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The motion of a drop on a rigid surface

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Abstract

The assumptions of a region of slip near a moving contact line (to remove the force-singularity) and a constant contact [illegible]le are used to obtain the equation for the shape of a thin drop of liquid resting on a [illegible] plane. Three asymptotic expansions are matched together to obtain an expression for [illegible] rate at which the drop spreads. Some cases of sliding motion are also examined. A[illegible]ugh the technique is presented here for thin drops only, it can also be applied to drops of arbitrary size.

Introduction

The chief difficulty that has to be overcome in an attempt to describe the motion of a drop in contact with a rigid surface is the determination of the correct boundary conditions to be applied at the contact line where the surface of the drop meets the rigid surface. If the drop is spreading over the surface, or if it is sliding along it, or both, the contact line is moving and it is well known that in these circumstances application of the no-slip boundary condition leads to a solution containing an unacceptable singularity. For certain purposes this singularity can be ignored but if, for example, we wish to determine the rate at which the drop spreads or the speed at which it slides, a dynamical balance of the forces acting must be achieved, which proves to be impossible in the presence of the force-singularity. To circumvent this difficulty, the most widely used device is to replace the no-slip boundary condition in the vicinity of the contact line by one allowing a certain amount of slip there. The argument in favour of this proposal is that large stresses occur near the contact line, associated with the rapid change in direction of the fluid motion there, and the molecular forces which are usually sufficient to prevent any slip between fluid and solid may be unable to control these large stresses. Of course, what is really required is a good molecular theory for the junction between drop, solid and surrounding air. Failing such a theory, some model boundary condition may be proposed in the hope that its exact form is of little consequence and that it will at least enable finite answers to be produced in answer to questions involving the force balances associated with the motion and that these answers can then be tested experimentally. The simplest model boundary condition is one which replaces the usual no-slip condition by one which allows a small amount of slip, proportional to the local velocity gradient. If u is the velocity parallel to the plane surface and z is measured normally away from it, the proposed boundary condition is

$$u - \tilde{\lambda}\, \partial u/\partial z = 0 \qquad (1)$$

for a fluid in contact with a solid boundary at rest. The slip coefficient $\tilde{\lambda}$ is a measure of the length over which slip is significant. Although its value is unknown, if the slip is produced by molecular effects we might expect a value of the order of 10^{-9} m. Such slip is only expected to occur close to the contact line and the boundary condition should revert to its usual form elsewhere. However, the very small size suggested for $\tilde{\lambda}$ indicates that the slip condition can be used everywhere with negligibly small error. As we shall see, allowing for slip near the contact line gives speeds proportional to $1/|\ln\tilde{\lambda}|$ which is of much greater significance than any erroneous inclusion of terms proportional to $\tilde{\lambda}$.

When we have decided to use a slip boundary condition for problems involving moving contact lines, the stresses near the contact line are still large and we may consequently expect that there will be a significant distortion of the shape of the free surface near the contact line. The large stresses will be balanced by capillary effects, which are proportional to the curvature of the surface. In order to provide sufficient boundary conditions for the shape of the free surface to be calculated, it is necessary to specify the angle at which the free surface meets the plane. Observations of contact angles seem to show that the angle increases with the speed of advance of the contact line, and decreases when the contact line is retreating. For stationary drops, the contact angle is not uniquely defined but can take any value between certain limits. The evidence for the dynamic behaviour of the contact angle is based on observations which do not take account of any rapid change of slope in the very small distance from the edge of the drop where, as we have seen, large stresses are present. It may well be that the contact angle measured at the edge itself does not change with speed and the dynamic behaviour refers only to an apparent contact angle, only relevant at some distance from the edge. Evidence in favour of this contention has been provided by Lowndes[1] who has produced numerical calculations for the motion of a meniscus along a tube using the slip hypothesis and keeping the actual contact angle fixed. He was able to show that apparent contact angles could be found from his calculated meniscus shapes which were in good agreement with observed values and that marked changes in slope occurred in the immediate vicinity of the edge.

The calculations of Lowndes[1] show that a self-consistent rational framework for dealing with moving contact lines is provided by the assumptions of slip at the edge and a fixed contact angle. This framework has been used to discuss the spreading and sliding of a drop which is thin enough for lubrication theory to be used[2]. These problems are time-dependent and an estimate of the speeds involved depends crucially on the slip hypothesis. Both the meniscus problem and the drop problems needed considerable numerical calculation, although the use of lubrication theory reduced the amount required to a large extent. The equations for the spreading and sliding drop problems involve a small parameter, the slip coefficient, which suggests that matched asymptotic expansions could yield the desired answers without recourse to extensive numerical calculation. An attempt at such a procedure was made before the numerical results were obtained, but was not successful. The present paper, however, shows that matched asymptotic expansions can be used to obtain the rate of spread of a thin drop and, with certain restrictions, the rate at which a drop slides down a plane. The key to success was the realisation that, as well as expected inner and outer expansions, an intermediate region was required across which the inner and outer regions could be matched. The method employed has some similarities to the one set out by Lacey[3], except that he used a multiple scale approach and did not carry the solution sufficiently far.

Although the methods to be described here can be applied to a variety of problems, for simplicity they are explained with reference to the problems examined before[2]. The drop is assumed to be thin and two-dimensional and it is also assumed that it is small enough for the Bond number to be small, that is, for gravity to be less significant than capillarity. In the first problem, the drop is placed on a horizontal plane and allowed to spread until its equilibrium position is reached. The quantity to be determined is the rate of spread of the drop as a function of its width. In the second problem, the drop is placed on an inclined plane, when both spreading and sliding may occur. The final width of the drop and the speed at which it slides are the quantities to be determined in this case.

Formulation

The application of lubrication theory to the problems to be solved is straightforward and has been described in detail before[2]. The simplified forms of the Stokes equations enable the velocity components to be found in terms of the pressure and the application of the normal stress condition and the kinematic boundary condition at the free surface yields an equation for the height $\tilde{h}(\tilde{x},\tilde{t})$ of the drop, where $\tilde{x}$ is measured parallel to the plane surface and $\tilde{t}$ is the time. The equation for $\tilde{h}$ is

$$\frac{3\mu}{\sigma}\frac{\partial \tilde{h}}{\partial \tilde{t}} + \frac{\partial}{\partial \tilde{x}}\left[\tilde{h}^2(\tilde{h} + 3\tilde{\lambda})\left\{\frac{\partial^3 \tilde{h}}{\partial \tilde{x}^3} + \frac{g\rho \sin\theta}{\sigma}\right\}\right] = 0 , \quad (2)$$

where μ is the fluid viscosity, g gravity, σ surface tension, $\tilde{\lambda}$ the slip coefficient and θ the inclination of the plane to the horizontal. Lubrication theory is only valid if the slope of the drop surface is everywhere small, so the contact angles must be small. A non-dimensional form of (2) is

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}\left[h^2(h + \lambda)\left\{\frac{\partial^3 h}{\partial x^3} + K\right\}\right] = 0 , \quad (3)$$

where

$$\tilde{h} = a_o\alpha_a h,\ \tilde{x} = a_o x,\ \tilde{t} = 3\mu a_o t/\sigma\alpha_a^3,\ \tilde{\lambda} = a_o\alpha_a\lambda/3,\ K = a_o^2\rho g \sin\theta/\sigma\alpha_a, \quad (4)$$

and a_o is a length scale associated with the size of the drop and α_a is a typical value of the (small) contact angle.

The extent of the plane covered by the drop can be fixed by two more unknowns, $a_1(t)$ and $a_2(t)$, so that $a_2 \leq x \leq a_1$ and

$$h(a_1(t),t) = h(a_2(t),t) = 0. \quad (5)$$

The volume of fluid in the drop remains constant throughout the motion and the length scale can be chosen so that

$$\int_{a_2}^{a_1} h(x,t)\,dx = \frac{2}{3} . \quad (6)$$

The other conditions on h relate to the slope of the surface of the drop at its edges. The proposal indicated in the introduction shows that, when the contact line is moving in a direction from the interior of the drop to the exterior (an advancing edge), the contact angle is fixed at its static value, which we can take to be the scaling factor α_a. For a retracting edge, when the motion is in the opposite direction, the contact angle is equal to the minimum static angle α_r. At a stationary edge the contact angle can lie anywhere between α_r and α_a. The boundary conditions to be applied at the edges are, therefore,

$$\text{at } x = a_1: \quad \begin{aligned} -\partial h/\partial x &= 1 &\quad \text{if } da_1/dt > 0, \\ \beta \leq -\partial h/\partial x &\leq 1 &\quad \text{if } da_1/dt = 0, \\ -\partial h/\partial x &= \beta &\quad \text{if } da_1/dt < 0, \end{aligned} \tag{7}$$

$$\text{at } x = a_2: \quad \begin{aligned} \partial h/\partial x &= \beta &\quad \text{if } da_2/dt > 0, \\ \beta \leq \partial h/\partial x &\leq 1 &\quad \text{if } da_2/dt = 0, \\ \partial h/\partial x &= 1 &\quad \text{if } da_2/dt < 0, \end{aligned} \tag{8}$$

where $\beta = \alpha_r/\alpha_a$ and $0 \leq \beta \leq 1$.

The final information needed to specify the problem completely is the initial state, that is, the values of $a_1(0)$, $a_2(0)$ and $h(x,0)$. From arbitrary initial states, one expects a fairly rapid transient phase during which the shape of the drop changes without significant spreading taking place. This is because the rate of spread is controlled by conditions at the contact line where large stresses resist the motion. No such restriction is placed on the distortion of the drop surface when the edges are fixed. Since the initial phase is of little significance to the general spreading problem it will be ignored here. The height of the drop is then a function of time only through its dependence on the positions of the edges. Thus the solutions to be obtained are of similarity type and the initial shape of the drop will be assumed to agree with these solutions for the given initial positions of the edges.

Spreading

The simplest problem of the type being considered is when the drop spreads on a horizontal surface. If we suppose that the drop starts from a position where the apparent contact angles are greater than the static value, the edges of the drop will move outwards. If the drop is initially symmetric about its mid-position, it will remain so and we may write $a_1(t) = -a_2(t) = a(t)$ and consider the interval $0 \leq x \leq a$ only. The problem then takes the form

$$\dot{a}\,\frac{\partial h}{\partial a} + \frac{\partial}{\partial x}\left[h^2(h+\lambda)\,\frac{\partial^3 h}{\partial x^3} \right] = 0\,, \tag{9}$$

$$h = 0, \quad -\partial h/\partial x = 1 \qquad \text{at} \quad x = a\,, \tag{10}$$

$$\partial h/\partial x = 0 \qquad \text{at} \quad x = 0\,, \tag{11}$$

$$\int_0^a h\,dx = 1/3, \tag{12}$$

where $\dot{a} = da/dt$ and h is a function of x and a, in line with the intention to ignore any initial transient phase. As already explained, the rate of spread is expected to be small so that we can expand in powers of some small parameter $\varepsilon(\lambda)$, where $\lambda \ll \varepsilon \ll 1$ but the dependence of ε on λ is yet to be determined. Hence we can write

$$\dot{a} = \varepsilon u_1 + \varepsilon^2 u_2 + \dots\,, \tag{13}$$

and, in the outer region where x is $O(1)$, $h = h_0 + \varepsilon h_1 + \dots$ From equation (9) the equations satisfied by h_0 and h_1 are

$$\frac{\partial}{\partial x}\left[h_0^3\,\frac{\partial^3 h_0}{\partial x^3} \right] = 0\,, \tag{14}$$

$$\frac{\partial}{\partial x}\left[h_0^3\,\frac{\partial^3 h_1}{\partial x^3} \right] = -\,u_1\,\frac{\partial h_0}{\partial a} \tag{15}$$

and these have to be solved subject to the conditions (10), (11) and (12), except that the condition on the slope at the edge of the drop is not to be applied in this outer region. The solutions are

$$h_0 = \frac{1}{2a^3}(a^2 - x^2) , \tag{16}$$

$$h_1 = u_1 a^4 \left[(a + x) \ln(a + x) + (a - x) \ln(a - x) - 2a \ln 2a + \frac{3}{2a}(a^2 - x^2) \right] \tag{17}$$

so that, near the edge of the drop where $a - x$ is small,

$$h \sim \frac{a - x}{a^2} + \varepsilon\, u_1 a^4 (a + x) \left[\ln \frac{a - x}{2a} + 2 \right] . \tag{18}$$

The inner region is close to the edge of the drop and is where slip is important. In this region we write

$$x = a - \lambda X, \quad h(x,a) = \lambda H(X,a), \quad H = H_0 + \varepsilon H_1 + \ldots \tag{19}$$

The equation satisfied by H with a term $0(\lambda)$ omitted is

$$\dot{a} \frac{\partial H}{\partial X} + \frac{\partial}{\partial X} \left[H^2 (H + 1) \frac{\partial^3 H}{\partial X^3} \right] = 0 \tag{20}$$

and the boundary conditions are

$$H = 0, \quad \partial H/\partial X = 1 \quad \text{at} \quad X = 0 , \tag{21}$$

and $\partial H/\partial X$ is not more than logarithmically infinite as $X \to \infty$. The solution is

$$H = X + \tfrac{1}{2}\varepsilon u_1 \left[(X + 1)^2 \ln(X + 1) - X^2 \ln X - X) \right] + \ldots , \tag{22}$$

so that, for $X \to \infty$,

$$H \sim X + \varepsilon u_1 X \ln X . \tag{23}$$

Although (18) and (23) both contain logarithmic terms, it is not possible to match these two expansions together and an intermediate expansion is required. This region is of width $0(\varepsilon)$, and the match can be achieved if we choose

$$\varepsilon = 1/ \ln(\lambda^{-1}) . \tag{24}$$

The variables to be used in this region are defined by

$$y = \varepsilon \ln X , \quad Q(y) = H/X , \tag{25}$$

and the governing equation (20) becomes, after one integration,

$$\dot{a} + Q(Q + e^{-y/\varepsilon})(\varepsilon^3 \frac{\partial^3 Q}{\partial y^3} - \varepsilon \frac{\partial Q}{\partial y}) = 0 . \tag{26}$$

Neglecting the exponentially small term, the solution is

$$Q^3 = c_0 + \varepsilon c_1 + 3(u_1 + \varepsilon u_2)\, y + 0(\varepsilon^2) , \tag{27}$$

which matches with the inner solution (23) if we choose $c_0 = 1$, $c_1 = 0$. To match with the outer solution (18) we write

$$y = 1 + \varepsilon \ln(a - x) \tag{28}$$

and obtain

$$h \sim (a - x)\left[(1 + 3u_1)^{1/3} + \varepsilon (1 + 3u_1)^{-2/3}(u_1 \ln(a - x) + u_2) + 0(\varepsilon^2) \right] . \tag{29}$$

Comparing this with the outer solution, we can see that the logarithmic term and the constant term both match if

$$1 + 3u_1 = a^{-6} , \quad u_2 = u_1(2 - \ln 2a) , \tag{30}$$

so that the rate of spread of the drop is given approximately by

$$\dot{a} = \varepsilon\{1 + \varepsilon(2 - \ln 2a)\}\ (a^{-6} - 1) , \tag{31}$$

or, to the same order of accuracy,

$$3 \ \ln\left(\frac{2a}{\lambda e^2}\right) \frac{da}{dt} = a^{-6} - 1 \ . \tag{32}$$

The objective of determining the rate of spread of the drop as a function of its width has thus been achieved. If the leading term only in the outer expansion is included an apparent contact angle is given by the value of a^{-2}, from (18). With variables in their dimensional forms, equation (32) yields the expression

$$\alpha_a\left\{1 + \frac{9\mu U}{\sigma\alpha_a^3} \ \ln\left(\frac{2\tilde{a}\alpha_a}{3\tilde{\lambda}e^2}\right)\right\}^{1/3} \tag{33}$$

for the apparent contact angle at the edge of a drop of width $2a$ advancing with speed U when the static contact angle is small. But the inclusion of the second term in the outer expansion destroys the validity of the concept of an apparent contact angle as a directly measurable quantity since, with the extra term included, the slope does not tend to a constant at the edge of the drop within the outer region. It is, however, still possible to define the quantity (33) as a derived contact angle as it could be measured by finding the curvature of the drop at its mid-point, for example, thus taking into account the outer solution but not requiring any measurement to be made in the vicinity of the edge.

Sliding

The second problem is when the drop is placed on an inclined plane. The drop is no longer symmetric and both edges have to be treated. As before, the Bond number is small, and gravity enters the problem only through the positive parameter K defined in (4), which measures the component of gravity down the plane. Any transient behaviour is again ignored, so that we suppose the height of the drop to depend on the co-ordinate x measured along the plane and on the positions of the two edges, but not directly on the time. The same three regions encountered in the spreading problem are present, but because both edges have to be treated, it is convenient to introduce a change of variable. If we write $h(x,t) = f(s,a_1,a_2)$, where

$$x = \tfrac{1}{2}(a_1 + a_2) + \tfrac{1}{2}(a_1 - a_2)\ s \ , \tag{34}$$

the range covered by the independent variable s is from -1 to 1. In the outer region, we can write $f = f_o + f_1 + \dots$, and the equation for f_o is

$$\frac{\partial^3 f_o}{\partial s^3} + K = 0 \ , \tag{35}$$

and the solution which vanishes at the edges and which satisfies the volume condition (6) is

$$f_0 = \frac{1 - s^2}{a_1 - a_2}\ \left\{1 + \frac{Ks}{48}(a_1 - a_2)^4\right\} \ . \tag{36}$$

Since f_0 must be non-negative for s in $[-1,1]$, this solution is only acceptable if $0 < b \leq 1$, where

$$b = \frac{K}{48}\ (a_1 - a_2)^4. \tag{37}$$

This condition may be broken either in the initial stage or during the spreading of the drop. In either case, a different approach from that used here must then be employed. The failure of the condition implies that regions are developing where the drop becomes very thin and although this is an interesting possible behaviour, this aspect of the problem is not investigated here, and we assume that $b < 1$ throughout the motion.

The second term in the expansion in the outer region satisfies the equation

$$\frac{16}{(a_1-a_2)^5}\ \frac{\partial^3 f_1}{\partial s^3} = \frac{\dot{a}_1(1+s)(1+b) + \dot{a}_2(1-s)(1-b)}{(1-s^2)^2(1 + bs)^3} \ . \tag{38}$$

The boundary conditions on f_1 are

$$f_1 = 0 \ \text{ at } \ s = -1 \ \text{ and at } \ s = 1, \ \int_{-1}^{1} f_1\, ds = 0 \ , \tag{39}$$

and the solution can be found in closed form after a great deal of algebra. The only quantities of interest are the asymptotic values for the height of the drop near the two edges and these are given by

$$h \sim \frac{4(a_1-x)(1+b)}{(a_1-a_2)^2} + \frac{(a_1-a_2)^4(a_1-x)}{16(1+b)^2}\left[\dot{a}_1\left\{\ln\frac{(1-b)(a_1-x)}{(1+b)(a_1-a_2)} + \frac{1-2b}{1-b}\right\} - \dot{a}_2\,\frac{1}{1-b}\right], \tag{40}$$

$$h \sim \frac{4(x-a_2)(1-b)}{(a_1-a_2)^2} + \frac{(a_1-a_2)^4(x-a_2)}{16(1-b)^2}\left[-\dot{a}_2\left\{\ln\frac{(1+b)(x-a_2)}{(1-b)(a_1-a_2)} + \frac{1+2b}{1+b}\right\} + \dot{a}_1\,\frac{1}{1+b}\right]. \tag{41}$$

The solutions in the inner and intermediate regions are similar to those found in the spreading problem, except that the edges may be moving in either direction or be stationary. The conditions (7) apply at the lower edge $x = a_1$ and when they are applied, and the resulting inner expansions matched via the intermediate expansion to the outer solutions, we obtain the equation

$$\left\{\ln\left(\frac{(a_1-a_2)(1+b)}{\lambda(1-b)}\,S(\dot{a}_1)\right) - \frac{1-2b}{1-b}\right\}\dot{a}_1 + \frac{\dot{a}_2}{1-b} = \frac{1}{3}\left\{\frac{2^6(1+b)^3}{(a_1-a_2)^6} - S^3(\dot{a}_1)\right\} \tag{42}$$

where S is a step function, defined by

$$S(x) = 1 \quad \text{for} \quad x > 0, \quad S(x) = \beta \quad \text{for} \quad x < 0\,, \tag{43}$$

When the edge is at rest, (42) is replaced by $\dot{a}_1 = 0$. The corresponding results for the upper edge $x = a_2$, where the conditions (8) apply, are

$$\left\{\ln\left(\frac{(a_1-a_2)(1-b)}{\lambda(1+b)}\,S(-\dot{a}_2)\right) - \frac{1+2b}{1+b}\right\}\dot{a}_2 + \frac{\dot{a}_1}{1+b} = -\frac{1}{3}\left\{\frac{2^6(1-b)^3}{(a_1-a_2)^6} - S^3(-\dot{a}_2)\right\} \tag{44}$$

when the edge is moving, and $\dot{a}_2 = 0$ when it is at rest.

These equations are sufficient to determine the future behaviour of the drop from any given initial position of the edges. The drop may not move at all, or one or both edges may move in either direction as the drop spreads or contracts. The most interesting possibility is when the drop spreads and slides, approaching a final state in which the width of the drop and its speed down the plane attain constant values. This final state can be found by setting $\dot{a}_1 = \dot{a}_2 = U$ and $a_1 - a_2 = 2a$. From (42) and (44), with b replaced by its value in terms of K and a from (37), we obtain the equations

$$U = \frac{\frac{2K}{a^2}\left(1 + \frac{1}{27}a^8K^2\right) - 1 + \beta^3}{3\ln\left(\frac{4a^2\beta}{\lambda^2}\right) + \frac{12a^8K^2}{9 - a^8K^2}}\,, \tag{45}$$

$$\frac{\ln\left(\frac{2a}{\lambda}\,\frac{3+a^4K}{3-a^4K}\right) + \frac{6a^4K}{3-a^4K}}{\ln\left(\frac{2a}{\lambda}\,\frac{3-a^4K}{3+a^4K}\beta\right) - \frac{6a^4K}{3+a^4K}} = \frac{a^6 - \left(1 + \frac{1}{3}a^4K\right)^3}{\left(1 - \frac{1}{3}a^4K\right)^3 - \beta^3a^6}\,. \tag{46}$$

There are too many parameters for it to be easy to make general statements about the motion. An approximate set of criteria can be found by retaining only the dominant terms on the left-hand sides of (42) and (44), that is, the logarithmic terms. Then it follows that

$$\begin{aligned} \dot{a}_1 &= 0 \quad \text{if} \quad \beta < a^{-2}(1 + a^4K/3) < 1\,, \\ \dot{a}_2 &= 0 \quad \text{if} \quad \beta < a^{-2}(1 - a^4K/3) < 1\,. \end{aligned} \tag{47}$$

A static final state is only possible if these two conditions on the width of the drop overlap, which they do if $0 \leq K \leq K_c$, where

$$K_c = \frac{3}{4}(1 - \beta^2) . \tag{48}$$

while for $K > K_c$ the drop will slide. If there is no contact angle hysteresis, that is, if $\alpha_r = \alpha_a$, the drop will slide however small the inclination of the plane.

Extensions and conclusions

Although only thin two-dimensional drops have been considered here, the method is applicable to many other cases. The spreading of a thin drop by both capillarity and gravity and without the restriction to two-dimensionality has been examined[4]. The capillary spreading of a drop which is not thin, so that the simplifications of lubrication theory are not available, has also been examined and the results compared with those obtained experimentally[5]. Further work on the sliding problem, with the extension to three-dimensionality and the lifting of the restriction on the gravity parameter K is planned.

The aim of this paper has been to show that the moving contact line problem can, in certain circumstances, be solved in a satisfactory manner. The solutions for which experimental corroboration is available[1,5] indicate that the proposed boundary conditions can be used with some confidence. The results obtained here and elsewhere[4,5] show that the application of these conditions need not involve a large amount of refined numerical analysis to resolve the solution near the contact line.

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