Capillary Height in Inclined Tubes

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The surface form and the length of the liquid column in a cylindrical capillary tube inclined against the vertical direction are studied by a method of successive approximations. The results are obtained as expansions in powers of $\lambda = \rho G a^3 / 2C$, where a is the radius of the tube, G the acceleration of gravity, ρ the density and C the surface tension of the liquid. The length of the liquid column is given to third order in λ .

Expressions for the form and height of the surface of a liquid in a vertical, cylindrical capillary tube are known from the literature¹. They are, *e.g.*, used in precision measurements of surface tension by the method of capillary rise.

Recently Koefoed and Villadsen² have improved this method by using capillary tubes which are not vertical. For this reason we have found it worthwhile to derive expressions analogous to those in Ref.¹, but valid also for tubes inclined against the vertical direction.

We have only treated the case in which the angle of contact between the liquid and the tube is 180°, this being the most important from the metrological point of view.

This note describes the principles and results of the calculations. The detailed and somewhat lengthy derivations are largely omitted, since they do not present any novel features.

NOMENCLATURE AND METHOD

We consider a free surface in a capillary tube, the radius of which is a . We want to treat both cases shown in Fig. 1 in one calculation. We therefore introduce a cylindrical system of coordinates (r, φ, z) according to the following rules (*cf.* Fig. 1):

The origin is at the level of the undisturbed surface of the liquid outside the tube. The z -axis is the axis of the tube, oriented *from liquid to gas*. The angle from the z -axis to the upward vertical is denoted by α .

The height and form of the surface will adjust itself in such a way that the free energy F of the system is a minimum. The variable part of F has

Fig. 1. Cylindrical coordinate systems used for surfaces turned upward and downward, respectively. A—A is the level of the undisturbed surface.†

three components, the gravitational energy F_G , the energy of the free surface in the tube F_S , and the energy due to the interface between the liquid and the wall of the tube, F_T . Let $z = z(r, \varphi)$ be the equation of the surface. The three contributions to F can then be written in the following forms valid for all values of α . (The arbitrary additive constants are chosen so as to give simple expressions):

$$F_G = \rho G \int_0^{2\pi} d\varphi \int_0^a r dr \left(\frac{1}{2} z^2 \cos \alpha - z r \cos \varphi \sin \alpha \right) \quad (1)$$

$$F_S = C \cdot S = C \int_0^{2\pi} d\varphi \int_0^a r dr \sqrt{1 + (z'_r)^2 + (z'_\varphi)^2 / r^2} \quad (2)$$

$$F_T = -C \int_0^{2\pi} d\varphi \cdot a z(a, \varphi) \quad (3)$$

Here G is the acceleration of gravity, C the surface tension and ρ the density of the liquid. (Strictly speaking ρ should be the difference between the densities of the liquid and the medium outside the surface.) S is the area of the free surface in the tube. z'_r and z'_φ mean $\partial z / \partial r$ and $\partial z / \partial \varphi$, respectively. The integral in (3) is the area of the interface between liquid and tube.

The function $z(r, \varphi)$ is now a solution of the variational equation

$$\delta F \stackrel{\text{def}}{=} \delta(F_G + F_S + F_T) = 0 \quad (4)$$

where $z(r, \varphi)$ is to be varied subject to the boundary condition that the angle of contact shall be constant and equal to 180° , i.e. z'_r must go to plus infinity when r goes to a . Furthermore we assume that $z(r, \varphi)$ is at least twice differentiable.

By varying the height, but not the form, of the surface, *i.e.* by letting $\delta z = \text{const.}$, we are able to derive one exact equation from eqn. (4). In this case only F_G and F_T contribute to δF , and we get

$$\frac{1}{\pi a^2} \int_0^{2\pi} d\varphi \int_0^a r dr \cdot z \stackrel{\text{def}}{=} \bar{z} = \frac{h}{\cos \alpha} \quad (5)$$

where $\bar{z}$ is written for the mean value of z over the surface, and where

$$h \stackrel{\text{def}}{=} \frac{2C}{\rho G a} \quad (6)$$

is the expression valid for the capillary height in a very narrow, vertical tube. Eqn. (5) may also be derived from an elementary consideration of the equilibrium between the forces from the walls of the tube and those due to gravity.

It is not possible to give the solution to eqn. (4) in closed form by means of tabulated functions. We therefore try to solve it by successive approximations, $z(r, \varphi)$ being written as an expansion in a suitable dimensionless perturbation parameter. As such we shall choose

$$\lambda \stackrel{\text{def}}{=} \frac{a}{h} = \frac{\rho G a^2}{2C} \quad (7)$$

When λ is very small the surface will be a hemisphere of radius a . It has the parametric representation (with Θ as a parameter defined by eqn. (8)):

$$r = a \sin \Theta \quad (8)$$

$$z = A - a \cos \Theta \quad (9)$$

The single adjustable constant A is most easily found by inserting eqns. (8) and (9) in eqn. (5). The result is

$$A = h / \cos \alpha + \frac{2}{3} a \quad (10)$$

This, then, has led to the terms in z/h proportional to λ^0 and λ^1 , respectively, *i.e.* to the wellknown first and second order approximations.

In order to improve the result two ways are possible. First, one may choose for $z(r, \varphi)$ a suitable trial function with a number of adjustable constants to be determined from eqn. (4). The simplest trial function, which takes into account both the departure from spherical form and from axial symmetry, is an inclined ellipsoid: $z = k_1 - k_2 \cos \varphi + k_3 \cos \varphi \sin \Theta$, where Θ is still defined by eqn. (8). The use of this function leads to a result which is sufficiently accurate for many purposes. The other method is a consistent perturbation calculation. We put

$$\frac{z}{h} = \frac{1}{\cos \alpha} + \lambda \left(\frac{2}{3} - \cos \Theta \right) + \lambda^2 f_1(\Theta, \varphi) + \lambda^3 f_2(\Theta, \varphi) + \dots \quad (11)$$

and by means of eqn. (4), where F is also expanded in powers of λ , we derive differential equations for the unknown functions f_1, f_2 . The first few of these equations turn out to be exactly soluble. We therefore prefer this way of attack and shall not give the results of the first method mentioned.

THE THIRD AND FOURTH ORDER APPROXIMATIONS

Eqns. (11), (1), (2) and (3) lead to an expansion of F in powers of λ . The first term, which depends on the unknown functions in eqn. (11), is the following:

$$F_4 = \frac{2C^2\lambda^3}{\rho G} \cdot \int_0^{2\pi} d\varphi \int_0^{\pi/2} L_1 d\Theta \quad (12)$$

where $L_1 = \sin\Theta \cos\Theta [(\frac{4}{3} \cdot \cos\alpha - 2\cos\alpha \cos\Theta - 2\sin\alpha \cos\varphi \sin\Theta) \cdot f_1$

$$+ \frac{1}{2} \cos\Theta (f'_{1,\Theta})^2 + \frac{1}{2} \frac{\cos\Theta}{\sin^2\Theta} (f'_{1,\varphi})^2] \quad (13)$$

The first step in the perturbation calculus now consists in determining f_1 so that F_4 is a minimum. On varying f_1 (and later f_2) we keep the boundary values $f_1(\frac{\pi}{2}, \varphi)$ (and $f_2(\frac{\pi}{2}, \varphi)$) fixed, but on the other hand we require, in agreement with eqn. (5), that $\bar{f}_1 = 0$ (and $\bar{f}_2 = 0$). This fixes an otherwise arbitrary constant in f_1 (and f_2). The variational problem is of standard form and leads to the Euler-Lagrange differential equation

$$\frac{\partial}{\partial\Theta} \frac{\partial L_1}{\partial f'_{1,\Theta}} + \frac{\partial}{\partial\varphi} \frac{\partial L_1}{\partial f'_{1,\varphi}} = \frac{\partial L_1}{\partial f_1} \quad (14)$$

From the differential equation or directly from the variational problem and the way in which φ appears in L_1 , it follows that f_1 must be of the form

$$f_1(\Theta, \varphi) = g_1(\Theta) + g_2(\Theta) \cos\varphi \quad (15)$$

Eqn. (14) thus separates into two equations, one for g_1 and one for g_2 .

The differential equation determining g_1 becomes

$$\frac{d}{d\Theta} \left(\sin\Theta \cos^2\Theta \frac{dg_1}{d\Theta} \right) = \frac{4}{3} \cos\alpha \sin\Theta \cos\Theta - 2\cos\alpha \cos^2\Theta \sin\Theta \quad (16)$$

The integration is elementary. The first constant of integration follows from the requirement that $dg_1/d\Theta$ must be finite for $\Theta = 0$. The second is determined from the condition $\bar{f}_2 = 0$. The result is

$$g_1 = \frac{1}{3} \cos\alpha (2 \ln(1 + \cos\Theta) - 1) \quad (17)$$

The equation determining g_2 is

$$\frac{d}{d\Theta} \left(\sin\Theta \cos^2\Theta \frac{dg_2}{d\Theta} \right) = \frac{\cos^2\Theta}{\sin\Theta} g_2 - 2\sin\alpha \sin^2\Theta \cos\Theta \quad (18)$$

The condition that g_2 must be finite at both ends of the interval $0 \leq \Theta \leq \frac{\pi}{2}$ determines both constants in the complete integral to this equation.

We find

$$g_2 = \frac{2}{3} \sin\alpha \sin\Theta \left(\frac{\ln(1 + \cos\Theta)}{\cos\Theta} + \frac{1}{1 + \cos\Theta} \right) \quad (19)$$

For $r \rightarrow a$, the partial derivative $f'_{1,r}$ must not go so rapidly to negative infinity that the boundary condition for the complete function $z(r, \varphi)$ can not be fulfilled. This puts a limit on the magnitude of λ , but it is found from eqns. (15), (17) and (19) that the condition ($\lambda \lesssim 1$, dependent on α) is fulfilled for all values of λ which lead to a useful perturbation expansion.

We are now able to carry the perturbation calculus one step further. The known function f_1 is introduced into the free energy and the first term in the expansion which depends on f_2 is minimized. This leads to an equation like (14), from which it is seen that f_2 is of the form

$$f_2(\Theta, \varphi) = G_1(\Theta) + G_2(\Theta) \cos \varphi + G_3(\Theta) \cos 2\varphi \quad (20)$$

We have only determined $G_1(\Theta)$. The reason is that G_2 and G_3 vanish (like Θ and Θ^2 , respectively) for $\Theta \rightarrow 0$; their contributions to the height of the meniscus will therefore be of higher order in λ than the contribution from G_1 .

G_1 is found in the same way as g_1 . We omit the details in the calculations. The result is

$$\begin{aligned} G_1(\Theta) = & \frac{2}{3} \cos^2 \alpha \left[\frac{\ln(1+u)}{u} - 2 \ln(1+u) + u \right] \\ & + \frac{1}{9} \sin^2 \alpha \left[(\ln(1+u))^2 \left(\frac{1}{u} + \frac{1}{u^3} \right) + 2 \ln(1+u) \left(\frac{5}{u} - \frac{1}{u^2} \right) + \frac{4}{1+u} + \frac{1}{u} - 3u \right] \\ & - \frac{8}{3} \ln 2 + \frac{14}{9} - \frac{2}{3} \sin^2 \alpha, \end{aligned} \quad (21)$$

where, for brevity, $\cos \Theta$ has been denoted by u .

THE CAPILLARY HEIGHT

From eqn. (11) we now find the parameters of that point of the surface where the tangential plane is perpendicular to the axis of the tube ($z'_\Theta = 0$). The value of z/h for this point is denoted by z_m/h and is found on inserting the said parameters in eqn. (11). z_m/h is written as an expansion in λ :

$$\begin{aligned} \frac{z_m}{h} = & \frac{1}{\cos \alpha} - \frac{1}{3} \lambda + \frac{1}{3} \cos \alpha [2 \ln 2 - 1] \cdot \lambda^2 - [\cos^2 \alpha (\frac{1}{3} \ln 2 - \frac{2}{9}) + \sin^2 \alpha (2 \ln 2 - \frac{5}{6})] \cdot \lambda^3 + \dots \\ = & \frac{1}{\cos \alpha} - \frac{1}{3} \lambda + 0.129 \cos \alpha \cdot \lambda^2 - [0.088 \cos^2 \alpha + 0.553 \sin^2 \alpha] \cdot \lambda^3 + \dots \end{aligned} \quad (22)$$

For $\alpha = 0$ the first three terms in this expansion have been found by Poisson and Volkmann¹. On considering the way in which the acceleration of gravity enters into h and λ , one sees that the first three terms in (22) are obtained from Poisson's expression on replacing G by $G \cos \alpha$, *i.e.* by the component of the acceleration of gravity along the negative z -axis. However, it is also seen that the term in (22) proportional to λ^3 is affected by the asymmetry of the surface and consequently it depends also on the component of G perpendicular to the axis of the tube.

The results obtained are valid for both positive and negative values of $\cos \alpha$. However, it must be remembered that the z -axis is oriented downwards

for $\cos\alpha$ negative (hanging surface). In the method of Koefoed and Villadsen ², the distance is measured between two surfaces in tubes of different radii (a_1 and a_2) and with different values of α ($\alpha_1 = \alpha$; $\alpha_2 = \pi + \alpha$). This distance l will be

$$\begin{aligned} l = z_1 - |z_2| &= z_1 + z_2 \\ &= \frac{h_1 - h_2}{\cos\alpha} - \frac{1}{3} (a_1 + a_2) + 0.129 \cos\alpha \left(\frac{a_1^2}{h_1} - \frac{a_2^2}{h_2} \right) - \\ &\quad - (0.088 \cos^2\alpha + 0.553 \sin^2\alpha) \left(\frac{a_1^3}{h_1^2} + \frac{a_2^3}{h_2^2} \right) + \dots \end{aligned} \quad (23)$$

where $h_1 = 2C/\rho Ga_1$, and $h_2 = 2C/\rho Ga_2$.

For the purpose of measuring surface tension, the formula (23) is most easily utilized when inverted so as to give $2C/\rho G$ as an expansion in powers of, *e.g.*, a_2/l .

We conclude with a few words about the practical convergence of the expansion found. The last term in eqn. (22) becomes equal to 0.1 % of the first term at a value of λ approximately equal to 1/5, but somewhat dependent on α . For water this corresponds to a tube diameter of $2a \approx 3.5$ mm. When $\sin^2\alpha$ is small, an accuracy of about 0.1 % may be expected even for values of λ as large as 1/3 ($2a \approx 4.5$ mm for water). However, for larger values of $\sin^2\alpha$ this is presumably not the case, because the fourth term in eqn. (22) becomes larger than the third term, a fact that points to a slow convergence of the expansion.

REFERENCES

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