Contact-line motion of shear-thinning liquids

D. E. Weidner and L. W. Schwartz[a)]
Department of Mechanical Engineering, University of Delaware, Newark, Delaware 19716

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It is demonstrated that, for the slow advance of a viscous liquid onto a previously dry substrate, the well-known moving contact line paradox is alleviated for liquids exhibiting power-law shear-thinning behavior. In contrast to previous models that allow contact-line motion, it is no longer necessary to abandon the no-slip condition at the substrate in the vicinity of the contact point. While the stress is still unbounded at the contact point, the equations of motion are shown to be integrable. A three-constant Ellis viscosity model is employed that allows a low-shear Newtonian viscosity, and may thus be used to model essentially Newtonian flows where shear thinning only becomes important in the immediate vicinity of the contact point. Calculations are presented for the model problem of the progression of a uniform coating layer down a vertical substrate using the lubrication approximations. The relationship between viscous heating and shear-thinning rheology is also explored.

I. INTRODUCTION

The classical problem of a liquid advancing onto a previously dry surface has received much attention in the fluid mechanics literature. (For reviews see, e.g., Dussan V,[1] Davis,[2] de Gennes,[3] and Tuck and Schwartz.[4]) If the liquid is Newtonian and the no-slip boundary condition is enforced at the leading edge of the liquid, known as the contact line, then an infinite force is required to move this front over the dry substrate.[5,6] The standard method of removing this singularity is to allow for fluid slip in a small region near the moving contact line.[2,6–8] In these slip models, the boundary conditions at the front include the moving contact angle and a "slip length." Another method of alleviating the force singularity is to assume that the substrate is never perfectly dry, but that evaporation and condensation at the front always produces a thin "precursor layer."[3,9,10] In this case there is no contact line, and a complete specification of the problem requires the thickness of the precursor layer. In this work we suggest an alternate approach to mitigating the moving contact line singularity: shear-thinning rheology. If the viscosity of the liquid decreases monotonically with increasing shear stress, then there will still be an infinite shear stress at the front, but the stress singularity will be integrable, yielding a finite force at the substrate. For this case, complete specification of the problem requires a knowledge of the rheological properties of the liquid and the advancing contact angle.

The fundamental equations for the draining of a non-Newtonian liquid layer using a lubrication model are derived below. A three-parameter Ellis viscosity model is used, which allows for power-law shear-thinning behavior at high shear stress. An analytical expression for the speed of the advance is derived, as well as a differential equation for the steady-state shape of the layer. The numerical solution to this differential equation is then discussed, and results are presented showing profiles as a function of various dimensionless parameters. An expression for the shear stress near the contact point is derived and is shown to be integrable for shear-thinning liquids. The relationship between viscous heating and shear-thinning rheology is also explored.

II. PROBLEM FORMULATION AND SOLUTION METHODOLOGY

Consider the progression of a semi-infinite uniform coating layer draining down a previously dry, vertical substrate, as shown in Fig. 1. Here x is the coordinate parallel to the substrate, y the coordinate perpendicular to the substrate, and $h(x)$ the thickness of the coating layer. The front of the coating layer moves downward at constant speed U, relative to the fixed substrate. The (x,y) coordinate system is fixed to the moving front; in this coordinate system the substrate moves upward at speed U and the profile has reached steady state. Far upstream, corresponding to large negative x, the film has a constant thickness h_1. At $x=0$, the contact point, the free surface meets the substrate at a contact angle θ_c.

Under the assumptions that the liquid layer is thin, the motion is slow, and the free surface is almost parallel to the substrate, the x and y momentum equations reduce to

$$0=-p_x+\tau_y+\rho g, \tag{1}$$

$$0=p_y. \tag{2}$$

Here p is the pressure, τ is the shear stress, ρ is the liquid density, and g is the acceleration of gravity. Subscripts indicate partial differentiation. Equations (1) and (2) are the basis of the so-called lubrication theory (see, e.g., Sherman[11]).

The pressure jump at the free surface $h(x)$ is given by

$$p=-\frac{\sigma}{R}=-\frac{\sigma h_{xx}}{(1+h_x^2)^{3/2}}\approx-\sigma h_{xx}, \tag{3}$$

where σ is the surface tension and the surface curvature $1/R$ is approximated by assuming $h_x^2\ll 1$. The no-slip boundary condition is enforced at the substrate

$$u=-U \quad \text{at } y=0, \tag{4}$$

where u is the x component of velocity.

[a)]Corresponding author. Also at Department of Mathematical Sciences, University of Delaware, Newark, Delaware 19716.

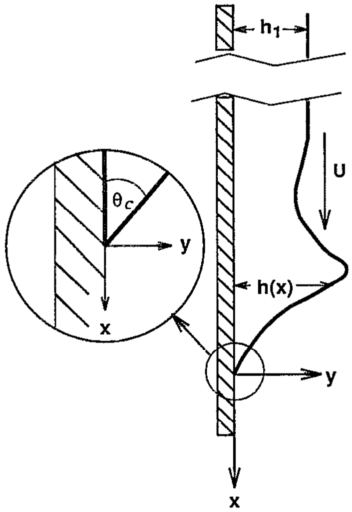

FIG. 1. Liquid layer draining down a vertical wall under gravity.

Since p is not a function of y, the pressure $p(x)$ in the liquid is given by Eq. (3). The free surface is stress free, and by integrating Eq. (1) we find that the shear stress in the liquid is a linear function of y:

$$\tau=(\sigma h_{xxx}+\rho g)(h-y). \tag{5}$$

The liquid is assumed to obey an Ellis constitutive law,[12]

$$\tau=\eta u_y,$$

where

$$\frac{1}{\eta}=\frac{1}{\eta_0}\left(1+\left|\frac{\tau}{\tau_{1/2}}\right|^{\alpha-1}\right).$$

Here η is the viscosity, η_0 is the viscosity at zero shear stress, $\tau_{1/2}$ is the shear stress at which the viscosity is reduced by a factor of $\frac{1}{2}$, and α is a power-law index. When $\alpha=1$, the liquid is Newtonian, while for $\alpha>1$, the liquid is shear thinning. The Ellis viscosity model incorporates power-law behavior at high shear stresses, while allowing for a Newtonian plateau at low shear stresses. Because the free surface of the coating is stress free, and the shear stress in the liquid far away from the contact point may be quite small, this is a particularly appropriate rheological model.

Incorporating the Ellis constitutive law in Eq. (5), integrating, and employing the no-slip boundary condition yields an expression for the velocity u. By integrating u over the thickness of the coating layer, the flux is obtained as

$$Q(x)=\int_0^h u(x,y)dy$$

$$=\frac{1}{\eta_0}\left(\frac{(\sigma h_{xxx}+\rho g)h^3}{3}+\frac{(\sigma h_{xxx}+\rho g)^\alpha h^{\alpha+2}}{(\alpha+2)(\tau_{1/2})^{\alpha-1}}\right)-Uh. \tag{6}$$

Since the profile is steady in the (x,y) coordinate system, Q must be independent of x. But $Q(0)=0$, thus the flux everywhere must equal zero. Far upstream $h_{xxx}=0$ and $h=h_1$, and the speed U may be evaluated from Eq. (6) as

$$U=\frac{h_1\rho g}{3\eta_0}\left[1+\frac{3}{\alpha+2}\left(\frac{\rho g h_1}{\tau_{1/2}}\right)^{\alpha-1}\right]. \tag{7}$$

Note that the speed of the front is not an explicit function of either the surface tension or the contact angle.

With the substitution (7), Eq. (6) is a third-order nonlinear ordinary differential equation for the shape of the liquid surface. It may be written in dimensionless form as

$$(\hat{h}_{\hat{x}\hat{x}\hat{x}}+1)\hat{h}^3\left(1+\frac{3}{\alpha+2}\,|(\hat{h}_{\hat{x}\hat{x}\hat{x}}+1)B\hat{h}|^{\alpha-1}\right)$$

$$=\hat{h}\left(1+\frac{3}{\alpha+2}\,B^{\alpha-1}\right), \tag{8}$$

where

$$\hat{h}=h/h_1, \tag{9a}$$

$$\hat{x}=(\rho g/\sigma h_1)^{1/3}x, \tag{9b}$$

and

$$B=\rho g h_1/\tau_{1/2}. \tag{9c}$$

The nondimensional quantity B is the ratio of the maximum shear stress far upstream to $\tau_{1/2}$. Large values of B indicate that substantial shear thinning occurs far away from $\hat{x}=0$, while for small values of B the shear thinning is largely restricted to the vicinity of the contact point.

With $\hat{h}(0)=0$, the boundary conditions for Eq. (8) are

$$\hat{h}\to 1, \quad \text{as } x\to-\infty, \tag{10}$$

and the contact angle condition,

$$\hat{h}_{\hat{x}}(0)=-\tan\,\hat{\theta}_c=-\left(\frac{\sigma}{\rho g h_1^2}\right)^{1/3}\tan\,\theta_c. \tag{11}$$

Using the scaling (9), $\hat{h}_{\hat{x}}$ is an order unity quantity, in general. The physical contact angle θ_c will be small for thin coating layers, corresponding to small values of the Bond number $\rho g h_1^2/\sigma$.

Equation (8) is solved by a shooting method, following Tuck and Schwartz,[4] who treated Newtonian flows where slip is allowed. A formal linearization of Eq. (8) near $\hat{h}=1$ shows that the upstream boundary condition can be strengthened to

$$\hat{h}\to 1+a\,\exp(D^{1/3}\hat{x}/2)\cos(D^{1/3}\sqrt{3}\hat{x}/2), \quad \text{as } \hat{x}\to-\infty, \tag{12}$$

where

$$D=\frac{\alpha(2+3B)+4+3B}{\alpha(1+3B)+2}.$$

For given B and α, initial conditions $\hat{h}(\hat{x}_0)$, $\hat{h}_{\hat{x}}(\hat{x}_0)$, and $\hat{h}_{\hat{x}\hat{x}}(\hat{x}_0)$ are found using Eq. (12) at some arbitrary starting value $\hat{x}=\hat{x}_0$.

Integration is carried forward in $\hat{x}$ using a fourth-order Runge–Kutta scheme. Suitably small increments in $\hat{x}$ are used to ensure accuracy as the contact condition $\hat{h}=0$ is approached. For each value of the shooting parameter a, a well-defined contact slope $\hat{h}_{\hat{x}}(0)$ is calculated. Since $\hat{x}$ does not appear explicitly in the differential equation, each such solution can then be shifted in $\hat{x}$ so that the contact point

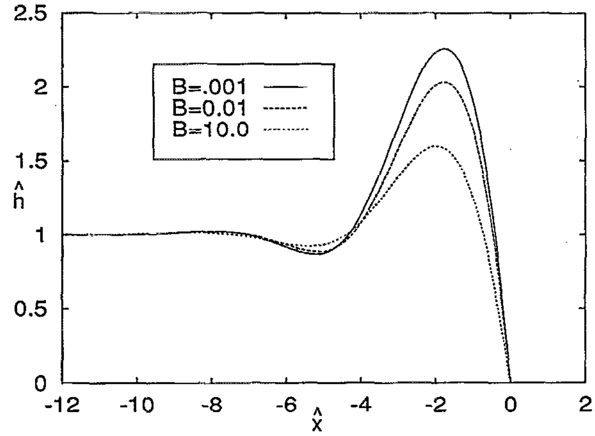

FIG. 2. Nondimensional surface profiles for several values of the stress ratio B. Here $\tan \hat{\theta}_c = 1.0$ and $\alpha = 2$.

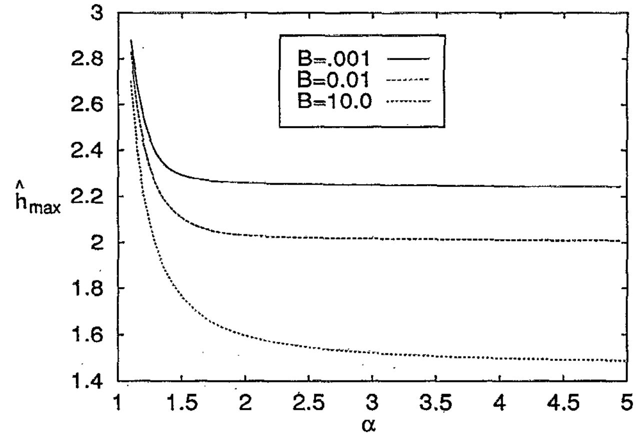

FIG. 3. Maximum coating thickness versus the shear-thinning exponent α for several values of the stress ratio B. Here $\tan \hat{\theta}_c = 1.0$.

corresponds to $\hat{x}=0$. For the linearization (12) to be valid, the parameter a must be small. However, all solutions to Eq. (8), for a particular choice of parameters B and α, can be generated by allowing a to vary by a factor between 1 and $\exp(2\pi/\sqrt{3}) \approx 37.62$, as explained by Tuck and Schwartz.[4] Note that the numerical integration of (8) requires that the functional form $\hat{h}_{\hat{x}\hat{x}\hat{x}} = f(\hat{h};B,\alpha)$ be known. For integer values of α between 1 and 4 inclusive, the resulting polynomial equation for $\hat{h}_{\hat{x}\hat{x}\hat{x}}$ can be solved explicitly; for other values of α, a Newton–Raphson iteration is used.

III. CALCULATED RESULTS

Figure 2 shows the free surface profiles for several values of the stress ratio B, illustrating the effect of shear-thinning rheology. As B is increased, the size of the shear-thinning region increases. For $B=0.001$, substantial shear thinning occurs only in the vicinity of the contact line. A scaling analysis of Eq. (8) readily shows that the size of the contact region, where the shear-thinning term is dominant for $B \ll 1$, is given by

$$\hat{x} \sim \hat{h} \sim O(B).$$

Conversely, for large B, non-Newtonian effects are present at large distances from the contact region.

The size of the shear-thinning region determines the magnitude of the maximum coating thickness or "overshoot." Small values of B cause a large overshoot. The magnitude of the overshoot is also a function of the power-law index α. Figure 3 shows the overshoot, given by $\hat{h}_{\max}$, as a function of α for three values of B. As either $\alpha \to 1$ or $B \to 0$, the Newtonian case is recovered and $\hat{h}_{\max} \to \infty$.

Figure 4 is a plot of $\hat{h}_{\max}$ versus the reduced contact angle $\hat{\theta}_c$. Here the magnitude of the overshoot is an increasing function of contact angle. Note that for a contact slope of less than approximately 1.0, the magnitude of the overshoot is a weak function of contact angle. For larger values of $\tan \hat{\theta}_c$, the overshoot is a weak function of B.

IV. CHARACTER OF THE SOLUTION IN THE CONTACT REGION; RELEVANCE TO NOMINALLY NEWTONIAN LIQUIDS

For both Newtonian and the class of shear-thinning liquids considered here, the stress is singular at the contact point. In the vicinity of the contact point, τ becomes large and the Ellis viscosity law reduces to a power-law model,

$$\tau \approx K(u_y)^{1/\alpha}, \quad \text{for } \tau \gg \tau_{1/2}, \tag{13}$$

where

$$K = [\eta_0(\tau_{1/2})^{\alpha-1}]^{1/\alpha}. \tag{14}$$

Solving for u in Eq. (13), integrating over the layer thickness to find the flux, and setting the flux to zero, yields the differential equation

$$\sigma h_{xxx} + \rho g = \frac{K(\alpha+2)^{1/\alpha} U^{1/\alpha}}{h^{(\alpha+1)/\alpha}}. \tag{15}$$

Thus, the shear stress at the substrate, using (5), is

$$\tau_{\text{sub}} = (\sigma h_{xxx} + \rho g) h = \frac{K(\alpha+2)^{1/\alpha} U^{1/\alpha}}{h^{1/\alpha}}. \tag{16}$$

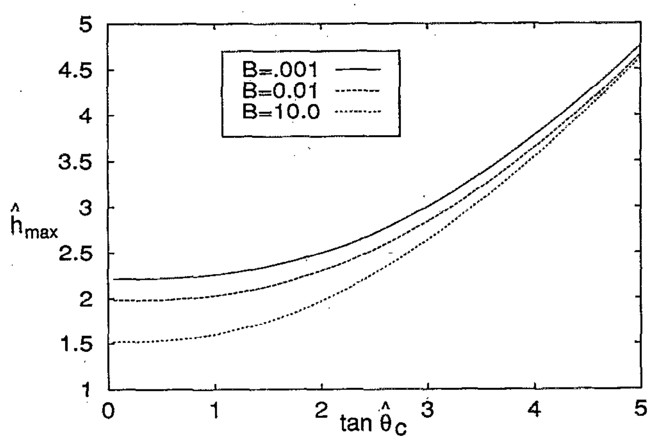

FIG. 4. Maximum coating thickness versus contact slope for several values of B and $\alpha=2$.

For $\alpha>1$, corresponding to a power-law liquid, the force on the substrate between the contact point $x=0$ and $x=-a$, where a is a small distance, is given by

$$F(a)=\int_0^{-a}\tau_{\text{sub}}\,dx=-K\left(\frac{(\alpha+2)U}{\tan\,\theta_c}\right)^{1/\alpha}\frac{a^{1-1/\alpha}}{1-1/\alpha}. \tag{17}$$

Note that the shape of the liquid surface in the contact region has been approximated simply as $h=-x\tan\theta_c$. For the Newtonian case, $\alpha=1$, the force F is clearly singular, thus exhibiting the well-known impossibility of moving a contact line unless the no-slip condition is relaxed.

Because the shear stress in the liquid goes to infinity at the contact point, the effective viscosity of the power-law liquid goes to zero there. (Note that the local Reynolds number also goes to zero, as $h^{1/\alpha}$.) Hence, we can retain the no-slip boundary condition in the vicinity of the moving contact line, while still allowing the contact line to move on the substrate. Note that the fluid must obey a power-law shear-thinning law at high shear rates; a fluid exhibiting a Newtonian plateau at high shear rates will retain the force singularity.

It has been reported that some nominally Newtonian fluids exhibit shear-thinning behavior at high shear rates.[13,14] It is not clear whether such viscosity reductions are due to a modification of the liquid structure, as is characteristic of complex fluids, or are merely caused by viscous heating. Most liquids exhibit a decrease in viscosity with increasing temperature, and the observed shear thinning at high shear rates may be due to temperature effects. But the preceding analysis is valid regardless of the mechanism that causes the shear thinning. In fact, if the viscosity is assumed to have power-law dependence on temperature, it is possible to show that the power-law index relating the viscosity to the temperature is identical to the power-law index relating viscosity to shear stress.

Compare the variation in viscosity with position, in the contact region, for two cases: (i) a shear-thinning liquid and (ii) a nominally Newtonian, nonevaporating liquid, whose viscosity decreases with increasing temperature. In the first case, it follows immediately from Eq. (13) that

$$\eta\sim K(h/U)^{(\alpha-1)/\alpha}, \tag{18}$$

as $h=h(x)\to 0$, and η may be interpreted as a layer-averaged viscosity.

For the Newtonian liquid, viscous work is assumed to adiabatically heat the liquid and the energy balance, per unit volume, is

$$\frac{D}{Dt}(c_pT)=\mathbf{V}\cdot\boldsymbol{\nabla}(c_pT)\sim\tau u_y, \tag{19}$$

where c_p is the specific heat. Again, interpreting quantities in a layer-averaged sense, (19) may be rewritten as

$$c_pU\frac{dT}{dx}\sim c_pU\tan\,\theta_c\frac{dT}{dh}\sim\eta\frac{U^2}{h^2}. \tag{20}$$

Assume that the viscosity-temperature law is of the form

$$\eta\sim C/T^{\delta-1}, \tag{21}$$

for large temperature, where C is a constant and $\delta>1$. Replacing T in favor of η in (20) and integrating readily yields

$$\eta\sim(h/U)^{(\delta-1)/\delta}. \tag{22}$$

The two cases are essentially identical, provided that $\delta=\alpha$. Since the temperature dependence in (21) can, in principle, be determined by macroscopic measurements, δ could be used as an *a priori* estimate of the shear-thinning exponent for the present purpose.

V. CONCLUSION

We have considered the progression of a uniform coating layer draining down a previously dry, vertical substrate. If the coating liquid is shear thinning, it is possible to retain the no-slip boundary condition at the front while still allowing for contact line motion. When the advancing contact angle is small, we have used lubrication theory to derive an expression for the speed of the advancing front and a differential equation for the profile of the front. The speed and shape of the front are functions of the physical properties and rheological parameters of the liquid, the upstream coating thickness, and the advancing contact angle.

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