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Classification

Physics Abstracts

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Capillary rise in tubes with sharp grooves

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Abstract . — Liquid in grooved capillaries, made by e.g. inserting a plate in a cylindrical tube, exhibits unusual spreading and flow properties. One example is capillary rise, where a long, upward tongue on top of the usual meniscus has been observed along the groove. We attribute the underlying mechanism to a thermodynamic instability against spreading for a (partial or complete wetting) liquid in a sharp groove whose opening angle α is less than a critical value $\alpha_c = \pi - 2\theta$. The equilibrium shape of the tongue is determined analytically. The dynamics of liquid rising is studied in the viscous regime. When the diameter of the tube is smaller than the capillary length, the center part of the meniscus rises with time t following a $t^{1/2}$ -law, while the tongue is truncated at a height which grows following a $t^{1/3}$ -law. Sharp groove also facilitates release of gas bubbles trapped inside a capillary under the action of gravity.

1. Introduction.

It is well-known that capillary rise in a thin tube is inversely proportional to the diameter of the tube [1]. This law holds for partial as well as complete wetting. In this paper we show that, when a sharp, vertical groove of sufficiently small opening angle is constructed in the tube, a liquid tongue of macroscopic thickness appears inside the groove. The tongue extends to arbitrarily high altitudes, independent of the diameter of the tube.

Our work started with the need to fill thin glass tubes with certain kind of ionic solution, to be used as microelectrodes in physiological experiments. A practical problem is to avoid trapping of gas bubbles in the tube. When tubes with a circular cross-section are used [see Fig. 1a], it is very difficult to get rid of bubbles particularly in the sharp tip region. A simple solution was found by inserting a plate inside the raw tube before stretching it into the final shape using standard glass-making technique [see Fig. 1b]. Tubes with cross-sectional shapes shown in figures 1c-1e were found to be equally good for this purpose [2].

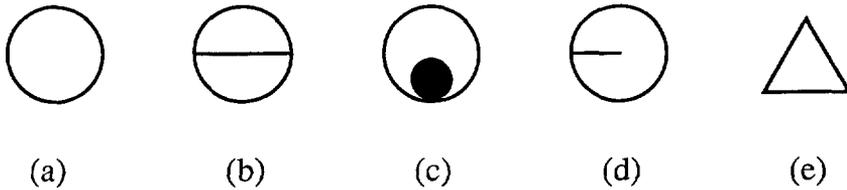


Fig. 1. — Cross-sectional shape of tubes used in the experiment. (b)-(e) contain sharp grooves along the tube. The groove opening angles are: (b) $\alpha = \frac{1}{2}\pi$; (c) $\alpha = 0$; (d) $\alpha = \frac{1}{2}\pi$; (e) $\alpha = \frac{1}{3}\pi$.

The tubes which do not trap gas bubbles have a common feature that there are sharp grooves inside. When such a tube is held vertically, liquid on top of a trapped bubble develops tongues which extend down along these groove. As a result, trapped bubbles rise easily to the top under gravity. The spontaneous flow of liquid along the grooves suggests that there is no free energy barrier for spreading. Indeed, when these tubes (about 1 mm in diameter and initially empty) are placed vertically in contact with the solution, we discover that, on top of the normal capillary rise, the liquid creeps up along the grooves to very high altitudes.

The new physics introduced by the groove geometry is the increased tendency for the liquid to spread. The bottom part of the grooves which appear in the constructions shown in figures 1b-e can be approximated by a wedge of opening angle α . As we shall show below, within the classical thermodynamic theory, one can identify a critical angle

$$\alpha_c = \pi - 2\theta, \quad (1)$$

where θ is the equilibrium contact angle. For $\alpha < \alpha_c$, spreading occurs even when the liquid does not wet the wall completely. Depending on the initial state of the liquid, gravity may either enhance or act against spreading. In this paper we focus on capillary rise against gravity. In this case there is an equilibrium liquid-air interface profile which can be determined analytically. The dynamics of the rising process will also be considered.

The paper is organized as follows. In section 2 we discuss the static aspects of the problem. Section 3 contains an analysis on the dynamics of the rising process in the viscous regime. Discussion and conclusions are presented in section 4.

2. The equilibrium problem.

2.1 CRITICAL ANGLE FOR SPREADING. — In the absence of gravity, the instability of a liquid drop against spreading in a sharp groove with an opening angle $\alpha < \alpha_c$ can be seen as follows. Consider a (fictitious) liquid column of length L that fills the bottom part of the groove. The cross-section of the column is taken to be an isosceles triangle with the two equal sides on the wall and a perpendicular of length d . For $L \gg d$, the total surface free energy of the liquid is given by

$$F = 2dL\gamma \tan(\alpha/2) + 2dL(\gamma_{SL} - \gamma_{SG}) \sec(\alpha/2), \quad (2)$$

where γ , γ_{SG} , and γ_{SL} are the surface tensions of liquid and gas, solid and gas, and solid and liquid, respectively. Using the Young's formula

$$\gamma \cos \theta = \gamma_{SG} - \gamma_{SL}, \quad (3)$$

Equation (2) may be rewritten as

$$F = 2dL\gamma[\sin(\alpha/2) - \cos\theta] / \cos(\alpha/2). \tag{4}$$

Equation (4) shows that, for $\sin(\alpha/2) < \cos\theta$ or $\alpha < \alpha_c = \pi - 2\theta$ and a fixed volume $V = d^2L \tan(\alpha/2)$, the free energy of the column decreases without bound as $L \rightarrow \infty$. We are thus led to the conclusion that any liquid drop of finite extent is unstable against spreading for $\alpha < \alpha_c$.

2.2 EQUILIBRIUM SHAPE OF THE TONGUE. — When the groove is placed vertically, spreading is countered by gravity. In a cylindrical tube, the macroscopic rise z of the liquid is limited to a finite value even in the case of complete wetting. In contrast, for tubes with sharp grooves, the finite free energy gain per unit length in the groove [see Eq. (4)] is able to overcome the gravitational energy $\rho g z$ per unit volume, provided the product $d z$ is sufficiently small. Thus a thin tongue of the liquid can climb up to an arbitrary height along the bottom of the groove. The width d of the tongue, however, should be inversely proportional to the height. Note that the tongue is not a precursor film. It is completely describable within the classical thermodynamic framework.

To determine the equilibrium profile of the liquid-air interface $z(x, y)$, one has to solve the equation [1]

$$\rho g z = 2\gamma H, \tag{5}$$

subjected to the boundary condition that the contact angle of the liquid at the wall is θ . Here ρ is the mass density of the liquid (or more precisely, the difference between the mass density of the liquid and that of the gas), and H is the mean curvature of the interface. To obtain a complete solution to (5) for the geometries illustrated in figure 1, one has to resort to numerical means. Here we are mainly interested in the profile of the tongues. The problem can then be simplified by considering liquid rise in an infinite wedge formed by two planar vertical walls at an angle α , as shown in figure 2a.

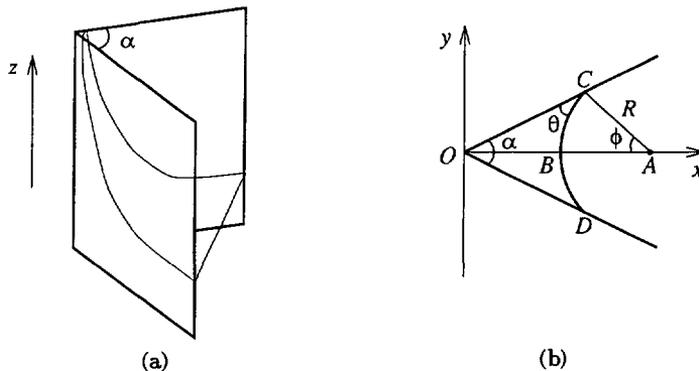


Fig. 2. — (a) A wedge of angle α formed by two vertical planes. Thin lines illustrate equilibrium capillary rise. (b) Horizontal cross-section of (a). Liquid is confined in the region OCBDO.

Anticipating a slow variation of the cross-sectional shape of the tongue with the height at high altitudes, one may, in a first approximation, ignore the interface curvature in the vertical

direction. According to equation (5), the horizontal cross-section of the tongue should then take the form of a dart with a circular base, as illustrated by the closed area OCBDO in figure 2b. The radius R of the arc is given by

$$R = a^2 / (2z), \tag{6}$$

where $a = [2\gamma / (\rho g)]^{1/2}$ is the capillary length. The angle between the tangent of the circle and the wall at the point of intersection is θ . From the geometry one obtains the following equation relating the distance $d = OB$ and the radius R of the circle,

$$d = R \left(\frac{\cos \theta}{\sin \frac{1}{2}\alpha} - 1 \right). \tag{7}$$

Combining (7) with (6), we see that the width of the tongue is inversely proportional to the height when the opening angle α is less than α_c .

It turns out that the leading order correction to (7) can also be calculated analytically when the ratio $R/z = \frac{1}{2}(a/z)^2$ is small. For this purpose let us introduce polar coordinates (r, ϕ) in the horizontal xy -plane centered at A ,

$$x = X - r \cos \phi, \quad y = r \sin \phi, \tag{8}$$

where $X = d + R$ is the distance between O and A . The liquid-gas interface position is specified, for small R/z , by

$$r(\phi, z) = R \left[1 + \left(\frac{R}{z} \right)^2 \epsilon(\phi) + \dots \right]. \tag{9}$$

The mean curvature H can now be expressed in ϵ . After some algebra the final result is given by

$$H = \frac{1}{2R} \left[1 - \left(\frac{R}{z} \right)^2 \left(\frac{d^2 \epsilon}{d\phi^2} + \epsilon + 1 - \chi^2 + \frac{3}{2}(1 - \chi \cos \phi)^2 \right) + \dots \right], \tag{10}$$

where $\chi = X/R = \cos \theta / \sin(\alpha/2)$. Inserting (10) into (5) and using (6), we obtain, to leading order in $(R/z)^2$,

$$\frac{d^2 \epsilon}{d\phi^2} + \epsilon + 1 - \chi^2 + \frac{3}{2}(1 - \chi \cos \phi)^2 = 0. \tag{11}$$

Equation (11) has a general solution which respects the $\phi \rightarrow -\phi$ symmetry,

$$\epsilon(\phi) = C \cos \phi - \frac{5}{2} + \frac{3}{2}\chi\phi \sin \phi + \frac{1}{2}\chi^2 \cos^2 \phi. \tag{12}$$

The constant C in (12) is to be determined by the contact angle θ at the wall. From the geometry we see that the polar angle $\phi_1 (> 0)$ at which curve (9) intersects the wall satisfies

$$r \sin(\phi_1 + \frac{\alpha}{2}) = X \sin \frac{\alpha}{2} \tag{13}$$

Setting the angle between the interface and the wall (in three dimensions) to θ , we obtain,

$$\epsilon \cos \theta + \frac{d\epsilon}{d\phi} \cos(\phi_1 + \frac{1}{2}\alpha) + \frac{1}{2} \cos \theta (1 - \chi \cos \phi_1)^2 = 0. \tag{14}$$

Combining equations (12-14) gives

$$C = \frac{\cos \theta}{2 \sin \frac{1}{2} \alpha} \left[4 + 3 \sin^2 \theta - \frac{3}{2} (\pi - 2\theta - \alpha + \sin 2\theta) \cot \frac{\alpha}{2} \right]. \quad (15)$$

Figure 3a shows cross-sectional profiles of the interface calculated using (12) (solid lines) for the case $\alpha = \frac{1}{3}\pi$ and $\theta = \frac{1}{12}\pi$. The heights of the cross-sections are at $z/a = 1.5, 2, 2.5$ and 3 . The convergence to the circular profiles (shown by the dashed lines) is very fast as z/a increases. Figure 3b shows the vertical profiles of the interface for the same set of parameter values. Solid line gives the contact line of the liquid with the wall, while the dashed line is the profile on the bisector of the wedge.

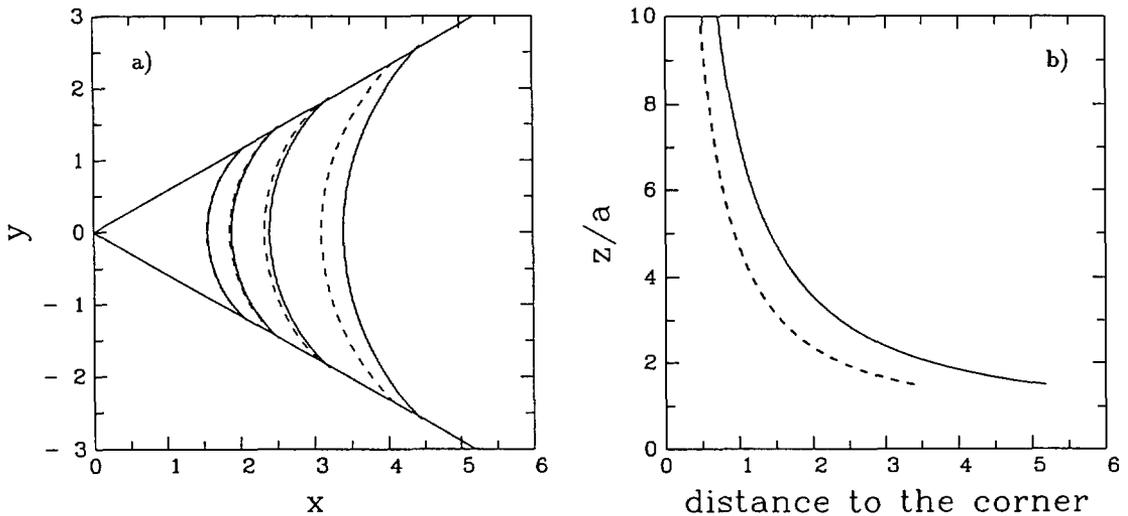


Fig. 3. — Equilibrium profile of the tongue in an infinite wedge of opening angle $\alpha = \frac{1}{3}\pi$. The contact angle is chosen at $\theta = \frac{1}{12}\pi$. a) Horizontal cross-sections of the tongue (thin solid lines) at heights $z/a = 1.5, 2, 2.5$ and 3 (from right to left). Dashed lines give the zeroth order approximation. b) The contact line (solid) on the wall and the vertical profile (dashed) on the bisector of the wedge.

3. Dynamics.

When a thin tube with sharp grooves is made in contact with a liquid, the build-up of the equilibrium height consists of three stages: (i) an initial “rush” into the tube, which typically takes less than 10^{-2} s [3]. The flow in this period can be quite turbulent. (ii) viscous rising in the center part of the tube towards equilibrium. (iii) development of tongues. In the following we only consider stages (ii) and (iii). Here the dynamics is controlled by the viscous flow of the liquid which limits transport of matter needed to reach final equilibrium. For simplicity we assume that processes (ii) and (iii) are separated in time, though in practice there may well be

an overlap. Our considerations follow closely previous work on wetting dynamics as reviewed by de Gennes [4] and by Leger and Joanny [5].

3.1 VISCOUS RISE IN A CIRCULAR TUBE. — Let us first consider rising in a thin circular tube without grooves. The hydrodynamic equation governing the viscous flow of the liquid in the tube is given by [6]

$$-\nabla \left(\frac{p}{\rho} + gz \right) + \nu \nabla^2 \mathbf{v} = 0, \quad (16)$$

where ν is the viscosity coefficient of the liquid. The inertia term has been ignored. As usual, no-slip boundary condition on the wall is imposed.

The driving force for the flow is the unbalanced pressure drop across the liquid-gas interface at height h ,

$$\delta p = \rho gh - 4\gamma \cos \theta / D = \rho g(h - h_{\text{eq}}), \quad (17)$$

where D is the diameter of the tube and $h_{\text{eq}} = 2a^2 \cos \theta / D$ is the equilibrium height of the interface [7]. The contact angle θ has a weak dependence on velocity which we ignore here [4, 5]. In the following we make the further approximation that \mathbf{v} has only a vertical component. For an incompressible fluid, this implies that v_z depends only on the horizontal coordinates (x, y) . In this case equation (16) reduces to the Laplace equation

$$(\partial_x^2 + \partial_y^2)v_z = \delta p / (\nu \rho h). \quad (18)$$

The solution to (18) is given by

$$v_z = \frac{1}{4} [\delta p / (\nu \rho h)] [r^2 - (D/2)^2], \quad (19)$$

where r is the distance to the center of the tube.

From equation (19) we obtain the flow rate per unit area

$$\frac{1}{\pi(D/2)^2} \int dx dy v_z = -\frac{1}{8} \frac{\delta p}{\nu \rho h} \left(\frac{D}{2} \right)^2 \quad (20)$$

Identifying (20) with the velocity of the interface and using (17), we obtain,

$$\frac{dh}{dt} = \frac{g}{8\nu} \left(\frac{D}{2} \right)^2 \frac{h_{\text{eq}} - h}{h} \quad (21)$$

This equation can be easily integrated to give

$$-\frac{h}{h_{\text{eq}}} - \ln \left(1 - \frac{h}{h_{\text{eq}}} \right) = \frac{1}{8 \cos \theta} \left(\frac{D}{2a} \right)^3 \frac{t}{t_0}, \quad (22)$$

where $t_0 = \nu / (ga)$ is a characteristic relaxation time of the liquid, typically less than 10^{-2} s. For $h/h_{\text{eq}} \ll 1$ or $t \ll t_0(2a/D)^3$ the rising is diffusive,

$$h = \frac{h_{\text{eq}}}{2 \cos^{1/2} \theta} \left(\frac{D}{2a} \right)^{3/2} \left(\frac{t}{t_0} \right)^{1/2} \quad (23)$$

It crosses over to an exponential decay

$$h = h_{\text{eq}} \left[1 - \exp \left\{ -1 - \frac{1}{8 \cos \theta} \left(\frac{D}{2a} \right)^3 \frac{t}{t_0} \right\} \right] \tag{24}$$

at $t \simeq t_0(2a/D)^3$.

The important result of the above calculation is that the typical rising time of the liquid is inversely proportional to the third power of the diameter of the tube. Another interesting phenomenon is that, although the equilibrium rise h_{eq} is higher when the tube is thinner, the time it takes to reach a given height $h \ll h_{\text{eq}}$ is actually longer, $t(h) \simeq t_0 h^2 / (aD)$. The diffusive regime exists only when the diameter is significantly smaller than the capillary length. The approximation that \mathbf{v} has only a vertical component is not correct close to the top of the liquid column or at the root of tongues. However, we expect that the qualitative behavior of viscous rising is captured by (22).

3.2 DEVELOPMENT OF TONGUES. — In the above discussion we assumed that the equilibrium meniscus shape (but not the height) at the center of the tube is established at the end of stage (i). The rising in stage (ii) is then governed by the unbalanced pressure drop, compensated by the viscous forces in the liquid. This description does not apply directly to the tongue region: the equilibrium interface extends to infinite height which can not be established in any finite time. A more plausible picture is that, at a given time t , there is a fully-developed tongue truncated at some height $h_m(t)$. In addition, there can be an incipient tongue above $h_m(t)$.

A simple estimate for $h_m(t)$ can be made from equation (23). The equilibrium thickness of the tongue at h_m is of the order of a^2/h_m [see Eq. (6)]. Assuming that the viscous flow up to this level is similar to the one in a tube of diameter $D = a^2/h_m$, we obtain from equation (23)

$$h_m \simeq a(t/t_0)^{1/3} \tag{25}$$

Equivalently, the time for the tongue to reach a height h is given by

$$\tau \simeq t_0(h/a)^3. \tag{26}$$

It turns out that a more detailed calculation presented below gives the same result as the simple-minded estimate (26). Let us start with the approximate equation

$$(\partial_x^2 + \partial_y^2)v_z = \Phi(z), \tag{27}$$

where

$$\Phi(z) = \frac{1}{\nu} \left(g + \frac{1}{\rho} \partial_z p \right). \tag{28}$$

The term $\partial_z^2 v_z$, which is omitted in (27), will be shown to be small. In addition to the no-slip boundary condition $v_z = 0$ on the solid walls, we demand that the tangential stress vanishes on the liquid-gas interface, $\partial_n v_z = 0$.

To fix the solution to (28), one has to specify the shape of the cross-sectional area. For simplicity we assume that all cross-sections of the tongue have the same shape, and are parametrized only by the linear dimension $R(z)$. In this case solution to (28) can be written as

$$v_z(x, y, z) = -\hat{v}(x/R, y/R)R^2\Phi, \tag{29}$$

where \hat{v} is the solution to a dimensionless equation which vanishes on the walls and is positive inside the region of interest. We are now in a position to justify that $\partial_z^2 v_z$ is indeed negligible: it is smaller than Φ by a factor $(R/z)^2$, which is a small number in the tongue.

The final step is to write down an equation for $R(z, t)$, which can be done using the continuity equation for an incompressible liquid,

$$\partial_t A + \partial_z U = 0. \quad (30)$$

Here $A = A_0 R^2$ is the cross-sectional area, $U = \int dx dy v_z(x, y) = -U_0 R^4 \Phi$ is the total velocity in the vertical direction, and A_0 and U_0 are positive numbers which depend only on the geometry. Combining (30) with (28) and using $P = P_0 - \gamma/R$, we obtain

$$\partial_t R^2 = (U_0/A_0) \partial_z \left(\frac{g}{\nu} R^4 + \frac{\gamma}{\rho \nu} R^2 \partial_z R \right). \quad (31)$$

Equation (31) has a stationary solution (6). We now consider a linearized form of (31) around this solution. Writing $R = (a^2/2z)(1 + \delta)$, we obtain,

$$t_1 \partial_t \delta = \frac{a^3}{z} \partial_z^2 \delta - \frac{2a^3}{z^2} \partial_z \delta - \frac{4a^3}{z^3} \delta, \quad (32)$$

where $t_1 = 8t_0 A_0/U_0$. Equation (32) admits a scaling solution

$$\delta(z, t) = \Delta \left(\frac{(z/a)}{(t/t_1)^{1/3}} \right). \quad (33)$$

The scaling function Δ satisfies

$$\frac{d^2 \Delta}{du^2} + \left(\frac{1}{3} u^2 - \frac{2}{u} \right) \frac{d\Delta}{du} - \frac{4}{u^2} \Delta = 0. \quad (34)$$

Thus the characteristic relaxation time for the build-up of the fully-developed tongue at height z is given by (26).

In the long-time limit, $\delta \rightarrow 0$, so that $\Delta(0) = 0$. The second boundary condition may be chosen to be $\Delta(\infty) = -1$. A numerical integration of (34) then yields the solution shown in figure 4. For $u \gg 1$ we have $\Delta = -1 + 4u^{-3} + O(u^{-6})$. In the opposite limit $u \ll 1$ we have $\Delta \simeq -0.0317u^4 [1 - \frac{1}{18}u^3 + O(u^6)]$.

4. Discussion and conclusions.

In this paper we have shown that a liquid drop of finite extent is unstable against spreading in a groove whose opening angle is less than some critical value α_c . Spreading to infinite heights takes place even when the liquid has to climb upwards against gravity. However, the thickness of the liquid tongue decreases with increasing height. In addition, the total amount of liquid in the tongue is finite: it is of the order of $a^2 D$ where D is the diameter of the tube.

Since the equilibrium thickness of the tongues is proportional to a^2/z [Eq. (6)], at very high altitudes, microscopic interactions such as van der Waals and double-layer forces become important [1, 3-5]. Taking $a = 1$ mm and the range of molecular interactions at $1 \mu\text{m}$, the macroscopic description used in this paper breaks down when the height exceeds 1 m. This regime is left for future investigation.

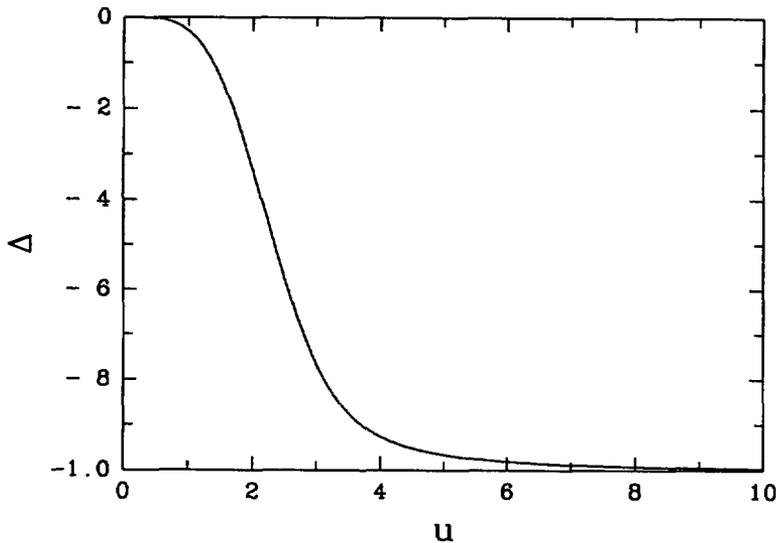


Fig. 4. — The scaling function that appears in equation (33).

In a tube whose diameter is smaller than the capillary length, the approach to equilibrium is controlled by viscous flow of the liquid, which yields a $t^{1/2}$ -law for rising of the center meniscus and, at a later stage, a slower $t^{1/3}$ -law for rising of the tongues. For pure water at room temperature, the surface tension and kinematic viscosity coefficients are given by $\gamma \simeq 73$ dyn/cm and $\nu \simeq 10^{-2}$ cm²/s, respectively. This yields $a = 0.38$ cm and $t_0 = \nu/(ga) \simeq 3 \times 10^{-5}$ s. Using equation (26), we find that the time it takes for the liquid to reach 1 cm, 10 cm, and 1 m are then 10^{-3} s, 1 s, and 10 min, respectively. In our experiments with colored solutions, rising seems to be much slower than that predicted above. This may possibly due to contact-line pinning by dirt on the wall of the tube or a change of wetting properties by ions in the solution, or a combination of both effects. We have not, however, checked quantitatively whether the scaling laws break down as well.

The analysis presented in this paper offers an explanation for the fast release of bubbles in tubes with sharp grooves. Such tubes may be more of a common occurrence than rarity in living bodies, for which liquid transport is of crucial importance, and where capillary forces are of relevance. Our findings may also be of use in solving engineering problems where trapping of bubbles is hazardous. We hope our preliminary study will inspire further theoretical and experimental investigations in this area, particularly on the dynamical side.

Acknowledgements.

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