

Hydrodynamic Model of Steady Movement of a Solid/Liquid/Fluid Contact Line

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Received May 2, 1970; August 7, 1970

Movement of the contact line over a solid surface violates the adherence, or "no slip," boundary condition which is otherwise obeyed by flowing liquids. A flat fluid interface moving steadily over a flat solid is modeled with the creeping flow approximation, which turns out to be self-consistent. Adherence is required except at the contact line itself. Though the velocity field appears to be realistic, stresses and viscous dissipation are found to increase without bound at the contact line. The way the hydrodynamic model breaks down suggests that in reality there may be steep gradients, rheological anomalies, and discontinuous processes around the contact line. Slip and the role of long-range forces are explored with the aid of the lubrication flow approximation.

INTRODUCTION

Movement over a solid surface of the three-phase contact line where the interface between liquid and a second, immiscible fluid intersects the solid is a *prima facie* violation of the adherence, or "no-slip," boundary condition of fluid mechanics. For if one fluid displaces another from the solid surface, both clearly must move relative to the surface sometime during the process. Yet the hypothesis that fluid immediately next to a solid does not move, or slip, relative to the solid has proved successful throughout the continuum mechanics of ordinary liquids and of gases in most common circumstances (1-5; for the view of one uncritical dissenter see reference 6). The exceptions occur under the relatively extreme conditions of gas-kinetic flows and are well understood to arise in inadequacies of the continuum description when the molecular mean free path approaches the dimensions of the flow

channel (7). Contact line movement does not seem directly analogous. Thus from the viewpoint of fluid mechanics there is a fundamental issue of how fluid displacement at a solid surface is to be understood. Whereas the ultimate resolution must of course rest on molecular considerations—of nonequilibrium kinetics in particular—the problem can be approached and delineated through kinematics and dynamics of fluids, and this we do here.

Contact lines between solid, liquid, and fluid have attracted considerable scientific attention, largely in the field of surface chemistry (8, 9(a)). The bulk of published research treats *static* systems; relatively few experimental studies of *dynamic* situations have been reported, and scarcely any theoretical investigations (see below). Previous workers seem not to have been well informed by fluid mechanics. Our purpose here is to construct a hydrodynamical model of flow near a moving contact line and to analyze quantitatively the behavior of that line movement. Eventually we want to describe

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the process in terms of fluid mechanical boundary conditions that will support accurate, predictive calculations.

Historically, West (10) appears to have been the first to pay attention to flow near a moving contact line. Studying resistance to motion of an isolated mercury index in an otherwise air-filled capillary tube he reasoned that owing to the adherence boundary condition at the solid wall, liquid should push forward and spread outward from the center portion of the front meniscus and roll inward toward the central region of the rear meniscus. In a similar study Yarnold (11) argued for the same sort of flow pattern, which was later named by Rose (12) the fountain effect. Yarnold suggested in passing that mercury in contact with the tube wall may be only "very nearly" at rest as the index moves. He recognized that there must be departures from Poiseuille flow near the ends of the index—a point also raised by investigators of capillary rise and forced liquid displacement (*cf.* reference 13). Yarnold noted that movement of indexes produced electrification of the glass tube, that at very low velocities the indexes tended to stick, and, in published discussion, that certain of his results were sensitive to slight contamination and presumably to the nature of the glass surface. Neither West nor Yarnold was able to observe particle paths within indexes, but Schwartz *et al.* (14) by injecting a little dye at one end of an index of transparent liquid were able to visualize the fountain effect: "The index proceeds forward by rolling away from the tube wall and inward toward its center axis at the rear, while rolling outward from its center axis and onto the tube wall at the front. There is no apparent sliding of liquid along the tube wall." Similar naked-eye observations of mercury drops running down glass slides and of droplets of high-contact-angle liquids on inclined plates of Teflon and polyethylene also convey strong impressions of rolling motion (11, 14). Investigators of other systems either fail to characterize the motion or write

of "sliding," however (*e.g.*, reference 15). Ablett (16) spoke of "slipping" but also referred to the motion as rolling.

The local contact angle at which fluid interface meets solid is, strictly, the angle between the normals \mathbf{n}_1 and \mathbf{n}_2 to the two surfaces at a given common point: contact angle varies along the contact line, in general, and measurements yield some manner of local average—a fact stated by Sumner (17) but seldom restated. Contact angle can be measured between one particular pair of tangents to the surfaces. If \mathbf{t} is the unit tangent to the contact line itself, that pair consists of $\mathbf{n}_1 \times \mathbf{t}$ and $\mathbf{n}_2 \times \mathbf{t}$. Indeed, $(\mathbf{n}_1 \times \mathbf{t}) \cdot (\mathbf{n}_2 \times \mathbf{t}) = \mathbf{n}_1 \cdot \mathbf{n}_2 \equiv \cos \phi$. When this pair is not specifically sought the accuracy of measurements is suspect. On the other hand, reported average deviations are commonly $\pm 2^\circ$, though sometimes only $\pm 1^\circ$ (17–21).

Recorded data on "dynamic contact angles" fall into two distinct categories. Upon causing rapid displacement of a contact line over a solid surface to a new location, experimenters generally find the new static contact angle depends on the *direction* of recent movement of the contact line (*cf.* 16, 17). The difference between the so-called advancing, *i.e.*, advanced, and receding, *i.e.*, receded, contact angle has come to be called contact angle hysteresis (22–24). The difference (Fig. 1) can depend on the time interval between movement and measurement, on contamination, and on many aspects of the state of the solid surface. These are known to include its roughness, heterogeneity, and content of liquid dissolved or "penetrated" in it (24). In a few systems under special circumstances the hysteresis is less than the average deviation in contact angle measurement: such findings have been reported by Ray and Bartell (18) for sessile water drops on fresh, vapor-deposited films of highly purified paraffin on glass, by Timmons and Zisman (25) for a long-chain perfluoro-hydrocarbon monolayer deposited by "melt retraction" on very smooth, clean

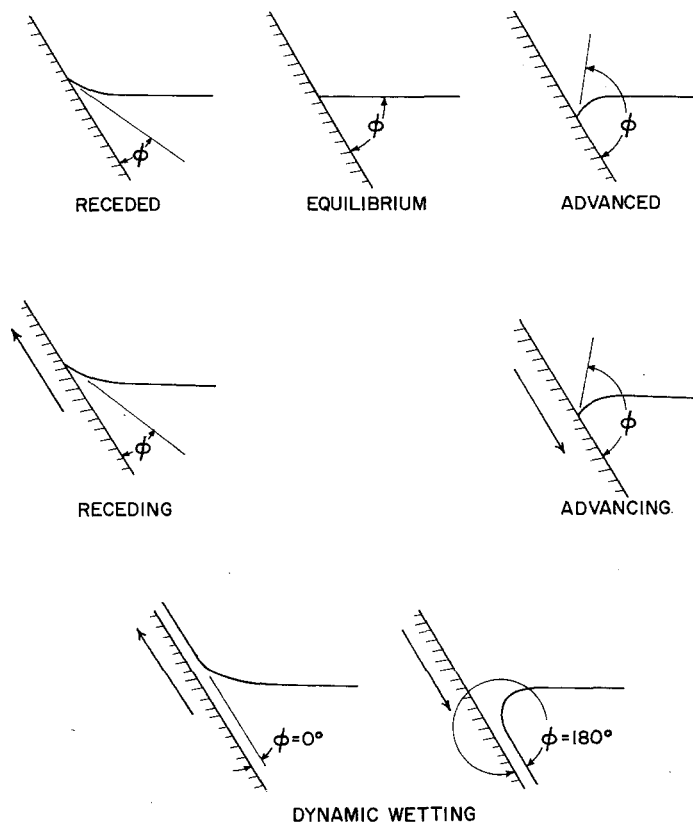


FIG. 1. Contact angles

chromium, and in less detail by Schulman and Zisman (26). Despite these exceptions and references in the literature to contact angle as a thermodynamic equilibrium property, virtually all the published data for which reproducibility is claimed are measurements of advanced contact angles within a minute or so of contact line displacement, the most popular technique being that of Sumner (17, 19, 20).

The second category is that of truly dynamic contact angles. The angle made by the tangent plane to the solid surface with a tangent to the fluid interface very near the line of contact has been measured under low magnification when the contact line was moving over the solid. The first to do so was Ablett (27), who employed a slowly rotating drum carefully coated with paraffin and partially immersed in a pool of water; among the most recent are Blake *et al.*

(13) and Elliott and Riddiford (28). In the systems investigated by the latter (*e.g.*, air/water/siliconed glass) it appeared that when the contact line is caused to move sufficiently slowly over the solid, *viz.*, up to 1 mm/min, the dynamic contact angle remains constant at the recently advanced or recently receded static value, depending on the direction of movement—a behavior also observed by Yarnold and Mason (29). At slightly higher speeds the dynamic contact angle becomes quite velocity dependent until it achieves another constant value above speeds of about 10 mm/min. Such velocity-independent behavior was also seen by Yarnold (11) and Schwartz *et al.* (14). Experimentation on far higher speed film-coating operations by Derjaguin and Levi (30(a)) and Perry (31) indicates a third regime, in which dynamic contact angle again becomes velocity dependent and with further

increase of speed into the range 10–75 cm/sec reaches 180° (or 0° , a matter of convention). This value signals entrainment of a continuous, visible film of the fluid originally in contact with the solid—and thus *disappearance* of the three-phase contact line. This may be termed dynamic wetting; see Fig. 1. Derjaguin and Levi have published some ideas about the mechanism underlying this transition, as have Hansen and Miotto (32) about the lowest speed regime and the transition that terminates it. Recently some letters have been published in which rationalizations in terms of the theory of absolute reaction rates are put forward (33, 34).

Many of the observations of truly dynamic contact angles were corroborated in this laboratory by Seward (35), whose experience emphasized the fact that forced contact line movement tends, especially in practical circumstances, to be irregular, short lengths of line remaining temporarily stuck while interspersed portions are breaking loose and moving rapidly over short distances. The contact line is anything but straight or smooth and its motion is scarcely steady—except when seen from some distance. This “stick-and-slip” phenomenon is strongly influenced by surface finish and contamination and probably by minute capillary waves propagating along the fluid interface.² Local “stick-and-slip” and irregularities of contact line and contact angle are also emphasized in the paper by Elliott and Riddiford (28). Careful observations of one liquid displacing another are scarce. The same authors do report some observations of siliconed glass/Bayol/water. The relationship between advancing contact angle and contact-line speed is similar to that in solid/liquid/gas systems except that the domain of constant contact angle at lowest speeds appears to be absent. Owing to the irregularities and the “stick-and-slip” phenomenon already cited, reced-

ing contact angle could not be measured meaningfully. Blake *et al.* (13) report more success, except at the lowest speeds, with water displacement by benzene and *vice versa* in silane-coated glass capillaries as well as untreated ones.

There are several pieces of direct evidence about contact-line movement still missing. Furthermore it is already plain that in practical circumstances the flow patterns very near a moving contact line are three-dimensional and unsteady (13, 28, 35). Nevertheless, it is instructive to set up, as we do in the next section, a hydrodynamical model on the assumptions of steady, two-dimensional flow at low Reynolds number with a perfectly flat fluid interface.

Investigators of moving indexes and rolling or sliding drops have neglected viscous forces near the contact line when they went about correlating their velocity data (10, 11, 14, 15). In contrast, the analyses by Bhat-tacharji and Savic (36), Bataille (37), and Moffat (38), of steady, creeping flow of liquid with a flat, free surface intersecting a moving solid wall all show a *singularly large* effect of viscosity near the contact line, which in these instances is the juncture of solid, liquid, and, strictly speaking, void. In the next section we generalize Moffatt's analysis to cover a creeping-flow model of contact-line movement. This model includes a number of interesting special cases. In one the fluid phase is a thin wedge resembling a film; in another the interface is an inextensible membrane of film. This last bears on the remarkable “zippering action” in certain monolayer deposition operations first described by Blodgett (39) and Langmuir (40). In following sections we diagnose the failure of the creeping flow model, suggest some remedies, incorporate some of these in a second hydrodynamic model, one based on the lubrication approximation (independently invoked several times in recent literature), which also fails to describe contact-line movement adequately, although it sheds light on effects of surface curvature,

² Such waves are evidently the agents of vibrations which are said to be impossible to remove from systems of contact angle measurement (24).

long-range forces, slip, and other matters for further investigation.

CREEPING FLOW MODEL

As one approach to understanding the behavior of fluids near a moving contact line we consider the simple situation diagrammed in Fig. 2. A perfectly flat, solid surface translates with steady velocity U in its own plane, which is inclined at the angle ϕ from a perfectly flat fluid interface between liquid below (Phase B) and a second, immiscible fluid above (Phase A). The situation is plainly two-dimensional. It is convenient to take the three-phase contact line as the origin of a polar coordinate system (r, θ) , as shown.

We take both bulk fluid phases to be incompressible Newtonian fluids, and regard both as extending to indefinitely large distances from the origin. Thus there is no geometrical length scale in the system and so the creeping flow approximation may be satisfactory near the contact line. Its linearity is ample reason for trying it immediately, and it does prove to be self-consistent at small radii (Eq. [29]). Far from the contact line the viscous stresses turn out to transport less momentum than does convection and accordingly the approximation fails at large radii.

In the creeping flow approximation the solid can just as well be at rest and the fluid interface translating parallel to itself—filling or emptying rather than immersion or withdrawal.

In terms of the stream function $\psi(r, \theta)$ for incompressible, two-dimensional flow we have velocity components $v_r = -r^{-1} \partial\psi/\partial\theta$

and $v_\theta = \partial\psi/\partial r$. In the creeping flow approximation the Navier-Stokes equation for velocity is linearized and leads, for steady flow, to the two-dimensional biharmonic equation in ψ (cf. reference 3):³

$$\nabla_2^4 \psi = 0. \quad [1]$$

This equation together with many of its solutions is well known in elasticity theory as well as viscous flow theory. The boundary and interface conditions to be imposed are:

- (i) Kinematic conditions: vanishing normal component of velocity at the solid surface and fluid interface

$$0 = v_{B\theta} = \partial\psi_B/\partial r \quad [2, 3]$$

$$\text{at } \theta = 0 \text{ and } \theta = \phi, r \geq 0;$$

$$0 = v_{A\theta} = \partial\psi_A/\partial r \quad [4, 5]$$

$$\text{at } \theta = \phi \text{ and } \theta = \pi, r \geq 0.$$

- (ii) Kinematic condition: no slip, i.e., continuity of velocity at the interface

$$v_{Ar} = v_{Br}, \quad \text{i.e.,} \quad [6]$$

$$\partial\psi_A/\partial\theta = \partial\psi_B/\partial\theta \quad \text{at } \theta = \phi, r > 0.$$

- (iii) Dynamic condition: continuity of tangential stress at the interface

$$\tau_{Ar\theta} = \tau_{Br\theta}, \quad \text{i.e.,} \quad [7]$$

$$\mu_A \frac{\partial^2 \psi_A}{\partial \theta^2} = \mu_B \frac{\partial^2 \psi_B}{\partial \theta^2} \quad \text{at } \theta = \phi, r > 0.$$

Equations [3] and [4] have been invoked to simplify the second expression.

- (iv) Kinematic condition: no slip, i.e., no tangential relative motion of fluid at the solid surface

$$+ U = v_{Br}$$

$$= -\frac{1}{r} \frac{\partial\psi_B}{\partial\theta} \quad \text{at } \theta = 0, r > 0; \quad [8]$$

³ This equation would be a valid approximation for *unsteady* creeping flow near a moving contact line as pictured here, provided the characteristic period or imposed time scale is not too small.

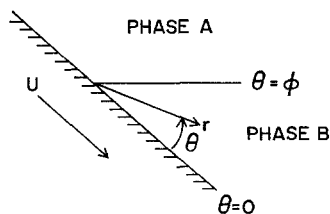


Fig. 2. Model of contact line movement

$$-U = v_{Ar} \\ = -\frac{1}{r} \frac{\partial \psi_A}{\partial \theta} \quad \text{at } \theta = \pi, r > 0, \quad [9]$$

This condition is called into question later. Because the interface is idealized as being perfectly flat, no condition can be imposed on the normal stresses acting at it. The reasonableness of the idealization is discussed later (Eq. [23]).

The general solution of the biharmonic equation in plane polar coordinates has been known at least since Michell's 1899 paper (41); from it one finds that the solution of [1] corresponding to bounded velocity both at $r = 0$ and as $r \rightarrow \infty$ is simply

$$\psi(r, \theta) = r(a \sin \theta + b \cos \theta + c\theta \sin \theta + d\theta \cos \theta). \quad [10]$$

This form of solution applies to both fluid Phase A and liquid Phase B and so there are eight constants to satisfy the eight conditions [2]–[9], which constitute a set of simultaneous, linear, algebraic equations. It is convenient to let

$$S \equiv \sin \phi, \quad C \equiv \cos \phi, \\ \delta \equiv \phi - \pi, \quad R \equiv \mu_A/\mu_B. \quad [11]$$

By standard methods the constants are found to be

$$a_A = -U - \pi c_A - d_A, \\ b_A = \pi d_A, \quad [12, 13]$$

$$c_A = US^2[S^2 - \delta\phi + R(\phi^2 - S^2)]/D \quad [14]$$

$$d_A = USC[S^2 - \delta\phi + R(\phi^2 - S^2) - \pi \tan \phi]/D, \quad [15]$$

$$a_B = -U - d_B, \quad b_B = 0, \quad [16, 17]$$

$$c_B = US^2[S^2 - \delta^2 + R(\delta\phi - S^2)]/D, \quad [18]$$

$$d_B = USC[S^2 - \delta^2 + R(\phi\delta - S^2) - R\pi \tan \phi]/D, \quad [19]$$

where

$$D \equiv (SC - \phi)(\delta^2 - S^2) + R(\delta - SC)(\phi^2 - S^2). \quad [20]$$

It can be shown that this last is nonvanishing and so too is c_A , at least.⁴ Therefore the solution of the boundary value problem is unique. The velocity components in the two phases are

$$v_{Ar} = [U + (\pi - \theta)c_A] \cos \theta - [c_A + (\pi - \theta)d_A] \sin \theta; \quad [21]$$

$$v_{A\theta} = -[U + (\pi - \theta)c_A + d_A] \sin \theta - (\pi - \theta)d_A \cos \theta; \quad [22]$$

$$v_{Br} = (U - \theta c_B) \cos \theta - (c_B - \theta d_B) \sin \theta; \quad [23]$$

$$v_{B\theta} = (U - \theta c_B + d_B) \sin \theta + \theta d_B \cos \theta. \quad [24]$$

The solution may be characterized by the velocity of the fluid interface, which occupies the plane $\theta = \phi$:

$$v_r(r, \phi) = U[(\phi C - S)(S^2 - \delta^2) + R(\delta C - S)(\phi^2 - S^2)]/D. \quad [25]$$

The velocity is independent of r , the distance from the contact line; this is in fact true of velocity throughout both phases (see Eqs. [21]–[24]). According to Eq. [25] the direction of motion along the interface reverses as the viscosity ratio R is varied at a fixed dynamic contact angle ϕ . The critical viscosity ratio at which the interface should remain motionless ($v_r = 0$) is given by ($S \equiv \sin \phi$ and $C \equiv \cos \phi$ still):

$$R_c = \frac{(\phi C - S)(\delta^2 - S^2)}{(\delta C - S)(\phi^2 - S^2)}. \quad [26]$$

Sample velocity fields for a dynamic contact angle $\phi = 30^\circ$ and a range of viscosity

⁴ Indeed, because $R > 0$ and $0 < \phi < \pi$ and $0 < -\delta < \pi$, we have $\phi > S > SC$, $-\delta > \sin(-\delta) = S > \sin(-\delta) \cos(-\delta) = -SC$, and, accordingly, both $D < 0$ and $c_A < 0$.

ratios, including R_c , are shown in Figs. 3-6. Other examples, with $\phi = 5^\circ$, are diagrammed in Figs. 7-9.

Away from the moving solid surface there are three rays (planes) along which the radial velocity component vanishes. Besides the fluid interface there is a single ray along which the azimuthal velocity component vanishes. The location of this dividing ray depends on dynamic contact angle as well as viscosity ratio, but it tends to fall in the

phase of lower viscosity. The direction of radial movement along this ray is opposite to that of the solid surface in contact with the same phase. It is also opposite to the direction of radial movement of the interface (Eq. [25]). Because careful experimental observations are still lacking it is not yet possible to say to what extent all of the foregoing predictions are borne out in reality.

When one of the phases is a thin film such that $\phi \rightarrow 0$, approximations of $\sin \phi$ and

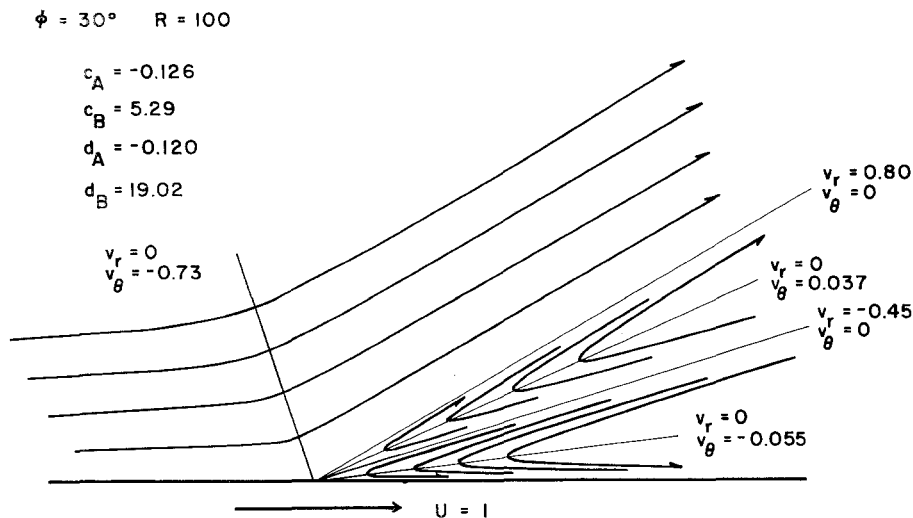


FIG. 3. Stream lines and characteristic velocity values: $\phi = 30^\circ$, $R = 100$

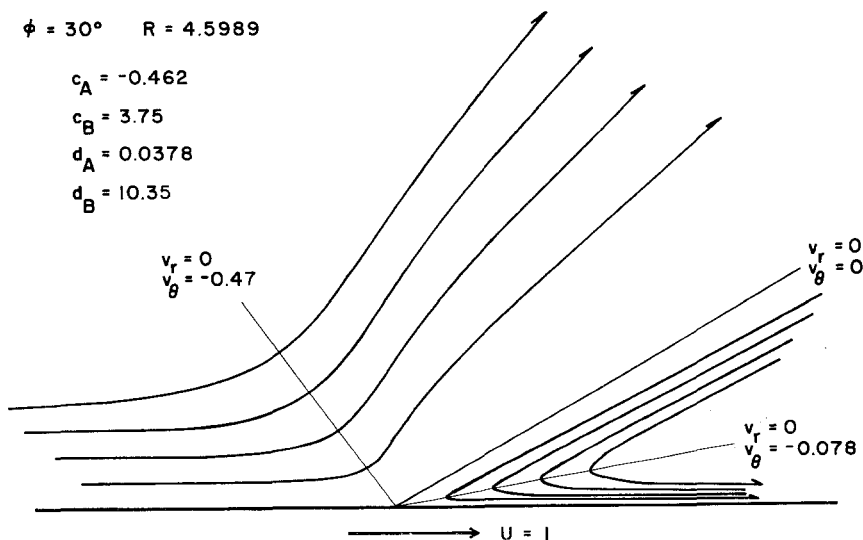


FIG. 4. $\phi = 30^\circ$, $R = R_c = 4.59890$

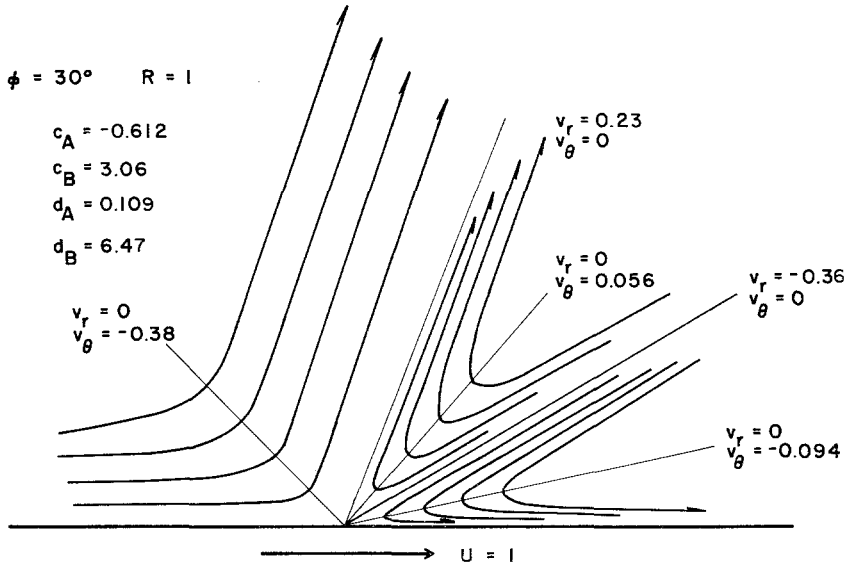


FIG. 5. $\phi = 30^\circ, R = 1$

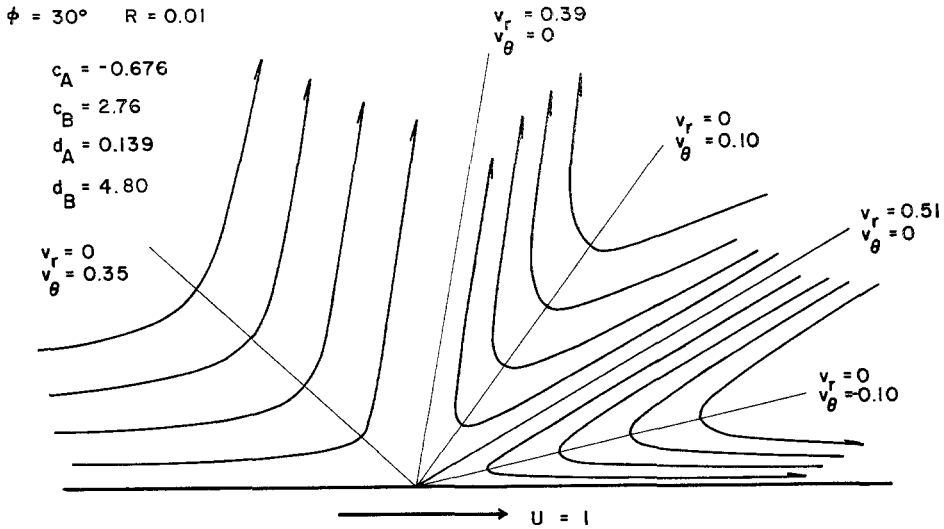


FIG. 6. $\phi = 30^\circ, R = 0.01$.

$\cos \phi$ are in order. It is found that to the indicated orders of ϕ ,

$$c_A \simeq -\frac{U}{\pi} \left(\frac{3\pi + R\phi^3}{2\pi + R\phi} \right), \quad [14', 15']$$

$$d_A \simeq -\frac{U\phi}{\pi} \left(\frac{-\pi + R\phi}{2\pi + R\phi} \right),$$

$$c_B \simeq \frac{3U}{\phi} \left(\frac{\pi + R\phi}{2\pi + R\phi} \right), \quad [18', 19']$$

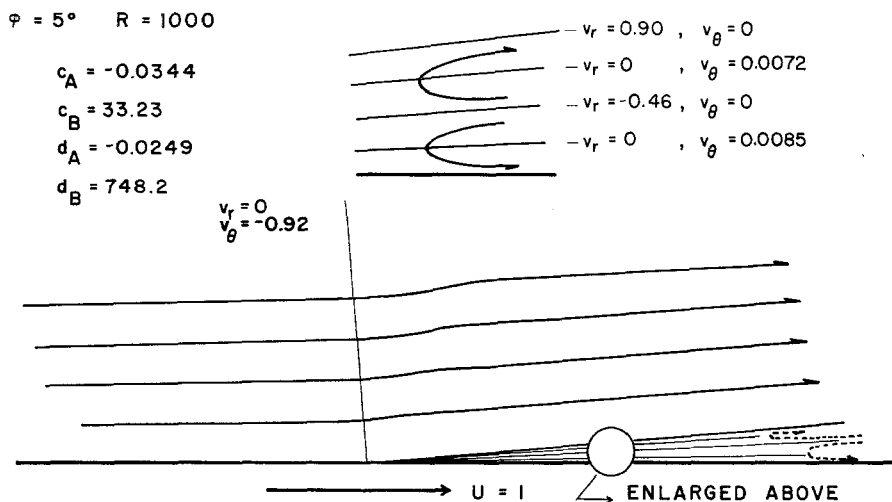
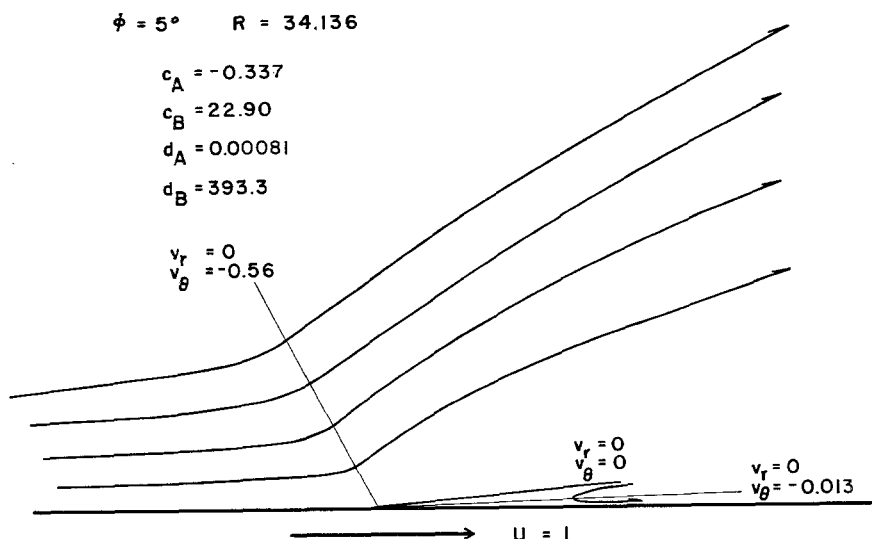
$$d_B \simeq \frac{3U}{\phi^2} \left(\frac{\pi + 2R\phi}{2\pi + R\phi} \right),$$

and that

$$v_{Br} \simeq U - 2c_B\theta + d_B\theta^2 + \mathcal{O}(\phi^2), \quad [23']$$

$$v_{B\theta} \simeq -U - d_B(1 - \theta - \theta^2/2) + \mathcal{O}(\phi). \quad [24']$$

Similar formulas can be written for Phase A. Values calculated from these formulas for $\phi = 5^\circ$ are within 0.5% of the exact values when $R = 1000$, and within about 5% when $R = 0.01$. It is noteworthy that

FIG. 7. $\phi = 5^\circ, R = 1000$ FIG. 8. $\phi = 5^\circ, R = R_c = 34.13619$

even when the slender phase is far less viscous than its ample partner its small viscosity still plays an important role if the product of R and ϕ (in radians) is appreciable. As the viscosity of the slender phase diminishes the dynamic contact angle at which the interface remains motionless is, to a good approximation, $\phi \simeq \pi/R$, demonstrating the strong effect of even a film of gas.

At all values of the dynamic contact angle the viscous stress components are given by

$$\tau_{r\theta} = \frac{2\mu}{r} (c \cos \theta - d \sin \theta), \quad [27]$$

$$\tau_{rr} = \tau_{\theta\theta} = 0,$$

and the pressure field by (p_0 is the hydrostatic datum)

$$p - p_0 = -\frac{2\mu}{r} (c \sin \theta + d \cos \theta) \quad [28]$$

(in both formulas phase-labeling subscripts have been omitted). Whereas the velocity field seems unexceptionable apart from at

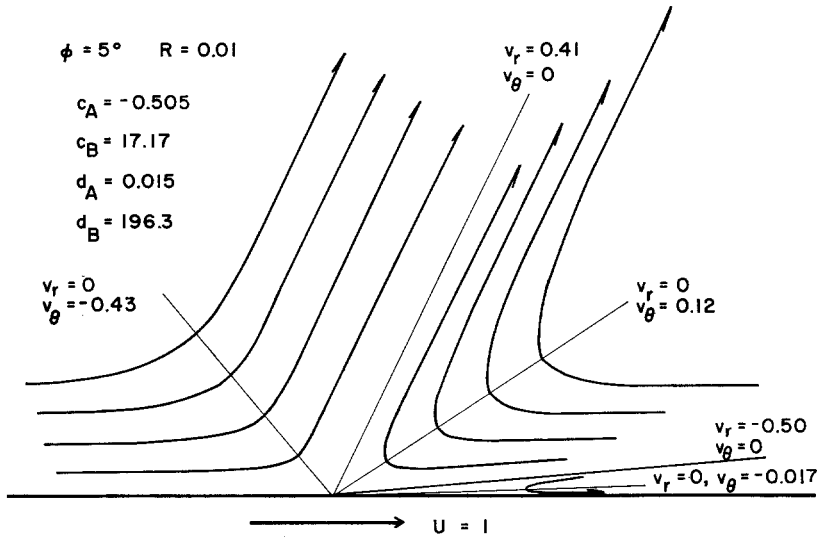


FIG. 9. $\phi = 5^\circ$, $R = 0.01$

the contact line itself, where it is multiple-valued, the shear stress and pressure fields vary as r^{-1} and so increase in magnitude without bound as the contact line is approached. The total force exerted on the solid surface is logarithmically infinite: not even Herakles could sink a solid if the physical model were entirely valid, which it is not.

Locally the ratio of the magnitude of "inertial force" to that of "viscous force" is

$$\frac{\rho |\mathbf{v} \cdot \nabla \mathbf{v}|}{\mu |\nabla^2 \mathbf{v}|} = \left(\frac{rU}{\nu} \right) \frac{|a \sin \theta + b \cos \theta + c \theta \sin \theta + d \theta \cos \theta| \cdot |c \cos \theta - d \sin \theta|}{U \sqrt{c^2 + d^2}} \quad [29]$$

Because the constants are all proportional to the velocity U the second part on the right is independent of that velocity and so in each phase the ratio is of the order of the local Reynolds number rU/ν . According to Eq. [29] convective momentum transport becomes vanishingly small compared to viscous transfer as the contact line is approached ($r \rightarrow 0$). The creeping flow approximation is self-consistent provided $r \ll \nu/U$. This upper bound is 1 cm for water wetting a surface at a speed of 6 mm/min.

Integrating the kinetic energy equation over a semicylinder centered on the contact line establishes that not only work done by wall stress but also viscous dissipation are logarithmically infinite, which brings even the assumption of uniform properties into question. And according to Eq. [21] the normal stress difference across the fluid interface varies as r^{-1} . This difference should be balanced by the action of interfacial tension σ in an interface of mean curvature H , where

$$\begin{aligned} 2H\sigma &= p_B - p_A \\ &= \frac{2}{r} [\mu_A(c_A \sin \phi + d_A \cos \phi) - \mu_B(c_B \sin \phi + d_B \cos \phi)]. \end{aligned} \quad [30]$$

This curvature should increase rapidly as the contact line is approached—in direct conflict with the hypothesis that the fluid interface is perfectly flat, on which the physical model is based. However, the local radius of curvature would have to be about 10^5 times greater than the distance to the contact line when water at a moderate dynamic contact angle wets a surface at 6 mm/min. The curvature in this instance would be imperceptible by optical means.

The model is plainly defective in the

immediate neighborhood of the moving contact line. Nevertheless, it may approximate reality well in a slightly removed region where the fluid interface is substantially flat and the flow qualifies as creeping. We present a few special cases involving just one phase before turning to implications of the defects of the model.

SPECIAL CASES

If Phase A could be regarded as a void one would need to consider only Phase B and on setting $R = 0$ one would find from Eqs. [16]–[19] that

$$\begin{aligned} a_B &= -U - d_B, \\ b_B &= 0, c_B = \frac{US^2}{(\phi - SC)}, \\ d_B &= \frac{USC}{(\phi - SC)}. \end{aligned} \quad [31]$$

This is the case touched on by Moffatt (38). Formulas given above reveal that when the dynamic contact angle is small, taking Phase A as a void can lead to serious error, quite apart from the peculiar degeneracy of the model at the contact line.

Steady translation of a flat, free surface which separates liquid from void in an infinitely long tube and makes a right angle with the tube wall is a variant of Moffatt's case. This hypothetical situation was adopted as a model for certain purposes by Bhat-tacharji and Savic (36) and Bataille (37) and was analyzed by them. It can be shown that the integral transform method they

used is applicable to our case of $R = 0$, $\phi = \pi/2$ and gives in fact the same solution. The method cannot, however, be extended to other situations (for it to succeed the kinematic and dynamic conditions at the interface must have a special compatibility).

If the interface were covered by an inextensible film or membrane translating with a prescribed, constant velocity $v_r = \kappa U$ at $\theta = \phi$, the dynamic condition [7] would not apply, its place being taken by the kinematic condition

$$\begin{aligned} \kappa U &= v_{Br} \\ &= -\frac{1}{r} \frac{\partial \psi_B}{\partial \theta} \quad \text{at } \theta = \phi, r > 0. \end{aligned} \quad [32]$$

This leads to the constants (where κ is the ratio $v_r(\phi)/v_r(0)$)

$$\begin{aligned} a_B &= \frac{U\phi(\phi + \kappa \sin \phi)}{\sin^2 \phi - \phi^2}, \quad b_B = 0, \\ d_B &= \frac{U \sin \phi (\sin \phi + \kappa \phi)}{\sin^2 \phi - \phi^2}, \\ c_B &= \frac{U[(\sin \phi \cos \phi - \phi) + \kappa(\phi \cos \phi - \sin \phi)]}{\sin^2 \phi - \phi^2}, \end{aligned} \quad [33-36]$$

from which the velocity field is readily constructed. Of special interest is the case $U = -V$ and $\kappa = 1$, *i.e.*, $v_r(\phi) = v_r(0) = -V$, as can occur when a relatively inextensible film floating on liquid is taken up by a moving solid surface. A sample velocity field calculated for a deposition angle of $\phi = 30^\circ$ is shown in Fig. 10. The azimuthal velocity component of course vanishes on the ray

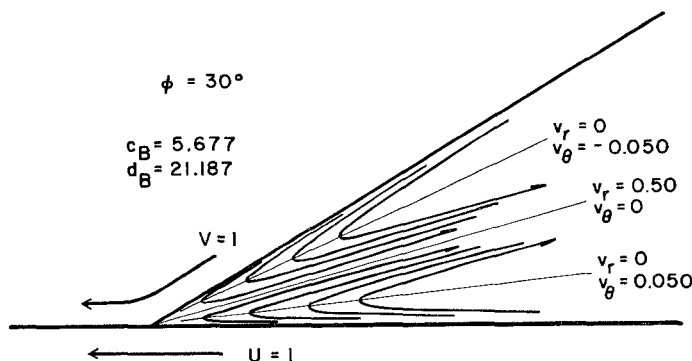
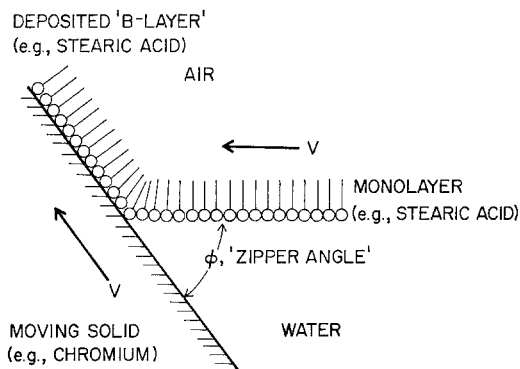


FIG. 10. Stream lines and characteristic velocity values when $U = \kappa U = -V$; $\phi = 30^\circ$



FILM DEPOSITION WITH 'ZIPPERING ACTION', AFTER LANGMUIR (1938)

FIG. 11. Film deposition with "zippering action," after Langmuir (40).

(plane) $\theta = \phi/2$. All the singularity of the moving contact line is present in this case too. Nevertheless, it can serve as a simplified model of flow when certain monolayers under constant and relatively high surface pressure are deposited from a liquid surface onto a high-energy solid surface that is sufficiently slowly withdrawn from the liquid for Langmuir's "zippering action" to occur, as diagrammed in Fig. 11. According to Langmuir (40), "The water appears to peel back from the slide as this is slowly⁵ withdrawn from the water, leaving the slide dry but with a B-layer which has been deposited on its surface. Actually, however, the water is forced out from under the B-layer by attractive forces exerted by the polar groups of the B-layer on the underlying polar atoms of the chromium surface.... The angle ϕ is conveniently measured by withdrawing the slide from the water in an inclined position and so altering ϕ that the water surface *remains horizontal right up to the line of contact with the plate.*" (Italics added.) This circumstance warrants further mention below.

Another special case, of particular interest in connection with wiping and lubri-

cation, is that of $\kappa = 0$, corresponding to G. I. Taylor's (43) model of one plate scraping another, to which Eqs. [33]–[36] do indeed lead when κ is set equal to zero.

DISCUSSION

The creeping flow model is singular and therefore unrealistic in the corner of each of the two fluid phases at a moving line of contact. Shear stresses, pressure, and viscous dissipation rate increase without bound as the contact line is approached. Neither the shape of the solid surface nor the nature of the bulk fluids is primarily responsible. From a mathematical viewpoint these deficiencies of the model stem from the velocity discontinuity on the boundary: the adherence condition is imposed (Eqs. [8] and [9]) at the solid where $r > 0$ but at $r = 0$ perfect slip of the contact line itself is demanded.

Now singularities in mathematical physics usually signal failure of one or more hypotheses underlying the model, for nature abhors local infinities. The most obvious culprit here is the adherence, or "no-slip," condition but there are other suspects: where pressure in the liquid plunges and viscous dissipation mounts there may be cavitation; short of that there may be steep gradients of viscosity and density and appreciable compressibility effects; just as ordinary fluid no longer follows bulk equations of state when it is in interfacial transition zones, so also may it behave still differently when it is in contact-line zones—the Newtonian constitutive relation may very well fail as the contact line is approached in either fluid phase; accumulation or depletion of surfactant or heat in the interface might cause an interfacial tension gradient in the interface near the contact line. The presence of the corners of fluid insures that there is a neighborhood of the contact line in which long-range intermolecular forces (electrostatic and dispersion forces) take on special importance, and a still smaller neighborhood the linear dimensions of which approach molecular dimensions and in which the conventional continuum

⁵ Up to 50 mm/min and even faster, according to the original publication by Blodgett (39). For a review and references to more recent investigations see Gaines (42).

approach either fails or must be drastically reinterpreted. On this scale the contact line is seen as a zone and it is not at all clear how it might grade into the three zones that merge into it (44).

Although it is useful to think of steady movement of a contact line over a perfectly flat and homogeneous solid surface it cannot be forgotten that real surfaces, with only the rarest of exceptions, are geometrically rough and chemically and electrically heterogeneous. The ubiquity on solids of traces of gas that reveal themselves as bubble nucleating sites in surface boiling is a frequent reminder of how imperfectly liquids usually displace gases from rough surfaces. Yet roughness and heterogeneity neither remove nor explain the hydrodynamic model's singularity, which is still present when it is applied to contact-line movement through distances smaller than the length scales of roughness and heterogeneity. The question, already raised in the Introduction, is: How is forced fluid displacement at a solid surface to be understood in dynamical terms?⁶

The hydrodynamical model studied here might be rehabilitated for many practical purposes involving common surfaces by introducing "smoothing" features in the boundary conditions to remove the kinematic discontinuity at the contact line. Such a feature to be useful should involve only one or two empirical parameters; that these might eventually be estimated from considerations of microscopic and molecular details is to be hoped. The leading possibility is to replace the adherence condition (Eqs. [6], [8], [9]) by a dynamic condition that allows slip yet is still linear (2(b), 45):

$$\begin{aligned}\tau &= -\beta(x)(v_x - U) \\ \alpha(x) \frac{\partial v_x}{\partial y} &= v_x - U, \quad \alpha \equiv \mu/\beta.\end{aligned}\quad [37]$$

⁶ Spontaneous fluid displacement, *i.e.*, migration of a contact line under conditions of mechanical equilibrium, appears from a macroscopic point of view as a different process, to be understood in the somewhat different terms appropriate to diffusional processes.

Here the parameter β is the slip, or momentum transfer, coefficient. In some sense it represents the extent of "adhesion" of fluid to solid. Putting it equal to zero corresponds to unimpeded tangential slip between fluid and solid, whereas assigning small values may be appropriate to the production of new solid/fluid interface and destruction of old as the contact line advances. At the other extreme, passing to the limit as $\beta \rightarrow \infty$ corresponds to imposing the no-slip condition, which implies no mass flux of fluid next to the solid relative to the solid. It should be noted that the adherence boundary condition is freely abandoned in mathematical modeling of plastic processing (46) as well as of metal working (47). (Relaxing the normal component of the adherence condition, Eqs. [2] and [5], in the immediate vicinity of the contact line—to allow for fracture, for example—is another possibility, but seems to demand slip anyway, along the fluid interface.)

Unfortunately Eq. [37] cannot be satisfied by any stream function of the form of Eq. [10]: the dynamic slip condition and the creeping flow solution that has velocity remaining finite as $r \rightarrow \infty$ are incompatible, and so the model developed above cannot be generalized directly. A more general solution of the biharmonic equation [1] must be used, bringing with it velocity fields that are unbounded in the limit as $r \rightarrow \infty$ and raising formidable mathematical difficulties.

The model should also be modified to allow for curvature of the fluid interface. All that is needed is the normal force condition (Eq. [30] is a special version) together with the interfacial profile, but the latter is unknown beforehand, strictly speaking, and this also greatly complicates the task of mathematical analysis. Furthermore, long-range forces in the neighborhood of the contact line should be accounted for in the normal force condition.

As it happens there is another type of hydrodynamic model, found in the theory of lubrication, which is mathematically more tractable, but it pertains only to flow in

thin layers. The approximation on which it rests necessarily fails short of the contact line when it is applied to displacement flow. Though the lubrication flow model begs the fundamental question of contact-line movement it provides insights into effects of surface curvature, long-range forces, slip, and perhaps of non-Newtonian rheology as well. For this reason it is illustrated in the Appendix by application to a case of "zippering action" of a monomolecular film riding on a thin layer of liquid. The results in the Appendix support the expectation that long-range interactions dominate the local force balance on the interface near the contact line; they also indicate that these interactions are responsible for expulsion of the last of the entrained liquid and that increasingly free slip as the contact line is approached can relieve the otherwise enormous shear stress generated in the neighborhood of the contact line. It can also be seen that an interfacial-tension gradient might substantially affect the rate of expulsion of entrained liquid and the shear stress distribution, but that it brings no new force to bear on the contact line itself. Effects of density and viscosity gradients and non-Newtonian fluid behavior have not been analyzed, but none of these could relieve the kinematic discontinuity inherent in juxtaposing moving contact line and the "no-slip" boundary condition. The possible roles of cavitation or plastic flow and fracture of material under high stress in the vicinity of the contact line remain to be explored.

ACKNOWLEDGMENT

This research was supported by Grant GK-41 from the National Science Foundation.

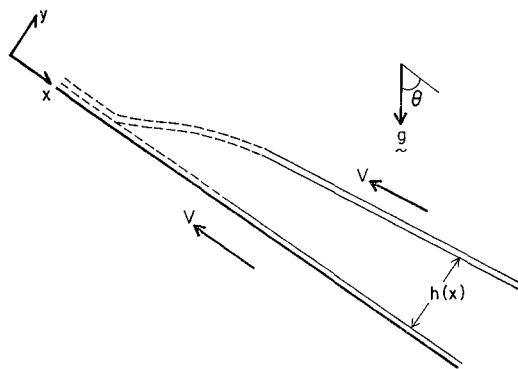
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APPENDIX

To illustrate another type of hydrodynamic model proposed in the literature we consider the situation in Fig. 11, except that the zipper angle is much smaller and the interface may be somewhat curved, as in



MODEL OF FILM DEPOSITION WITH 'ZIPPERING ACTION'

Fig. 12. Lubrication flow model of film deposition with "zippering action."

Fig. 12. We must focus on flow in the region sufficiently far from the contact line that velocity of the liquid is nearly parallel to the plane of the plate, yet the thickness h of the liquid layer is still small. In this region $v_y \ll V$, the streamlines are nearly straight and unidirectional, and inertial "forces" are negligible, making appropriate the lubrication approximation, the limits of validity of which are discussed by, among others, Bretherton (48). Thus the Navier-Stokes equation simplifies to an equation well known in lubricating theory:

$$\mu \frac{\partial^2 v_x}{\partial y^2} = \frac{\partial p}{\partial x} - \rho g \cos \theta. \quad [38]$$

From the outset it is clear that the lubrication flow approximation breaks down short of the moving contact line, except possibly when the dynamic contact angle vanishes. Still, for describing flow in a thin film it is a more powerful tool than the creeping flow approximation and its results supplement those at Eqs. [23']-[24'].

The boundary conditions to be imposed on Eq. [38] are:

- (i) Dynamic conditions leaving open the possibility of slip at the solid surface and at the inextensible film (cf. Eq. [37]):

$$\alpha_s(x) \frac{\partial v_x}{\partial y} = v_x + V \quad \text{at} \quad y = 0; \quad [39]$$

$$\alpha_f(x) \frac{\partial v_x}{\partial y} = v_x + V \quad \text{at} \quad y = h(x). \quad [40]$$

- (ii) Dynamic condition of balanced normal components of forces acting on the film (cf. Eq. [30])

$$p - p_0 \simeq -\sigma \frac{d^2 h}{dx^2} + \frac{dW}{dh} \quad [41]$$

at $y = h(x)$.

Here p_0 is the ambient pressure in the gas phase; $d^2 h/dx^2$ approximates the mean curvature of the film because $dh/dx \ll 1$; and $W(h)$ is a potential function accounting for long-range forces of interaction among the assembled molecules of film, liquid layer, and solid (and absorbates on the solid). In the form

$$W(h) = -\frac{k}{m(m+1)h^m} \quad [42]$$

coulombic, van der Waals, and retarded dispersion interactions are represented by $m = 1, 2$, and 3 , respectively (9(b), 49, 50). Besides the boundary conditions the continuity equation must be imposed in the form

$$0 = \int_0^{h(x)} v_x dy. \quad [43]$$

Taking viscosity as a constant, integrating Eq. [38], applying Eqs. [39]–[42], and substituting the result in Eq. [43] yields an ordinary differential equation governing film thickness:

$$\sigma \frac{d^2 h}{dx^2} + \frac{k}{h^{m+2}} \frac{dh}{dx} \quad [44]$$

$$+ \rho g \cos \theta - \mu V F(h) = 0,$$

where

$$F(h) \equiv \frac{12(h + \alpha_s - \alpha_f)}{h[4h(\alpha_s - \alpha_f) + 3h^2 - \alpha_s \alpha_f]}.$$

Three boundary conditions on $h(x)$ are needed to specify a unique solution. In Eq. [44] the first term represents the curvature-dependent pressure force, which tends to drive liquid from a zone of higher surface curvature to an adjacent zone of lower curvature; the second term represents the effect of long-range forces, which (except for electrostatic repulsion) tend to expel liquid from thinner toward thicker film; the third term stands for the effect of gravity, which is usually secondary; and the last term represents the viscous resistance to squeezing liquid along the film. This viscous resistance of course increases as the film thins, but it can be reduced somewhat if slip occurs at the boundaries, as the auxiliary function $F(h)$ indicates.

As the contact line is approached the viscous resistance becomes so great that the film surface would have to be increasingly sharply curved in order to develop sufficient capillary pressure to expel liquid carried toward the contact line by viscous drag. But the surface can turn through no more than the dynamic contact angle *in toto*; and anyway the approximations at Eqs. [38] and [41] break down where the surface is highly curved. So capillary pressure cannot account for late stages of thinning. However, in the limiting case in which a *continuous* liquid film of finite thickness is deposited, *i.e.*, dynamic wetting as shown in Fig. 1, curvature-induced capillary pressure may suffice because the entrained liquid does not have to be squeezed out completely. Bretherton in 1961 (48) and, more recently, Friz (51) and Ludviksson and Lightfoot (52) have made analyses of this limiting case with the aid of the lubrication approximation.

Actually, as the contact line is approached the long-range forces dominate the others that cause flow; in Eq. [44] the first and third terms can be neglected as $h \rightarrow 0$, leaving (30(b)):

$$\frac{k}{h^{m+2}} \frac{dh}{dx} - \frac{12\mu V}{h^2} = 0. \quad [45]$$

This simplification is written for the case of solid, adherence, $\alpha_s = \alpha_f = 0$. The solution of [45] is

$$\begin{aligned} m = 1, \quad k \ln (h/h_0) &= 12\mu V(x - x_0) \\ m > 1, \quad \frac{k}{m-1} \left(\frac{1}{h_0^{m-1}} - \frac{1}{h^{m-1}} \right) &= 12\mu V(x - x_0). \end{aligned} \quad [46]$$

Thus according to the lubrication flow model a contact line could be realized ($h = 0$) only in the limit as the long-range forces have an excessive time to work ($x \rightarrow \infty$, *i.e.*, $t \equiv -x/V \rightarrow \infty$). And even then the transfer of monolayer to the solid surface would take place at zero dynamic contact angle. The shear stress exerted by the liquid on the

$$\mu \left(\frac{\partial v_x}{\partial y} \right)_{y=0} = \frac{6\mu V}{h}, \quad [47]$$

unfortunately would become indefinitely large in the neighborhood of the contact line. However, the magnitude of this runaway shear stress would not mount as rapidly if adherence were less than perfect near the contact line, *i.e.*, if $\alpha_s \neq 0$ and $\alpha_f \neq 0$. Examination of the extreme situation in which liquid slips perfectly freely at the film, *i.e.*, $\alpha_f \rightarrow \infty$ with $\alpha_s \neq 0$ (53), indicates that the shear stress could remain finite were there increasingly free slip as the contact line is approached. But even in this extreme the lubrication flow model can properly be applied only to an asymptotically zero dynamic contact angle.