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The film drainage problem in droplet coalescence

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A small drop of liquid 1 falls through a less dense liquid 2 and approaches the horizontal interface between liquid 2 and an underlying layer of liquid 1. After a short time the drop will be brought to rest (or nearly) in a hollow in the interface. Before the drop can coalesce with its bulk phase, the thin film of liquid 2 trapped between them must be squeezed out, and become sufficiently thin that rupture can occur. This is the film drainage problem. Early calculations, based on simple lubrication theory, fail to take proper account of two effects which are investigated here and shown to be decisive. They are the circulation induced in the drop and in the lower bulk fluid, which tends to speed up drainage, and the constriction in the film thickness at its periphery, which tends to slow it down. This constriction has been observed and some existing theories have attempted to model it in an *ad hoc* manner. We give here a physical explanation and calculate the minimum thickness explicitly. The effect of circulation in the adjacent fluids is also calculated.

1. Introduction

In the chemical-engineering process known as liquid–liquid extraction, two immiscible liquids are stirred up so that one liquid is dispersed in the other in the form of small droplets. The large interfacial area thus created enables (for example) a solute to pass efficiently from one liquid to the other. In the final stages of the process the liquids must be separated again and it is often important to prevent contamination of each liquid by small droplets of the other. The two liquids soon form two bulk layers, with the lighter liquid uppermost, but each will contain small drops of the other which approach the interface under the influence of buoyancy forces. The speed and efficiency with which these drops can be removed is often a key factor in the overall efficiency of the process.

As an idealization of this problem we consider a single drop of dense liquid (phase 1) sinking through a less dense liquid (phase 2) towards the horizontal interface between the two bulk phases. As the drop approaches the interface a thin layer of fluid 2 is trapped between the drop and its bulk phase. This thin layer must be squeezed away until there remains a film so thin that it can rupture, allowing coalescence. It is well established that most of the time required for coalescence is the time needed for this film to drain. Once the film has ruptured coalescence is effectively instantaneous (except that sometimes a secondary droplet is formed; Charles & Mason 1960).

With this in mind we assume that the drop has already reached the interface, where it is resting almost stationary, in quasi-static equilibrium, as the thin fluid

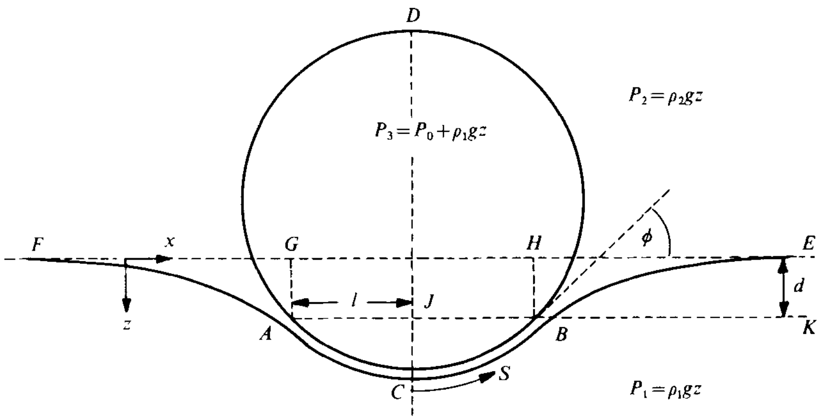

FIGURE 1. Cross-section of a drop resting on a phase boundary.

film drains. The drop rests in a depression in the interface with the weight of the drop partly supported by Archimedes' principle and partly by the surface tension of the interface. We take the initial film thickness as given since this is equivalent to choice of the time origin. The problem is to determine the subsequent changes in the film thickness and in particular how long it will take for the film to reach such a size that rupture can occur. How this rupture process is initiated is not well established but the current belief is that it is caused by an instability due to the van der Waal's forces between the molecules themselves. Such effects are likely to be important once the film thickness reaches 10^{-7} m or so. Certainly experiments indicate that rupture becomes more likely as the film gets thinner and it is natural to conjecture that rupture is most likely at the spot where the film is thinnest. If this is so, and the film thickness varies substantially from place to place, it will not be enough to estimate the average film thickness; instead the detailed dynamics of the film must be studied in order to find the minimum thickness. This is the principal aim of this paper. We also determine the overall behaviour of the film thickness as a function of time for large times and show that the models studied by most earlier workers give incorrect results. It is the models which are inadequate, not (usually) the calculations.

The film drainage problem has of course been studied by many writers and the literature up to 1971 is well covered in the survey article by Jeffreys & Davies (1971). The overall shape of the drop and liquid interface is well established; see, for example, Princen (1963) and Hartland (1967). One must make the reasonable assumption that the contour of the bulk-phase interface closely follows that of the lower surface of the drop until a definite point is reached, after which the two surfaces diverge, the drop closing over and the bulk-phase interface levelling off to a horizontal plane (figure 1). Only such an extended thin gap can explain the long times often needed for coalescence, and such gaps are observed experimentally.

We now present an argument to show that the problem of the flow in the film and the problem of the overall shapes of the interfaces can be decoupled. The shapes of the drop and of the bulk-fluid interface can be determined entirely by global arguments without any reference to the film flow at all; we show how this can be done without giving the detailed solution, which can be found elsewhere (see references earlier). The solution of this geometrical problem then provides the geometrical data for the study of the film drainage problem.

Since the lower surface of the drop and the bulk-fluid interface are so close over such a large region, their curvatures will be equal as a first approximation. Further, since the lower bulk fluid and the drop have the same density and the gap is so small, the pressure difference P_0 between the lower bulk phase and the drop is effectively a constant owing to the effect of surface tension γ, so that $2\gamma\bar{\kappa} = P_0$, and we can conclude that the curvature $\bar{\kappa}$ is a constant. Since we also assume that the configuration is axially symmetric the lower region of contact, ACB in figure 1, must be a spherical cap. At this stage we have therefore two free parameters at our disposal when describing the surface ACB: the value of $\bar{\kappa}$ and the value of the angle ϕ at which the spherical cap terminates. We now show how the solution of the interface equation may be continued beyond B and obtain two conditions that must be met by the solution. These will serve to determine the parameters $\bar{\kappa}$ and ϕ.

Beyond the region of contact each surface is an elastica with the pressure change due to surface tension balancing the difference between the hydrostatic pressure fields on either side. Besides the obvious fact that the curves must be continuous at the horizontal circle through AB, the gradients of the curves must also be continuous there for a discontinuity would produce a force which could not be balanced in a fluid medium. The elastica satisfies a second-order differential equation so with these conditions the equation for the surface of the drop can be integrated round from A (or B) to D. There are two restrictions that must be satisfied. One is that, at the point D which is vertically above C the curve must have zero gradient. This is in order that the drop does not have a pointed apex, gradient discontinuities being forbidden. The other restriction is that a given volume V is contained in the drop. These two restrictions determine the values of our parameters, the angle ϕ and the curvature $\bar{\kappa}$ of the spherical cap. Further, since ϕ is now known, the elastica describing the interphase boundary BE/AF is also well determined. We have one free parameter d in this case, the height of the level surface EF above AB. Only if this is chosen correctly will the elastica level off properly into a horizontal surface. Thus we see that the problems describing the large features of the interface shapes are well posed and can be solved independently. Below we refer to these as the exterior solution and the results will be presented in terms of parameters (such as ϕ) which can be determined by a separate investigation in any particular case.

The details of the interface shapes can only be obtained numerically, but various integral constraints can be obtained using only the assumptions just mentioned. Although this is not our main purpose we give some of these here since erroneous versions have appeared earlier. Details are given in appendix A.

Of general interest is that the drop displaces a volume from the lower bulk phase equal to its own volume. Of more practical value is the result that

$$2\pi l\gamma \sin\phi = \Delta\rho g V_1,$$

where ρ is the density, $\Delta\rho = \rho_1 - \rho_2$ and V_1 is the volume $AGHBDA$ in figure 1. We can use this equation to find an approximate value for ϕ in the case where the bubble remains approximately spherical with radius R_s (except over the lower portion ACB) by assuming that V_1 can be replaced by the full volume V of the drop. The radius of curvature R of the spherical cap will be given by $R = 2R_s$ (the two interfaces at the spherical cap double the effect of surface tension and produce the factor 2) and hence

$$\sin^2\phi = \tfrac{1}{12}\lambda, \tag{1.1}$$

where $\lambda = \Delta\rho g R^2/\gamma$. This formula is valid when the hydrostatic pressure variations are small in comparison with the surface-tension forces, i.e. when $\lambda \ll 1$. For benzene and water $\lambda = 0{\cdot}54$ if we choose $R_s = 2\,\mathrm{mm}$, whereupon $\phi = 12^\circ$ in agreement with numerical solutions of Princen. Equation (1.1) was derived by Charles & Mason (1960) for a bubble supported by a liquid interface although they seemed to believe this equation was exact. They found good agreement both with their own experimental results and with those of Derjaguin & Kussakov (1939).

Thus the exterior problem is well understood. The same cannot be said for the finer details, viz. the drainage of the fluid from the narrow gap. All attempts to derive this which are based on a viscous fluid model have been made under the assumption that at least one (and usually both) of the interfaces is rigid. Thus Charles & Mason (1960) took both surfaces to be rigid, which leads to a parabolic velocity profile for the flow, and then calculated the rate at which the gap closed by assuming that the change in the potential energy of the system is equal to the amount of energy dissipated by viscous friction in the gap. (This second assumption is also incorrect.) Their work was later extended by Jeffreys & Hawksley (1965), who attempted to calculate details of the gap shape. A correct approach was made by Hartland (1969) (again keeping one boundary rigid), who related the pressure within the gap to the pressure in the surrounding fluids. Unfortunately he made no approximations in his derivation, and this led to a partial differential equation for the gap profile which could only be solved numerically. We shall solve the same problem by an analytical technique and show how the resulting profiles have a fairly simple physical explanation. We also compare our theoretical results with his experimental results. The imposition of the no-slip condition at one boundary is appropriate in this case because the experiments were carried out with a hollow aluminium sphere (instead of a liquid drop). The no-slip condition may also be appropriate when surfactants are present in substantial amounts.

The gap boundaries are not rigid in general, however, and the realization that circulation in the drop and in the lower bulk phase must be accounted for is not new (see, for example, Jeffreys & Davies 1971). The possibly more natural assumption that the boundaries should be stress free leads to a subtle complication. If the boundaries are unable to support tangential stress then however viscous the fluid may be there is nothing for it to grip on to, and it should therefore be rapidly squeezed out of the gap. The solution of this difficulty is to take proper account of the circulation in the drop and in the lower bulk phase, as follows. The velocity profile in the film can be regarded as the sum of two terms. We refer to figure 2 and let u be the s component of velocity in the film, whose thickness is of order H_0, say. Then the tangential stress in the film is of order $\mu_2 u/H_0$. The velocities in the drop and lower bulk phase will also be of order u by continuity of velocity, and so the tangential stresses there will be of order $\mu_1 u/R$. These stresses cannot balance to leading order in the small parameter $H_0/R = \delta$. We therefore solve this problem by proposing an expansion for u in powers of δ in which the leading term u_0 satisfies $\partial u/\partial n = 0$ at the boundary and thus is roughly a plug flow. The requirement that the tangential stress be continuous is met by the terms of next order. However it turns out that this procedure is not

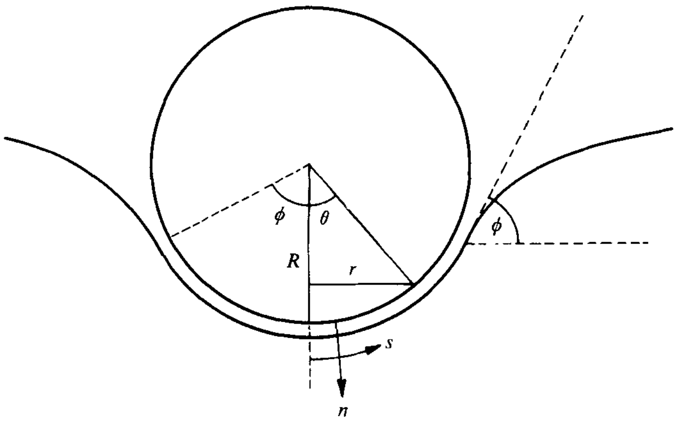

FIGURE 2. Cross-section of a rigid cylinder resting on an elastic sheet.

necessary in the main part of the film but only in a narrow region at its periphery, for a reason to be given presently, and the details are explained in § 3. Note further that if one interface of the film is rigid the circulation across the other interface will, by the above arguments, produce terms of order δ, which in that case can be ignored.

An entirely different treatment has recently been attempted by Chesters (1975), who considered the gap to be filled by an inviscid fluid and so sidestepped the rigid/free boundary dilemma. Such a model will be correct when the inertia forces in the gap are larger than the viscous forces, and clearly this happens when the Reynolds number based on the gap thickness and the fluid velocity in the gap is large. Clearly this can always be achieved if the drop impinges on the bulk-liquid interface with a sufficiently high initial velocity. Conversely viscosity must dominate when the gap thickness becomes sufficiently small. Which is the correct model in any individual case can be decided only by evaluating the Reynolds number. In this paper we shall assume throughout that viscous forces dominate.

A problem of a different nature arises when one considers the pressure and pressure gradients along the gap. The pressure in the gap just before the gap terminates at the point B (see figure 1) cannot be equal to the pressure just beyond that point, still in phase 2. This is easily seen by comparing these pressures with the pressure just on the other side of the adjacent lower boundary. Assuming equilibrium, the pressure in phase 1 just below the boundary will be continuous. However the curvature of the surface changes suddenly at B, so surface tension will ensure a finite pressure drop on the other side in phase 2. Its effect will be to increase the fluid velocity in the film until the increased viscous stresses that are produced balance the large pressure gradient. By continuity, it follows that the gap must contract at this point, becoming even smaller than before. These contractions have been observed, but the explanation in terms of the pressure gradient does not appear to have been given. As noted above, it is important to understand and predict this narrowing of the gap because it is here (when it exists) that rupture of the film is most likely. Furthermore it is plain that the constriction will have a major effect on the overall rate of drainage of the film.

In § 2 we re-examine the problem of Hartland (1969), in which the 'drop' is a rigid sphere. This is a much simplified problem because of the presence of a rigid boundary.

The constriction at the edge of the film is examined in detail. There are two distinct cases depending on whether or not the hydrostatic pressure gradient due to gravity can be neglected. Solutions are found in each case.

In § 3 we examine a liquid drop, and so have low-stress boundary conditions. However, we consider only the case when hydrostatic pressure variations along the gap can be neglected. Again a contraction exists at the edge. We find that the fluid in the main gap is essentially motionless with the pressure there constant. It needs only a very slight approach of the boundary surfaces over the area of contact to cause a flux which, when magnified by the contraction at the boundary edge, leads to appreciable velocities through the contraction. These velocities are driven by the high local pressure gradient at that point. Otherwise the solution is as outlined earlier, local circulation being set up in the phase 1 fluid on either side of the contraction and the resulting stresses balancing those in the gap. The circulation is driven by the high velocities in the contraction, and is therefore on the scale of the contracted region, the main gap length playing a passive role.

In § 2 the analysis leads to the study of single nonlinear ordinary differential equations whose solutions can be, and are, found once and for all. The relevant piece of information in the solution is, in each case, in fact a pair of numbers. For the complicated situation of § 3 we arrive instead at a nonlinear integro-differential equation, which, if it could be solved, would presumably yield similar information. The solution has not been attempted for reasons given in § 3 and the results therefore contain two unknown numerical constants.

2. The settling of a rigid sphere

We consider here a rigid sphere of radius R and weight W which is sinking through a liquid of density ρ_2 towards the interface between that liquid and a liquid of density ρ_1 ($>\rho_2$). The interface will be horizontal at large distances from the sphere (see figure 2). We assume that the sphere has sunk sufficiently far that it is almost touching the interface and is separated from it by only a thin layer of fluid 2 of thickness $H(\theta, t)$ which extends symmetrically around the sphere as far as $\theta = \phi$.

This is the configuration studied experimentally by Hartland so the results obtained here can be compared directly with his. The model also has the simplifying feature that the film flow must satisfy the no-slip condition at the upper boundary and will therefore have a Poiseuille velocity distribution, rather than a plug-flow distribution, which means that we can ignore temporarily the problems of fluid circulation in the drop and lower bulk phase. The important feature of the draining film, the contraction at its periphery caused by the large pressure gradient, can be studied without complications.

We consider the system to be in quasi-static equilibrium, i.e. to first order all the forces in the system are balanced and changes relative to this equilibrium take place only slowly. The viscosity of the liquid in the film prevents it from draining away too quickly. Since the film thickness is slowly varying we must assume that we are given a quantity defining its initial size. (It is not obvious that this is sufficient. Conceivably one might have to specify the entire initial distribution $H_0(\theta)$ of the gap thickness and consider the motion as an initial-value problem. However, under the quasi-static assumption the functional dependence of the gap size on θ is determinate, as will be shown, and only a constant representing its order of magnitude need be specified. This is equivalent to specifying the amount of fluid remaining in the gap.) Thus we take $H(0, 0) = H_0$ as given. Then the statement that the gap is small means that

$$\delta = H_0/R \ll 1.$$

A further consequence of the quasi-static assumption is that the angle ϕ, which is the slope of the interface as it leaves the sphere, is determined from the exterior problem, as explained in §1, and can be regarded as known.

We now analyse the motion in the thin film. Again using the quasi-static approximation, we neglect the acceleration terms in the equations of motion. The balance of forces will be between the pressure gradient and the viscous drag. Further, if a boundary-layer approximation (based on the assumption $\delta \ll 1$) is made the momentum equations are

$$\partial p/\partial n = \rho_2 g \cos\theta, \tag{2.1}$$

$$\rho_2 g \sin\theta + \partial p/\partial s = \mu_2 \partial^2 u/\partial n^2. \tag{2.2}$$

Here u is the s component of velocity, p is the pressure and μ_2 the viscosity.

The solution of (2.1) is

$$p = P(s, t) + \rho_2 g n \cos\theta$$

and we shall henceforth omit the second term on the right-hand side because it leads to terms of order δ relative to those retained.

Then the solution of (2.2), with the condition of zero tangential stress at the lower boundary, is

$$u = \frac{1}{2\mu_2}\left(\rho_2 g \sin\theta + \frac{\partial p}{\partial s}\right) n(n-2H). \tag{2.3}$$

(As explained in §1, a more accurate boundary condition, allowing for the drag produced by the motion of the lower bulk fluid, yields a correction term of order δ.)

The continuity equation may be written in the form

$$-r\frac{\partial H}{\partial t} = \frac{\partial}{\partial s}\left\{r\int_0^H u\,dn\right\} = -\frac{1}{3\mu_2}\frac{\partial}{\partial s}\left\{rH^3\left(\rho_2 g \sin\theta + \frac{\partial P}{\partial s}\right)\right\}, \tag{2.4}$$

where (2.3) has been used to eliminate u from the right-hand side. The length r is indicated in figure 2.

Continuity of normal stress at the lower boundary of the film yields the equation

$$P = \gamma\bar{\kappa} + \rho_1 g R \cos\theta + \text{constant}, \tag{2.5}$$

where $\bar{\kappa}$ is the curvature. The hydrostatic term in this equation is correct to leading order in δ; the surface-tension term $\gamma\bar{\kappa}$ will be approximated presently.

We now use (2.5) to eliminate the pressure from (2.4). At the same time we introduce the dimensionless quantities $h = H/H_0$, $\kappa = R\bar{\kappa}$ and $t = Tt'$, although the time scale T is as yet unknown and will have to be determined subsequently. We also set $r = R\sin\theta$, which gives

$$\frac{\partial}{\partial\theta}\left\{h^3 \sin\theta\left(\lambda\sin\theta - \delta\frac{\partial\kappa}{\partial\theta}\right)\right\} = -\frac{3\mu_2 R}{\gamma T\delta^2}\sin\theta\frac{\partial h}{\partial t'}, \tag{2.6}$$

where $\lambda = \Delta\rho g R^2/\gamma$ as defined earlier.

Next we introduce into this equation the approximation

$$\kappa \sim 2-\delta\left(\frac{\partial^2 h}{\partial\theta^2}+\cot\theta\frac{\partial h}{\partial\theta}+2h\right). \tag{2.7}$$

(Hartland's formula equivalent to (2.7) appears to be in error.) To obtain the equation in a convenient form for what follows we integrate with respect to θ:

$$\delta\frac{\partial}{\partial\theta}\left(\frac{\partial^2 h}{\partial\theta^2}+\cot\theta\frac{\partial h}{\partial\theta}+2h\right)+\lambda\sin\theta=\frac{3\mu_2 R}{\gamma T\delta^2}\,\frac{1}{h^3\sin\theta}F(\theta,t'), \tag{2.8}$$

where

$$F(\theta,t') = -\int_0^\theta \frac{\partial h}{\partial t'}\sin\theta\, d\theta.$$

The solution must satisfy the boundary condition

$$\partial h/\partial\theta = 0 \quad \text{where} \quad \theta = 0$$

and the initial condition

$$h = 1 \quad \text{when} \quad t' = 0, \quad \theta = 0.$$

These conditions are not sufficient to determine the solution, of course. Further conditions will be obtained by studying in more detail the structure of the solution near $\theta = \phi$. Equation (2.8) holds in the film as far as $\theta = \phi$, and also just beyond as the gap begins to widen. It will fail when the gap width is comparable to R (i.e. h is of order δ^{-1}) since then the boundary-layer approximations and the curvature approximations fail simultaneously.

To obtain solutions of (2.8) it is necessary to understand the physical structure of the equation. The function $F(\theta,t')$ is the dimensionless flux of liquid in the gap at any position and time, and the term on the right-hand side of (2.8) represents the viscous drag due to this flow. On the left-hand side the first term is the pressure gradient due to the surface tension and the change in curvature of the lower surface, while the second term is the pressure gradient due to the action of gravity. We now outline how these terms balance and describe the structure of h as a function of θ.

Over the main area of the film the interface remains close to the sphere and since $h = 1$ at $\theta = 0, t' = 0$ we expect h to be $O(1)$. The pressure inside the gap is thus approximately hydrostatic but exceeds the ambient pressure by an amount $\gamma\bar{\kappa}$. It is this excess pressure which supports the weight of the sphere. Near the edge of the gap ($\theta = \phi$), h will have to decrease in order to equalize the pressures of the film and the bulk phase. The mechanism for this has been given in § 1 but bears repeating. The large pressure jump at the film periphery accelerates the fluid leaving the gap until the increased viscous drag of the faster moving fluid is sufficient to prevent any further acceleration. Since the fluid flux must remain approximately constant, the gap must then contract, by continuity. Within the contraction it is thus necessary that at least the surface-tension and viscous terms of (2.8) balance, although we shall see that it is possible for the gravity term to be important also. (There is an implicit assumption here that the pressure variations in the exterior region remain small. While this will be true once a quasi-static equilibrium has been attained, it will not invariably be the case. For instance, a gas bubble rising towards an interface through a fluid with relatively low viscosity will initially cause large exterior pressure changes, and a contraction need not form in that case. This feature of the exterior pressure field was overlooked by Chesters 1975.) Finally, h will have to increase by a net factor of δ^{-1} just beyond $\theta = \phi$ so that it matches into the exterior solution.

We have argued that the pressure in the main portion of the film is approximately hydrostatic with an excess pressure of order $\gamma\bar{\kappa}$ to support the weight of the sphere. However the pressure gradients which produce the fluid motion are small and might be dominated either by gravity or by surface tension via small variations in the boundary curvature, according as the ratio λ/δ is large or small. Thus the detailed structure of the flow depends on this ratio.

We begin by considering the case $\lambda \ll \delta$. The solution so obtained cannot be valid for all times, of course, since H must decrease with time and this must be equivalent to having chosen a smaller initial value for H_0, i.e. to a reduced value for δ. Thus eventually gravity must dominate, and the solution we are about to find will apply only to the early stages of the settling of the drop. We consider the case $\lambda \gg \delta$ subsequently.

Neglecting gravity, then, (2.8) becomes

$$-\frac{1}{\delta}\frac{\partial \kappa}{\partial \theta} = \frac{\partial}{\partial \theta}\left(\frac{\partial^2 h}{\partial \theta^2} + \cot\theta\frac{\partial h}{\partial \theta} + 2h\right) = \frac{\epsilon}{h^3 \sin\theta}F(\theta, t'), \tag{2.9}$$

where $\epsilon = 3\mu_2 R/\gamma T\delta^3$ is effectively an arbitrary parameter since at present the time scale T has not been determined.

We now argue that $\epsilon \to 0$ as $\delta \to 0$ in order to obtain a solution with the required structure. This can be verified *a posteriori* from the solution we obtain and essentially follows from the requirement that the solution for h must change by an order of magnitude δ^{-1} just beyond $\theta = \phi$. Since ϵ is our only disposable parameter it must be functionally related to δ. It is not possible for ϵ to be $O(1)$ for then, while h might increase numerically beyond the contraction, it would still have to remain formally $O(1)$. Since supposing that ϵ is large leads immediately to a contradiction a solution of the required form can be possible only if ϵ is formally small. We now obtain a solution based on this using matched asymptotic expansions.

In accordance with the usual terminology of matched asymptotic expansions, we call the solution that is valid over the main portion of the film the outer solution and the solution that is valid over the contraction the inner solution. The reader is reminded that the term 'exterior solution' is being used to denote the solution outside the film entirely.

Taking ϵ to be small, we can neglect the right-hand side of (2.9) to obtain the equation $\partial\kappa/\partial\theta = 0$, so that the lower interface has the form of the cap of a sphere. This result cannot be uniformly valid over the entire gap, however, for if so the lower surface would have completely to envelop the solid sphere. The spherical cap is therefore an outer solution and must intersect the solid sphere in a horizontal circle. (Note that it is impossible for two spheres to touch tangentially and also symmetrically, so the intersection must be at a finite angle with h decreasing linearly.) Near this intersection h becomes small so the right-hand side of (2.9) is no longer negligible. This region of non-uniformity corresponds to the reduction in film thickness mentioned earlier and so must be located at $\theta = \phi$. We term the solution in this contraction region the inner solution. Moreover, as mentioned previously, it is necessary that just beyond the contraction h increases to $O(\delta^{-1})$ and we shall see that the equation for the contraction region has the appropriate behaviour to achieve this.

We now obtain the solution in detail. For the outer solution we set the right-hand side of (2.9) to zero to obtain

$$\frac{\partial}{\partial\theta}\left(\frac{\partial^2 h}{\partial\theta^2}+\cot\theta\frac{\partial h}{\partial\theta}+2h\right) = 0,$$

with boundary conditions at $\theta = 0$ as above and with the further condition

$$h = 0 \quad \text{at} \quad \theta = \phi,$$

which is the condition for first-order matching to the inner solution at the contraction. The solution is

$$h = j(t')f_1(\theta,\phi), \tag{2.10}$$

where

$$f_1 = \frac{\cos\theta-\cos\phi}{1-\cos\phi} \sim 1-\frac{\theta^2}{\phi^2} \tag{2.11}$$

and $j(t')$ contains the time dependence of the outer solution. It must satisfy the initial condition $j(0) = 1$ but is otherwise determined by matching to the inner solution. In fact we shall show that $j(t') = (4t'+1)^{-\frac{1}{4}}$. The spatial dependence of h is contained in f_1 and we have given an approximate form valid for small ϕ ($0 \leqslant \theta \leqslant \phi$) since this makes its shape easily appreciated.

We continue by finding the inner solution valid near $\theta = \phi$. The scaled variables appropriate to this region can be found in the usual manner but are somewhat complicated:

$$h = \frac{\epsilon}{2m}j^2(t')\,J(\xi), \quad \theta-\phi = \frac{\epsilon}{2m}j(t')\,\xi, \tag{2.12}$$

where

$$m = \sin\phi/(1-\cos\phi).$$

The factors of m are introduced for convenience to cancel a similar factor that occurs in the equation. The factors of ϵ are necessary to bring the viscous drag on the right-hand side of (2.9) into balance with the left-hand side while also allowing matching to the outer solution. The time dependence of the scalings is necessary to achieve matching with the outer solution on the one hand and with the exterior solution, which is time independent, on the other. It is interesting to note that, unlike the outer solution, which is of separable type, the inner solution is of similarity form, so a simple composite solution for both regions would not be easily attainable from the original equation.

We now substitute (2.12) into (2.9) and retain only the terms of largest order. We see that only the value of the fluid flux at $\theta = \phi$ is important. This is to be expected since on the stretched ξ scale the flux is constant to $O(\epsilon)$, and depends only on the time. The variation in the viscous drag is accounted for by the h^{-3} factor and not the flux variation. Thus

$$F(\phi+\epsilon\xi,t') \sim -\int_0^\phi \frac{\partial h}{\partial t'}\sin\theta\,d\theta = -\frac{1-\cos\phi}{2}\frac{dj}{dt'},$$

where we have used (2.10) to evaluate the integral. On substituting we find that the equation to first order is

$$\frac{d^3 J}{d\xi^3} = -\frac{1}{j^5}\frac{dj}{dt'}\frac{1}{J^3}.$$

For a solution to exist we must have

$$dj/dt' = \text{constant} \times j^5$$

and the constant can be arbitrarily selected as unity since other choices are equivalent to altering the time scale T. Thus

$$j(t') = (4t'+1)^{-\frac{1}{4}} \tag{2.13}$$

and the spatial dependence J satisfies

$$d^3J/d\xi^3 = 1/J^3 \tag{2.14}$$

with the condition that J matches into the outer solution (2.10) as $\xi \to -\infty$:

$$dJ/d\xi \to -m, \quad d^2J/d\xi^2 \to 0 \quad \text{as} \quad \xi \to -\infty.$$

Since (2.14) does not contain ξ explicitly this amounts to a complete specification of the boundary conditions: the solution will be determinate to within an arbitrary displacement of the origin. Such a displacement is equivalent to changing ϕ by an amount $O(\epsilon)$ and this is negligible to first order. To determine this displacement one would need to examine higher-order terms. Thus one has no control over the asymptotic behaviour of J for large positive values of ξ, so one must expect that as J becomes large and the term on the right-hand side of (2.14) becomes negligible, the solution becomes

$$J \sim a\xi^2 \quad \text{as} \quad \xi \to \infty, \tag{2.15}$$

where a is a constant which must be determined by solving the equation. In fact a numerical computation gives

$$a = \alpha m^5, \quad \text{where} \quad \alpha \simeq 0{\cdot}61$$

(see appendix B).

It is necessary that (2.15) matches the exterior solution. The quadratic dependence of J on ξ shows that the interface between the upper and lower bulk fluids must approach the sphere tangentially, as was assumed when solving the exterior problem. The form of H from the exterior solution can then be shown to be

$$H \sim \frac{R}{E}\left(\frac{R+E}{2}\right)(\theta-\phi)^2 \quad \text{as} \quad \theta \to \phi+, \tag{2.16}$$

where E is the radius of curvature of the curve formed by the intersection of the bulk-fluid interface and a vertical plane through the axis of symmetry, evaluated at $\theta = \phi$. (Referring to figure 1, it is the radius of curvature of EB at B.) Thus E is determined by the exterior solution and will be regarded as known. The derivation of (2.16) is given in appendix C.

Matching (2.15) and (2.16) finally enables us to determine ϵ:

$$\epsilon = 2\alpha m^6 \left(\frac{2E}{R+E}\right)\delta.$$

Thus we see that ϵ is $O(\delta)$, i.e. formally small as predicted. This enables us to find the only remaining unknown, the time scale T:

$$T = \frac{3\mu_2 R}{2\alpha m^6 \gamma}\left(\frac{R+E}{2E}\right)\frac{1}{\delta^4}. \tag{2.17}$$

In the above analysis we have used the initial value H_0 to form the small parameter δ which was used as the basis for an asymptotic expansion of the solution. The time dependence of the solution was kept clearly separate. However, the distinction must be an artificial one since by altering our choice of the time origin $t' = 0$ we could obtain the same problem but with a different initial condition. The solutions must all have the same form under this transformation, which is possible only if δ and $j(t')$ do not occur independently but only as $\Delta(t')$, where

$$\Delta(t') = H(0,t')/R = \delta j(t'), \tag{2.18}$$

whenever any real, i.e. dimensional, quantity is considered. It can be verified that this is the case with the main film thickness $O(\Delta R)$, the contraction thickness $O(\Delta^2 R)$ and the contraction length $O(\Delta R)$. The scalings are thus quasi-static scalings, depending on the current gap thickness.

The solution obtained so far is a rather specialized one in that it does not satisfy arbitrary initial conditions. If, at $t' = 0$, the surface did not have the shape prescribed by (2.11), but the other assumptions were valid, (2.9) would have to be solved as a proper initial-value problem. The right-hand side of (2.9) could then no longer be small and would presumably be brought into balance by $\partial h/\partial t'$ being large. Thus the initial changes would occur on a short time scale and one would expect the solution to decay into the one we have found above, although we have no proof that this happens.

We continue by finding the correction to the above solution due to gravity. In the main gap length the correct equation is

$$\frac{\partial}{\partial\theta}\left(\frac{\partial^2 h}{\partial\theta^2} + \cot\theta\frac{\partial h}{\partial\theta} + 2h\right) + \frac{\lambda}{\delta}\sin\theta = 0$$

with the boundary conditions as before. The solution is

$$h = j(t')f_1(\theta,\phi) + (\lambda/\delta)f_2(\theta,\phi), \tag{2.19}$$

where f_1 has already been defined by (2.11) and

$$\begin{aligned} f_2 &= \frac{2}{3}\left[\frac{\cos\phi\log\cos\frac{1}{2}\phi}{1-\cos\phi}(1-\cos\theta) - \cos\theta\log\cos\tfrac{1}{2}\theta\right] \\ &\sim \tfrac{1}{32}\theta^2(\phi^2-\theta^2). \end{aligned}$$

The nature of these solutions is most easily seen by the approximate forms which are valid for small ϕ $(0 \leqslant \theta \leqslant \phi)$. Thus f_1, which represents the cap of a sphere, has a parabolic shape decreasing monotonically from unity at $\theta = 0$ to zero at $\theta = \phi$. The function f_2, which represents the distortion of the spherical cap due to hydrostatic forces, has a double zero at $\theta = 0$, increases slowly to its maximum value at $\theta = \phi/2^{\frac{1}{2}}$, then decreases fairly sharply to zero. The behaviour is much the same when ϕ is of order unity.

It is interesting now to consider the solution as $j(t')$ changes with time. The balance between the two terms is decided by the ratio $\lambda/\delta j(t') = \lambda/\Delta$. Initially this is small since we are taking $\lambda/\delta \ll 1$ and so the gap thickness is largest at $\theta = 0$ and decreases monotonically to $\theta = \phi$. As $j(t')$ decreases and λ/Δ increases, the gravitational term eventually becomes of comparable importance. The effect is to level off the gap thickness over the centre region with a much sharper decrease near $\theta = \phi$. Letting $j(t')$ be even smaller, one can even obtain a mild increase in the gap thickness before it finally decreases.

The behaviour just described is evident in the experimental results of Hartland (1969). He photographed a hollow aluminium sphere rising through golden syrup into liquid paraffin and took measurements from enlargements of these photographs. His paper shows tracings of the gap thickness at five different times, and a transition of the form just described is clearly noticeable. The transition curve that he sketched has $H_0 = 5{\cdot}2 \times 10^{-4}\,\mathrm{m}$, the nearest curve above it having $H_0 = 9{\cdot}5 \times 10^{-4}\,\mathrm{m}$ and the nearest curve below it having $H_0 = 2{\cdot}3 \times 10^{-4}\,\mathrm{m}$. His physical parameters are

$$R = 6{\cdot}325 \times 10^{-3}\,\mathrm{m}, \quad \gamma = 4{\cdot}01 \times 10^{-2}\,\mathrm{kg/s^2}, \quad \Delta\rho = 530\,\mathrm{kg/m^3},$$

from which one can calculate $\lambda = 5{\cdot}2$. It is still possible to use the solution (2.18) even with the large values of λ/Δ that this produces because the numerical values taken by the function $f_2(\theta, \phi)$ are so small. Transition to gravity-dominated flow should occur when $R\lambda f_2(\max)$ is comparable to H_0. Taking $\phi = 65°$ (from Hartland's sketches), these two quantities are equal when $H_0 = 4{\cdot}3 \times 10^{-4}\,\mathrm{m}$, which, of course, is an underestimate of the transition thickness since the non-uniformity of the solution will already be rendering (2.19) invalid.

A more detailed comparison with the experiments shows that the theory seriously underestimates the rate of thinning of the film in the early stages. This may be ascribed to the failure of the quasi-static approximation, which seems in Hartland's experiments to hold only in the final stages of the motion when $\delta \ll \lambda$. However the regime $\lambda \ll \delta$ might well occur in other cases, for example where $\Delta\rho$ or R is small.

We turn now to the consideration of (2.8) in the case $\delta \ll \lambda$. On the left the curvature terms in h will be negligible compared with the hydrostatic terms, and a balance can be achieved only by retaining the term on the right due to viscous drag, giving the equation

$$\lambda h^3 \sin^2\theta = -\frac{3\mu_2 R}{\gamma\delta^2}\int_0^\theta \frac{\partial h}{\partial t}\sin\theta\, d\theta.$$

This is properly treated as an initial-value problem, but here we simply assume that the solution develops into a separable form and see what features can be deduced from that. Only one form of separable solution is possible, namely

$$\delta h = \frac{H}{R} = \left(\frac{\mu_2 R}{\gamma\lambda t + C}\right)^{\frac{1}{2}} i(\theta), \tag{2.20}$$

where C is a constant and

$$i^2(\theta) = \frac{1}{(\sin\theta)^{\frac{4}{3}}}\int_0^\theta (\sin\theta')^{\frac{1}{3}}\, d\theta'. \tag{2.21}$$

This solution will either be valid for all times (if $\delta \ll \lambda$), in which case C may be determined from the initial conditions, or else will be valid only for large times (if $\delta \gg \lambda$), in which case C is not immediately determinate but would anyway become negligible as $\gamma\lambda t$ increases. In principle C could be found in the latter case by considering the full initial-value problem.

We see that h decreases as $t^{-\frac{1}{2}}$ for large t. Note that (2.13) has the consequence $h \propto t^{-\frac{1}{4}}$; this does not mean that the rate of thinning actually increases since (2.13)

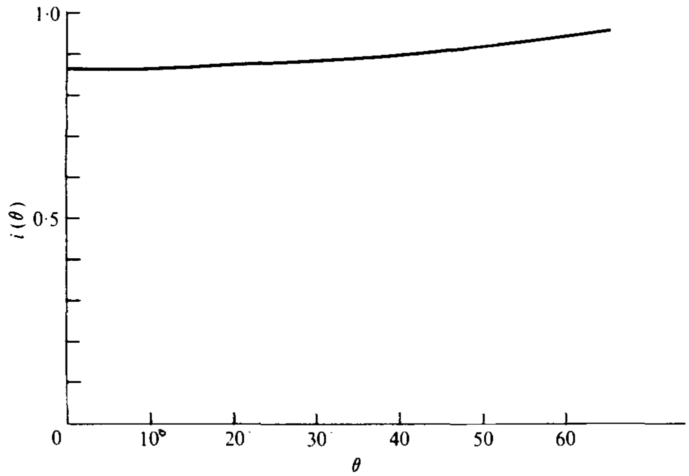

FIGURE 3. Graph of the function $i(\theta)$ [equation (2.21)].

holds for smaller values of t. (The two expressions represent different approximations of the same function, valid in different ranges of t.) The form of $i(\theta)$ is sketched in figure 3. It is almost constant with a very gradual rise from its minimum at $\theta = 0$. This is also a noticeable feature of the experimental curves sketched by Hartland. (The singularity at $\theta = \pi$ is outside the range of interest.)

To show that (2.20) is a possible solution of the problem it is necessary to consider the region at the edge of the film and to show how the solution (2.20) merges with the exterior solution. To do this we introduce appropriate variables which bring the order of magnitude of the surface-tension terms in (2.8) to that of the others. These are

$$\Delta(t) = \frac{H(0,t)}{R} = \frac{3^{\frac{1}{2}}}{2}\left(\frac{\mu_2 R}{\gamma\lambda t + C}\right)^{\frac{1}{2}}, \tag{2.22a}$$

$$h = \frac{2}{3^{\frac{1}{2}}}\frac{\Delta(t)\, i(\phi)}{\delta} G(\zeta, t), \tag{2.22b}$$

$$\theta = \phi + \left(\frac{2\Delta(t)\, i(\phi)}{3^{\frac{1}{2}}\lambda \sin\phi}\right)^{\frac{1}{3}} \zeta. \tag{2.22c}$$

Since Δ is small the flux term $F(\theta, t)$ is approximately independent of position in the neighbourhood of $\theta = \phi$, just as in the previous case. Neglecting small terms, the equation thus reduces to

$$\partial^3 G/\partial\zeta^3 = G^{-3} - 1 \tag{2.23}$$

and this must be solved subject to the boundary conditions that $G \to 1$ as $\zeta \to -\infty$ and G matches the exterior solution. It should be noted, however, that the solution does not match in the usual sense of asymptotic overlap. The solution is given in appendix D and a typical sketch of a solution curve is given in figure 4.

3. The settling of a drop

In this section we consider a genuine fluid drop settling into a bulk phase, but we make the assumption that the hydrostatic pressure variations in both phases can be neglected. The gross features of the solution have already been established in § 1.

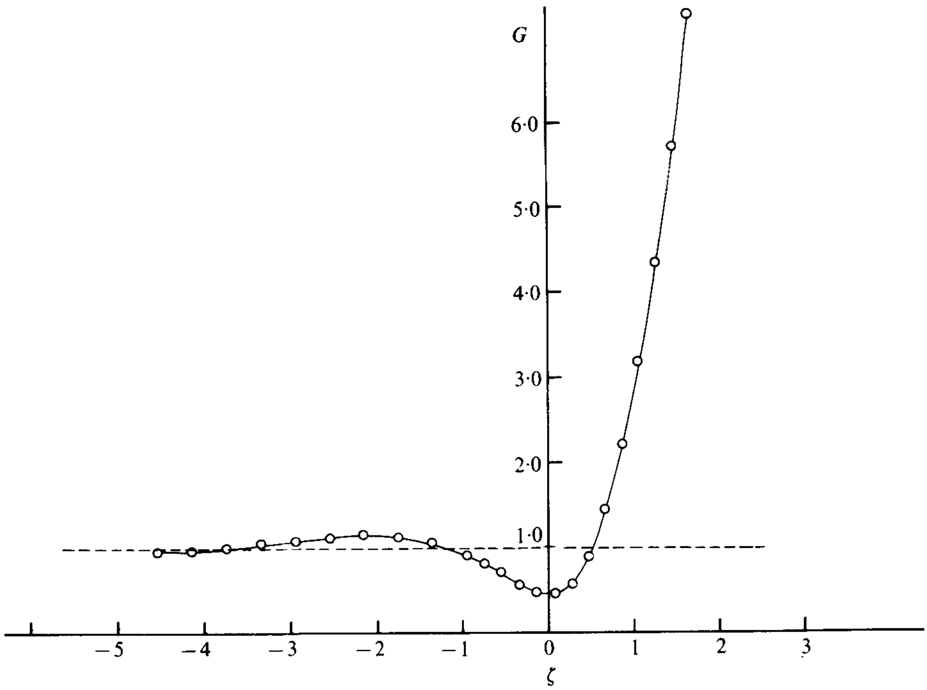

FIGURE 4. A typical curve $G(\zeta)$ (appendix D). The ζ origin has been shifted to coincide with the minimum of G.

The touching faces of the drop surface and the bulk interface will form a spherical cap whose radius R can be determined without reference to the details of the flow in the narrow gap which separates them. We use this to define our co-ordinate system for the gap. We let the co-ordinate $\bar{s}$ be the length of an arc measured along the sphere surface from the centre of the cap and let $\theta = \bar{s}/R$. As usual, $\bar{n}$ is the co-ordinate normal to $\bar{s}$. The exact interfaces will then have the equations

$$R_l = R + \bar{F}_l(\bar{s}), \quad R_u = R + \bar{F}_u(\bar{s}),$$

where $R_{l,u}$ is the distance from the centre of curvature of the spherical cap to the surface. The subscript l refers to the (lower) bulk interface and the subscript u to the (upper) drop interface. The functions $\bar{F}$ are unknown. We are, of course, assuming axial symmetry. The gap thickness at any point is thus

$$H(\bar{s}) = \bar{F}_l(\bar{s}) - \bar{F}_u(\bar{s}). \tag{3.1}$$

The equation of normal momentum yields $\bar{P} = \bar{P}(\bar{s})$ as usual. The solution of the equation of tangential momentum

$$\partial\bar{p}/\partial s = \mu_2\, \partial^2\bar{u}/\partial\bar{n}^2$$

must satisfy the condition that the tangential stress is continuous at the boundary. As explained in § 1, this means that the stress must be of a smaller order of magnitude than the terms we are examining because of the difference in order of magnitude of the spatial derivatives. The drop motion would be on the scale R while the gap motion would have as its scale $H(0) = H_0$. So we must take $\partial\bar{u}/\partial\bar{n} = 0$ at the interface, in which case the only possible solution is

$$\bar{u} = \bar{u}(\bar{s}),$$

from which it follows that

$$\bar{P} = \text{constant} = P_0.$$

The condition that the normal stress is continuous at both interfaces gives the two equations

$$\gamma\bar{\kappa}_l = \bar{P}, \tag{3.2}$$

$$\gamma(\bar{\kappa}_l + \bar{\kappa}_u) = \text{constant}, \tag{3.3}$$

from which it is easy to deduce that both curvatures are constant over the main region of the gap.

Just as in the previous section, this solution cannot be applied uniformly. There must be a contraction of the gap thickness at the edge of the spherical cap, which alters the orders of magnitude of the variables. Thus the gap thickness over the main gap length must satisfy

$$H = \begin{cases} H_0 & \text{when} \quad \theta = 0, \\ 0 & \text{when} \quad \theta = \phi \end{cases}$$

and is therefore

$$H = H_0\left(\frac{\cos\theta - \cos\phi}{1 - \cos\phi}\right). \tag{3.4}$$

Although the contraction changes the orders of magnitude of the variables, the solution scheme that we have just outlined still applies in the contraction. But we must now pursue the solution in more detail since the dynamics of this region determine the rate at which the fluid drains from the gap. The velocity increases by $O(\delta^{-1})$ but in spite of this we can still conclude that $\bar{u} = \bar{u}(\bar{s})$ only, and that the pressure gradient can be neglected to first order. Since the velocity at the interface is continuous, fluid on the other side of the interface will be set in motion, forming localized flows on both sides of the gap. These drag flows will be on the scale of the gap length δR and will lead to small but non-vanishing stresses at the interface. These stresses are balanced by a second-order flow in the gap driven by the pressure gradient, which can now no longer be neglected.

We introduce scaled dimensionless variables as follows:

$$\bar{s} - \bar{s}_\phi = \delta R s, \quad \bar{n} = \delta H_0 n, \quad \bar{P} = (\gamma/R)P,$$

$$\bar{u} = (\gamma\delta^2/\mu_2)(u_0(s) + \delta u_1(s)\ldots),$$

$$\bar{\kappa} = R^{-1}\kappa(s), \quad \bar{F} = \delta^2 RF(s), \quad H = \delta H_0\mathscr{H}(s),$$

where $\bar{s}_\phi$ is the value of s at $\theta = \phi$.

The first-order flow $u_0(s)$ is as yet unknown. It can be related to the gap thickness by means of the continuity equation

$$u_0(s)\mathscr{H}(s) = \Omega,$$

where Ω is the dimensionless flux per unit perimeter, which, as previously, we take to be an unknown constant. This first-order velocity in the narrow gap will drive flows in the adjacent phase 1 regions across the interfaces whose length scale will be that of the narrowed region, i.e. δR. Since the shape of each interface changes only on the scale R, the smaller length scale of these drag flows means that the interface will appear locally plane as far as they are concerned. (The reader is reminded that at the narrow gap the interfaces undergo a change in curvature but not in slope.) Furthermore, since the radii of curvature of the interfaces are also of order R, the flows can be considered two-dimensional. From these considerations the following canonical boundary-value problem emerges. We have a two-dimensional slow viscous flow in a semi-infinite region with the velocities $u = u_0(s)$ and $v = 0$ specified along its plane boundary $y = 0$, where y and v are the normal co-ordinate and velocity component respectively. This problem is solved in appendix E, where we show that the stream function ψ is given by

$$\psi = \operatorname{Re}\frac{y}{\pi i}\int_{-\infty}^{\infty}\frac{u_0(z)\,dz}{z-(s+iy)}, \quad y > 0. \tag{3.5}$$

Thus we can find the stress at the boundary $y = 0$:

$$\mu_1\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial s}\right)_{y=0} = \mu_1\left(\frac{\partial^2\psi}{\partial y^2}-\frac{\partial^2\psi}{\partial s^2}\right)_{y=0} = \frac{2\mu_1}{\pi}\int_{-\infty}^{\infty}\frac{u_0'(z)\,dz}{z-s},$$

where the integral is a Cauchy principal value and the subscript on μ refers to the phase. This stress must be balanced by the stress of the second-order gap flow, whose equation is

$$dP/ds = \partial^2 u_1/\partial n^2.$$

Integrating this equation across the gap gives

$$\frac{dP}{ds}\mathscr{H} = \left[\frac{\partial u_1}{\partial n}\right]_u^l = \frac{4\mu_1}{\pi\mu_2}\int_{-\infty}^{\infty}\frac{u_0'(z)\,dz}{z-s}. \tag{3.6}$$

Finally we can relate the pressure to the curvatures and hence to the gap thickness. The usual approximation $\kappa = 1+F''(s)$ is employed for the curvature. Hence we may combine (3.1) and (3.3) to obtain (in dimensionless form)

$$F_l'''' = \tfrac{1}{2}\mathscr{H}''''$$

and so from (3.2)

$$dP/ds = F_l''' = \tfrac{1}{2}\mathscr{H}'''.$$

Substituting this into (3.6) and also using (3.5) to eliminate u_0 from the integrand produces our final equation:

$$\mathscr{H}\frac{d^3\mathscr{H}}{ds^3} = \frac{8\Omega\mu_1}{\pi\mu_2}\int_{-\infty}^{\infty}\frac{\mathscr{H}'(z)\,dz}{\mathscr{H}^2(z)\,(z-s)}. \tag{3.7}$$

The flux Ω is determined by the requirement that this equation has a solution which satisfies the boundary conditions

$$d\mathscr{H}/ds = -\sin\phi/(1-\cos\phi) = -m \quad \text{as} \quad s\to-\infty$$

in order to match the gap solution (3.4). Also, in order that the solution matches the exterior solution we require that

$$d^2\mathscr{H}/ds^2 \to 2(1+R/E_l) \quad \text{as} \quad s\to\infty,$$

where E_l is the same as the quantity E of the previous section. Equation (3.7) and its boundary conditions can be reduced to a canonical dimensionless form by introducing the scaled variables

$$\mathscr{H} = \left(\frac{8\mu_1 \Omega m^2}{\mu_2 \pi}\right)^{\frac{1}{5}} G, \quad s = \left(\frac{m^3 \mu_2 \pi}{8\Omega\mu_1}\right)^{\frac{1}{5}} x = px, \quad t = pT.$$

Then we have

$$\left.\begin{aligned} G\frac{d^3G}{dx^3} &= \int_{-\infty}^{\infty} \frac{G'(z)\,dz}{G^2(z)\,(z-x)}, \\ dG/dx &\to -1 \quad \text{as} \quad x \to -\infty. \end{aligned}\right\} \tag{3.8}$$

There seems to be no theory for equations of this type, and the best advice available to the authors is that at present there is no real prospect of finding the solution numerically. One can only conjecture that, if the equation represents a sensible approach to the physics, the solution will exist and be unique. We therefore complete the solution in terms of the two unknown constants

$$G_{\min} = \alpha, \quad G''(\infty) = \beta.$$

We deduce that

$$\Omega = \left\{\frac{m^4}{\beta^5}\left(1 + \frac{R}{E_l}\right)^5\right\}^{\frac{1}{3}}, \tag{3.9}$$

and the actual dimensional flux per unit span $\bar{\Omega} = \bar{u}H$ is related to Ω by

$$\bar{\Omega} = (\gamma H_0^4/\mu_2 R^3)\,\Omega. \tag{3.10}$$

From (3.4) we have

$$\begin{aligned} \bar{\Omega} 2\pi R \sin\phi &= -\frac{dH_0}{dt} 2\pi R^2 \int_0^{\phi} \frac{\cos\theta - \cos\phi}{1-\cos\phi} \sin\theta\, d\theta \\ &= -2\pi R^2 \sin^2 \tfrac{1}{2}\phi\, dH_0/dt \end{aligned}$$

and hence

$$\dot{\delta} = -\frac{\gamma\Omega\sin\phi}{\mu_2 R \sin^2\frac{1}{2}\phi}\,\delta^4,$$

with the consequence that $\delta \propto t^{-\frac{1}{3}}$ as $t \to \infty$. The ratio of the minimum film thickness to that at $\theta = 0$ is

$$H_{\min} = \alpha\delta(8\mu_1 \Omega m^2/\pi\mu_2)^{\frac{1}{5}}$$

and Ω is given by (3.9).

Finally in this section we justify the assumption that the circulating motion in the drop and lower bulk phase is steady. The time scale on which these motions are established is H_0^2/ν_1 since their length scale is H_0. The time scale of the film drainage may be found from the form of $\bar{\Omega}$, the flux per unit perimeter out of the film, which is given by (3.10). The value of Ω is unknown since β is unknown, but assuming that it is an order-one number, the time scale of the film drainage is $\mu_2 R^4/\gamma H_0^3$. Thus the assumption that the circulating motion is steady is valid provided that $\gamma H_0^5/\nu_1 \mu_2 R^4 \ll 1$, which is generally satisfied.

4. Concluding remarks

Simple theories of film drainage based on lubrication theory neglect two effects, which have been evaluated and shown to be decisive. The first is the effect of circulation in the drop and the lower bulk phase, which tends to speed up the rate of drainage.

The second is the narrowing of the film at its periphery in order to smooth out the sharp pressure drop. This tends to slow down the rate of drainage.

If either or both of the surfaces bounding the film is immobile in the tangential direction, so that it can support tangential stress in the same fashion as a solid surface, the effect of circulation is irrelevant and the rate of drainage is substantially reduced (by comparison with existing models) by the constriction at the periphery. This theory will also apply when the 'drop' is actually a solid body, and may be appropriate as an approximation when significant quantities of surfactants are present.

For the case when both surfaces are mobile the problem has been analysed only for the case in which hydrostatic forces in the film are negligible. There results an integro-differential equation whose solution has not been found, but the analysis is complete except for a numerical constant which is the solution of that equation. There seems little point in extending the theory to include hydrostatic effects until these computational difficulties can be overcome. On the other hand, a solution which is complete up to a constant will still be useful for comparison with experiment.

Two features of the solutions are of particular interest. The rate at which the film thins out as a function of time has been determined and it turns out that for large times we have $H \propto t^{-\alpha}$, where α depends on the model. Standard lubrication theory gives the value $\alpha = \frac{1}{2}$. From the present theory we have, for one rigid boundary, the value $\alpha = \frac{1}{4}$ when gravity is negligible and $\alpha = \frac{1}{2}$ when gravity is dominant. These results are derived in § 2. For the case of two free boundaries and gravity negligible we have $\alpha = \frac{1}{3}$.

The minimum value of the film thickness, when it occurs at the periphery, has been found. This is important because it is likely that it is this minimum thickness, not the average thickness, which determines the probability that the film will rupture. The results are given at the ends of §§ 2 and 3.

Finally, it should be pointed out again that the theory is based on the quasi-static approximation and the thin-film approximation. The former approximation may well be inappropriate if the drop approaches the interface at high speed in the initial stages; this would occur with gas bubbles or large liquid drops where the density difference is large. As regards the thin-film approximation, the results are asymptotic and thus are formally valid in the limit as the thickness tends to zero if other quantities are held fixed; but they may be useless in practice if another quantity turns out to be very large. For example, it has been assumed that the viscosity ratio of the fluids is not large and for this reason also the results will not hold for air bubbles.

We wish to extend our thanks to Mr G. Siemieniuch, who performed the numerical computations, and to Dr G. R. Wickham for assistance with the boundary-value problem in appendix E. We are also indebted to the referees for pointing out an error in formula (2.7) and for other suggestions which improved the paper.

Appendix A

In this appendix we obtain various integral constraints on the basic drop profile (the exterior solution). The notation is the same as that in figure 1, which also displays the expressions for the pressures P_i in the different regions. For simplicity we shall derive the results for two-dimensional drops only, then quote the corresponding result for axially symmetric three-dimensional drops. The volumes referred to in the two-dimensional case are thus really cross-sectional areas (volume per unit length). We denote the total volume of the drop by V, the volume $AGHBDA$ by V_1, the volume $ABHGA$ by V_2, the volume $ACBJA$ by V_3 and the volume $2(BEHB)$ by V_4.

We begin by resolving the vertical forces on the volume V_3:

$$2\gamma \sin\phi + \int_{ACB} P_4\, dx + \int_{BJA} P_3\, dx = \rho_1 g V_3,$$

where P_4 is the pressure in the gap, $P_4 = P_1 + \gamma\kappa$. The integrals are easy to evaluate, and

$$2\gamma \sin\phi + [2\gamma \sin\phi - 2lP_0 + \rho_1 g V_3] = \rho_1 g V_3$$

so

$$2lP_0 = 4\gamma \sin\phi. \tag{A 1}$$

The corresponding expression for axial symmetry is

$$\pi l^2 P_0 = 4\pi l \gamma \sin\phi.$$

Next we resolve the vertical forces on the combined volume $V_1 + V_2$:

$$\int_{BDA} P_2\, dx + \int_{AJB} P_3\, dx - 2\gamma \sin\phi = \rho_1 g (V_1 + V_2),$$

which can be evaluated to give

$$\rho_2 g V_1 + 2P_0 l + \rho_1 g V_2 - 2\gamma \sin\phi = \rho_1 g (V_1 + V_2).$$

Combining this with (A 1) gives

$$2\gamma \sin\phi = \Delta\rho g V_1. \tag{A 2}$$

The corresponding expression for axial symmetry is

$$2\pi l \gamma \sin\phi = \Delta\rho g V_1.$$

This equation can be used to find an approximate value for ϕ when $V_1 \simeq V$. If now we consider the equation of the elastica BE/AF and integrate with respect to x across its entire length

$$\int_{BE} -\gamma\kappa\, dx = \int_{BE} \Delta\rho g z\, dx,$$

then the result is

$$2\gamma \sin\phi = \Delta\rho g V_4 \tag{A 3}$$

since V_4 is defined to be twice the volume $BEHB$. Thus, with (A 2), this shows that the drop displaces an amount of fluid equal to its own volume. The same conclusion also holds in the case of axial symmetry. The equation corresponding to (A 3) is

$$2\pi\gamma l \sin\phi = \Delta\rho g V_4,$$

where V_4 denotes the total volume generated when the area $BEHB$ is rotated about the axis of symmetry.

Finally we resolve the horizontal forces on the volume $BKEB$:

$$\gamma - \gamma\cos\phi = \int_{EK} P_1\, dz + \int_{BE} P_2\, dz.$$

The integrals can be evaluated to give

$$\gamma(1-\cos\phi) = \tfrac{1}{2}\Delta\rho g d^2, \tag{A 4}$$

where d is the depth that the point B is below the horizontal level of the bulk interface. This equation can be used to find d, and hence the curvature E^{-1} of the elastica at the point B.

Unfortunately there is no equivalent formula for the three-dimensional axially symmetric problem. The evaluation of E needed in § 2 for comparison with Hartland's experiments can be carried out only by numerical computation. This seemed to involve undue effort and we used (A 4) instead since, considering the other approximations made, one would expect this to provide an acceptable approximation for the value of E.

Appendix B

We obtain the solution of the equation

$$d^3J/d\xi^3 = 1/J^3$$

with the boundary condition $dJ/d\xi \to -m$ as $\xi \to -\infty$. If the scaled variables $J = m^{-3}p$ and $\xi = m^{-4}z$ are introduced then the equation transforms to

$$\left.\begin{aligned} d^3p/dz^3 &= 1/p^3, \\ \text{with} \qquad dp/dz &\to -1 \quad \text{as} \quad z \to -\infty. \end{aligned}\right\} \tag{B 1}$$

For large negative values of z we can then obtain the asymptotic expansion

$$p \sim -z - \tfrac{1}{2}\log(-z) - \tfrac{1}{4}z^{-1}\log(-z) - \tfrac{11}{24}z^{-1}.$$

Equations (B 1) were then solved numerically by integrating forwards from $z = -10$ to $z = +10$, the asymptotic expansion being used to provide the initial conditions. The curve $p(z)$ is sketched in figure 5. It has a minimum value of 1·2537 and $d^2p/dz^2 \to 1{\cdot}2205$ as $z \to \infty$. Another integration was performed which checked the accuracy of the initial conditions by integrating forwards from $z = -15$. The minimum value found was 1·2571 and $d^2p/dz^2 \to 1{\cdot}2147$. Thus we conclude that

$$J_{\min} \simeq 1{\cdot}25/m^3$$

and

$$J \sim \alpha m^5 \xi^2 \quad \text{as} \quad \xi \to \infty,$$

where $\alpha \simeq 0{\cdot}61$.

Appendix C. The exterior matching condition

We wish to find the rate of divergence of two touching curves (see figure 6). We choose a convenient co-ordinate system where the angle θ is measured from the normal line at the point of contact. The centre from which θ is measured is at a distance R from the point of contact, where, in applications, R is the radius of the spherical cap formed by the two interfaces where they almost touch. We take these two interfaces then to diverge with local radii of curvature r and ρ for the drop interface and bulk interface respectively.

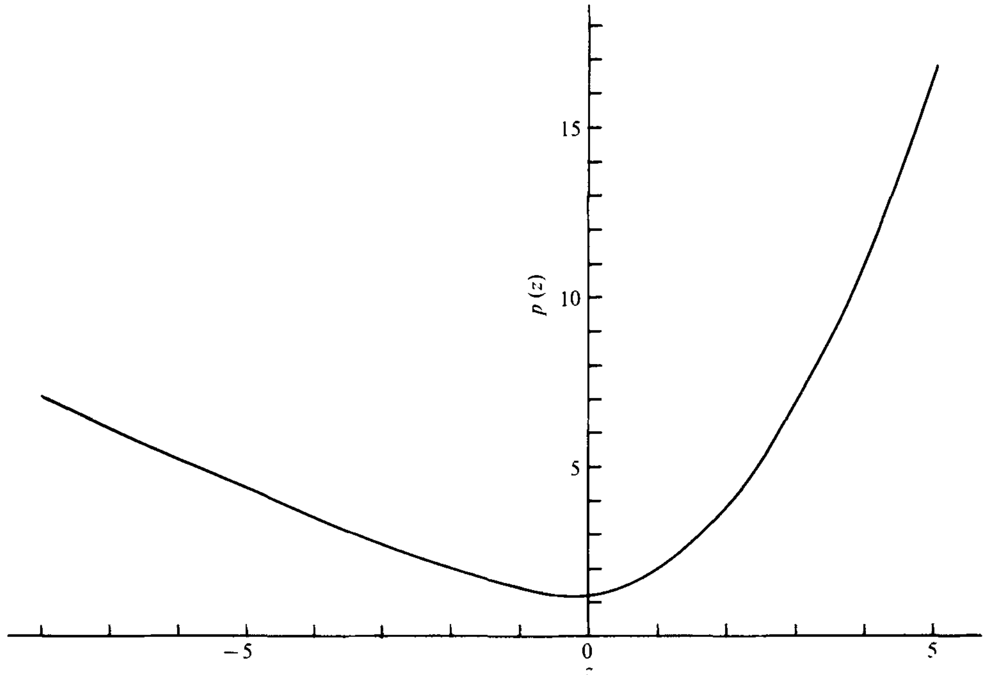

FIGURE 5. Graph of the function $p(z)$.

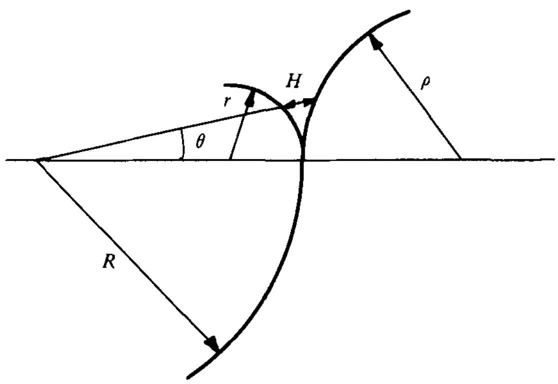

FIGURE 6. The gap $H(\theta)$ between two tangential circles measured from the centre of a third tangential circle.

It is a matter of elementary geometry to show that

$$H = \cos\theta\{R+\rho-[(R+\rho)^2-(R^2+2R\rho)\sec^2\theta]^{\frac{1}{2}}+r-R-[(R-r)^2-(R^2-2Rr)\sec^2\theta]^{\frac{1}{2}}\},$$

which can be approximated by

$$H \sim \tfrac{1}{2}R^2\theta^2(\rho^{-1}+r^{-1}) \quad \text{as} \quad \theta\to 0.$$

We have applied this formula to two cases.

(i) When $r = R$ and $\rho = E$ (§ 2)

$$H \sim \frac{R}{E}\left(\frac{R+E}{2}\right)\theta^2,$$

where E is the radius of curvature of the elastica of the bulk interface at the point of contact. This can be found only by actually solving the exterior problem, or looking up the solution in tables. This can always be done, since the exterior problem is well posed, but considerable effort might be needed in that there seems to be no short cut. There is a short cut, however, for two-dimensional problems since the curvature can be related to the depth of the point of contact below the mean level of the bulk interface, and for the two-dimensional problem an explicit expression can be found for this depth (see appendix A). We used this two-dimensional result in § 2 to obtain a value for E in Hartland's experiment. There is no reason why this need be correct, of course, but it avoided the large amount of work needed to find the exact value of E.

(ii) When $r = E_u$ and $\rho = E_l$ (§ 3)

$$H = \tfrac{1}{2}R^2(E_l^{-1}+E_u^{-1})\,\theta^2,$$

where E (taken to be positive) is the radius of curvature of the plane-section curve of the elastica evaluated at the point of contact. The subscripts u and l refer to the upper drop interface and the lower bulk interface respectively.

The comments on E above apply to both E_u and E_l, although they are dependent on one another and it is necessary to calculate only one of them numerically. This can be shown as follows. We refer to the notation of figure 1. We remain near to the point B and so can neglect any hydrostatic variations in the pressure. Then

$$P_1+\gamma\kappa_l^* = P_2, \quad P_2+\gamma\kappa_u^* = P_3,$$

where κ^* denotes total curvature and we shall use κ to denote planar curvature. Since also

$$P_3 = P_1+4\gamma/R$$

we can deduce that

$$4/R = \kappa_l^*+\kappa_u^*,$$

or

$$2/R = \kappa_u+\kappa_l,$$

because, since the gradients of the curves and the spherical cap are all equal at that point, the curvature due to axial symmetry is R^{-1} for each curve. Finally we have $\kappa_u = E_u^{-1}$ and $\kappa_l = -E_l^{-1}$, so

$$H = R\theta^2(1+R/E_l).$$

Appendix D

We consider the solution of the differential equation

$$\partial^3 G/\partial\zeta^3 = G^{-3}-1,$$

i.e. (2.23), with the boundary condition $G\to 1$ as $\zeta\to-\infty$ and the requirement that G merges into the exterior solution as $\zeta\to\infty$. We use the word 'merges' since matching of the solutions in the conventional sense is not possible. To explain this we must consider the nature of the solutions. As $\zeta\to-\infty$ we can obtain the asymptotic solution

$$G \sim 1+A\exp(\tfrac{1}{2}k\zeta)\cos(\tfrac{1}{2}k3^{\frac{1}{2}}\zeta)+A^2\exp(k\zeta)\{\tfrac{1}{2}-\tfrac{1}{7}\cos(k3^{\frac{1}{2}}\zeta)\},$$

where $k = 3^{\frac{1}{3}}$. Thus the solution begins at $\zeta = -\infty$ as a constant, unity, plus a small oscillation which grows in amplitude as ζ increases. (See figure 4.) Once this oscillation becomes of order unity its linear character vanishes. As G becomes small a large value for G''' results because of the term G^{-3} on the right-hand side of (2.23). This has the effect of turning the oscillation round very sharply and shooting it outwards, so that G achieves large values. Once G has become large the term G^{-3} becomes negligible and the -1 on the right-hand side of (2.23) very slowly bends the oscillation back, so that the solution once more heads towards $G = 0$. An even sharper reflexion then results and the process is repeated.

Now, using the scalings (2.22) and the results of appendix C, we can deduce that for G to match the exterior solution

$$G \sim \left(\frac{R+E}{2E}\right)\left\{\frac{3^{\frac{1}{2}}}{2\delta(t)\, i(\phi)\, \lambda^2 \sin^2\phi}\right\}^{\frac{1}{3}} \zeta^2 = D\zeta^2 \tag{D 1}$$

as ζ becomes large. Thus G would have to increase by an order of magnitude equal to the dimensionless group of constants D. Formally this is impossible since, formally, this is properly considered as a limiting operation, so that D can be arbitrarily large, and to increase G by an arbitrary amount would involve an infinite number of ever growing loops and reflexions. But in practice G increases by an extremely large factor after each reflexion. A numerical factor of 10^4 is quite easy to obtain with only a single reflexion, and such a factor can easily equal the numerical value taken by D in any real situation, since then D will merely be large and not infinite.

With this in mind we computed a set of solution curves of (2.23) as far as the first major reflexion. A typical curve is sketched in figure 4. On the rebound from this reflexion the curves always had the form

$$G \sim -\tfrac{1}{6}\zeta^3 + \tfrac{1}{2}D\zeta^2$$

where the second term $\frac{1}{2}D\zeta^2$, although formally small, was much bigger than the other term because of the large value of D. We took this part of the solution to merge into the exterior solution. No re-looping of the solution for G occurs in practice, of course, because before the term $-\frac{1}{6}\zeta^3$ can operate to turn the solution back towards smaller values of G, the approximations which led to this equation become invalid and the full equations have to be used.

In the numerical computation of these curves, initial conditions were obtained using the asymptotic expansion quoted at the beginning of this appendix with values of A chosen between 0·5 and 10. Special care had to be taken in the numerical computation in the region where G became small. The constant was found in different cases from

$$D = G''(\zeta) + \zeta \quad \text{as} \quad G \to \text{large values},$$

where the origin for ζ was taken as the point where G was minimum. As we have mentioned elsewhere, there is an arbitrary choice for this origin which can be resolved only by considering higher approximations. Theoretically this is not a problem since D is nominally an order of magnitude larger than ζ and such a change should alter D by only a relatively small amount. As a practical point, however, the value of D given by (D 1) is principally determined as the cube root of a large quantity, and the effect of this is to produce values of which are much smaller than one would ideally wish. In Hartland's experiment, for instance, $D = 6$, and clearly the exact position of the ζ origin is of importance in such cases if one wishes to make exact calculations. In taking our ζ origin to be at the position of minimum G we have ignored this problem.

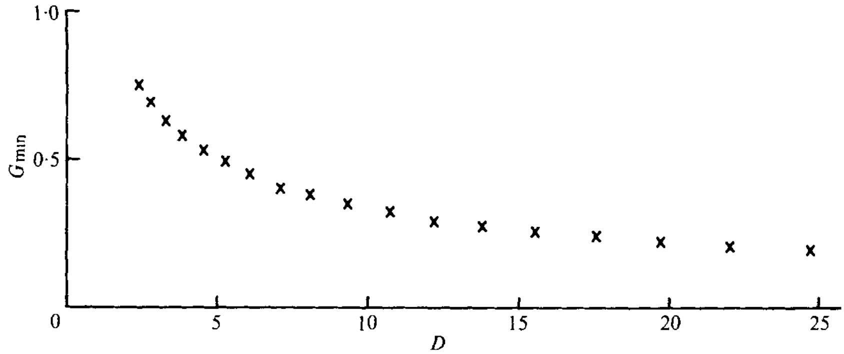

FIGURE 7. The minimum value of G plotted as a function of the matching coefficient D for the corresponding curve (appendix D).

In figure 7 we have plotted the values obtained for D against the corresponding minimum value of G. The curve cannot be continued for larger values of G_{min} since G does not subsequently increase sufficiently for G^{-3} to be negligible, so D does not approach a satisfactory constant value in such cases. The curve can be continued for smaller values of G_{min}, but values of D greater than 25 seem unlikely in physical situations.

An interesting paper with which to compare these results is that of Bretherton (1961), who considers the passage of an air bubble along a capillary tube which is otherwise full of a viscous fluid with a high surface tension. A thin film of liquid remains on the wall as the bubble passes and the equations for this thin film are similar to ours. He, too, solves his problem by matching to the exterior solutions, which in his case are the caps on the top and bottom of the moving bubble. In the case when the bubble rises against gravity his equation is identical with (2.23) except for a difference in sign due to the fact that ζ is measured in the opposite direction. The same difficulty over matching that we have discussed also occurs in Bretherton's problem but seems to have been overlooked, possibly because it occurs in the region which (in his problem) is not of interest.

Appendix E

We wish to find the two-dimensional viscous flow generated in a half-space by the boundary conditions $u = u_0(x)$ and $v = 0$ along its plane boundary $y = 0$. In terms of the stream function ψ defined by $u = \partial\psi/\partial y$ and $v = -\partial\psi/\partial x$, the equation for viscous motion is the biharmonic equation

$$\nabla^4\psi = 0$$

and the boundary conditions are

$$\psi = 0, \quad \partial\psi/\partial y = u_0(x) \quad \text{on} \quad y = 0$$

and that ψ is bounded as $x^2+y^2 \to \infty$. We look for a solution of the form $\psi = y\phi(x,y)$, where ϕ satisfies

$$\nabla^2\phi = 0, \quad \phi(x,0) = u_0(x).$$

Since ϕ is harmonic we can use complex-variable theory and set

$$\phi = \operatorname{Re} w(z),$$

where $z = x+iy$ and w is an analytic function which is regular in the upper half-plane and satisfies

$$w(x+i0)+w^*(x-i0) = 2u_0(x)$$

and

$$w \to 0 \quad \text{as} \quad |z| \to \infty,$$

where the asterisk denotes the complex conjugate. If we consider the analytic function

$$W(z) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{u(t)}{t-z}dt$$

then we see that it has the property

$$\begin{aligned} W(x+i0)+W^*(x-i0) &= \frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{u_0(t)\,dt}{t-x} + \tfrac{1}{2}u_0(x) \\ &\quad -\frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{u_0(t)\,dt}{t-x} + \tfrac{1}{2}u_0(x) = u_0(x). \end{aligned}$$

It follows that the regular function w that we want is

$$w = 2W$$

and the solution of the original boundary-value problem is

$$\psi(x,y) = \mathrm{Re}\frac{y}{\pi i}\int_{-\infty}^{\infty} \frac{u(t)\,dt}{t-z},$$

assuming, of course, that the integral on the right-hand side of this equation actually exists.

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