J. Fluid Mech. (1982), *vol.* 121, *pp.* 425–442
Printed in Great Britain

The spreading of a drop by capillary action

By L. M. HOCKING
Department of Mathematics, University College London
AND A. D. RIVERS
Pilkington Bros, Lathom, Ormskirk, Lancs

(Received 9 November 1981)

A small drop placed on a horizontal surface will spread under the action of capillary forces until it reaches an equilibrium position. The rate at which it spreads provides a means for testing certain hypotheses about moving contact lines; namely that there must be slip between the fluid and the solid boundary near the rim of the drop to avoid a force singularity there, and that the contact angle measured at the rim itself does not show the dynamic behaviour observed by measurements that ignore rapid changes in slope in the immediate vicinity of the rim but remains equal to its static value.

By the use of matched asymptotic expansions, an equation for the rate of spread of a drop as a function of the radius of the contact circle is obtained. Experiments on the spreading of small drops of molten glass allow a comparison to be made between the spreading of a drop determined experimentally and that predicted theoretically, which supports the use of the proposed hypotheses as appropriate for the study of fluid motions containing moving contact lines.

1. Introduction

The object of this paper is to test certain proposals about the dynamics of fluid motions when the boundary contains a moving contact line by evaluating the rate of spread of a drop of fluid placed on a horizontal surface and comparing the predicted values with those determined experimentally. It is well-known that in such flows a force singularity appears if a solution of the Navier–Stokes equations with a no-slip boundary condition is attempted. The most usual hypothesis made to circumvent this difficulty is to relax the no-slip condition in the vicinity of the moving contact line and to replace it by a Maxwell condition in which the amount of slip is proportional to the local velocity gradient, the constant of proportionality being the slip coefficient. The magnitude of this coefficient is a measure of the extent of the region where slip is significant. There is no firm physical basis for this hypothesis, although Hocking (1976) argued that the flow over a rough surface could be modelled by a flow with slip over a smooth surface, the slip coefficient then being a measure of the scale of the roughness. For a smooth surface, there is no doubt that what is required is an analysis of the effects of molecular attraction near the contact line. Failing such an analysis, it seems plausible to postulate that its macroscopic effect would be the proposed slip boundary condition, with a slip coefficient of the molecular scale. Certainly this hypothesis is the simplest one that can be incorporated into a continuum model and that achieves the aim of removing the force singularity.

This slip hypothesis has been used to examine the motion of a meniscus (Hocking 1977; Huh & Mason 1977; Lowndes 1980). The shape of the meniscus as calculated by Lowndes is in good agreement with experiment, but his solution does not provide a satisfactory test of the dynamics of the motion. The contribution to the total pressure gradient needed to drive the fluid from the neighbourhood of the contact line is only a small fraction of the total. A better model for experimental comparison is provided by the spreading of a drop, and it is this example of flow with a moving contact line which will be discussed here.

In all problems that contain a moving contact line, it is necessary to make some statement about the contact angle. This is a complicated topic (for a review see Dussan V. 1979), and there is evidence that the contact angle is velocity-dependent. But it has also been suggested that this evidence does not relate to the actual contact angle but to the slope measured at some distance from the contact line or derived from an assumed form of the free surface. Since, as we have already seen, there is a small region near the contact line where large stresses are present, it is reasonable to suppose that there will be large changes in slope in the same region, so the variation of contact angle with velocity may only reflect the presence of this region and the real contact angle may remain unaltered. Accordingly, it will be assumed here that the contact angle is a constant throughout the motion. (Since the drop spreads outwards, it is the advancing contact angle which must be used.) These two hypotheses, of a constant contact angle and of a slip boundary condition, have been used by Hocking (1981) to discuss the spreading of a thin drop using lubrication theory. Lowndes (1980) used these hypotheses in his numerical solution of the moving meniscus, and he was able to show how the rapid change of slope near the contact line led to derived contact angles in good agreement with those observed experimentally by a number of authors.

Recently, the equation for the spreading of a thin drop has been re-examined, and a solution based on matched asymptotic expansions has been obtained (Hocking 1982*a*). The key point in the analysis is that it is not enough to use simply an outer region covering the major part of the drop and an inner region of the same size as the slip coefficient; an intermediate region is needed as well, for which an expansion in terms of the logarithm of the slip coefficient is appropriate. Lacey (1982) independently recognized the importance of an expansion in terms of this variable in his study of the spreading of thin drops. Moreover – and this is the feature that makes the analysis of the present paper possible – these three regions are also present when the restrictions of lubrication theory are lifted.

In this paper, we consider the spreading of a fluid drop placed on a horizontal surface when the drop is small enough for the spreading to be effected by capillarity, with gravity playing no part in the process. We obtain an equation for the rate of spread of the drop as a function of the contact radius, and hence are able to determine the radius as a function of the time from any given initial configuration. These results can then be compared with those obtained experimentally.

The experiments that provide the data for this comparison were performed prior to the development of the theory presented in this paper and consist of observations of molten glass drops on a platinum plate (Copley, Rivers & Smith 1975). The contact between molten glass and certain metals has important technological significance. It is necessary to avoid the sticking of molten glass to metal forming tools, but a controlled degree of wetting is required in the drawing of glass fibres from a metal bushing. A greater understanding of the wetting process would contribute to the control of interactions between metals and glasses, with particular applications to the development of glass-to-metal seals.

A comparatively simple way of examining some features of this interaction in a controlled situation is in the spreading of a glass drop on a metal substrate. For this reason, and to obtain quantitative measurements of the shape and rate of spread of a drop, a number of experiments were made, which are described in this paper, and the results obtained are directly comparable with the theoretical ones.

2. Formulation

The parameters that govern the spreading of a liquid drop on a horizontal surface are the density ρ and the viscosity μ of the liquid, the surface tension σ and the advancing static contact angle α_s for the liquid/air/solid system, the gravitational acceleration g, the volume V of the drop and the slip coefficient λ. We assume that these parameters have values that ensure that the following three assumptions are valid: the Reynolds number of the motion is small enough for the Stokes equations to be used; the Bond number, which measures the relative importance of gravity to capillarity in the spreading process, is small; the slip coefficient is small compared to the size of the drop.

In equilibrium, the surface of the drop is part of a sphere, and the equilibrium radius a_s of the drop is given by

$$\frac{\pi a_s^3}{3V} = \frac{(1+\cos\alpha_s)^2}{\sin\alpha_s(2+\cos\alpha_s)}. \tag{2.1}$$

We assume that the drop is placed on the horizontal surface with some initial shape and that the combined effect of surface tension and the fixed contact angle at the rim drives the drop towards the equilibrium position. We also assume that the drop is initially, and remains, symmetric about a vertical axis, so that, if we define cylindrical polar co-ordinates (r, ϕ, z), all quantities are independent of ϕ, and we can introduce a stream function ψ. If u and v are the velocity components in the r- and z-directions respectively, and if μp is the pressure, the Stokes equations can be written in the form

$$\psi_{rr} - r^{-1}\psi_r + \psi_{zz} = \zeta, \quad \zeta_{rr} - r^{-1}\zeta_r + \zeta_{zz} = 0, \tag{2.2}$$

and the velocity components and pressure are given by

$$u = r^{-1}\psi_z, \quad v = -r^{-1}\psi_r, \quad p_r = r^{-1}\zeta_z, \quad p_z = -r^{-1}\zeta_r. \tag{2.3}$$

The boundary conditions on the plane $z = 0$ are

$$\psi = 0, \quad \psi_z - \lambda\psi_{zz} = 0, \tag{2.4}$$

since we are assuming a slip boundary condition with coefficient λ. These conditions hold for $0 \leqslant r \leqslant a$, where $a(t)$ is the radius of the rim of the drop. On the axis $r = 0$, ψ must be $O(r^2)$. The other boundary conditions must be applied at the surface of the drop which we define by $S(r, z, t) = 0$, with $S(a, 0, t) = 0$ at the rim of the drop. The condition that this is a material surface is $DS/Dt = 0$ or

$$S_t + r^{-1}(\psi_z S_r - \psi_r S_z) = 0,$$

which, in integrated form, becomes

$$\psi = \int_0^r \frac{rS_t}{S_z}\,dr \quad \text{along} \quad S = 0. \tag{2.5}$$

Note that, if $S \equiv z - h(r,t)$, we have

$$\psi = -\int_0^r h_t r\,dr,$$

$$\psi(a,0,t) = -\int_0^a h_t r\,dr = -\frac{d}{dt}\int_0^a hr\,dr,$$

since $h = 0$ at $r = a$, and this is zero because the volume of the drop is constant. Hence we can write, as an alternative to (2.5),

$$\psi = -\int_r^a \frac{rS_t}{S_z}\,dr. \tag{2.6}$$

The vanishing of the tangential stress on the drop surface is expressed by the condition

$$(S_z^2 - S_r^2)(\psi_{zz} - \psi_{rr} + r^{-1}\psi_r) + 2S_z S_r(2\psi_{rz} - r^{-1}\psi_z) = 0, \tag{2.7}$$

in which the derivatives of ψ are to be evaluated on $S = 0$. The difference between the normal stress in the liquid at the drop surface and the pressure on the air outside is accounted for by the surface-tension contribution, which is proportional to the mean curvature. This condition has the form

$$\frac{\sigma}{\mu}K = p - p_a + (S_z^2 + S_r^2)^{-1}\{2(S_z^2 - S_r^2)\,r^{-1}\psi_{rz} + 2S_r^2 r^{-2}\psi_z - 2S_r S_z(r^{-1}\psi_{zz} - r^{-1}\psi_{rr} + r^{-2}\psi_r)\}, \tag{2.8}$$

where p_a is an unknown constant and

$$K = (S_z^2 + S_r^2)^{-\frac{3}{2}}\{S_z^2 S_{rr} - 2S_z S_r S_{rz} + S_r^2 S_{zz} + r^{-1}S_r(S_r^2 + S_z^2)\}.$$

If we denote the downward angle of slope at an arbitrary position on the drop surface by δ, so that

$$\cos\delta = \frac{S_z}{(S_z^2 + S_r^2)^{\frac{1}{2}}}, \quad \sin\delta = \frac{S_r}{(S_z^2 + S_r^2)^{\frac{1}{2}}},$$

the curvature K can be written more simply as

$$K = \frac{1}{r}\frac{d}{dr}(r\sin\delta) \quad \text{along} \quad S = 0. \tag{2.9}$$

The condition at the rim $z = 0, r = a$ is

$$\delta = \alpha_s,$$

and the constant-volume condition is

$$2\pi\int_0^a hr\,dr = V, \tag{2.10}$$

where $S(r,h,t) = 0$.

A key parameter in the motion of fluid interfaces is the capillary number $Ca = \mu U/\sigma$, which measures the relative importance of viscous to capillary forces. In meniscus

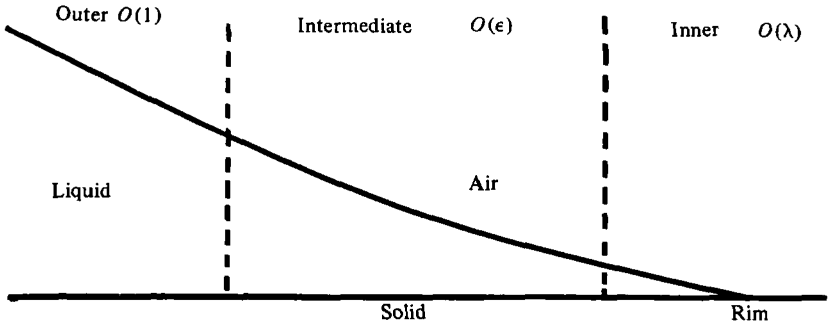

FIGURE 1. Schematic representation of the vicinity of the rim of the spreading drop.

problems, the typical speed U can be controlled and it is possible to ensure that $Ca \ll 1$. It is then possible to expand the solution in powers of Ca, the leading term for the position of the interface being fixed before the corresponding stream function has to be evaluated. Consequently, the Stokes equations have to be solved in a previously determined domain. In the present case, however, the motion is driven by surface tension, and it looks at first sight that the capillary number will be $O(1)$, with the consequence that the Stokes equations and the equation determining the position of the surface would have to be solved simultaneously. However, the large stresses present at the contact line, even when the slip boundary condition is used, slow down the rate of spread of the drop so that Ca is proportional to $\epsilon = 1/|\ln \lambda|$, which is small, and we can still validly expand in powers of this parameter.†

The plan of the method of solution is as follows (see figure 1). In the outer region, where r and z are $O(1)$, we first determine the leading term in the expansion of S from the constant-curvature condition. The stream function for this geometry can then be obtained, and the correction to the shape of the surface found. A similar process is performed in the inner region, where $a-r$ and z are $O(\lambda)$. These two regions are then matched together by means of an intermediate expansion. This expansion and matching procedure determines the speed at which the drop spreads, in principle to any order, and we obtain the first two terms in the expansion of the rate of spread in powers of ϵ.

3. The outer region

We consider first the outer region where spatial variations are on the length scale of the drop as a whole. Since the rate at which the drop spreads is small, we start by solving the normal stress balance equation (2.8) with $\psi = 0$, which gives the leading term in the expansion of the drop shape. If this is written as $S_0 \equiv z - h_0(r,t) = 0$, we have

$$h_0 = (a^2 \operatorname{cosec}^2 \alpha - r^2)^{\frac{1}{2}} - a \cot \alpha,$$

since the surface tension ensures that the drop surface is part of a sphere. The radius of the rim of the drop is $a(t)$ and the slope of the drop surface at the edge of the outer

† A non-dimensional quantity should strictly be used in the definition of ϵ, but the logarithmic terms in the final result (5.8) do combine to form a non-dimensional expression.

region is $\alpha(t)$; these two quantities are related by the constant-volume condition (2.10), which gives

$$\frac{\pi a^3}{3V} = \frac{(1+\cos\alpha)^2}{\sin\alpha(2+\cos\alpha)}. \tag{3.1}$$

To this order, the pressure inside the drop is constant, and the pressure difference across the surface is fixed by (2.8).

The next step is to determine ψ in the region bounded by $z = 0$ and $z = h_0$. For this purpose it is convenient to introduce bispherical co-ordinates ξ and η, defined by

$$z = \frac{a\sin\xi}{\cosh\eta+\cos\xi}, \quad r = \frac{a\sinh\eta}{\cosh\eta+\cos\xi}. \tag{3.2}$$

The axis and the rim of the drop are defined by $\eta = 0$ and $\eta = \infty$ respectively, the plane surface by $\xi = 0$, and the curved surface of the drop by $\xi = \alpha$. The boundary conditions (2.4) satisfied by ψ at $z = 0$ become

$$\psi = \psi_\xi = 0 \quad \text{at} \quad \xi = 0. \tag{3.3}$$

Since we are expanding in powers of ϵ and will not reach terms which are $O(\lambda)$ in the expansion of ψ, we can ignore the slip term in this region. The boundary condition (2.5) fixes the value of ψ on the free surface. With $S \equiv z - h_0$, the value of $\partial h_0/\partial t$ can be calculated in terms of da/dt, since the constant-volume condition (3.1), when differentiated and simplified, shows that

$$\frac{d\alpha}{dt} = -\frac{1}{a}\frac{da}{dt}\sin\alpha(2+\cos\alpha). \tag{3.4}$$

After some manipulation we obtain

$$\psi = a^2\frac{da}{dt}\frac{\cosh\eta - 1}{(\cosh\eta+\cos\alpha)^2}, \tag{3.5}$$

as the boundary condition which forces a non-zero solution for ψ. The other condition to be applied at the drop surface is the tangential stress condition (2.7), which in the new co-ordinates becomes

$$\psi_{\xi\xi} - \psi_{\eta\eta} + \psi_\eta \coth\eta - 3(\cosh\eta+\cos\alpha)^{-1}(\psi_\xi\sin\alpha + \psi_\eta\sinh\eta) = 0. \tag{3.6}$$

These conditions are sufficient to determine the solution of the Stokes equations uniquely. The normal stress condition can then be used to find the correction to the drop shape.

The Stokes equations in bispherical co-ordinates can be written in terms of the operator

$$L \equiv \frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} - \frac{1+\cosh\xi\cos\eta}{(\cosh\xi+\cos\eta)\sinh\eta}\frac{\partial}{\partial\eta} - \frac{\sin\xi}{\cosh\xi+\cos\eta}\frac{\partial}{\partial\xi},$$

and the equations (2.2) become

$$a^2\zeta = (\cosh\eta+\cos\xi)^2 L\psi, \quad L\zeta = 0. \tag{3.7}$$

The relations (2.3) between the pressure and the vorticity become

$$p_\eta = \frac{\cosh\eta+\cos\xi}{a\sinh\eta}\zeta_\xi, \quad p_\xi = -\frac{\cosh\eta+\cos\xi}{a\sinh\eta}\zeta_\eta. \tag{3.8}$$

Following the suggestions of Payne & Pell (1960), who considered the solution of the Stokes equations in lenticular regions, we write

$$\psi = \frac{z}{a}\phi_1 + \frac{a^2-r^2-z^2}{2a}\phi_2 = \frac{\phi_1 \sin\xi + \phi_2\cos\xi}{\cosh\eta + \cos\xi},$$

where ϕ_1 and ϕ_2 are solutions of $L\phi = 0$ which are regular at $\eta = 0$. The corresponding value of ζ is

$$a^2\zeta = 2a\frac{\partial\phi_1}{\partial z} - 2z\frac{\partial\phi_2}{\partial z} - 2r\frac{\partial\phi_2}{\partial r} - \phi_2. \tag{3.9}$$

Appropriate expressions for ϕ_1 and ϕ_2 can be built up from solutions of the form

$$(\cosh\eta + \cos\xi)^{-\frac{1}{2}} \exp(\pm q\xi)\,\Phi_q(\eta),$$

where q is a separation parameter. The function Φ_q can be written in terms of the Legendre functions of complex order as

$$\Phi_q(\eta) = \int_1^{\cosh\eta} P_{-\frac{1}{2}+iq}(x)\,dx.$$

With a suitable choice of ϕ_1 and ϕ_2 we can ensure that the conditions (3.3) at $\xi = 0$ are satisfied, and we write

$$\psi = a^2\frac{da}{dt}(\cosh\eta+\cos\xi)^{-\frac{3}{2}}\int_0^\infty \{A(q)\sin\xi\sinh q\xi + B(q)(\cos\xi\sinh q\xi - q\sin\xi\cosh q\xi)\}\,\Phi_q(\eta)\,dq. \tag{3.10}$$

In order to satisfy the condition (3.5) at $\xi = \alpha$, it is necessary to express the function of η appearing in that condition in terms of $\Phi_q(\eta)$. This can be done by means of the result, quoted by Payne & Pell,

$$(x+\cos\alpha)^{-\frac{1}{2}} = 2^{\frac{1}{2}}\int_0^\infty \frac{\cosh q\alpha}{\cosh q\pi} P_{-\frac{1}{2}+iq}(x)\,dq. \tag{3.11}$$

Manipulation of this equation and the application of the condition (3.5) eventually leads to an equation linking $A(q)$ and $B(q)$, namely

$$A\sin\alpha\sinh q\alpha + B(\cos\alpha\sinh q\alpha - q\sin\alpha\cosh q\alpha) = \frac{1}{2^{\frac{1}{2}}\cosh q\pi}\{\sin\alpha\cosh q\alpha + 2q(1+\cos\alpha)\sinh q\alpha\}. \tag{3.12}$$

When the value (3.10) is substituted for ψ in the tangential stress condition (2.7), and further manipulation of (3.11) is used, we obtain a second equation relating $A(q)$ and $B(q)$, namely

$$A(\cos\alpha\cosh q\alpha + q\sin\alpha\sinh q\alpha) - B(1+q^2)\sin\alpha\cosh q\alpha = \frac{1}{2^{\frac{1}{2}}\cosh q\pi}\left\{2q^2(1+\cos\alpha)\sinh q\alpha - \frac{3q(1+\cos\alpha)^2}{\sin\alpha}\cosh q\alpha + \frac{(1+\cos\alpha)^2(2+\cos\alpha)}{\sin^2\alpha}\sinh q\alpha\right\}. \tag{3.13}$$

These two equations, (3.12) and (3.13), determine A and B, and hence the stream function is known.

The pressure to this order can be determined from the vorticity (3.9) and the relations (3.8). The other terms making up the normal stress can also be found, and after considerable manipulation the normal stress equation (2.8) takes the form

$$\frac{\sigma a}{\mu(da/dt)}\frac{1}{r}\frac{d}{dr}(r\sin\delta) = \int_0^\infty Z(q,\eta)\,dq + \text{const}, \tag{3.14}$$

where

$$\begin{aligned} Z(q,\eta) = {} & 2(\cosh\eta+\cos\alpha)^{-\frac{1}{2}}\left\{q(\cosh\eta+\cos\alpha)\left(\frac{\cosh\eta+\cos\alpha}{\sinh\eta}\Phi_q'(\eta)-\tfrac{3}{2}\Phi_q(\eta)\right)C(q)\right.\\ & \left.-\tfrac{3}{2}\sin\alpha\left(\frac{\cosh\eta+\cos\alpha}{\sinh\eta}\Phi_q'(\eta)-\tfrac{1}{2}\Phi_q(\eta)\right)D(q)\right\}\\ & -3\int_0^\eta \frac{q(\cosh\eta_1+\cos\alpha)\cosh q\alpha+\frac{1}{2}\sin\alpha\sinh q\alpha}{\sinh\eta_1(\cosh\eta_1+\cos\alpha)^{\frac{1}{2}}}\Phi_q(\eta_1)B(q)\,d\eta_1, \end{aligned} \tag{3.15}$$

with

$$C(q) = A\sin\alpha\cosh q\alpha + B(\cos\alpha\cosh q\alpha - q\sin\alpha\sinh q\alpha),$$
$$D(q) = A\sin\alpha\sinh q\alpha + B(\cos\alpha\sinh q\alpha - q\sin\alpha\cosh q\alpha).$$

If we write $\delta = \delta_0+\delta_1$, where δ_0 is the angle of slope associated with S_0 and δ_1 the correction forced by the motion, we can integrate (3.14) and obtain to first order

$$\begin{aligned} \frac{\sigma}{\mu(da/dt)}\delta_1 = {} & \frac{(\cosh\eta+\cos\alpha)^2}{\sinh\eta(1+\cos\alpha\cosh\eta)}\int_0^\eta \frac{\sinh\eta_1(1+\cos\alpha\cosh\eta_1)}{(\cosh\eta_1+\cos\alpha)^3}\int_0^\infty Z(q,\eta_1)\,dq\,d\eta_1\\ & +\frac{c_1\sinh\eta}{1+\cos\alpha\cosh\eta}, \end{aligned} \tag{3.16}$$

since $r\sin\alpha = a\sin\delta_0$; c_1 is a constant, as yet undetermined.

If the drop surface is written as $S \equiv z-h_0(r,t)-h_1(r,t) = 0$,

$$\frac{dh_1}{dr} = -\delta_1\sec^2\delta_0,$$

and so

$$h_1 = a\int_\eta^\infty \frac{\delta_1}{1+\cos\alpha\cosh\eta_1}\,d\eta_1,$$

since $h_1(a,t) = 0$. The constant c_1 can be determined by the condition (2.10) that the volume of the drop is constant, so that

$$\int_0^a h_1 r\,dr = 0.$$

With the value of c_1 so determined, the expression (3.16) for δ_1 becomes

$$\begin{aligned} \delta_1 = {} & \frac{\mu}{\sigma}\frac{da}{dt}\frac{(\cosh\eta+\cos\alpha)^2}{\sinh\eta(1+\cos\alpha\cosh\eta)}\left[\int_0^\eta \frac{\sinh\eta_1(1+\cos\alpha\cosh\eta_1)}{(\cosh\eta_1+\cos\alpha)^3}\int_0^\infty Z(q,\eta_1)\,dq\,d\eta_1\right.\\ & \left.-\frac{(1+\cos\alpha)^2\sinh^2\eta}{(\cosh\eta+\cos\alpha)^2}\int_0^\infty \frac{\sinh\eta_1}{(\cosh\eta_1+\cos\alpha)^3}\int_0^\infty Z(q,\eta_1)\,dq\,d\eta_1\right]. \end{aligned} \tag{3.17}$$

We require the value of δ_1 near the rim, where $\eta = \infty$. Using the value of Z given by (3.15), with A and B determined by the conditions (3.12) and (3.13), we can show that

δ_1 is a linear function of η for large η. Some of the components of the integrals in (3.17) can be evaluated exactly, and we obtain the following asymptotic result:

$$\delta_1 = \frac{\mu}{\sigma}\frac{da}{dt}\left[\frac{\sin^2\alpha}{\cos\alpha} + \frac{2\sin\alpha}{\alpha - \sin\alpha\cos\alpha}\left(-\eta + \ln\{2(1+\cos\alpha)\} + 2\right) + J(\alpha)\right], \tag{3.18}$$

where

$$J(\alpha) = \frac{1}{\cos\alpha}\int_0^\infty \frac{\cosh\eta - 1}{\sinh\eta(\cosh\eta + \cos\alpha)^{\frac{1}{2}}}\int_0^\infty \frac{2^{\frac{1}{2}}\Phi_q(\eta)}{\cosh q\pi}\left\{-q(q^2+1)\cosh q\alpha E_1(q,\alpha)\right.$$
$$\left. + \tfrac{3}{4}\sin\alpha\frac{q\sin\alpha\cosh q\alpha - \cos\alpha\sinh q\alpha}{(\cosh\eta + \cos\alpha)^2}E(q,\alpha)\right\}dq\,d\eta, \tag{3.19}$$

$$E(q,\alpha) = \frac{\begin{array}{l}4\sin\alpha(1+\cos\alpha)^2 q\sinh q\alpha\cosh q\alpha \\ \qquad + \sin^2\alpha\cos\alpha\cosh^2 q\alpha - (1+\cos\alpha)^2(2+\cos\alpha)\sinh^2 q\alpha\end{array}}{\sin\alpha(\sinh q\alpha\cosh q\alpha - q\sin\alpha\cos\alpha)},$$

$$E_1(q,\alpha) = E(q,\alpha) - \frac{(1+4q^2)\sin\alpha\cos\alpha}{q(1+q^2)(\alpha - \sin\alpha\cos\alpha)}.$$

Hence the angle of slope at the edge of the drop in this outer region is given by

$$\delta \sim \alpha + \frac{\mu}{\sigma}\frac{da}{dt}\left[\frac{2\sin\alpha}{\alpha - \sin\alpha\cos\alpha}\left\{\ln s + \ln\left(\frac{(1+\cos\alpha)e^2}{a}\right)\right\} + \frac{\sin^2\alpha}{\cos\alpha} + J(\alpha)\right], \tag{3.20}$$

where s is the arc length measured from the edge and is given by $s \sim 2a\exp(-\eta)$ as $s \to 0$.

4. The inner region

The inner region extends to distances $O(\lambda)$ from the rim of the drop. We follow the same order of solution as in the outer region, and the first result is that the curvature of the interface is constant, so that to leading order

$$S_0 \equiv z - (a-r)\tan\alpha_s,$$

since we know that the contact angle at the edge is α_s. Using this result we can calculate the value of the stream function on the interface from (2.6), and this gives

$$\psi = a\frac{da}{dt}(a-r)\tan\alpha_s \tag{4.1}$$

as one of the conditions that ψ must satisfy on $S_0 = 0$.

It is convenient to work in polar co-ordinates with origin at the rim, defined by

$$r = a - \lambda r_1\cos\theta, \quad z = \lambda r_1\sin\theta.$$

Because the size of this region is so small, the curvature of the rim is unimportant and the solution is locally two-dimensional. The stream function and vorticity satisfy the appropriate forms of the equations (2.2), so that

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1}\frac{\partial}{\partial r_1} + \frac{1}{r_1^2}\frac{\partial^2}{\partial\theta^2}\right)\psi = \lambda^2\zeta, \quad \left(\frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1}\frac{\partial}{\partial r_1} + \frac{1}{r_1^2}\frac{\partial^2}{\partial\theta^2}\right)\zeta = 0, \tag{4.2}$$

and the pressure–vorticity relations (2.3) become

$$\frac{\partial p}{\partial r_1} = -\frac{1}{r_1}\frac{\partial\zeta}{\partial\theta}, \quad \frac{1}{r_1}\frac{\partial p}{\partial\theta} = \frac{\partial\zeta}{\partial r_1}.$$

The plane boundary of the drop is given by $\theta = 0$, and the conditions (2.4) to be applied there are

$$\psi = 0, \quad \frac{1}{r_1}\frac{\partial \psi}{\partial \theta} - \frac{1}{r_1^2}\frac{\partial^2 \psi}{\partial \theta^2} = 0, \tag{4.3}$$

since slip is important in this region. In terms of the polar co-ordinates, the drop surface is given to leading order by $\theta = \alpha_s$, and the conditions to be satisfied there are (4.1) and the tangential stress condition (2.7), which reduce to

$$\psi = -\frac{\partial^2 \psi}{\partial \theta^2} = \lambda a \frac{da}{dt} r_1 \sin \alpha_s \quad \text{on} \quad \theta = \alpha_s. \tag{4.4}$$

If we write

$$\psi = \lambda a \frac{da}{dt} r_1 (\sin \theta + f),$$

the equation for f is identical with that solved previously for the problem of a plane meniscus (Hocking 1977). The solution was obtained there by writing $r_1 = \exp \rho$ and using a two-sided Laplace transform, which reduced the problem to that of finding the solution of an integral equation for the value of $\partial^2 f/d\theta^2$ on the boundary $\theta = 0$. With this quantity denoted by $k_1(\rho)$, the integral equation was shown to be

$$1 - e^{-\rho} k_1(\rho) = \int_{-\infty}^{\infty} L_1(\rho - \rho_1)\, k_1(\rho_1)\, d\rho_1, \tag{4.5}$$

where the kernel L_1 was given by

$$L_1(\rho) = \frac{\pi}{4\alpha_s^2} \int_{\rho}^{\infty} \frac{\sinh \rho_1}{\cosh(\pi \rho_1/\alpha_s) - 1}\, d\rho_1.$$

The asymptotic value of k_1 for large ρ was found to be

$$k_1 \sim \frac{2 \sin^2 \alpha_s}{\alpha_s - \sin \alpha_s \cos \alpha_s}\, \rho + j(\alpha_s), \tag{4.6}$$

where j, which was denoted by h_1 in that paper, can only be found by a numerical solution of (4.5).

The normal stress condition (2.8) in the co-ordinates currently being used becomes

$$\frac{a\sigma}{\mu} \frac{d\delta}{dr_1} = \left[\frac{2}{r_1} \frac{\partial^2 \psi}{\partial r_1 \partial \theta} - \frac{2}{r_1^2} \frac{\partial \psi}{\partial \theta} - p \right]_{\theta = \alpha_s} + \text{const},$$

and the terms on the right-hand side can be expressed in terms of $k_1(\rho)$. After integration, we obtain

$$\delta = \alpha_s - \frac{\mu}{\sigma} \frac{da}{dt} \int_{-\infty}^{\ln r_1} F(\rho)\, d\rho,$$

where F has the Laplace transform

$$\frac{\tilde{k}_1}{\omega} \left(\frac{1}{\sin(\omega - 1)\alpha_s} + \frac{2(\omega \cos \omega\alpha_s \sin \alpha_s - \sin \omega\alpha_s \cos \alpha_s)}{\cos 2\alpha_s - \cos 2\omega\alpha_s} \right);$$

$\tilde{k}_1$ is the transform of k_1, defined by

$$\tilde{k}_1(\omega) = \int_{-\infty}^{\infty} k_1(\rho)\, e^{-\rho\omega}\, d\rho.$$

Making use of (4.6), we find the asymptotic value of the angle of slope as we leave the inner region to be

$$\delta \sim \alpha_s + \frac{\mu}{\sigma}\frac{da}{dt}\left\{\frac{2\sin\alpha_s}{\alpha_s - \sin\alpha_s\cos\alpha_s}\ln\frac{s}{\lambda} + \frac{2\sin\alpha_s}{\alpha_s - \sin\alpha_s\cos\alpha_s} + \frac{j(\alpha_s)}{\sin\alpha_s}\right\}, \tag{4.7}$$

where, as before, s is the arc length measured from the edge, and is equal to λr_1.

If this result is compared with the value found in the outer region as the rim is approached, it will be noted that both expressions contain a term in $\ln s$, but that these terms do not match, and it is not legitimate to try to obtain an equation for da/dt by matching the constant parts of the two expressions. It is clear that the remedy is to introduce an intermediate region, across which the two asymptotic values of δ, (3.20) and (4.7), can be smoothly matched.

5. The intermediate region

To bridge the gap between the inner and outer regions, we start with the equations written in terms of the polar co-ordinates with origin at the rim used in the inner region and define a new variable x by

$$r_1 = \exp(x/\epsilon),$$

where the small parameter ϵ is defined, as previously, by

$$\epsilon = \frac{1}{|\ln\lambda|}.$$

We expand the solution in powers of ϵ, and neglect terms $O(\epsilon^2)$ throughout, as well of course as all terms $O(\lambda)$. The surface of the drop is defined by

$$\theta = \beta(x),$$

so that the angle of slope of the surface is given by

$$\delta = \beta + \arctan\left(r_1\frac{d\theta}{dr_1}\right) = \beta + \epsilon\frac{d\beta}{dx} \tag{5.1}$$

to the chosen order, and we also have the result

$$\beta = \delta - \epsilon\frac{d\delta}{dx}.$$

The slow variation of the boundary position with distance from the rim implies that the solution is locally similar to that between plane boundaries, but with coefficients which are slowly varying functions of r_1. If we write the stream function as

$$\psi = \lambda a\frac{da}{dt}r_1 g(x,\theta),$$

the equations (4.2) reduce to

$$\left(\frac{\partial^2}{\partial\theta^2} + 1\right)^2 g = 0,$$

with an error which is $O(\epsilon^2)$ and not $O(\epsilon)$. The boundary conditions (4.3) and (4.4), neglecting the $O(\lambda)$ term, are

$$g = \frac{\partial g}{\partial \theta} = 0 \quad \text{on} \quad \theta = 0,$$

$$g = \sin\beta, \quad \frac{\partial^2 g}{\partial \theta^2} + g = 0 \quad \text{on} \quad \theta = \beta,$$

and the solution is

$$g = \frac{\sin\beta\{\theta\cos(\beta-\theta) - \sin\theta\cos\beta\}}{\beta - \sin\beta\cos\beta}.$$

The pressure can now be determined, and the normal stress condition (2.8) then gives the equation

$$\frac{d\delta}{dx} = \frac{\mu}{\epsilon\sigma}\frac{da}{dt}\left(1+\epsilon\frac{d}{dx}\right)\frac{2\sin\beta}{\beta-\sin\beta\cos\beta},$$

or, in view of (5.1),

$$\frac{d\beta}{dx} = \frac{\mu}{\epsilon\sigma}\frac{da}{dt}\frac{2\sin\beta}{\beta-\sin\beta\cos\beta}. \tag{5.2}$$

If we now define

$$G(\beta) = \int_0^\beta \frac{\beta_1 - \sin\beta_1\cos\beta_1}{\sin\beta_1}d\beta_1, \tag{5.3}$$

we can integrate (5.2) to obtain

$$G(\beta) = \frac{2\mu}{\epsilon\sigma}\frac{da}{dt}x + \text{const.} \tag{5.4}$$

The constant can be determined by matching this solution to that in the inner region. If we write (4.7) in the current variables, we obtain

$$\delta \sim \alpha_s + \frac{2\mu}{\epsilon\sigma}\frac{da}{dt}\frac{1}{G'(\alpha_s)}(x+\epsilon) + \frac{\mu}{\sigma}\frac{da}{dt}\frac{j(\alpha_s)}{\sin\alpha_s},$$

since $x = \epsilon \ln r_1$. It follows that

$$\beta \sim \alpha_s + \frac{2\mu}{\epsilon\sigma}\frac{da}{dt}\left(\frac{x}{G'(\alpha_s)} + \epsilon\frac{j(\alpha_s)}{2\sin\alpha_s}\right),$$

and so (5.4) becomes

$$G(\beta) = G(\alpha_s) + \frac{2\mu}{\epsilon\sigma}\frac{da}{dt}\left(x + \epsilon\frac{j(\alpha_s)\,G'(\alpha_s)}{2\sin\alpha_s}\right). \tag{5.5}$$

The value of δ as the rim of the drop is approached from the outer region is given by (3.20). From this result we obtain

$$G(\beta) = G(\alpha) + \frac{2\mu}{\sigma}\frac{da}{dt}\left\{\ln s - 1 + \ln\left(\frac{1+\cos\alpha}{a}e^2\right) + \left(\frac{\sin^2\alpha}{2\cos\alpha} + \tfrac{1}{2}J(\alpha)\right)G'(\alpha)\right\}. \tag{5.6}$$

To match the corresponding function in the intermediate region with this result, we write $x = 1 + \epsilon \ln s$ in (5.5), and obtain

$$G(\beta) = G(\alpha_s) + \frac{2\mu}{\sigma}\frac{da}{dt}\left\{\frac{1}{\epsilon} + \ln s + \frac{j(\alpha_s)\,G'(\alpha_s)}{2\sin\alpha_s}\right\}. \tag{5.7}$$

Comparing these two values, (5.6) and (5.7), for $G(\beta)$, we see that the two terms in $\ln s$ are identical, and the remaining parts agree, provided that

$$G(\alpha)-G(\alpha_s) = \frac{2\mu}{\sigma}\frac{da}{dt}\left\{-\ln\lambda-\ln\left(\frac{1+\cos\alpha}{a}e\right)-\left(\frac{\sin^2\alpha}{2\cos\alpha}+\tfrac{1}{2}J(\alpha)\,G'(\alpha)+\frac{j(\alpha_s)\,G'(\alpha_s)}{2\sin\alpha_s}\right)\right\},$$

which is the equation for the rate of spread of the drop. Simplifying this expression, we have

$$\frac{2\mu}{\sigma}\frac{da}{dt} = \frac{G(\alpha)-G(\alpha_s)}{-\ln\lambda+\ln a-Q_0(\alpha)+Q_1(\alpha_s)}, \tag{5.8}$$

where

$$Q_0(\alpha) = 1+\ln(1+\cos\alpha)+\frac{\alpha-\sin\alpha\cos\alpha}{2\sin\alpha}\left(\frac{\sin^2\alpha}{\cos\alpha}+J(\alpha)\right), \tag{5.9}$$

$$Q_1(\alpha_s) = \frac{\alpha_s-\sin\alpha_s\cos\alpha_s}{2\sin^2\alpha_s}\,j(\alpha_s). \tag{5.10}$$

The leading term in the denominator of (5.8) could have been found from the leading terms in the inner and outer regions, which can be easily found without the effort needed to determine the functions Q_0 and Q_1. If a comparison with experimental results is to be attempted, however, it is essential that these terms be included; otherwise any multiple of λ could replace λ with equal jusitfication. Since the denominator in (5.8) has an error $O(\epsilon)$, the given solution contains the first two terms in an expansion in powers of ϵ.

6. Numerical work

There are three numerical tasks to be performed if the spreading of the drop is to be calculated. The functions Q_0 and Q_1 have to be evaluated for arbitrary angles, and the differential equation (5.8) must be solved. To evaluate Q_0 we have to find the value of the infinite double integral $J(\alpha)$, defined by (3.19), which itself requires the evaluation of the function $\Phi_q(\eta)$. This function can be defined in terms of hypergeometric functions, for which series solutions are available, but different series have to be used for different parts of the range of integration, and it proved simpler to evaluate it by direct solution of the differential equation it satisfies. Some care is needed to ensure that the infinite extent of the two variables in the integral is correctly accounted for. For most values of α there proved to be no difficulty in obtaining accurate values for the integral, but when α was close to π the convergence of the q-integral was slow and the solutions obtained were less accurate. The evaluation of Q_1 requires the solution of the integral equation (4.5). A few values were given in Hocking (1977), and the method of solution described there was extended to give a more detailed set of results. Some values of Q_0 and Q_1 for angles in the range from zero to π are given in table 1.

Before solving (5.8), it is convenient to express it in non-dimensional form. If we introduce a length scale a_0 equal to the radius of a sphere with the same volume as the drop, and define non-dimensional variables by

$$\hat{a} = a/a_0, \quad \tau = \sigma t/2\mu a_0,$$

(5.8) becomes

$$\frac{d\hat{a}}{d\tau} = \frac{G(\alpha)-G(\alpha_s)}{\ln(a_0/\lambda)+\ln\hat{a}-Q_0(\alpha)+Q_1(\alpha_s)}. \tag{6.1}$$

α (rad)	Q_o	Q_i	α (rad)	Q_o	Q_i
0·1	1·6852	−3·3982	1·6	0·2470	−0·0696
0·2	1·6614	−2·7011	1·7	0·1067	0·0974
0·3	1·6223	−2·2880	1·8	−0·0196	0·2805
0·4	1·5687	−1·9905	1·9	−0·1560	0·4850
0·5	1·5017	−1·7519	2·0	−0·2896	0·7181
0·6	1·4226	−1·5509	2·1	−0·4247	0·9888
0·7	1·3326	−1·3745	2·2	−0·5529	1·3112
0·8	1·2334	−1·2143	2·3	−0·6737	1·7053
0·9	1·1263	−1·0653	2·4	−0·7841	2·2010
1·0	1·0127	−0·9231	2·5	−0·8807	2·8487
1·1	0·8938	−0·7853	2·6	−0·9604	3·7349
1·2	0·7705	−0·6489	2·7	−1·0209	5·0312
1·3	0·6437	−0·5116	2·8	−1·0629	7·0840
1·4	0·5140	−0·3710	2·9	−1·0810	10·6700
1·5	0·3816	−0·2246	3·0	−1·1370	21·6400

TABLE 1. Values of Q_o and Q_i

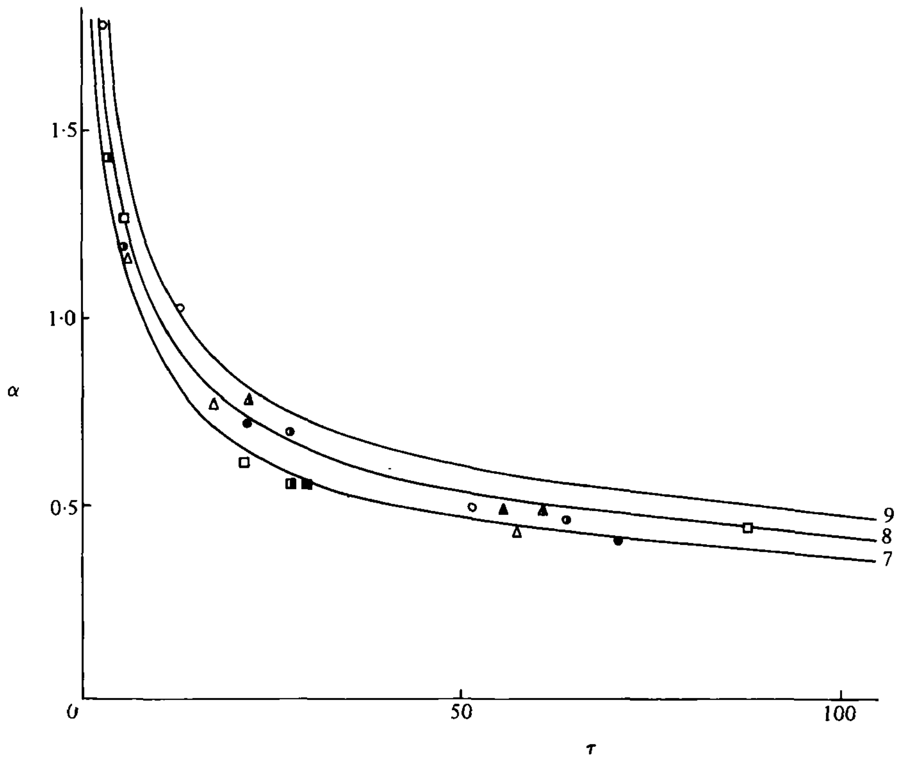

FIGURE 2. The outer contact angle as a function of the time. The curves show the results calculated from (6.1). The number by each curve is the value of the index n where the slip coefficient λ is equal to 10^{-n} m. The symbols refer to the experimental results, and the key is given in table 2.

The value of $\hat{a}$ for any value of α can be found from (3.1), which in the present variables becomes

$$\hat{a}^3 = \frac{4(1+\cos\alpha)^2}{\sin\alpha(2+\cos\alpha)}, \tag{6.2}$$

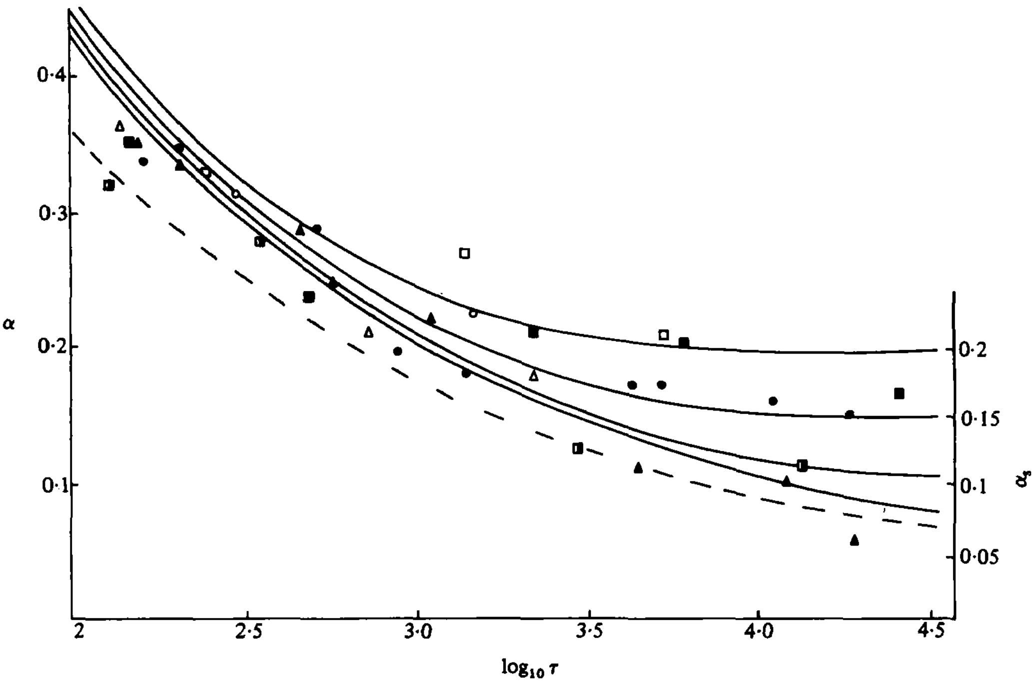

FIGURE 3. The later stages in the spreading. Note the changes in the scale of both axes. The solid curves are for $\lambda = 10^{-8}$ m and for static contact angles 0·05, 0·1, 0·15, 0·2 rad. The dashed curve is for $\lambda = 10^{-7}$ m and for $\alpha_s = 0{\cdot}05$.

and from (3.4) we also have

$$\frac{d\alpha}{d\tau} = -\sin\alpha(2+\cos\alpha)\frac{1}{\hat{a}}\frac{d\hat{a}}{d\tau}.$$

The rate of spread of the drop when the rim has any radius or the contact angle in the outer region has any value can be found from (6.1). The time taken for the drop to spread from an initial position with $\alpha = \alpha_0$ is given by evaluating

$$\tau = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{d\alpha/d\tau}.$$

It is therefore possible to find α as a function of τ, starting from any initial position and with given values of the parameters α_s, a_0 and λ.

For comparison with the experimental results described in § 7, solutions for the spread of the drop were obtained for $a_0 = 0{\cdot}5\times10^{-3}$ m, $\alpha_0 = 2{\cdot}8$, for $\alpha_s = 0{\cdot}05$, $0{\cdot}1$, $0{\cdot}15$, $0{\cdot}2$ and for $\lambda = 10^{-n}$ m ($n = 6, 7, 8, 9$). Some of the results obtained are shown in figures 2 and 3.

In these calculations, and in the theory presented, it has been assumed that the initial configuration of the drop is consistent with the form taken in the outer region, that is it is part of a sphere. If the drop were started from any other shape, it would quickly distort into the spherical shape because of the dominance of surface tension in the outer region. Such initial transient behaviour is ignored here. It is not likely ever to be significant in the parameter range for which the theory is valid, and the experiments were conducted so that the initial shape was close to the required spherical form.

Temperature (°C)	TiO_2 (%) 5		10		20	
1010	5600	○	4000	□	2500	△
1105	1500	◑	1100	◨	630	◭
1180	630	●	470	■	280	▲

TABLE 2. Viscosity in poise for each experiment. Also shown are the symbols used in figures 2 and 3.

7. Experiments

The experiments were undertaken to measure the time history of a small drop of molten glass on a horizontal surface. The substrate was a thin platinum sheet, ground and polished (on a lap wheel using a 1–3 μm diamond grit), and then degreased. The glasses used were ternary silicate glass containing SiO_2 and NaO_2 in a 4:1 mole ratio, with additions of TiO_2 at the 5, 10 and 20 mole % levels. Beads of an approximately spherical shape were made from these glasses, and the specimens used were chosen by weight to have a diameter close to 1 mm. The metal substrate was placed in a furnace with accurate temperature control and, after the temperature had equilibrated, the cold glass bead was placed on the heated platinum surface, whereupon it rapidly melted and began to spread.

The change in shape of the vertical profile of the drop was recorded at measured times by photographs taken through a microscope. It was always possible to fit a circle to the drop profiles, and the apparent contact angle was measured from the photographs. No variation in shape was observed when the platinum sheet and drop were inverted in the furnace.

The experiments were performed at three different temperatures, and the viscosity for each glass at each temperature was measured; the results are given in table 2. The surface tension was practically the same in all cases, and its value was $0{\cdot}33\ \mathrm{N\,m^{-1}}$. The static contact angle was estimated from the shape of the drop after a very long time had elapsed. It proved difficult to obtain a very precise measurement, but in all cases it was in the range 5° to 15°.

The experiments performed in the inverted position show that gravity was not important in the spreading process, so that the experimental results should be comparable with those of the theory. The spherical shape of the drop profile over most of its surface agrees with the leading term of the outer solution in the theory. The results of the experiments can be scaled in the same way as were the numerical ones, and they are shown as points on the diagrams in figures 2 and 3. There is some doubt about the time origin to be used, as there may be some spreading before the drop is completely molten. However, the theory shows that the initial spreading is very rapid, and the drop had usually spread to an approximately hemispherical shape before the first measurements were made, so that this initial uncertainty is of no importance.

The results of figure 2 are not affected noticeably by a change in the static contact angle in the chosen range (0·05–0·2 rad). It can be seen that, though there is some scatter, the experimental results agree reasonably well with the theoretical curve for some value of the slip coefficient between 10^{-7} and 10^{-8} m. The values in figure 3 relate to a later stage in the spreading process, as the drop approaches its equilibrium shape. The static contact angle is now important, and the curves separate as they asymptote to different values. Variation of the slip coefficient is now of less significance.

Another set of experiments on the rate of spread of drops has been reported by Karnik (1977). In our notation his results are for $\tau < 500$ and most of them are for static contact angles within the range we consider. The scale of the diagrams in Karnik's paper is such that accurate results cannot be taken from them for inclusion in figures 2 and 3, but our estimates for them do lie within the scatter of our results at the appropriate values of τ, thus providing further evidence for the acceptability of our model of the spreading phenomenon.

8. Conclusions

The agreement between the experimental results and the theoretical predictions is sufficiently good to strengthen the case for regarding the hypotheses put forward at the beginning of this paper as a satisfactory basis for the solution of problems involving moving contact lines. It is disappointing that it is not possible to determine the slip coefficient more accurately, especially as the most likely value lies midway between the values expected if surface roughness or molecular interaction are regarded as the primary cause of slip.

The restriction that the Bond number is small enough to ensure that gravity is unimportant in the spreading process limits the application of the theory presented here to very small drops. There is no difficulty in principle preventing an extension of the theory to Bond numbers that are $O(1)$. The inner and intermediate regions are unchanged, but the outer region is no longer spherical to leading order, and has a shape determined by the static sessile-drop problem. If we then tried to find the stream function, we could no longer use any simple co-ordinate system but would have to resort to a numerical solution of the Stokes equations in the region between the plane and curved boundaries of the drop. If we are content to determine the gross features only, then, as pointed out before, we do not need to find the solution in this region, and to leading order we would have an equation like

$$\frac{d\hat{a}}{d\tau} = \frac{G(\alpha) - G(\alpha_s)}{\ln(a_0/\lambda)},$$

but now the connection between $\hat{a}$ and α would be given, not by (6.2), but by the solution of the sessile-drop problem. For large Bond numbers the drop may be sufficiently flattened for lubrication theory to be applied in the outer region, although the full equations would still be needed in the other regions, where the slope of the drop would not be small. If, however, the slope is everywhere small, lubrication theory can be applied over the whole of the drop and the spreading problem in those circumstances has been solved for all Bond numbers by Hocking (1982*b*).

The model for the spreading process used in this paper is probably the simplest possible one. There are many features present in the experimental situation which have not been included. As Copley, Rivers & Smith (1972) have shown, grain boundaries impede the spreading, and droplets form by condensation of the vapour on the substrate ahead of the contact line; there are no doubt other microstructural features present which affect the spreading process. Our aim has been to concentrate on the dynamics in the simplest case, to provide a basis to which these further refinements can be added.

We wish to thank Mr A. S. Robinson, Director of Research and Development, and the Directors of Pilkington Brothers Ltd for their permission to publish the experimental work. We wish to thank a referee for the reference to the paper by Karnik.

REFERENCES

COPLEY, G. J., RIVERS, A. D. & SMITH, R. 1972 *Glass Tech.* **13**, 50.

COPLEY, G. J., RIVERS, A. D. & SMITH, R. 1975 *J. Materials Sci.* **10**, 1285.

DUSSAN V., E. B. 1979 *Ann. Rev. Fluid Mech.* **11**, 371.

HOCKING, L. M. 1976 *J. Fluid Mech.* **76**, 801.

HOCKING, L. M. 1977 *J. Fluid Mech.* **77**, 209.

HOCKING, L. M. 1981 *Q. J. Mech. Appl. Math.* **34**, 37.

HOCKING, L. M. 1982*a* The motion of a drop on a rigid surface. In *Proc. 2nd Int. Coll. on Drops and Bubbles, Monterey. JPL Publication* no. 82-7 (NASA-JPL, Pasadena, Cal.), p. 315.

HOCKING, L. M. 1982*b* The spreading of a thin drop by gravity and capillarity. Submitted to *Q. J. Mech. Appl. Math.*

HUH, C. & MASON, S. G. 1977 *J. Fluid Mech.* **81**, 401.

KARNIK, A. R. 1977 *J. Photo. Sci.* **25**, 197.

LACEY, A. A. 1982 The motion with slip of a thin viscous droplet over a solid surface. Submitted to *Stud. Appl. Math.*

LOWNDES, J. 1980 *J. Fluid Mech.* **101**, 631.

PAYNE, L. E. & PELL, W. H. 1960 *J. Fluid Mech.* **7**, 529.