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Considerations on the moving contact-line singularity, with application to frictional drag on a slender drop

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It has previously been shown that the no-slip boundary condition leads to a singularity at a moving contact line and that this forces one to admit some form of slip. Present considerations on the energetics of slip due to shear stress lead to a yield stress boundary condition. A model for the distortion of the liquid state near solid boundaries gives a physical basis for this boundary condition. The yield stress condition is illustrated by an analysis of a slender drop rolling down an incline. That analysis provides a formula for the frictional drag resisting the drop movement. With the present boundary condition the length of the slip region becomes a property of the fluid flow.

1. Introduction

The three-phase contact line, where liquid, solid and gas meet, is encountered frequently in everyday experience and is of concern to many areas of science. Movement of this contact line causes considerable embarrassment to a fluid dynamicist; for, when the contact line is in motion with respect to the solid surface, the usual no-slip boundary condition of viscous flow gives rise to a non-integrable singularity in the surface shear stress. Thus, if the liquid and gas are immiscible, so that the contact line maintains its integrity, motion of the contact line would be resisted by an infinite force. As Huh & Scriven (1971) aptly describe it, 'not even Herakles could sink a solid if the physical model were correct, which it is not'.

The stress singularity is an immediate consequence of the inconsistency of the no-slip condition at a line where two surfaces in relative motion meet. The no-slip condition says that particles of fluid adjacent to each surface assume the velocity of that surface, so the velocity of particles at the line of intersection between surfaces in relative motion must be multiple valued (Batchelor 1967, p. 226; Dussan V. & Davis 1974).

From another point of view, one can regard the moving contact-line singularity as arising when equations derived for continuous motion (the Navier–Stokes equations plus no-slip imply that within the fluid motion is continuous, and that at a solid boundary, motion of the fluid is continuous with that of the solid) are applied to a situation in which the continuum motion is discontinuous. Dussan V. & Davis (1974) observe that if one allows a singularity at the contact line, there is no inconsistency between the discontinuous motion and the no-slip condition. However, the singularity takes the form of a physically unacceptable infinite shear stress, so it is not allowable. That the motion at a moving contact line is discontinuous is made clear by the observation that as a solid is submerged into a liquid, portions of the solid which were initially adjacent to the gas phase will subsequently be adjacent to the liquid phase, assuming the gas and liquid to be immiscible. Hence, there are points on the solid surface and in the liquid which initially were at finite separation and subsequently have infinitesimal separation: see Dussan V. & Davis (1974) for a more lengthy discussion of the kinematics.

The point of view that the singularity arises from applying inherently continuous governing laws to a discontinuous process leads to the conclusions that a fundamental modification of these laws must be made, and that singularities will arise in other cases of discontinuous motion, such as the break up of a capillary jet into drops, unless similar modifications are made. In the present case, it will be supposed that the discontinuous motion can be incorporated by allowing slip of the fluid relative to the solid boundary: it will be assumed that the Navier–Stokes equations do not break down. The purpose of the present paper is to present ideas about the form which a modification of the no-slip condition might take.

It will be further supposed here that slip can be described by a relation between slip velocity and surface shear stress. Such a constitutive equation will unavoidably involve undetermined constants, requiring experimental evaluation. The goal of the present paper is to arrive at a constitutive relation, and thereby to suggest the nature of the required constants. To this end we will consider, admittedly on a simplistic level, the mechanics and energetics of the slip process. We are led to infer that slip is a consequence of cohesive liquid–liquid bonds yielding within a thin layer near the solid surface. Consequently, our constitutive relation can be described as a yield stress boundary condition.

2. Survey

Analyses of moving contact lines have invoked several boundary conditions to eliminate the contact-line singularity, the most popular being the linear slip–shear relation (Lamb 1932, p. 586)

$$u_s = \frac{\lambda\tau}{\mu}. \tag{1}$$

Here u_s is the slip velocity, τ is the surface shear stress, μ is the liquid viscosity and λ is a slip length. Although this boundary condition has been applied to the contact-line problem by Huh & Scriven (1971), Huh & Mason (1977) and Hocking (1976), among others, it has not been arrived at by fundamental considerations, and indeed many of its practitioners have questioned its suitability. In an attempt to justify the linear model (1), Hocking (1976) proposed that on a microscopic scale slip does not actually occur. Rather, at an advancing contact line the liquid–gas interface might lay down on surface roughness elements, or jump between them, producing the appearance of slip at a large distance above the roughness. However, if slip did not occur, then displacement of the gas from the roughness elements by an advancing contact line would cause a singular stress, as we have previously described. Thus, in the surface roughness rationale, the contact-line singularity is simply transferred to the scale of the surface roughness, but is not resolved. Hocking recognized this difficulty.

Equation (1) receives its most fundamental justification when applied to slip at a gas–solid boundary: for this reason, it will be referred to as a 'gas dynamic' model. Near a stationary solid surface, randomly moving gas molecules collide with the surface and lose any directional bias they may have had. However, during the time between collisions, an imposed shear stress can transmit a mean momentum to the gas adjacent to the surface, and in a rarefied gas this can result in an appreciable slip velocity. Kinetic theory leads to the conclusion that λ is proportional to the mean free path of gas molecules.

It is well known that kinetic theory does not describe the liquid state. The density of a liquid is more nearly that of a solid than that of a gas. Consequently, stresses are transmitted through cohesive electrostatic forces, rather than through momentum transfer by random collisions. Thus, the concepts which underlie the gas-dynamic model (1) are of limited relevance to the liquid state. Despite its popularity, the gas-dynamic model is presently lacking in foundation.

Various other models have been used to eliminate the contact-line singularity. For instance, Dussan V. (1976) prescribes *a priori* a slip velocity as a function of distance to the contact line. Greenspan (1978) and Dussan V. & Chow (1983), among others, assume that contact angle is a known function of contact-line velocity, and determine the contact-line motion as a perturbation to a quasi-static solution. This approach avoids the contact singularity by delaying it to higher-order in the perturbation solution. It is also likely that the empirical dependence of contact angle on contact-line velocity is, at least in part, determined by velocity slip (Lowndes 1980); in this sense these analyses presuppose the solution.

Another model which warrants mention because of a similarity to the present model, is Huh & Mason's (1977) free-slip condition. Huh & Mason assume that within a given distance of the contact line the liquid slips freely over the solid, so that $\tau = 0$. Elsewhere a no-slip condition is imposed. This model produces a singularity where the boundary condition changes discontinuously from $u_s = 0$ to $\tau = 0$. Thus, τ rises to ∞ before dropping discontinuously to zero. Although Huh & Mason's free-slip model is substantially different from the present both in form and justification, it agrees with our conclusion that, to a large extent, the appropriate boundary condition should impose a criterion directly on the shear stress, with the slip velocity being determined indirectly. In the present theory, the surface stress is imagined to increase as the contact line is approached, until a critical level is reached at which the liquid begins to slip. The stress saturates at this level, with further increase being pre-empted by slipping of the liquid along the surface: this proposed behaviour is loosely analogous to the phenomenon of yield in metals. In the present model the location at which the liquid begins to slip is not prescribed, it is simply the location where the surface stress reaches its critical level, and this is a property of the fluid flow. The shear stress and slip velocity are continuous, and no singularity arises.

3. Energy considerations

When a wetted surface is pulled out of a liquid, its free energy is increased. This increase is produced by cohesive bonds between the bulk liquid and an adsorbed surface layer being broken. In the surface-tension model, an adhesive force between liquid and solid is associated with their line of contact, and the increment in free energy of the emerging surface can be attributed to work done against this force. Any slip velocity ought also to be associated with cohesive bonds being broken, in this case by the large shear stress existing in a neighbourhood of the contact line. The net rate at which shear stress does work on the surface is

$$\iint_{\text{surface}} \tau u_s, \tag{2}$$

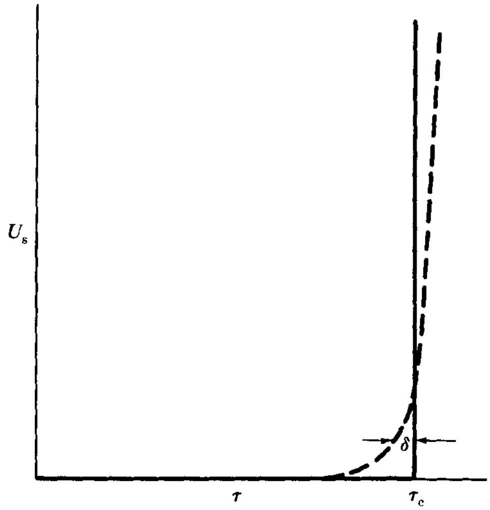

FIGURE 1. Illustrating the slip–stress relations. ——, relation (5); – – –, relation (6).

where the integral is over the submerged part of the solid. Surface slip increases the rate at which mechanical energy is dissipated by the amount of equation (2). In some sense this mechanical energy must be that expended in overcoming cohesion and causing slip.

A consideration of local energetics, along the lines of the previous paragraph suggests how to model slip. In the slip region the shear stress must break cohesive bonds, thereby enabling the liquid molecules at the surface to move with a finite velocity with respect to the solid. The local rate per unit area at which work is being done is τu_s; the local rate per unit area at which bonds are being broken will be denoted $\dot{N}$; and the energy needed to break a bond will be denoted E_b. The work of breaking a bond must be done by shear stresses, so the local energy balance is

$$\tau u_s = E_b \dot{N}, \tag{3}$$

assuming slip to be parallel to stress. If λ_s is a measure of bond spacing, then the number of bonds per unit area is $N = 1/\lambda_s^2$. In order to maintain bond spacing, the characteristic distance which layers slip when bonds are broken must also be λ_s. The slip velocity is then

$$u_s = (\dot{N}\lambda_s)\,\lambda_s^2. \tag{4}$$

Using (4) in (3) gives

$$\tau u_s = \tau_c u_s, \tag{5}$$

where $\tau_c = E_b/\lambda_s^3$. On rough surfaces, τ_c will be increased by a factor of $r^{\frac{3}{2}}$, where r is the ratio of the actual area of the surface to its area resolved in the plane of the mean surface.

As a moving contact line is approached, the surface stress increases. As long as $\tau < \tau_c$, equation (5) requires the no-slip condition, $u_s = 0$. However, when τ reaches the level τ_c, equation (5) is satisfied for arbitrary u_s. Thus, we are led to the idea of a yield stress, τ_c. The constitutive relation (5) is illustrated by figure 1: when $\tau < \tau_c$ the no-slip boundary condition is satisfied. When τ reaches τ_c the liquid begins to slip, preventing further increase of τ.

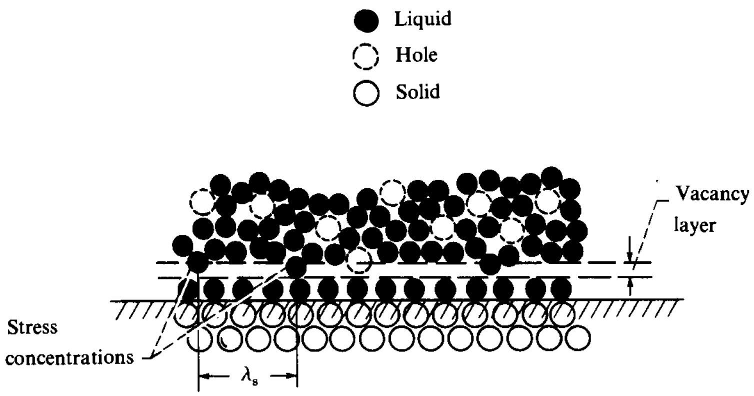

FIGURE 2. Extension of the significant structure model to include a solid–liquid interface. The vacancy layer is not meant to be void in the liquid; rather, it represents a layer in which adhesion to the solid weakens cohesive bonds.

4. The significant structure model

The constitutive equation (5) describes an abrupt change in boundary condition from $u_s = 0$ to $\tau = \tau_c$. One might expect this to be an approximation to an actual smooth curve of slip versus stress. A smoothing effect which the above simplistic line of reasoning ignores is the random thermal energy of the liquid. In order to incorporate this effect and to arrive at a more realistic slip–stress relation, we adopt the 'significant liquid structure' model of Eyring & Jhon (1969). Because the present discussion is by necessity intuitive, a graphic model such as that of Eyring & Jhon helps to fix ideas.

In this model, the molecular configuration of the liquid state is considered to be that of a solid with a high density of missing molecules. The disorder created by missing molecules makes the liquid fluid. The missing molecules leave holes which move randomly through the liquid, in analogy to the random thermal motion of molecules in a gas (Eyring & Jhon, figure 3.1). This random motion of holes makes a small gas-like contribution to liquid constitutive properties. To this extent, the slip–stress relation might be a linear combination of expressions (1) and (5) (or (6) below); however, we expect the gas dynamic contribution to slip to be rather small. In order to examine the yield stress contribution to slip in greater detail, we must extend the picture provided by the significant structure model to include the influence of an adjacent solid surface on the structure of the liquid phase.

In the significant structure model the liquid phase is a mirror image of the gas phase. To create this mirror image, gas molecules are replaced by holes and the void between gas molecules is filled with liquid molecules (figure 2 and Eyring & Jhon 1969).

Where a gas contacts a solid, a layer of molecules will be adsorbed on the surface. The spacing between gas molecules in this adsorbed phase is orders of magnitude smaller than that in the bulk of the gas phase (in fact, the surface number density of adsorbed molecules can approach that of the solid phase) and the adsorbed molecules are held tenaciously to the solid. Strict application of the mirror image approach would involve replacing the layer of adsorbed gas molecules by a layer of holes, held feebly by the surface. This is not a likely extension of significant liquid structure, but it provides guidance.

Beneath a wetting liquid phase, the solid will again be covered with a layer of tenaciously adsorbed molecules. Its strong adhesion to the surface is likely to reduce the cohesion of this layer to overlying layers of liquid. This weakened cohesion might be thought of as a 'vacancy layer', as is illustrated by figure 2. The vacancy layer is not a true void; the spacing between layers of molecules (which is exaggerated in figure 2) is imagined to be smaller than the molecular diameter. The significance of the vacancy layer is that it represents, in an idealized way, a weakness of the fluid phase at which stress concentration can result in slip. It is important that this layer exists, because it allows large stresses to be relieved by surface slip without the bulk of the fluid departing from Newtonian constitutive laws (or other continuum behaviour).

The vacancy layer is held from slipping by molecules which randomly span the layer. The illustration in figure 2 shows liquid molecules bridging the layer, but asperites on the solid surface could also impede slippage. These bridges serve to concentrate the surface shear stress. If the average spacing between bridging molecules is λ_s and the molecular diameter is a, and if a stress τ is acting on the bulk liquid phase, then the shear stress will typically be amplified to $(\lambda_s/a)^2\tau$ at these points.

Of course, we recognized that irregularities, or asperites on the surface can have an important influence on slippage and can affect the critical stress. Therefore, the ideas of Hocking (1976) have some relevance. However, the present point of view is that some real form of slip (as opposed to the apparent slip in Hocking 1976) must occur at the surface, and that the ideas described above have some bearing on that phenomenon.

In the Appendix, an analysis similar to those in Eyring & Jhon (1969) is used to argue that the slip relation might generally take the form

$$u_s = B\,\mathrm{e}^{((\tau/\tau_c-1))/\delta}, \tag{6}$$

where B and δ are dimensionless constants and $\delta \ll 1$. δ is proportional to temperature. Expression (6) is a smooth version of expression (5): when $\tau \ll \tau_c$, u_s is exponentially small; when $\tau \simeq \tau_c$, slip becomes significant, and the slip velocity becomes quite large when $\tau - \tau_c \gg \delta$. Despite the fact that (6) has been derived by considering a specific conceptual model, the form of this equation does not make explicit reference to that model and probably could be arrived at by other means.

Figure 1 compares (6) to (5). When $\delta \rightarrow 0$ these two formulae become equivalent in an asymptotic sense. Thus, expression (5) can be regarded as an approximation in two 'outer regions', with expression (6) describing an 'inner region' which interpolates smoothly between them. For many applications we expect (5) to be a suitable boundary condition, although the smooth boundary condition (6) is available when needed.

5. Illustration: Motion of a slender drop on an incline

To illustrate the model (5), it will be used to determine the speed with which a slender drop slides down an incline under the influence of gravity. We consider a two-dimensional drop and make the lubrication approximation (Huh & Scriven 1971; Hocking 1981). Indeed, our analysis follows that of Hocking (1981), except that we use the yield stress boundary condition (5) instead of the gas-dynamic condition (1). This change in boundary condition leads to a substantially different mathematical problem.

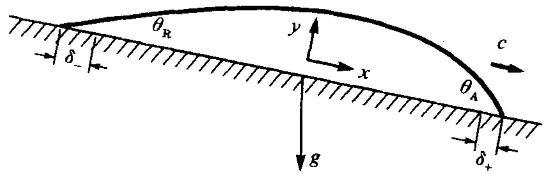

FIGURE 3. Defining sketch for analysis of a two-dimensional slender drop rolling down an incline.

The x-coordinate is normalized by the half length, L, of the drop, so that the drop meets the surface at $x = \pm 1$. The advancing and receding contact angles (figure 3) θ_A and θ_R are assumed to be known and independent of contact-line velocity: in the lubrication approximation, the average contact angle, $\bar{\theta} = \frac{1}{2}(\theta_A + \theta_R)$ must be small. Lowndes (1980) argues that the true contact angles are independent of drop speed; experiments showing dependence on speed are supposed to measure an angle at some distance from the wall and not the true contact angle. However, because contact-line motion involves breaking of cohesive bonds, it is conceivable that contact angles might depend on speed. If so, such dependence could be allowed in our analysis.

In regions of length δ_+ and δ_- on the liquid side of the contact lines, the stress boundary condition $\mu\, \mathrm{d}u/\mathrm{d}y = \tau_c$ on $y = 0$ is applied, while in the central part of the drop $u = 0$ on $y = 0$ (see figure 3). It will be assumed that any shear stress exerted on the drop by the gas phase is negligible. Thus, at the gas–liquid surface of the drop the shear stress $\mu\, \mathrm{d}u/\mathrm{d}y$ must vanish.

In the lubrication approximation (Batchelor §4.8), the horizontal momentum equation reduces to

$$\mu \frac{\partial^2 u}{\partial y^2} = \frac{\partial P}{\partial x} - \rho g \sin \alpha, \tag{7}$$

where α is the inclination of the surface to the direction of gravity. In the no-slip region the solution to (7) with the above boundary conditions is

$$u = \frac{(\partial P/\partial x - \rho g \sin \alpha)(y^2 - 2yh(x))}{2\mu}, \tag{8a}$$

where $y = h(x)$ is the surface of the drop. In the yield stress regions, $1 \mp x < \delta_\pm$ (see figure 3)

$$u = \tau_c \frac{2yh(x) - y^2}{2\mu h(x)} + u_s(x), \tag{8b}$$

where $u_s(x)$ is the slip velocity. Comparing (8b) to (8a) shows that

$$\frac{\partial P}{\partial x} = \rho g \sin \alpha - \frac{\tau_c}{h(x)} \tag{9}$$

in this region.

We seek a solution for a drop which is moving with constant velocity c. Then dependent variables will be functions of x and t only in the combination $x - ct$, so the equation of mass conservation is simply

$$\int_0^h u\, \mathrm{d}y = ch. \tag{10}$$

Substituting (8*a*) into (10) yields

$$\frac{\partial P}{\partial x}=\rho g\sin\alpha-\frac{3\mu c}{h^2} \tag{11}$$

in the no-slip region, while (8*b*) yields

$$u_s=c-\frac{\tau_c h}{3\mu} \tag{12}$$

in the slip regions.

Along the surface of the drop, the surface tension force must balance the pressure drop across the surface. In the slender-drop limit this balance becomes

$$\sigma\frac{d^2h}{dx^2}=-P.$$

If $\rho g L^2\cos\alpha/\sigma$ is sufficiently small, then the component of gravity normal to the incline has insignificant effect on the drop shape. Then with (9) and (11) determining P the above equation gives

$$\sigma h^2\frac{d^3h}{dx^3}+\rho g\sin\alpha h^2-3c\mu=0 \tag{13a}$$

in the no-slip region, $-1+\delta_- < x < 1-\delta_+$, and

$$\sigma h\frac{d^3h}{dx^3}+\rho g\sin\alpha h-\tau_c=0 \tag{13b}$$

in the end regions $1\pm x<\delta_\pm$.

At the junctions between the regions, the surface shear stress must be continuous. This is equivalent to requiring that the slip velocity (12) vanish at $x_+=1-\delta_+$ and at $x_-=-1+\delta_-$. Thus, with $h_\pm$ defined as $h(x_\pm)$,

$$h_+=h_-=\frac{3\mu c}{\tau_c}. \tag{14}$$

Equation (14) and the conditions $h(\pm 1)=0$, $dh(1)/dx=-\theta_A$ and $dh(-1)/dx=\theta_R$ provide boundary conditions to equations (13). In order that the solution to (13*a*) matches smoothly to the solutions to (13*b*), dh/dx and d^2h/dx^2 must be continuous at the junctions, x_+ and x_-.

The equations will be non-dimensionalized by introducing

$$\left.\begin{aligned}\bar{H},H&=\frac{h}{\theta L}, & T_c&=\frac{L\tau_c}{\sigma\theta^2},\\ C&=\frac{3c\mu}{\sigma\theta^3}, & K&=\frac{\rho g\sin\alpha L^2}{\sigma\theta},\end{aligned}\right\} \tag{15}$$

where $\bar{H}$ is the non-dimensional drop height in the slip regions and H is the height in the no-slip region. (Recall that x has already been scaled on L.)

In general the critical shear stress must be large, or else slip would commonly be observed: for instance, measurements of Poiseuille flow would not agree so well with the no-slip condition (Lamb 1932). Therefore, T_c is a large parameter, and it is appropriate to ignore gravity in the slip region ($T_c \gg K$). Then problem (13) reduces to solving

$$H^2H''' + KH^2 - C = 0 \quad (-1+\delta_- < x < 1-\delta_+), \tag{16a}$$

$$\bar{H}\bar{H}''' - T_c = 0 \begin{cases} (-1 \leqslant x < -1+\delta_-), \\ (1-\delta_+ < x \leqslant 1), \end{cases} \tag{16b}$$

where primes denote differentiation with respect to x, with boundary conditions

$$\bar{H}(\pm 1) = 0, \quad \bar{H}'(\pm 1) = \mp 1 - \epsilon, \tag{16c}$$

where $\epsilon = (\theta_A - \theta_R)/(\theta_A + \theta_R)$ and with

$$H_\pm = C/T_c.$$

It will evolve that when T_c is large, C is small (although only like $1/\ln(T_c)$). Therefore it is suitable to expand the solution to (16a) for small C. For simplicity, we follow Hocking (1981) and also consider the case of $K \ll 1$. Then to a first approximation (16a) reduces to $H''' = 0$. Solving this and then calculating the lowest-order correction gives

$$\begin{aligned} H = {} & \tfrac{1}{2}(1-x^2) - K\tfrac{1}{6}(x^3 - x) + C[(1-x)\ln(1-x) - (1+x)\ln(1+x) \\ & - \tfrac{1}{2}(1-x)^2\ln(1-x) + \tfrac{1}{2}(1+x)^2\ln(1+x)] + c_1\tfrac{1}{2}x^2 + c_2x + c_3 + O(C^2, CK), \end{aligned} \tag{17}$$

where c_1, c_2 and c_3 are constants of integration.

This solution for H, and its first two derivatives, must match with the solution to (16b) at $x_\pm = \pm(1-\delta_\pm)$. δ_+ and δ_- are small parameters $O(T_c^{-1}/\ln(T_c))$. Therefore it is suitable to evaluate (17) and its derivatives at $x_\pm$ keeping only the largest terms in $\delta_\pm$:

$$H_\pm = \delta_\pm(1 - \tfrac{1}{3}K) + \tfrac{1}{2}c_1 \pm c_2 + c_3 \pm C\delta_\pm \ln\delta_\pm, \tag{18a}$$

$$H'_\pm = \mp 1 - \tfrac{1}{3}K - C\ln\delta_\pm \pm c_1 + c_2, \tag{18b}$$

$$H''_\pm = \frac{\pm C}{\delta_\pm} + c_1. \tag{18c}$$

From (18a) and $H_\pm = C/T_c$

$$2c_2 = -C(\delta_+\ln\delta_+ + \delta_-\ln\delta_-) + (1 - \tfrac{1}{3}K)(\delta_- - \delta_+) = O(\delta_\pm \ln\delta_\pm);$$

hence, c_2 can be dropped from (18b). From (18b) and (16c) c_1 is $O(1)$ and so can be dropped from (18c). Thus (18) can be replaced by

$$\bar{H}_\pm = C/T_c, \tag{19a}$$

$$\bar{H}'_+ + \bar{H}'_- = -\tfrac{2}{3}K - C\ln(\delta_+\delta_-), \tag{19b}$$

$$\bar{H}''_\pm = \frac{\pm C}{\delta_\pm}. \tag{19c}$$

where H has been replaced by $\bar{H}$ to show that (19a–c) will be applied to the solution in the slip regions.

We must solve (16b) in the two end regions, subject to the boundary conditions (16c) and matching conditions (19). The differential equation (16b) is third-order, so the two end regions combined allow six integration constants. Additionally, the end region lengths $\delta_\pm$ and the drop speed C are unknown. These nine unknowns are determined by the four conditions (16*c*) and the five conditions (19).

Unfortunately, no closed-form general solution to (16*b*) seems to exist. A first integral is

$$\bar{H}\bar{H}'' - \tfrac{1}{2}\bar{H}'^2 = T_c(x \mp 1) - \tfrac{1}{2}(1 \pm \epsilon)^2. \tag{20}$$

Evaluating this at $x = \pm(1-\delta_\pm)$, using (19*a*) and (19*c*) yields

$$\bar{H}'_\pm = \mp[(1\pm\epsilon)^2 \pm 2T_c\delta_\pm \pm C^2/(\delta_\pm T_c)]^{\frac{1}{2}}. \tag{21}$$

Substituting this into (19*b*) yields

$$C \ln \delta_+ \delta_- = -\tfrac{2}{3}K + \left[(1+\epsilon)^2 + 2T_c\delta_+ + \frac{C^2}{\delta_+ T_c}\right]^{\frac{1}{2}} - \left[(1-\epsilon)^2 - 2T_c\delta_- - \frac{C^2}{\delta_- T_c}\right]^{\frac{1}{2}}. \tag{22}$$

Equation (21) determines C once $\delta_\pm$ are known. However, a full solution to (16*b*) is required in order to determine $\delta_\pm$.

An approximation for $\delta_\pm$ can be derived by expanding the solution to (16*b*) for small $T_c\delta_\pm$ (which is formally $O(1/\ln T_c)$ if $1-\epsilon$ is $O(1)$). In this approximation the solution to (16*b*) is expanded as

$$\bar{H} = (\mp 1 - \epsilon)\, z - \frac{T_c z^2 \ln|z|}{2(\epsilon \pm 1)} + \tfrac{1}{2}(\beta_\pm z^2) + O(T_c^2 z^3 \ln|z|), \tag{23}$$

where $z = x \mp 1$. Here β_+ and β_- are constants. Equation (23) must satisfy conditions (19) at $z = \mp\delta_\pm$. Thus, to lowest order in $\delta_\pm$, equation (23) substituted into (19*c*) gives

$$\beta_\pm + \frac{T_c \ln \delta_\pm}{\epsilon \pm 1} = \frac{\pm C}{\delta_\pm},$$

and substitution of (23) into (19*a*) gives

$$\delta_\pm = \frac{C}{T_c[1 \pm (\epsilon + \frac{1}{2}C)]}. \tag{24}$$

Using (23) in (19*b*) gives

$$2(\tfrac{1}{3}K - \epsilon) = -C \ln \delta_+ \delta_- \tag{25}$$

in place of the general formula (22). (Notice that (25) can be obtained directly from (22) by dropping the last two terms inside each square bracket.) Here $1 \ll -\ln \delta_+ \delta_-$ has been used for consistency. After substituting (24), (25) becomes

$$C = \frac{\frac{1}{3}K - \epsilon}{\ln\left[\dfrac{T_c(1-(\epsilon+\frac{1}{2}C)^2)^{\frac{1}{2}}}{C}\right]} \simeq \frac{\frac{1}{3}K - \epsilon}{\ln\left[\dfrac{T_c(1-\epsilon^2)^{\frac{1}{2}}}{C}\right]}. \tag{26}$$

Equation (26) implicitly determines the drop speed C as a function of the tangential component of gravity K, once the contact angle hysteresis ϵ and yield stress T_c are given. This equation expresses a balance between the external force acting on the drop and the frictional drag resisting movement of the drop.

6. Stick slip, and order of magnitude estimates

Expression (26) is similar to the formula obtained by Hocking (1981) using the gas-dynamic boundary condition (1), if his slip length λ is identified with $C/T_c(1-\epsilon^2)^{\frac{1}{2}}$. Note, however, that λ is regarded as a fixed constant, while here the slip length is a property of the flow, depending for that reason on the speed of advance and on the contact angles.

In order for a continuum model to apply, the slip length must be greater than a molecular diameter, a; thus in dimensional terms $c > \tau_c a(\theta_A \theta_R)^{\frac{1}{2}}/\mu$. This lower bound on c suggests an intriguing explanation for 'stick–slip' motion of contact lines (Huh & Scriven 1971): if the driving force is insufficient for c to be greater than its lower bound the contact line must move in spurts, at every instant either being stationary or moving with speed greater than $\tau_c a(\theta_A \theta_R)^{\frac{1}{2}}/\mu$. In other words, the critical stress is required to move the contact line, and if this level of stress is not reached far enough from the contact line, then the contact line cannot move. Microscopic surface roughness probably plays a role in stick–slip behaviour, so it might well be more appropriate to regard the length a as characteristic of roughness, rather than of molecular dimensions.

In cases of extremely slow contact-line movement, surface diffusion of the liquid phase probably becomes important. In that case, the present mechanical considerations would not apply and one would expect the contact line to move smoothly. It might be hypothesized that the yield-stress model becomes applicable at the onset of stick–slip behaviour, and that the slip region (dimensional) length $\delta_{\pm} L$ is then comparable to λ_s. Hypothesizing thus, we have

$$\lambda_s \simeq \delta_{\pm} L \simeq \frac{c\mu}{\tau_c} \simeq \frac{c\mu\lambda_s^3}{E_b}.$$

Elliot & Riddleford (1967) found that when $c \simeq 2$ mm/min a drop of water receding from a polyethelene surface moved in a stick–slip fashion. If we use this value and take $E_b \simeq 5$ kcal/mol as a reasonable value, then with $\mu = 10^{-2}$ g/cm s^{-1},

$$\lambda_s \simeq 10^{-4}\ \text{cm}.$$

Although this is a very crude estimate, and could very well be wrong by an order of magnitude, it gives an idea of the scales being considered. If this value of λ_s is used, we find

$$\tau_c \simeq \frac{E_b}{\lambda_s^3} \simeq 0.5 \frac{\text{g}}{\text{cm s}^{-2}}.$$

This estimate seems low, but it is also quite unreliable because a factor of two decrease of λ_s causes an order of magnitude increase of τ_c.

7. Further comments

Although the surface shear stress is continuous at $x = \pm(1-\delta_{\pm})$ in the above analysis, its derivative with respect to x is discontinuous. The discontinuity can be alleviated by invoking equation (6) to smooth the transition from no-slip to yield-stress boundary condition. Usually this would not be necessary, for the slip boundary condition was forced on us by a non-integrable shear stress singularity when no-slip is applied, and the yield-stress condition has removed that singularity. For most purposes the discontinuous derivative of surface stress can be tolerated.

A slightly more troubling feature of the slip boundary condition is that an integrable (logarithmic) singularity of the pressure can be shown to remain at the contact lines, $x = \pm 1$. This singularity is not a consequence of the slender-drop approximation, and occurs in solutions using boundary condition (1) as well (Huh & Mason 1977). The origin of the pressure singularity is the discontinuity in surface shear stress at the contact line: on the gas–solid side this stress is zero (or some non-zero value for a viscous fluid), while on the liquid–solid side it is finite. If necessary, the pressure singularity could be removed by introducing a thin region near the contact line in which the critical stress relaxes to zero (or in which values on either side of the contact line adjust). The considerations leading to (5) took no account of lateral inhomogeneity near the gas–liquid interface; presumably such consideration would justify yield-stress relaxation. However, the surface tension model represents the inhomogeneous region by a sharp interface, so it may be inconsistent to allow it finite thickness in the boundary condition: one may be forced to tolerate the pressure singularity if a continuum model is maintained.

The idea that observations of stick–slip behaviour might be used to estimate slip parameters was suggested to me by Professor S. H. Davis.

Appendix

Arguing as in §5.2 of Eyring & Jhon (1969), we suppose that an energy barrier E_a must be overcome for slip to occur and that the rate of slipping is described by an Arrhenius type equation. If the macroscopic slip velocity is a consequence of molecules in the vacancy layer slipping a distance λ_s, then the work done by the shear stress is $\tau\lambda_s^3 \cos\theta$ per microscopic slip, where θ is the angle between the stress and the direction of slip. Because of random thermal motion, microscopic slip is not parallel to the imposed macroscopic stress. We assume that slip takes place in a plane parallel to the surface. With these assumptions, the rate of slip is given by

$$\frac{kT}{f_s h}\, e^{(\tau\lambda_s^3 \cos\theta - E_a)/kT}, \tag{A 1}$$

where T = temperature, k = Boltzman constant, h = Planck constant and f_s is a partition function for the vacancy layer. It is through the energy barrier to slipping that the cohesive forces are incorporated.

The slip velocity is the slip distance, $\lambda_s \cos\theta$, multiplied by the rate of slip (A 1), averaged over angle:

$$\begin{aligned} u_s &= \frac{kT\lambda_s}{f_s h}\frac{1}{2\pi}\int_0^{2\pi} e^{(\tau\lambda_s^3 \cos\theta - E_a)/kT} \cos\theta\, d\theta \\ &= \frac{kT\lambda_s}{f_s h}\, e^{-E_a/kT} I_1((\tau\lambda_s^3/kT), \end{aligned} \tag{A 2}$$

where I_1 is a modified Bessel function. Assuming that $E_a/kT \gg 1$, the slip velocity is exponentially small when $\tau\lambda_s^3/kT$ is of order unity. When $\tau\lambda_s^3/kT \gg 1$, expression (A 2) can be approximated by

$$u_s = \frac{\beta^{\frac{3}{2}}\lambda_s^4}{f_s h(2\pi\tau)^{\frac{1}{2}}}\, e^{(\tau\lambda_s^3 - E_a)/kT}, \tag{A 3}$$

where $\beta = kT/\lambda_s^3$. The pre-exponential in (A 3) typically has a large magnitude. In order to obtain a smaller pre-exponential factor, expression (A 3) will be rewritten in terms of the fluid viscosity.

If E_l is an energy barrier to molecules randomly jumping into holes in the bulk liquid (Eyring & Jhon, equation (5.20)), f_l is the liquid phase partition function, λ_l is a characteristic spacing between liquid molecules, and Z is the number of nearest neighbours to a hole, then Eyring & Jhon's analysis gives

$$\mu^{-1} = \frac{Z\lambda_l^3(V-V_s)}{6f_l hV}\,\mathrm{e}^{-E_l/kT} \tag{A 4}$$

for the viscosity μ. Here $(V-V_s)/V$ is the ratio of the number of holes to the number of molecules plus holes per volume of liquid. A similar ratio might be incorporated into expression (A 3) if necessary. If we define

$$\tau_c = \frac{E_a - E_l}{\lambda_s^3}$$

then (A 3) and (A 4) give

$$u_s = \frac{6\lambda_s^4 f_l V\beta^{\frac{3}{2}}}{(2\pi\tau_c)^{\frac{1}{2}}\lambda_l^3 f_s Z(V-V_s)\,\mu}\,\mathrm{e}^{(\tau-\tau_c)/\beta}. \tag{A 5}$$

τ_c as defined here most likely is positive, because E_l is the barrier only to a molecule falling into a hole in the bulk liquid, while E_a is the barrier to a cohesive bond to the adsorbed layer being broken. Because u_s is exponentially small when $\tau - \tau_c \ll -\beta$, τ has been replaced by τ_c in the denominator of the pre-exponent in order to make (A 6) valid for all τ. Expression (A 5) has the form of (6), with $\delta = \beta/\tau_c$ ($\ll 1$).

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