the circle $\phi=s$. Hence, when ϕ is equal to π, the value of (ξ,η) should be $(0,2)$. The calculated values differed from these by 8×10^{-7} for ξ and 2×10^{-7} for η. (Part of this small error is certainly attributable to the rather crude interpolation used to determine the end point.)

Note added in proof: Dr M. E. O'Neill has brought to my notice a thesis (University of Minnesota 1972) by P. R. Pujado, who states that C. Huh in a thesis (ibid. 1969) analyses the stability of pendent drops with respect to perturbations to nearby equilibrium configurations. The end points are either fixed, or the contact angle for the perturbed shape is exactly the same as that for the unperturbed drop. For these restricted variations results are obtained for both axially and non-axially symmetrical perturbations.

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