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On the motion of bubbles in capillary tubes

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The average thickness of the wetting film left behind during the slow passage of an air bubble in a water-filled capillary tube of circular cross-section has been determined experimentally as a function of bubble speed and bubble length. For bubbles of length many times the tube radius, the ratio of film thickness to tube radius is found to be a function of the capillary number only, in agreement with previous experimental studies. As has been found previously, the asymptotic result of Bretherton (1961) significantly underpredicts the film thickness, the discrepancy being greatest at the lowest speeds. For bubbles of length less than about 20 tube radii, on the other hand, good agreement with the Bretherton theory is obtained over two orders of magnitude in bubble speed. The theoretical profile of long bubbles is shown to be unstable; however the explanation of the observed behaviour is, as yet, incomplete.

1. Introductory remarks

The flow of an air bubble in an otherwise liquid-filled tube has been the subject of study for the past half-century. In various laboratory experiments it is necessary to know the mean flow rate of a liquid through a clear tube of small bore; a simple estimate of this speed is obtained by introducing an air bubble into the system and measuring its travel time over a known distance. In an early work, Fairbrother & Stubbs (1935) realized that, if the liquid wets the glass tube, a thin liquid film will be left behind and the speed of the bubble will, in general, exceed the mean rate of the flow of the liquid. Reasoning on dimensional grounds, they established that, for small tube diameter and low speeds, the fractional error in the speed measurement will be a function only of the capillary number $Ca = \mu U/\sigma$, where U is the bubble speed, μ the viscosity of the driven fluid and σ is the liquid–air interfacial tension. Their experiments indicated that a satisfactory empirical correlation was

$$W = \frac{U-U_{\mathrm{m}}}{U} = 1.0\,Ca^{\frac{1}{2}} \tag{1.1}$$

over a range of capillary numbers between 10^{-3} and 10^{-2} approximately. Here U_{m} is the mean liquid speed. Taylor (1961) experimentally verified (1.1), extending its validity to $Ca = 0.1$, though his primary interest was for much higher speeds where W appears to achieve an asymptotic value of about 0.55. Later work by Cox (1962) indicated that this ultimate value was about 0.60. These workers calculated the thickness of the residual layer by measuring the rate of accumulation of the viscous liquid expelled from the tube and comparing this with the measured bubble velocity. Clearly this method is more appropriate to the higher capillary-number range where the difference in the two flow rates is substantial.

More recent interest in this problem arises because of its relevance to very slow two-phase flow in channels of microscopic dimensions. Such regimes are characteristic of flow within the porous rock of an oil reservoir where typically the driven fluid is significantly more viscous than the driver. When the two fluids are immiscible, capillary forces become important. Such forces are inversely proportional to the pore radius which, for a sandstone, may lie in the range 1 to 100 μm. Typical capillary numbers for reservoir applications vary from 10^{-6} or smaller up to perhaps 10^{-4}.

An important contribution to our understanding of this problem was made by Bretherton (1961). In the low-speed limit $Ca \to 0$, he found an approximate solution by, in effect, the method of matched asymptotic expansions. Using the assumption of quasi-unidirectional flow in the thin-film region, i.e. the so-called lubrication approximation, he found that

$$W = 1.29\,(3Ca)^{\frac{2}{3}} \tag{1.2}$$

to leading order. Bretherton's theory and certain extensions will be discussed further in §3.

Bretherton also performed experiments to validate his asymptotic result. He inferred the thickness of the wetting layer indirectly; rather than measure the rate of efflux of the expelled liquid, he measured the rate of shrinkage of driven slugs of two organic liquids in a tube otherwise filled with air. Since his theory predicted that film thickness would be determined by local behaviour near the bubble nose, his experiments employed semi-infinite bubbles; that is the liquid slug bridging the tube was blown downstream by a continuous stream of air. The agreement of theory with experiment was less than satisfactory. For capillary numbers in excess of 10^{-4}, the predicted $\frac{2}{3}$-power law was approximately obeyed. However at slower speeds, the measured value of effective film thickness greatly exceeded the theoretical value; at a capillary number of 10^{-6}, theory and experiment differed by about a factor of three. Since the theoretical result is based on the assumption of vanishingly small capillary number, the low-speed deviation places the entire theory in doubt. Bretherton systematically explored a number of possible causes for the discrepancy, yet none of these could provide a satisfactory explanation. In the light of our experimental finding, we shall review these various possibilities in §3. Another experimental study, by Marchessault & Mason (1960), used an air bubble in a dilute aqueous solution of potassium chloride. Film thicknesses were inferred from resistance measurements and were found to be substantially larger than Bretherton's findings.

Within the lubrication approximation, the problem of determining the asymptotic thickness of a soap film that is slowly pulled out of a liquid bath can be shown to be virtually identical to the Bretherton problem. In the physical chemistry community the result is known as Frankel's Law; its derivation is completely analogous to Bretherton's work. Unlike the bubble-in-tube problem where there is substantial disagreement between theory and experiment, Frankel's Law has been verified without difficulty. Discussions of this work are given in Mysels, Shinoda & Frankel (1959) and Lyklema, Scholten & Mysels (1965). The relationship between the two problems is discussed briefly in the Appendix to this paper. Similarly, the film-coating problem treated by Landau & Levich (1942) is also analogous to these two, within the lubrication approximation.

Recently this problem has been the subject of rather intensive study because of both its relevance to oil recovery and other applications, and also as a model for basic studies in wetting and spreading. Saffman (1982) employs the Bretherton solution to arrive at a prediction of the unrecoverable fraction of oil in a reservoir that is idealized as a network of capillary tubes. Prothero & Burton (1961) have considered bubbles in capillary tubes as a model for the motion of blood cells. Hirasaki & Lawson (1984) have extended the Bretherton solution by including a surface-tension-gradient effect in developing a model for flow of bubbly mixtures. This work is motivated, apparently, by the contemplated use of foams as pusher fluids in oil recovery. Experimentally they find that the effective viscosity of a chain of bubbles, in effect the pressure drop per bubble, exceeds the Bretherton prediction by about an order of magnitude. This large increase is attributed to surface dilation, and consequent variation in surfactant concentration, using ideas from the theoretical treatment of Levich (1962).

The inability of the Bretherton theory to correctly predict the wetting-layer thickness at very low speeds casts doubt on its prediction of bubble pressure drops; thus some or perhaps a large portion of the pressure drop increase measured by Hirasaki & Lawson (1986) may, in fact, occur in clean systems without surfactant. Recent theoretical studies by Teletzke (1983) and Teletzke, Davis & Scriven (1986*a*, *b*) treat thin liquid films in a more general sense; in this work the Bretherton solution is augmented, within the context of lubrication theory, by the inclusion of terms to model surface-tension-gradient effects, disjoining pressure in very thin films, and lack of perfect slip of the liquid on the bubble boundary.

The Bretherton problem also plays a role in the fingering instability in Hele-Shaw cells discussed first in the important paper by Saffman & Taylor (1958). Because multiphase flow in Hele-Shaw cells is often regarded as a model for porous-media flow, results obtained in these simple laboratory experiments may have implications for oil recovery and ground-water hydrology. At the fluid interface in a Hele-Shaw cell the pressure difference is essentially proportional to the mean curvature. Saffman & Taylor assumed that the component of the interface curvature between the plates was constant, thus only the variation in the curvature when the cell is viewed in planform is important. Under conditions of perfect wetting by the displaced liquid, the curvature between the plates and the thickness of the residual wetting layer will vary with the speed of advance of the interface. Park & Homsy (1984) demonstrate that the two-dimensional version of the Bretherton problem is the appropriate local solution to capture this effect.

Numerical studies of capillary-tube displacement of a wetting liquid by a semi-infinite inviscid slug of gas have recently appeared. Both Reinelt (1984), using a finite-difference method, and Shen & Udell (1985), using finite elements, solve the full creeping-motion equations with the exact continuity-of-stress conditions on the free surface. While Reinelt demonstrates strikingly good agreement with the high-speed experimental results of Taylor (1961), neither numerical method is able, apparently, to treat the low-speed regime $Ca \leqslant 10^{-3}$ because of the difficulty in adequately resolving the thin-film region. At $Ca = 0.01$, both solutions predict a thinner wetting film than that given by the Bretherton analysis.

In the next section details of our experimental procedure will be presented. While our technique is basically similar to Bretherton's, a number of modifications have been made. In particular, the injection system has been modified so that air bubbles of finite length can be investigated. The experimental results are given in §3. Essentially we find that short bubbles produce wetting films whose thickness is in close agreement with the Bretherton theory. The wetting films for sufficiently long bubbles, including the continuous gas-injection case, is thicker or much thicker, depending on the capillary number, but is also essentially independent of bubble length. At one particular speed, $Ca = 3 \times 10^{-5}$, for bubble lengths less than about 25

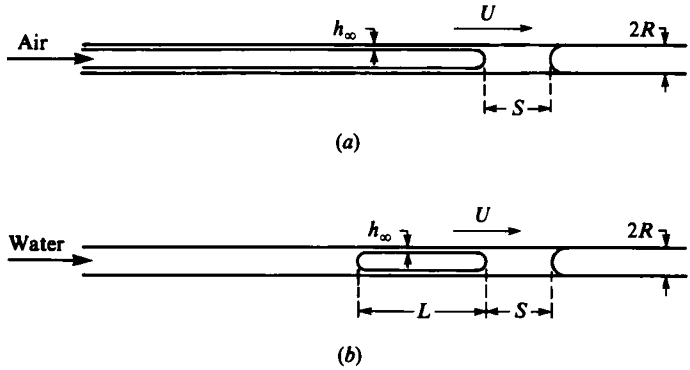

FIGURE 1. (a) Endless air bubble pushing liquid slug; (b) finite bubble pushing liquid slug.

tube radii, inferred film thicknesses agree well with the lubrication-theory result while for lengths greater than about 50 radii, film thickness is again virtually constant at about twice the theoretical result.

In §3 we compile various theoretical arguments in an effort to understand the new experimental results. It is shown that long stagnant wetting films are unstable suggesting that other steady-state solutions may exist for long bubbles. Potentially non-ideal experimental conditions are re-examined, though none yields an alternative explanation for the thicker films. In particular we consider and discard both lack of perfect slip, termed surface hardening by Bretherton, and surface-tension-gradient effects, due to contamination of the interface, for example, since both lead to reduction rather than increase of inferred film thickness.

Finally, in §4, we seek to put our new results in perspective and suggest additional avenues of attack, both experimental and theoretical, that may lead to a more complete understanding of this important problem.

2. Experimental procedure

Our approach was essentially that of Bretherton (1961) in which a slug of a wetting liquid is forced to move through an initially dry glass capillary tube at constant velocity U. The parameter W, defined in (1.1), is obtained from

$$W = \frac{\Delta S}{D}, \tag{2.1}$$

where ΔS is the decrease in length of the liquid slug and D is the distance of travel.

In some respects, our procedure differed from that of Bretherton: (i) We used water as the liquid phase, while Bretherton used aniline and benzene. (ii) In Bretherton's and some of our experiments, the slug was followed by an endless air bubble (figure 1 a), while we introduced the end-to-end bubble length L as a variable. In that case, the slug and air bubble are followed by liquid (figure 1 b). (iii) Bretherton moved the slug by applying hydrostatic suction at the upstream end of the tube, while we pushed the slug (or slug plus bubble) by injecting air (or water) from a glass syringe, driven by a positive displacement pump with adjustable flow rate (Sage Instruments Model 355). The link between the syringe and the capillary tube consisted of an 18- or 22-gauge hypodermic needle and Teflon connector.

The precision-bore Pyrex tubes were 95 cm long and had internal diameters of 1

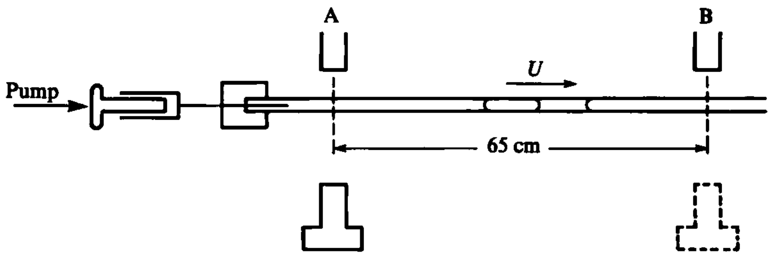

FIGURE 2. Schematic experimental arrangement.

or 2 mm (Lab-Crest Scientific Glass Co.). The stated tolerance of the tube diameters was ± 0.0075 mm. The tubes (and all other parts) were cleaned with chromic acid, and dried by passing dry filtered nitrogen through them for about 15 minutes. The water was distilled, and then passed through a Milli-Q Reagent-Grade Water System (Millipore Corp.) which consists of a prefilter, an activated-carbon filter, two ion-exchange cartridges, and a final 0.22 μm filter.

The dry tube was mounted on top of a heavy square brass bar, resting near its ends on two lab jacks, which permitted accurate levelling. A slug of water, between 1 and 3 cm long, was introduced at one end. In some experiments, the slug was pushed down the tube by injecting air. In most experiments, however, the slug was followed by an air bubble of length L, and slug plus bubble were driven by injecting water from the pump.

The slug was photographed as it moved past two fixed points A and B, exactly a distance $D = 65$ cm apart (figure 2). We used a Nikon FM2 35 mm camera, equipped with a PN 11 extension ring, a Nikkor 105 mm/f4 lens, and a Vivitar 283 electronic flash. The distance between the front of the lens and the tube was about 17 cm. A $\frac{1}{2}$-inch aluminium rod was mounted above the tube at A and B in the same focal plane as the slug. Its image on the negative provided the magnification factor, which was very close to unity. The slug length S was measured directly on the negative with a measuring microscope (Ernest F. Fullam, Inc.) to an accuracy of ± 0.001 cm. For short bubbles, the length L could be measured with the same accuracy from the negative. Since the longer bubbles did not fit on the negative their length was obtained with a ruler to 0.05 cm.

The slug's velocity U was obtained from the A-to-B travel time, while the surface tension and viscosity were taken as $\sigma = 72.0$ mN/m and $\mu = 0.93$ m Pa s (23 ± 0.5 °C). The resulting error in the capillary number should not exceed a few percent.

The error in ΔS and, therefore, in W can be considerably greater. Although the mean tube diameter $2R$ does not need to be known with great accuracy, slight deviations from uniformity can result in large errors, particularly at low velocities where ΔS is small. As a typical example, if the true diameters in the vicinity of A and B differ by 0.5%, then the slug lengths at A and B will differ by 1% for this reason alone. In a 1 mm tube, this amounts to an apparent ΔS of 0.02 cm for a 2 cm slug. As we shall see later, a typical value of W at, say, $Ca = 3 \times 10^{-5}$ is $W = 0.004$, or $\Delta S = 0.25$ cm. Therefore, in this particular case, non-uniformity, if unaccounted for, would cause an 8% error in W. Our tubes were tested for uniformity by measuring the length of a mercury slug in the vicinity of A and B. The difference in diameter was found to be extremely small (≈ 0.1%), so that the associated error in ΔS was comparable to that in the length measurements themselves.

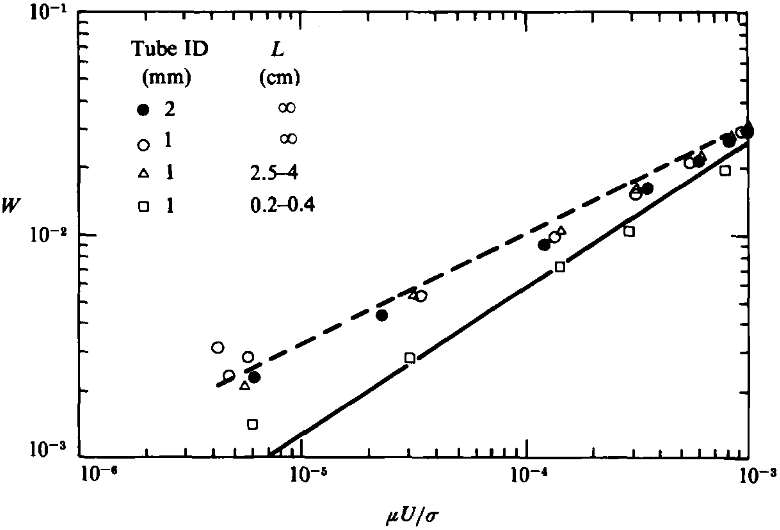

FIGURE 3. The variation in $W = 2h_{\infty}/R$ with capillary number: ——, Bretherton theory, $W = 1.29\,(3Ca)^{\frac{2}{3}}$; – – –, high-speed empirical correlation, $W = 1.0Ca^{\frac{1}{2}}$.

3. Discussion of results

We now discuss the experimental findings, which are presented graphically in figure 3. Our original apparatus used a capillary tube with a 2 mm inside diameter and, as was done by Bretherton, the liquid slug was followed by an endless stream of air. For values of capillary number between 6×10^{-6} and 10^{-3}, values of the speed difference or, equivalently, twice the wetting-film thickness, are given by the solid dots in the figure. As in Bretherton's experiments, using two other liquids, the discrepancy between theory and these measurements increases as the speed is reduced. In order to discern the effects of buoyancy, as explained below, a series of experiments with a 1 mm-inside-diameter tube was performed over the same range of speeds. As can be seen in the figure (open dots), no systematic change in the results is apparent.

For a given value of capillary number, the film thicknesses measured here, using water and an endless air stream, are somewhat greater than those measured by Bretherton. Bretherton used two organic liquids, aniline and benzene. It is perhaps interesting to note that, for these three liquids, film thicknesses increase with increasing interfacial tension.

The solid line in the figure is the theoretical result of Bretherton, obtained by invoking the 'lubrication' approximation. That is, by requiring quasi-unidirectional motion in the thin wetting layer and assuming the slope of the gas–liquid interface is small, it may be shown that the velocity profile is parabolic in y; this ordinate is measured inward from the tube wall. In a bubble-fixed coordinate system, the boundary conditions for this steady flow are no slip on the wall, $u(x,0) = -U$, and no shear on the interface $u_y(x, y_1) = 0$. Here U is the constant forward speed of the bubble in the direction of increasing x and $y_1(x)$ is the shape of the interface to be determined. The bubble viscosity is assumed to be zero and the pressure within it is constant. The pressure in the wetting layer is given by the interface pressure jump which is approximately equal to $\sigma y_1''$. With h_{∞} denoting the asymptotic film thickness, and requiring the backward mass flux in the layer to be constant, it may be shown that the equation of the interface is

$$y_1''' = \frac{3Ca(y_1 - h_\infty)}{y_1^3}. \tag{3.1}$$

The explicit dependence on capillary number $Ca = \mu U/\sigma$ may be removed by the non-dimensionalization and scaling

$$y_1 = h_\infty \eta, \quad x = h_\infty (3Ca)^{-\frac{1}{3}} \xi, \tag{3.2a,b}$$

which gives

$$\eta_{\xi\xi\xi} = \frac{\eta - 1}{\eta^3}. \tag{3.3}$$

This thin-film equation is then integrated numerically, using a shooting method, with initial conditions given by a linearized version of (3.3). Assuming the existence of an 'overlap' region, where η becomes large, yet the actual interface slope remains small, the asymptotic value of $y_1''(x)$ may be identified with the bubble nose curvature R^{-1}. For thin films, R is approximately equal to the tube radius. The final result is

$$\frac{h_\infty}{R} = 0.643(3Ca)^{\frac{2}{3}}. \tag{3.4}$$

Moreover the fractional speed difference W, plotted in figure 3, is simply equal to $2h_\infty/R$.

Further details of Bretherton's derivation and an extended result, to higher order in Ca, may be found in his original paper. Park & Homsy (1984) rederive the result (3.4) using the more modern formalism of matched asymptotic expansions. Note that the Bretherton solution gives the asymptotic layer thickness h_∞ using only local conditions at the bubble nose. This solution is independent of bubble length.

With a reasonable degree of rigour, Bretherton demonstrates that the lubrication equation (3.3) is a valid approximation to the full nonlinear problem and, when treated as an initial-value problem, yields a unique solution for the layer thickness given by (3.4). Because the original problem, without approximation, is highly nonlinear, other steady-state solutions are in no way ruled out.

Because of stability considerations, also to be discussed below, bubbles of finite length, between 2.5 and 4 cm, were then used to drive the water slug. Again, no change was apparent (cf. triangles in figure 3). Still shorter bubbles were then used. In each case the bubble length, including the front and rear menisci, was taken as close as possible to 3 mm. In the 1 mm tube, the thin film region is then about 2 mm in length. Even at the highest speed tested, therefore, the scaled film length $\Delta\xi$ was greater than 50, assuming the Bretherton theory to be correct. These data are shown using squares in figure 3. At last rather close agreement with the Bretherton theory was obtained except at the lowest speed tested, $Ca = 6 \times 10^{-6}$. This may well be due to experimental error which becomes quite appreciable in that region. Alternatively, agreement might have been obtained at this low speed, if even shorter bubbles had been used, but this was not investigated further.

A more detailed study was then made at a constant speed $Ca = 3 \times 10^{-5}$ using bubbles of various lengths. The actual value of Ca varied slightly from run to run ($3 \times 10^{-5} \pm 10\,\%$). The corresponding values of W were corrected for this via the $\frac{2}{3}$-power law. The corrected results are shown in figure 4 for a total of 65 runs. Also shown is the Bretherton result $W \approx 0.00259$ and the experimental value for the

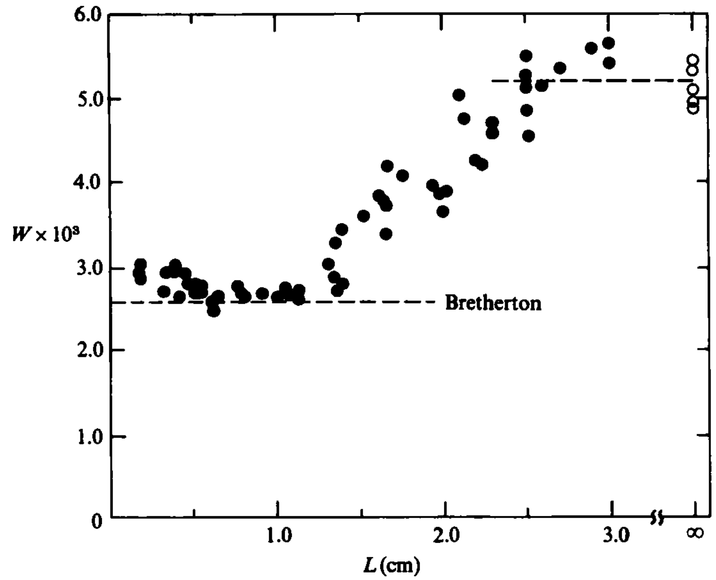

FIGURE 4. Variation in W with bubble length at capillary number $Ca = 3 \times 10^{-5}$, 1 mm ID tube.

endless bubble $W \approx 0.0052$. For bubbles between 0.18 and 1.20 cm in length, a total of 27 runs, the data are scattered around the Bretherton value with a maximum deviation of no more than 8%. Similarly, for bubbles longer than 2.5 cm, the data vary about the endless bubble result within 8%. In the transition region, where L lies between these values, somewhat greater scatter is observed. For very short bubbles the thin-film region is not long and values of W in excess of the Bretherton value are expected. Indeed, for bubbles less than the tube diameter in length, no thin-film region exists. The data do show an upward trend for small L. Teletzke (1983) has calculated the effective film thickness for very short bubbles by numerical integration of (3.3) in both the forward and backward directions. He finds that the semi-infinite result is valid unless the film length is less than a tube radius. The data seem to indicate a somewhat larger effect than his theory predicts.

Figures 3 and 4 considered together suggest that the problem may have multiple solutions: the lubrication result appropriate to bubbles of moderate length and a second solution for very long bubbles. Two questions naturally arise: (i) For what value of length does the Bretherton result cease to be valid and what is the cause? (ii) What is the origin of the second (conjectured) solution, assumed also to be of steady state? Paradoxically, of course, the Bretherton solution, which predicts a wetting-film thickness that is determined solely by conditions near the nose, works for the shorter bubbles where conditions at the rear meniscus might have been expected to have had greater influence. For comparison, in figure 3 we show the empirical expression of Fairbrother & Stubbs (1935)

$$W = 1.0Ca^{\frac{1}{2}},$$

which, while obviously closer to this second solution, does not predict the apparent deviation from simple power-law behaviour at low speeds. Bretherton neglected the variation in pressure due to changes in the transverse curvature. To the extent that wetting-film thickness is order $Ca^{\frac{2}{3}}$, he showed that the transverse curvature effect is of relative order $Ca^{\frac{2}{3}}$ smaller than those effects retained. Were the wetting-film thickness order $Ca^{\frac{1}{3}}$, on the other hand, the transverse curvature term would be of comparable magnitude to the y_{1xx} term. We note that the long-bubble data in figure 3 can be fit quite well with a linear combination of $Ca^{\frac{1}{3}}$ and $Ca^{\frac{2}{3}}$ terms. Such a semi-empirical fit is

$$W = 0.05(3Ca)^{\frac{1}{3}} + 2(0.643)(3Ca)^{\frac{2}{3}},$$

where the coefficient of the order-$\frac{2}{3}$ term is retained at the previous value.

A partial answer to the first question comes from stability considerations. An unsteady analogue of (3.3) can easily be derived. The wetting-layer volumetric flow rate Q is given, under the lubrication approximation, by

$$\frac{Q}{2\pi R} = -Uy_1 - \frac{y_1^3}{3\mu}\frac{\mathrm{d}p}{\mathrm{d}x}. \tag{3.5}$$

Mass conservation for unsteady flow is governed by

$$\frac{\partial Q}{\partial x} = -2\pi R\frac{\partial y_1}{\partial t}. \tag{3.6}$$

For slowly varying axisymmetric flow, the pressure jump across the interface is given by

$$\left.\begin{aligned} p &= -\sigma\left(\frac{\mathrm{d}^2 y_1}{\mathrm{d}x^2} + \frac{1}{R-y_1}\right) \\ &\approx -\sigma\left(y_{1xx} + \frac{1}{R} + \frac{y_1}{R^2} + \dots\right) \end{aligned}\right\} \tag{3.7}$$

for $y_1/R \ll 1$. Retaining this second component of the interface curvature and combining (3.5) and (3.6), we obtain

$$y_{1t} = Uy_{1x} - \frac{\sigma}{3\mu}y_1^3\left[\left(y_{1xxx} + \frac{y_{1x}}{R^2}\right)\right]_x \tag{3.8}$$

in a bubble-fixed coordinate system. In a laboratory coordinate system, on the other hand, the first term on the right of (3.8) is absent. Because of the no-shear interface condition, the uniform wetting film between the bubble end menisci is stagnant; let us therefore proceed in laboratory coordinates. Introducing dimensionless variables according to

$$y_1 = c\tilde{y}, \quad x = R\tilde{x}, \quad t = \frac{3\mu R^4}{\sigma c^3}\tilde{t},$$

(3.8) may be written in universal form, for $U = 0$, *as*

$$\tilde{y}_{\tilde{t}} = -[\tilde{y}^3(\tilde{y}_{\tilde{x}\tilde{x}\tilde{x}} + \tilde{y}_{\tilde{x}})]_{\tilde{x}} \tag{3.9}$$

where c is the wetting film thickness. The linearized form of (3.9) is simply

$$\tilde{y}_{\tilde{t}} = -(\tilde{y}_{\tilde{x}\tilde{x}\tilde{x}\tilde{x}} + \tilde{y}_{\tilde{x}\tilde{x}}). \tag{3.10}$$

For a long film, we can consider a continuous spectrum of disturbances of the form

$$\tilde{y} \sim \mathrm{Re}\,(\mathrm{e}^{\omega\tilde{t}+\mathrm{i}k\tilde{x}})$$

which, when inserted in (3.10), gives

$$\omega = k^2 - k^4.$$

The growth constant ω is positive for sufficiently small wavenumber. The wavelength of maximum growth is

$$\lambda_{\max} = 2^{\frac{1}{2}}2\pi R \approx 8.9R \tag{3.11\,a}$$

with a characteristic time given by

$$T_{\max} = \frac{12\mu R^4}{\sigma c^3}. \tag{3.11b}$$

Thus a thin stagnant annular film is unstable provided its length is greater than the tube circumference. Sometimes called the Rayleigh 'sausage' instability, the same result was obtained by Carroll & Lucassen (1974) for a thin stagnant film on the outside of a solid cylinder. In fact both can be shown to be special cases of the general linear stability results of Goren (1962) for thin films with negligible inertia.

We thus arrive at a criterion which distinguishes the longer from the shorter bubbles, the former being unstable. If we identify c with the Bretherton film thickness h_∞, however, we find the characteristic time for growth of a disturbance to be quite long. Using the total run time in a tube of length L as a reference, we find that

$$T_{\max}/T_{\text{run}} \sim Ca^{-1}.$$

Based on this simple argument one might conclude that the instability identified here could only be important at speeds much higher than those considered in the present experiments.

While the above stability calculation may also be criticized as not being as relevant as one performed in a bubble-fixed frame, the fact remains that long films are not stable and, if the problem as posed were to admit multiple solutions, this instability could be sufficient to cause transition to another steady-state solution. We deal here with a nonlinear free-surface problem for which no existence or uniqueness arguments are available. Certain other problems of this type, particularly those involving capillary forces, have been shown to possess multiple solutions, see, for example, Schwartz & Vanden-Broeck (1979), Chen & Saffman (1980), and Vanden-Broeck (1983).

In an effort to explain the difference between theory and experiment, Bretherton considered and rejected a number of potential experimental difficulties. We shall reconsider his list, augmented by some others, and, as he did, conclude that no single cause can explain the effectively thickened wetting layer.

We shall first dismiss those potential sources of error that can be treated most simply as follows.

(1) Inertial effects can be neglected since the Reynolds number based on tube diameter is $O(10^{-2})$ at low speeds where, for long bubbles, the deviation from theory is greatest.

(2) Undoubtedly the bubble rides high in the tube; however increasing the Weber number $\rho g R^2/\sigma$ by a factor of four, by going to the larger tube, caused no discernible change in W.

(3) Lack of perfect drying of the tube would lead to a reduction, not an increase, in inferred layer thickness.

(4) Disjoining pressure effects could only be important for films much thinner than those produced here.

(5) Evaporation of the film liquid into the bubble can be shown to be an insignificant effect.

(6) Aside from the contribution of the transverse curvature variation to the pressure, which we feel may have a qualitative effect, neglect of other terms in the lubrication approximation to the creeping-motion equations is shown to be self-consistent for $Ca < 5 \times 10^{-3}$ by Bretherton and also Teletzke (1983).

(7) Tube wall-roughness effects may be dismissed since long-bubble and short-bubble data were obtained in the same tube.

An additional argument leading to rejection of each of the above sources of error is that none of them would lead to a critical value of bubble length at which the error mechanism would become operative, as the data in figure 4 would seem to indicate.

Two related mechanisms that may lead to an effectively thicker residual film warrant more careful consideration. These are lack of perfect slip at the air–water interface and surface-tension gradients arising from contamination of the interface.

Lack of perfect slip at the interface can be modelled by assuming the bubble to contain a fluid of some arbitrary viscosity. We let the pressure within the bubble be p_1 and let the bubble fluid viscosity be μ_1. Similarly the pressure and viscosity of the liquid wetting the walls are denoted by p_2 and μ_2 respectively. Within the context of lubrication theory for axisymmetric flow, let the interface be denoted by $r^*(x)$ where x is the axial coordinate. In bubble-fixed coordinates we apply the conditions of no slip on the walls, continuity of tangential stress at the interface and zero net flux within the bubble to the solutions of the axial momentum equation for each fluid. The result is two coupled equations for the pressure gradients $p_1'(x)$ and $p_2'(x)$, assuming unidirectional motion:

$$p_1'\left[\tfrac{1}{8}r^{*2}-\tfrac{1}{4}M\,r^{*2}\log\frac{r^{*2}}{R^2}\right]+p_2'\,\tfrac{1}{4}M\left[R^2-r^{*2}+r^{*2}\log\frac{r^{*2}}{R^2}\right]=-\mu_2\,MU, \tag{3.12a}$$

$$p_1'\,r^{*2}\left[R^2-r^{*2}+r^{*2}\log\frac{r^{*2}}{R^2}\right]+p_2'\left[\tfrac{1}{2}(R^2-r^{*2})^2-r^{*2}(R^2-r^{*2})-r^{*4}\log\frac{r^{*2}}{R^2}\right]$$
$$=-4\mu_2\left[U(R^2-r^{*2})-\frac{Q_2}{\pi}\right]. \tag{3.12b}$$

Here M is the viscosity ratio μ_1/μ_2 and Q_2 is the volumetric flux of the outer fluid. Let

$$r^*=R-y_1(x)$$

and assume that the wetting film is thin, i.e.

$$H=y_1/R\ll 1.$$

We now expand (3.12) for small H and retain leading terms, order-one terms and order-(MH) terms. The simplified equations are

$$p_1'\,\tfrac{1}{8}R^2(1+4MH)+p_2'\,\tfrac{1}{2}MR^2H^2=-M\mu_2\,U \tag{3.13a}$$

and
$$p_1'\,2R^4H^2+p_2'\,\tfrac{8}{3}H^3=-4\mu_2\left[2R^2UH+\frac{Q_2}{\pi}\right]. \tag{3.13b}$$

Assume that the interface becomes straight and parallel to the tube walls far downstream, i.e. as $H\rightarrow H_\infty$. Then $p_1'=p_2'$ there and the flux Q_2 can be evaluated there as

$$Q_2=2\pi R^2\,UH_\infty\left(\frac{1-2MH_\infty}{1+4MH_\infty}\right). \tag{3.14}$$

Consistent with the assumption of small interface slope, we have

$$p_1'-p_2'=\sigma RH'''(x). \tag{3.15}$$

Equations (3.13) and (3.15) are three equations for the unknown pressure gradients and the interface profile $H(x)$. We can now eliminate p_1' and p_2' among them and introduce the Bretherton scaling

$$H=H_\infty\,\eta$$

and
$$x=RH_\infty(3Ca)^{-\frac{1}{3}}\xi.$$

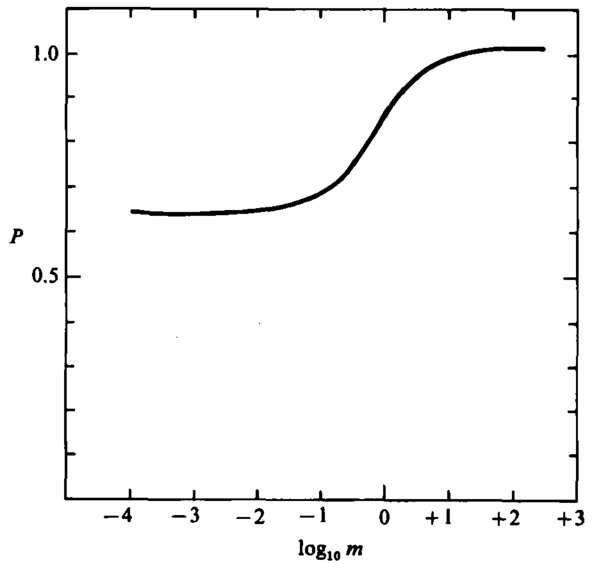

FIGURE 5. Similarity parameter P in the expression for wetting-film thickness, (3.18).

Again neglecting MH^2 terms relative to MH terms, we arrive at an equation for the interface

$$\eta_{\xi\xi\xi} = \frac{\eta-1}{\eta^3}\left\{\frac{1+2m+2m(1+4m)\eta}{(1+4m)(1+m\eta)}\right\}, \tag{3.16}$$

where

$$m = MH_\infty. \tag{3.17}$$

Thus the effect of finite bubble viscosity is to introduce the factor in curly brackets in (3.16). When the bubble viscosity is taken as zero, (3.3) is recovered.

Equation (3.16) has been integrated numerically, using a fourth-order Runge–Kutta method, for various values of m. As before, the limiting value of $\eta_{\xi\xi}$ as $\eta \to \infty$ gives the wetting-layer thickness in the form

$$H_\infty = (3Ca)^{\frac{2}{3}} P(m). \tag{3.18}$$

The function $P(m)$ is shown in figure 5. In the limit $m \to 0$, P assumes Bretherton's value 0.643. The other limiting case, $m \to \infty$, yields $P \approx 1.02$, exactly a factor of $2^{\frac{2}{3}}$ larger than the $m = 0$ case. In fact the form of $P(m)$ shown in figure 5 is closely approximated by the curve fit

$$P(m) = \frac{0.643}{2}\{1+2^{\frac{2}{3}}+(2^{\frac{2}{3}}-1)\tanh[1.2\log_{10} m+0.12]\}. \tag{3.19}$$

In any event, the wetting layer is always thicker for a finite value of the viscosity ratio. The amount of fluid left behind, equivalent to the rate of shrinkage of a driven slug, can be calculated from (3.14). It is always less than the inviscid-bubble case because the wetting film, while thicker, is no longer stagnant but has an average velocity in the direction of bubble motion.

That lack of perfect slip cannot explain the larger quantity of wetting fluid left behind in the experiment was numerically demonstrated for one particular value of capillary number, $Ca = 10^{-4}$, by Teletzke (1983). Bretherton himself showed that an infinite value of bubble viscosity leads to less fluid being left behind at any speed.

Here we have demonstrated that this is generally true for all viscosity ratios and capillary numbers consistent with the slowly varying, thin-film, and low-speed approximations. The problem has a similarity solution in the sense that the wetting-film thickness does not depend on the viscosity ratio and the capillary number separately, but only via the single parameter $(\mu_1/\mu_2)(h_\infty/R)$.

It is not *a priori* clear that a surface-tension-gradient effect will produce results analogous to finite driver viscosity. It can be demonstrated that this is true, however, at least in a qualitative sense. A full solution to this problem requires knowledge of the surface diffusion of contaminants as well as the details of the adsorption–desorption of these species between the interface and the bulk of the liquid. Levich (1962) describes such a coupled solution procedure for a spherical bubble or droplet in an unbounded liquid. We will be content here with a less exact treatment.

Assume that a steady-state distribution of surfactant exists on the interface in a bubble-fixed coordinate system. The concentration variation can be expected to be such that the surface tension is highest at the nose and decreases monotonically as one moves aft on the bubble. That is, the surface-tension gradient $\mathrm{d}\sigma/\mathrm{d}x$ is positive with x increasing in the direction of bubble motion. A force balance on an element of the interface yields, for the shearing stress,

$$\mu\frac{\partial u}{\partial y} = \frac{\mathrm{d}\sigma}{\mathrm{d}x} \quad \text{on } y = y_1. \tag{3.20}$$

The flux in the wetting layer, in the plane-flow problem, becomes

$$\begin{aligned} Q &= \frac{y_1^3}{3\mu}\frac{\mathrm{d}}{\mathrm{d}x}(\sigma y_1'') - Uy_1 + \frac{y_1^2}{2\mu}\frac{\mathrm{d}\sigma}{\mathrm{d}x}, \\ &= -cU, \end{aligned}$$

where c is the effective layer thickness to be determined. This equation may be rewritten as

$$y_1''' = \frac{3Ca(y_1-c)}{y_1^3} - \frac{1}{\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}x}\left(y_1'' + \frac{3}{2y_1}\right). \tag{3.21}$$

Introducing the Bretherton variables (ξ, η), (3.21) becomes

$$\eta''' = \frac{\eta-1}{\eta^3} - \frac{c}{2RCa\sigma}\frac{\mathrm{d}\sigma}{\mathrm{d}x}\left[\frac{3}{2\eta} + (3Ca)^{\frac{2}{3}}\eta''\right]. \tag{3.22}$$

The second derivative term in (3.22) is thus formally of order $Ca^{\frac{2}{3}}$ smaller than the η^{-1} term and will be discarded. We shall treat the coefficient of the η^{-1} term as a constant; this would indeed be the case if we assume that the surface-tension variation followed an exponential law near the nose of the form $\sigma = \sigma_0 \exp(\alpha x)$. It would also seem reasonable to expect that the surface-tension gradient is an increasing function of bubble speed, i.e. capillary number.

A model problem, including a surface-tension-gradient effect is, therefore,

$$\eta''' = \frac{\eta-1}{\eta^3} - \frac{B}{\eta}, \tag{3.23}$$

where B is a positive constant corresponding to positive $\mathrm{d}\sigma/\mathrm{d}x$, i.e. larger surface tension at the nose than in the thin-film region. Within the thin film η''' is taken to be zero and the constant film thickness is given by

$$\eta_0 = \frac{1-(1-4B)^{\frac{1}{2}}}{2B}.$$

B	η_0	P
0	1.000	0.6430
10^{-3}	1.001	0.6404
10^{-2}	1.010	0.616
0.1	1.127	0.349
0.15	1.225	0.151
0.17	1.277	0.036

TABLE 1.

Note that η_0 is greater than one for permissible positive values of B. The amount of fluid left behind, expressed as an effective thickness is, as before,

$$\frac{c}{R} = P(3Ca)^{\frac{2}{3}},$$

where P is the limiting value of η'' as $\eta \to \infty$. This equation may be integrated using a shooting method to find the dependence of P on B. Initial conditions are given by the linearized version of (3.23) with solution

$$\eta \approx \eta_0 + \epsilon e^{\beta\xi},$$

where

$$\beta = \left(\frac{1}{\eta_0^3} - \frac{2B}{\eta_0^2}\right)^{\frac{1}{3}}$$

and $\epsilon \ll 1$. Numerical values of P and η_0 are given in table 1. For values of B in excess of 0.173 matching is not possible because η ultimately tends to $-\infty$ rather than ∞. We see that our model of the surface-tension-gradient effect produces results that are qualitatively similar to finite bubble viscosity; the wetting-film thickness is increased, however the quantity of fluid left behind is reduced. A reverse surface-tension gradient, where the surface tension at the nose is lower than in the film, i.e. $B < 0$, is possible in principle, namely in the presence of rather high levels of simple electrolytes. This can be ruled out in our experiments. It may, however, have contributed to the large values of inferred film thicknesses obtained by Marchessault & Mason (1960) using their electrical-conductivity technique.

4. Concluding remarks

In this work we have reported experimental measurements of the thickness of the wetting film left behind after the slow passage of a bubble in a capillary tube. For sufficiently short bubbles, the film thickness agrees closely with the predictions of lubrication theory. For bubbles that are very long, on the other hand, a different 'solution curve' is measured; these results are also virtually independent of bubble length. The deviation between these two curves becomes quite large at low speeds.

We have shown that a long axisymmetric annular film is unstable to the Rayleigh 'sausage' mode. The wavelength of maximum growth is about 9 times the tube radius. This length may be compared with the bubble length at which the measured result, at one particular speed, begins to deviate from theory. From figure 4, this critical bubble length is between 20 and 25 tube radii. The rate of growth of the sausage instability, according to linear theory, is quite small, however. Many potential sources of error in the experiment have been investigated and no single one can provide an adequate explanation for this 'second' solution.

By analogy with the related problem of determining the shape of steady-state fingers in unstable displacement in Hele-Shaw cells, recently shown to possess multiple solutions by Vanden-Broeck (1983), we suggest that this problem also may admit multiple solutions. It seems clear that the lubrication version of this creeping-motion free-boundary problem has a unique solution. We feel it to be worthwhile to attack the full problem numerically using a boundary-integral technique. Such methods have been successful in producing multiple solutions to other problems where capillarity is important. Our experimental finding that long bubbles move faster than short ones has important implications for the stability and 'effective viscosity' of water–gas foams. Presumably the bubble-size distribution in a foam will be strongly influenced by the ultimate coalescence of bubbles moving at different speeds.

There is experimental evidence that the inability of lubrication theory to explain all the data may only occur for the axisymmetric case. The problem of predicting the thickness of soap films is directly analogous to the planar version of the Bretherton problem. Theoretical predictions of soap-film thickness, using Frankel's Law, are in very close agreement with experiment provided the soap film is thicker than about 1000 Å. Such results are reported in Mysels *et al.* (1959) and Lyklema *et al.* (1965). The range of capillary numbers in these experiments varies between approximately 10^{-7} and 10^{-4}. The strict equivalence of Frankel's Law and the Bretherton film-thickness result is discussed in the Appendix. Since the soap film is fundamentally two-dimensional, this suggests that the anomalous results may only occur in the axisymmetric version of the moving-bubble problem. Similarly, Levich (1962) reports confirmation of predicted layer thickness in film-coating experiments. If we accept this premise, the sausage instability may play an important role since it cannot occur in the two-dimensional case. It must be remembered, however, that the direct analogy among these various problems is strictly valid only in the lubrication approximation.

Our group is continuing its experimental investigation of this problem. It would be desirable to measure the possible dependence of the critical bubble length on Ca. In addition to determining the rate of shrinkage of driven-liquid slugs in capillary tubes, it is possible to simultaneously measure the pressure drop per bubble; these results can also be compared with predictions from lubrication theory. We hope to report on these experiments in the near future.

Appendix. Relation of Frankel's law and film coating to the Bretherton problem

The wetting-film thickness, as given by (3.4) may be written as

$$h_\infty = \frac{0.643}{\kappa}\left(\frac{3\mu U}{\sigma}\right)^{\frac{2}{3}}; \tag{A 1}$$

this approximation is valid for either axisymmetric or two-dimensional geometries. For axisymmetric flow, κ is the reciprocal of the tube radius R while for two-dimensional flow, κ is the reciprocal of the channel half-width. The form of (A 1) is determined by the balance of viscous and capillary forces within the transition zone, i.e. the region between the bubble-nose or outer region where the curvature is essentially constant and the thin-film or inner region, where the layer is stagnant in laboratory coordinates and is of constant thickness. Within the transition zone, the appropriate boundary conditions are no-slip on the tube wall and no-shear on the free surface.

Consider now the prediction of the thickness of a two-dimensional vertical film that is being drawn out of a soap solution, at low speed U, using a moving wire frame. The outer region does not have constant curvature; rather the shape of the free surface is determined by the balance of capillary and hydrostatic pressures. It is, in effect, a static meniscus whose shape is given by

$$\frac{\rho g y^2}{2\sigma} = 1 - \cos\theta. \tag{A 2}$$

Here y is measured vertically upward from the ambient water level and θ is the inclination of the tangent to the free surface. The free surface becomes vertical at a height

$$y_0 = \left(\frac{2\sigma}{\rho g}\right)^{\frac{1}{2}}. \tag{A 3}$$

The magnitude of the curvature there is

$$\kappa = \frac{2}{y_0} \tag{A 4}$$

using (A 2). The transition zone is centred about y_0; thus this value of κ is to be used in (A 1).

The lubrication-approximation boundary conditions for the film flow are analogous to those for the bubble-in-tube problem. One of them is a no-shear condition, applied here, by symmetry, on the film centreline. On the free surface, the no-slip condition is applied because the soap-film surface is assumed to be completely inextensible. This interchange of boundary conditions clearly has no effect on the lubrication-theory result.

Substituting for κ in (A 1), using (A 3) and (A 4), we arrive at Frankel's Law

$$T = \frac{C\mu^{\frac{2}{3}}U^{\frac{2}{3}}}{\sigma^{\frac{1}{6}}\rho^{\frac{1}{2}}g^{\frac{1}{2}}}, \tag{A 5}$$

where $T = 2h_\infty$ is the total width of the film. The constant C is $(0.643)\,3^{\frac{2}{3}}\,2^{\frac{1}{2}} \approx 1.88$, in agreement with Lyklema *et al.* (1965).

The Landau–Levich film-coating problem is more easily seen to be analogous to the Bretherton problem. The only modification required is the insertion of the curvature of the static meniscus as given by (A 3) and (A 4); this curvature replaces the reciprocal of the tube radius in the Bretherton problem.

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