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Rival contact-angle models and the spreading of drops

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The spreading of a drop of viscous fluid on a horizontal surface by capillarity has been studied by a number of authors. Different hypotheses have been advanced for the crucial questions of the contact angle at the moving rim of the drop. It is argued that there is one model that agrees with experiments and is economical in its hypotheses. On the basis of this model, the spreading rate is calculated for small static contact angles and for complete wetting (zero contact angle). The rates are also found when the spreading depends partially or dominantly on gravity.

1. The spreading of drops by capillarity

Consider a compact volume of clean fluid placed on a smooth rigid horizontal plane surface. We can also suppose, for simplicity, that the initial shape of the rim of the drop is circular and that it remains circular as the fluid spreads. An outward motion of the rim is produced by gravity, which acting alone would cause the fluid to spread out into a thin horizontal film, but for much of this paper the effect of gravity will be ignored. The other cause of the spreading of the fluid is capillarity. In equilibrium, capillarity causes the free surface to take the shape of a surface of constant curvature, but there is an additional quantity needed to fix the equilibrium shape, the static contact angle. If we suppose that the initial shape of the free surface is that of a spherical cap, with the slope at the rim greater than the static contact angle, then the drop will spread until the radius of the rim reaches a certain size, when the slope there will have its static value. If the static contact angle is zero, then the spreading will continue indefinitely.

It is clear that the process of spreading is completely described by finding the radius of the circular rim of the drop as a function of time. The relevant parameters defining the drop are its volume and the static contact angle, and we expect the rate of spreading to depend on the viscosity and surface tension of the fluid. If we assume that the slope of the free surface is small compared with unity at all times, the lubrication approximation can be applied, and the problem reduces to that of solving a nonlinear equation for the height of the drop as a function of the distance from the centre of the drop and of the time. The use of the lubrication approximation restricts consideration to systems in which the contact angle is small, although one of the proposed assumptions relating to the contact angle can be applied to angles of arbitrary size. Although this account of the formulation of the problem appears straightforward, it hides two difficulties. It is well-known that the usual no-slip boundary condition applied to a fluid in contact with a rigid surface is not acceptable for the vicinity of a moving contact line, since it leads to a force singularity (Dussan V. & Davis 1974). The relaxation of the boundary condition to allow for slip near the contact line (which is the preferred way in which this difficulty is overcome) introduces another parameter. Different prescriptions for the new form of the boundary condition have been suggested, but most involve a slip length as the new parameter. The second difficulty concerns the value of the contact angle under dynamic conditions. In order to provide the necessary conditions for the equation for the height of the drop it is necessary to prescribe the contact angle in the non-equilibrium state, and not only its static value. There are two possible assumptions, both of which have their supporters. One, used first by Greenspan (1978), is that the contact angle when the contact line is moving is some function of the velocity of the contact line. The spreading rate of a drop under various choices for this functional relation have been obtained recently by Ehrhard & Davis (1991). The second assumption, used for example by Hocking (1981), is that the contact angle at the rim of the drop remains equal to its static value even when the contact line is moving. The letters D (dynamic) and S (static) will be used in what follows when comparing results obtained using these alternative assumptions. It is immediately apparent that model D introduces an additional parameter with the dimensions of a velocity, as well as the functional relationship between velocity and angle, whereas model S requires no additional information.

The reason for the choice of model D stems from measurements of contact angles at moving contact lines (see, for example, Hoffman 1975), which clearly demonstrate the variation of angle with velocity. It might be thought that these experiments suffice to rule out model S immediately. However, as pointed out by Hanson & Toong (1971), it is important to recognize that most of the measurements of contact angles are not direct but are inferred from secondary observations, and that the slope changes rapidly in the vicinity of the contact line. Thus it is possible to make a distinction between the *apparent* contact angle, which is the angle to which the measurements relate, and the *real* contact angle at the contact line itself. It is not surprising that these two angles should differ when the contact line is moving; the relaxation of the no-slip condition to remove the force singularity results in finite but large stresses near the contact line. These in turn produce rapid changes in curvature since they must be balanced by the capillary pressure and hence a rapid change in slope near the contact line is to be expected. Nevertheless, the proponents of model D have ignored the distinction between real and apparent contact angles, and have taken the experimentally determined values of the apparent contact angle as defining the real contact angle. In this paper, the spreading problem is discussed on the basis of the two models, and arguments are given in favour of model S, which postulates that the contact angle at the edge of the drop is equal to the static contact angle even when the edge is moving. The modifications to the spreading rate required when there is complete wetting are found, and the effect of gravity on the spreading rate is also described briefly.

2. Formulation of the problem

The application of the lubrication approximation to the motion of a thin layer of fluid or a drop results in an equation that has been written down many times. The derivation given in Hocking (1983) is followed here, except that in that paper the small parameter defining the aspect ratio of the drop was chosen to be the static contact angle, but here it is defined independently. The reason for this change is so that the formulation holds for both zero and non-zero contact angles.

We consider an axisymmetric drop of liquid on a horizontal plane. We wish to determine the radius of the drop as a function of the time as capillarity and gravity cause it to spread over the plane, and also to find the shape of the top surface of the drop as a function of distance from the centre of the drop and of the time. The partial differential equation for the height of the drop when the lubrication approximation is used can be written in the form

$$\frac{\partial h}{\partial t}+\frac{1}{x}\frac{\partial}{\partial x}\left[h^2(h+\lambda)\,x\frac{\partial}{\partial x}\left(\frac{\partial^2 h}{\partial x^2}+\frac{1}{x}\frac{\partial h}{\partial x}-Bh\right)\right]=0. \tag{2.1}$$

Distance from the centre of the drop is denoted by $a_0 x$, where a_0 is the horizontal lengthscale. The vertical lengthscale is $a_0\epsilon$, where ϵ is the slope parameter or aspect ratio of the drop, and the height of the drop at the location x is denoted by $a_0\epsilon h(x,t)$. For the lubrication approximation to hold, ϵ must be small, and then (2.1) is the leading-order term in the expansion of the solution in powers of ϵ, provided the inertial terms in the Navier–Stokes equations are also small, that is, provided $\epsilon^2 Re \ll 1$, where Re is the Reynolds number. Because the slope of the top surface of the drop must be of order ϵ, it follows that the contact angle must also be of order ϵ.

The lengthscale and the aspect ratio are related to the volume V of the drop by

$$2\pi a_0^3\epsilon = V. \tag{2.2}$$

The dimensional time is equal to $(3\mu a_0/\sigma\epsilon^3)\,t$, where μ is the viscosity of the fluid and σ is the surface tension. The non-dimensional Bond number B expresses the ratio of gravitational and capillary forces and is defined by

$$B=\rho g a_0^2/\sigma, \tag{2.3}$$

where ρ is the density of the fluid and g is gravity. The form of the equation given by (2.1) is based on the assumption of a slip boundary condition of the form

$$u-\bar{\lambda}\,\partial u/\partial z = 0 \quad \text{on} \quad z=0, \tag{2.4}$$

where u is the radial velocity of the fluid at the plane surface $z=0$, and the non-dimensional parameter λ is defined in terms of the slip length $\bar{\lambda}$ and the height of the drop by

$$\bar{\lambda}=\tfrac{1}{3}a_0\epsilon\lambda. \tag{2.5}$$

The physical reason lying behind a condition like (2.4) is probably connected with roughness of the solid surface, either on a macroscopic or molecular level. There is no sound theoretical basis for the condition, other than the pragmatic one that it does enable the contact-line singularity to be removed. Variants of (2.4) have been proposed in problems of sliding and spreading, but they yield qualitatively similar results (see Dussan V. 1976). Since the object of this paper is to explore the differences arising from the contact-angle description it is sufficient to use (2.4) for both models.

The symmetry about the origin requires that

$$\partial h/\partial x = \partial^3 h/\partial x^3 = 0 \quad \text{at} \quad x=0. \tag{2.6}$$

Suppose that the rim of the drop is at $x=a(t)$, so that the drop has a radius $a(t)$ at time t. Then the vanishing of the height at the rim and the constancy of the fluid volume impose the conditions

$$h(a,t)=0, \quad \int_0^a x h(x,t)\,\mathrm{d}x = 1. \tag{2.7}$$

The final boundary condition relates to the slope of the surface at the rim of the drop, which must be of order ϵ. In model S, the contact angle has a constant value $\epsilon\alpha_s$, so that the boundary condition has the form

$$-\partial h/\partial x = \alpha_s \quad \text{at} \quad x = a(t). \tag{2.8S}$$

In model D, the static contact angle is also equal to $\epsilon\alpha_s$, but the contact angle when the contact line is moving is assumed to be velocity dependent. In a form that allows some flexibility, we can suppose that the excess of the contact angle over its static value is proportional to some power of the velocity of the contact line. Thus, in non-dimensional form the boundary condition has the form

$$-\partial h/\partial x = \alpha_d = \alpha_s + K\dot{a}^m \quad \text{at} \quad x = a(t), \tag{2.8D}$$

where $\dot{a} = \mathrm{d}a/\mathrm{d}t$ and K and m are positive constants. It should be made clear that there is no direct evidence for this assumption about the contact angle; other forms of the functional dependence on velocity could be postulated with equal validity.

We wish to find the solution of (2.1), subject to the conditions (2.6), (2.7) and either (2.8S) or (2.8D). The small parameter ϵ does not appear in this formulation of the problem, which is the leading-order term in an expansion in powers of ϵ. The solution will be found by expansions in terms of the remaining small parameter λ, although the precise forms of these expansions have still to be determined. The other parameter in (2.1) represents the effect of gravity on the spreading of the drop. In most of what follows in this paper, we concentrate on capillary-induced spreading and set the parameter B equal to zero. Then the equilibrium radius a_∞ and drop profile h_∞ are given by

$$a_\infty = (8/\alpha_s)^{\frac{1}{3}}, \quad h_\infty = \alpha_s(a_\infty^2 - x^2)/2a_\infty. \tag{2.9}$$

This steady state will be attained as $t \to \infty$. Of course, if $\alpha_s = 0$ there is no equilibrium configuration and the drop will spread indefinitely. Since the main interest is in the spreading of the drop after any initial transient adjustment of the drop shape has been accomplished, the precise form of the initial state is not important. We can suppose that, at $t = 0$,

$$a(0) = a_1, \quad h(x, 0) = 4(a_1^2 - x^2)/a_1^4, \tag{2.10}$$

where $a_1 < a_\infty$. An analysis of the initial motion for a variety of slip boundary conditions and contact-angle laws has been given by Haley & Miksis (1991).

The goal of the solution of the problem so formulated is the value of $a(t)$. When this has been determined, it is also possible to find the apparent contact angle α_a. As already explained, this is the contact angle measured outside the vicinity of the contact line, where the slope of the drop changes markedly. The quantity α_a can be found as a function of $\dot{a}$ and hence of t when $a(t)$ has been determined.

An important parameter in problems containing moving contact lines is the capillary number Ca, which measures the relative importance of viscous and capillary forces and is given by $Ca = \mu U/\sigma$. The velocity U which appears in this definition is, in the present case, proportional to $\dot{a}$, so that, with the chosen non-dimensionalization,

$$Ca = \tfrac{1}{3}\epsilon^3\dot{a}. \tag{2.11}$$

Hence, the contact-angle law (2.8D) can be written in terms of Ca instead of $\dot{a}$, and when the apparent contact angle α_a is determined, it too can be expressed as a function of Ca. An important consequence of the definition (2.11) of the capillary number is that Ca is not an input variable, but has to be determined from the solution. This is in contrast to other contact-line problems, such as the forced motion of a meniscus along a tube, when the capillary number can be prescribed.

3. Spreading rates

The quasi-static form for the drop height when gravity is unimportant can be found from (2.1) with $B = 0$ and the time-dependent term omitted. Since capillarity is the only remaining influence, the surface of the drop has constant curvature, which under the lubrication approximation means that it is a paraboloid. Applying the volume constraint (2.7), we find that, when the radius of the drop is a, the height h of the drop is given by

$$h = 4(a^2 - x^2)/a^4, \tag{3.1}$$

which is valid provided the time-dependent term in (2.1) is relatively small. This quasi-static solution is taken as the leading-order term in an expansion in terms of the spreading rate; the precise definition of the expansion parameter can be made *a posteriori* for both of the contact-angle models (2.8S) and (2.8D). The apparent contact angle α_a is given by the slope at $x = a$ of this leading-order solution so that

$$\alpha_a = 8/a^3. \tag{3.2}$$

Experiments reported by Tanner (1979) on the spreading of small volumes of fluid indicate that the spreading rate is proportional to the cube of the (apparent) contact angle. Of course, this relationship cannot hold when the drop is close to its equilibrium radius. A consequence of Tanner's experimental results is that the radius of the drop at time t is given by

$$a = ct^{\frac{1}{10}}, \tag{3.3}$$

where c is some constant, and this law has also been verified experimentally by Cazabet & Cohen Stuart (1986) and by Chen (1988). Any transient initial adjustment of the drop would not be covered by this theory, nor would it apply to drops so large that inertial effects destroy the validity of the lubrication approximation.

Theoretical predictions of the spreading rate must be tested against these experimental results. The leading-order solution (3.1) does not by itself determine the spreading rate, and the solution proceeds in different ways, depending on whether (2.8S) or (2.8D) is being used.

The solution with (2.8S) has been given by Hocking (1983). An inner region of width λ is needed near the contact line, and this has to be matched with the outer solution through an intermediate region of width $1/|\ln \lambda|$. The equation for $\dot{a}$ as given by Hocking (1983), when adjusted to allow for the change in definition of the aspect ratio has the form

$$3\dot{a} \ln\left(\frac{a\alpha_s}{2e\lambda}\right) = \left(\frac{8}{a^3}\right)^3 - \alpha_s^3. \tag{3.4S}$$

From this equation we see that $\dot{a}$ is proportional to the small parameter $1/|\ln \lambda|$, which is the appropriate expansion parameter in this case. We also see that, provided $a \ll a_\infty, a = (ct)^{\frac{1}{10}}$, where $c = \frac{5120}{3}/\ln(a\alpha_s/2e\lambda)$. Because of the presence of the drop radius a in the definition of c, it is not a constant but varies slowly with $\ln t$. A small adjustment to (3.3) is therefore needed, but is of only minor significance. When the radius is close to its equilibrium value the algebraic growth is replaced by an exponential approach of a to a_∞. The apparent contact angle α_a is defined by (3.2), and its values when the drop is far from, and close to, equilibrium have the respective forms

$$\alpha_a = c_1 \dot{a}^{\frac{1}{3}} \quad \text{for} \quad a \ll a_\infty, \qquad \alpha_a = \alpha_s + c_2 \dot{a} \quad \text{for} \quad a_\infty - a \ll a_\infty, \tag{3.5}$$

where c_1 and c_2 are known constants, depending on the parameters α_s and λ.

The spreading rate under one form of the alternative assumption (2.8D) was obtained by Greenspan (1978), and for a variety of slip laws and for different values of the power in the definition of α_d in (2.8D) by Haley & Miksis (1991) and Ehrhard & Davis (1991). As shown in these papers, the direct application of (2.8D) to the leading-order expression (3.1) for h determines the spreading rate as a function of radius in the form

$$K\dot{a}^m = 8/a^3 - \alpha_s, \tag{3.4D}$$

and the expansion parameter in this case is $K^{-1/m}$. If $m = \frac{1}{3}$, a is proportional to $t^{\frac{1}{10}}$ when $a \ll a_\infty$, so that (3.3) holds, but the approach to the equilibrium state is proportional to $t^{-\frac{1}{2}}$. In this model, and to leading order, the apparent contact angle α_a is equal to the assumed contact angle α_d. The spreading rate is proportional to K^{-3} when $m = \frac{1}{3}$. Although this result is obtained without reference to the difficulty associated with the force singularity at the contact line, a slip boundary condition is needed when the next term in the expansion is obtained. This correction requires an analysis parallel to that described when (2.8S) was used, and when this is done we find that the combined expression for the spreading rate when $m = \frac{1}{3}$ has the form

$$(\alpha_s + K\dot{a}^{\frac{1}{3}})^3 + 3\dot{a}\ln(a\alpha_s/2e\lambda) = (8/a^3)^3 = \sigma_a^3. \tag{3.6}$$

When $a \ll a_\infty$, this gives the spreading rate in the form

$$\dot{a}[K^3 + 3\ln(a\alpha_s/2e\lambda)] = (8/a^3)^3, \tag{3.7}$$

provided $K^3 \gg |\ln\lambda|$. This restriction means that the leading-order solution is only valid provided slip is present, and the slip coefficient, which is small compared to unity, must not be too small. The form for $\dot{a}$ given in (3.6) holds also when K^3 and $|\ln\lambda|$ are of the same order. The apparent contact angle can be found from (3.6): α_a is proportional to $\dot{a}^{\frac{1}{3}}$ when $a \ll a_\infty$, and, when $a_\infty - a$ is small,

$$\alpha_a = \alpha_s + K\dot{a}^{\frac{1}{3}} + \dot{a}\ln(a\alpha_s/2e\lambda)/\alpha_s^2. \tag{3.8}$$

Since the spreading rate tends to zero as a approaches a_∞, the apparent contact angle varies linearly with the velocity for large times, and not with the one-third power as (3.4D) predicts.

From these results we see that model D can give spreading at the observed rate only when m is equal to $\frac{1}{3}$ and when slip is present, with λ sufficiently large so that the condition $K^3 \gg |\ln\lambda|$ is satisfied. Model S also predicts the same form for the spreading rate, but the constant of proportionality depends only on the slip length λ and does not involve any other material constant. Model D predicts an algebraic approach to equilibrium when slip is completely neglected, but when it is included, the approach is exponential, as in model S. it follows from these results that there is nothing to be gained by postulating that the dynamic contact angle α_d is given by (2.8D). There is no direct evidence for the validity of this form, and it has been shown that the indirect evidence is consistent with the simpler assumption (2.8S), that is, that the real contact angle is constant. The spreading rate for the drop at any radius and the dynamic variation of the apparent contact angle can both be deduced from this single hypothesis.

A different conclusion is drawn by Ehrhard & Davis (1991). They accept as a postulate the dynamic contact angle as given by a form like that in (2.8D) and determine the spreading rate for various values of the two constants K and m (in the present notation). They include the special case of the constant contact angle, as discussed in Hocking (1983), which is given by setting $K = 0$ in (2.8D), and state that

Hocking's result holds when the capillary number that they define is very large, whereas their results hold when it is small. The effect of the differing assumptions is made clear by the composite expression (3.6). As explained in §2, in spreading problems the capillary number is not the most convenient quantity to use, since it is a variable of the motion. It is better to compare the two parameters K and $|\ln\lambda|$. From (3.6), which incorporates both the effect of the slip region and any assumed dynamic behaviour of the contact angle, we see that model D is only valid when $K^3 \gg |\ln\lambda|$, whereas model S and model D give equal spreading rates, to leading order, when $K^3 \ll |\ln\lambda|$. In the absence of any evidence to support the hypothesis of model D, there seems to be no reason for K to have any other value than $K=0$, in which case model D reduces to model S.

4. Small contact angles

The procedure described in Hocking (1983) that led to the equation (3.4S) for the spreading rate is valid when $\beta \gg 1$, where $\beta = \alpha_s/\dot{a}^{\frac{1}{3}}$. When a is close to a_∞, β is proportional to $|\ln\lambda|^{\frac{1}{3}}$, so the validity of the procedure is assured, provided α_s is not zero. For general values of a, $\dot{a}$ is proportional to $1/|\ln\lambda|$, so that the solution is valid only when $\alpha_s^3 \gg 1/|\ln\lambda|$. When this condition does not hold, that is, for sufficiently small values of α_s, and, in particular, when $\alpha_s = 0$, the solution given in Hocking (1983) must be modified. The most significant change is in the solution close to the contact line.

In this inner region, we write $h = \lambda H(\xi)$, where $\lambda\xi = a-x$, and, to leading order, the equation (2.1) for h becomes

$$\mathrm{d}^3H/\mathrm{d}\xi^3 = -\dot{a}/H(H+1), \tag{4.1}$$

with the conditions $H=0$, $\mathrm{d}H/\mathrm{d}\xi = \alpha_s$ at $\xi = 0$. When $\beta \gg 1$, the solution can be expanded in the form $H = \alpha_s\xi + \dot{a}H_1 + \dots$, with H_1 determined by repeated integration, as shown in Hocking (1983). For other values of β, the nonlinear equation (4.1) must be solved. If we introduce a new variable $\eta = \dot{a}^{\frac{1}{3}}\xi$, the equation for H becomes

$$\frac{\mathrm{d}^3H}{\mathrm{d}\eta^3} = -\frac{1}{H(H+1)}, \tag{4.2}$$

with $H=0$, $\mathrm{d}H/\mathrm{d}\eta = \beta$ at $\eta = 0$. In order to match with an outer solution, the solution for which $H \sim \eta^2$ must be excluded, and the asymptotic form for H can be written as

$$H \sim \eta\{3\ln\eta + q(\beta)\}^{\frac{1}{3}}, \tag{4.3}$$

where $q(\beta)$ must be determined numerically. This asymptotic value has the required form for the inner condition on the solution in the intermediate region, where $a-x$ is of order $1/|\ln\lambda|$, and the outer condition is obtained by matching with the outer solution, where $a-x$ is of order one. Repeating the procedure described in Hocking (1983), we find that

$$\dot{a}[3\ln(a/2e\lambda) + \ln\dot{a} + q(\beta)] = (8/a^3)^3. \tag{4.4}$$

When $\beta \gg 1$, the value of $q(\beta)$ can be found from the expansion of H in powers of $\dot{a}$ as in Hocking (1983), which in the present notation gives

$$q(\beta) \sim \beta^3 + 3\ln\beta \quad \text{as} \quad \beta \to \infty, \tag{4.5}$$

and then (4.4) is identical to (3.4S).

The value of $q(\beta)$ was determined numerically by solving (4.2). If we change the variable η to y, by writing $\eta = \exp(y)$, the range of y is from $-\infty$ to $+\infty$, and if we also write $H(\eta) = \eta S(y)$, (4.2) becomes

$$\frac{\mathrm{d}^3 S}{\mathrm{d}y^3} - \frac{\mathrm{d}S}{\mathrm{d}y} = -\frac{1}{S(S+\mathrm{e}^{-y})}, \tag{4.6}$$

with the boundary condition

$$S \sim (3y+q)^{\frac{1}{3}} \quad \text{as} \quad y \to \infty, \tag{4.7}$$

where $q(\beta)$ is a constant that has to be determined. The other boundary condition when $\beta \neq 0$ is that

$$S \sim \beta - y\mathrm{e}^{y}/2\beta \quad \text{as} \quad y \to -\infty. \tag{4.8}$$

By inverting the operator on the left-hand side of (4.6), we can write the equation in the form $S(y) = \mathscr{F}[S(y)]$, where the functional $\mathscr{F}$ is given by

$$\mathscr{F}[S(y)] = \beta + \int_{-\infty}^{y} \frac{2-\exp(y_1-y)}{P(y_1)}\,\mathrm{d}y_1 + \int_{y}^{\infty} \frac{\exp(y-y_1)}{P(y_1)}\,\mathrm{d}y_1, \tag{4.9}$$

with
$$P(y) = 2S(y)\{S(y)+\exp(-y)\}. \tag{4.10}$$

The value of $S(y)$ and hence of q was found from the iterative procedure

$$S_{n+1} = r\mathscr{F}[S_n] + (1-r)\,\mathscr{F}[S_n], \tag{4.11}$$

where r is a relaxation parameter and the iteration commenced from a guessed value of S_0 with the required behaviour at infinity. A value of 0.8 for r was found to be satisfactory for all β. The values of S were determined over a finite range from $-Y$ to $+Y$, and the values of the integrals in (4.9) from $-\infty$ to $-Y$ and from Y to ∞ were estimated by using the asymptotic forms of S as $y \to \pm\infty$.

When $\beta = 0$, which means that the static contact angle α_s is zero, the asymptotic form for H near the contact line, with H and $\mathrm{d}H/\mathrm{d}\eta$ zero there, can readily be found from (4.2) to be given by

$$H \sim (\tfrac{8}{3})^{\frac{1}{2}}\eta^{\frac{3}{2}}, \tag{4.12}$$

and the corresponding asymptotic form for S, replacing (4.8) when $\beta = 0$, is given by

$$S \sim (\tfrac{8}{3})^{\frac{1}{2}} \exp(\tfrac{1}{2}y) \quad \text{as} \quad y \to -\infty. \tag{4.13}$$

With this change in the asymptotic value of S, and the consequent adjustment to the evaluation of the first integral in (4.9) from $-\infty$ to $-Y$, the same procedure as that used for non-zero β could be applied. By taking a succession of values for Y from 10 to 20, and by choosing steplengths equal to 0.4, 0.2 and 0.1 in the evaluation of the integrals it was possible to determine the values of $q(\beta)$ to the accuracy shown in table 1. The value of q for $\beta = 3$ is close to the asymptotic value of 30.30 given by (4.5). For small β, $q(\beta)$ is approximately equal to $0.74+\beta^2$.

Since $q(\beta)$ is now known, (4.4) can be used to determine $\dot{a}$ for all values of a and α_s. As already explained, when $\alpha_s \neq 0$ the values of β will be large, except perhaps in the initial stages of the spreading, and (4.4) is then equivalent to (3.4S), with the radius of the drop proportional to $t^{\frac{1}{10}}$ until the radius is close to its equilibrium value, when the approach is exponential. When $\alpha_s = 0$, we can write (4.4) in the form

$$a^3\dot{a}\{\ln(a^3\dot{a})+c\} = \frac{512}{3a^6}, \quad c = -4.34-3\ln\lambda. \tag{4.14}$$

β	$q(\beta)$
0	0.74
0.1	0.75
0.2	0.78
0.4	0.92
0.6	1.21
0.8	1.68
1.0	2.37
2.0	10.46
3.0	30.44

TABLE 1. Determination of the value of $q(\beta)$

If we now write $b = \frac{1}{4}a^4$, the equation becomes

$$\dot{b}(\ln \dot{b} + c) = \frac{64}{3b^{\frac{3}{2}}}. \tag{4.15}$$

When $|\ln \dot{b}| \ll c$, the solution of this equation has the form

$$b = (160t/3c)^{\frac{2}{5}}, \tag{4.16}$$

so that a is proportional to $t^{\frac{1}{10}}$ as expected. There is, of course, no finite equilibrium solution when the static contact angle is zero, and $a \rightarrow \infty$. As can be seen from (4.15), when b is large, $\ln \dot{b}$ must be approximately equal to $-c$, from which it follows that

$$b = \mathrm{e}^{-c}t, \quad a = 4.19\lambda^{\frac{3}{4}}t^{\frac{1}{4}}. \tag{4.17}$$

The one-tenth power holds provided $a \ll \lambda^{-\frac{1}{2}}$, so the change to the more rapid growth only occurs when the radius of the drop has become so large that the height of the drop at its centre is of the same order as the slip length.

5. Spreading by gravity

When the Bond number B is not zero, spreading is produced by a combination of gravity and capillarity. It was shown in Hocking (1983) that, when $aB^{\frac{1}{2}} \ll 1$, the spreading rate is only slightly different from that induced by capillarity alone. When $1 \ll aB^{\frac{1}{2}} \ll |\ln \lambda|$, (3.4S) becomes

$$3\dot{a} \ln (a\alpha_s/2e\lambda) = (2B^{\frac{1}{2}}/a^2)^3 - \alpha_s^3, \tag{5.1}$$

and the radius is proportional to $t^{\frac{1}{7}}$. When $aB^{\frac{1}{2}} \gg |\ln \lambda|$, the radius of the drop is proportional to $t^{\frac{1}{8}}$ and the spreading is controlled by gravity alone, with capillarity an important factor in determining the profile of the drop near the contact line but not having a significant influence on the spreading rate, except when the drop is approaching its equilibrium radius. This spreading rate is in agreement with the experimental results of Cazabet & Cohen Stuart (1986). When $\alpha_s = 0$, the growth of the radius of the drop is, to leading order, given by $a \propto t^{\frac{1}{8}}$ without limit.

6. Conclusions

The results presented in this paper have shown that, for spreading problems, the dual assumptions of some form of slip at the contact line and a constant static contact angle provide an acceptable basis for the conditions to be imposed at the contact line. It has been possible to determine on this basis both the spreading rate and the dynamic variation of the apparent contact angle. The spreading of a drop has been successfully treated in this paper, even when the static contact angle is zero, which allows complete wetting. It had been thought that, in this case, there would have to be a precursor film extending to infinity ahead of the bulk of the drop. The model presented here has shown that there is still a definite finite edge to the drop during the spreading process. There is a region ahead of the bulk of the drop, of width proportional to $1/|\ln \lambda|$, within which the slope of the drop changes from the apparent contact angle to zero at the contact line itself.

Although the particular examples of spreading have been within the lubrication approximation, a similar formulation can be successfully applied to spreading problems when the slope of the drop is not small (Hocking & Rivers 1982; Cox 1986). Another example of a moving contact line is at the front of a sheet of viscous fluid moving down a plane. An analysis of this problem has been presented by Troian *et al.* (1989) who use the lubrication approximation and avoid the difficulties associated with a moving contact line and with the definition of the contact angle by supposing the existence of a thin precursor film ahead of the front. The thickness of this film is an unassigned parameter, and the maximum height of the fluid sheet is shown to depend weakly on this parameter. A similar problem is that of the motion of a ridge of fluid and this has been solved by Hocking & Miksis (1991) on the assumptions of the present paper, that is, a slip boundary condition, a constant static contact angle and the lubrication approximation. The solution they found is a weak function of the slip length.

In a recent paper, Goodwin & Homsy (1991) have argued against the use of lubrication theory in the treatment of the flow near the front of a gravity-driven fluid sheet. The basis for their criticism is that, while some of the singularities associated with the presence of the moving contact line can be removed by a slip boundary condition, the solution based on lubrication theory is still singular because the rate of change of curvature of the free surface is unbounded at the contact line. They relate this perceived difficulty to the use of the lubrication approximation; in order to avoid it they use instead the Stokes equations to describe the motion near the contact line. Of course, lubrication theory is only valid when the slope of the free surface is small, and this implies that the contact angle must also be small. The criticism made of the use of lubrication theory, however, is based on the unbounded rate of change of curvature of the free surface. In fact, the curvature itself is unbounded when lubrication theory is used, but this is no reason for the theory to be discredited. Examples of fluid motions in which the curvature of a fluid surface has a singularity have been given by Buckmaster (1972). Moreover, the solution given by Goodwin & Homsy (1991) is for the outer problem only, and hence includes a singularity at the contact line, which they do not remove by including slip into their model. Consequently, their solution cannot demonstrate the dependence on the conditions applied at the contact line which is a feature of the solutions of Troain *et al.* (1989) and of Hocking & Miksis (1991). Because they avoid the contact line itself by a suitable choice of collocation points, it appears that their solution must be grid-dependent. In their treatment of the spreading of an initially spherical drop, Hocking & Rivers (1982) solved the Stokes equations, not the lubrication approximation, both in the outer region and in the vicinity of the contact line as well. Their solution for the spreading rate was dependent on the choice of the slip parameter, and so demonstrated that the rate could not be determined without an adequate model for the slip region in the vicinity of the contact line.

No mention has been made here of the influence of long-range molecular forces on the spreading of a drop. Such effects have been thoroughly discussed by de Gennes (1985) and Joanny (1986), but their papers show that there are some difficulties in the definition of contact angles when such forces are included. I hope to discuss this aspect of the spreading problem in a subsequent paper.

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