From *Advances in Coating and Drying of Thin Films*, F. Durst & H. Raszillier, Eds., Shaker Verlag, Aachen, 1999.

Modeling Thin Layer Flows with Strong Surface Tension Gradient Effect

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Summary

Dramatic changes in flow behavior can be caused by nonuniformity in surface tension. We present results of a theoretical and numerical study of several flows where this nonuniformity is due to the presence of surfactant. Surfactants find general use in the coating and chemical process industries, food and personal care products, pharmaceuticals, agrochemicals and elsewhere. Their presence at interfaces can cause large shearing, or Marangoni, stresses during flow, because of developed gradients in concentration. We discuss both two and three dimensional unsteady flows. These are (i) leveling of a coating in the presence of an initially uniform distribution of surfactant, (ii) drainage of a vertical soap film, and (iii) flow behavior caused by a concentrated "bolus" of surfactant. This last example illustrates the mechanism responsible for "crater" formation in drying paint layers.

1. Anomalous behavior during leveling

Surfactants are polar molecules that locate themselves preferentially on material interfaces and lower the surface tension there by their presence. Because of resulting surface tension gradients, they strongly influence wetting and spreading behavior of thin liquid films. They have beneficial effects in many industrial processes. Particles of dust that fall on the surface of a freshly applied liquid coating layer behave in a similar fashion. Because surface tension is the principal agent responsible for leveling of the irregularities in an applied coating, the presence of dust is generally undesirable and extreme cleanliness is often maintained during coating operations. We present a model for flow in thin liquid films when surfactant is included. We will show that, under certain circumstances, a surprising effect may appear. It can happen that, assuming that environmental contamination cannot be reduced past a certain level, that adding additional "dust" can actually improve leveling. Here we only give results of a linear analysis[1]; numerical studies using unsteady lubrication theory and finite element solution of the unapproximated Stokes flow problem confirm the effects.[1,2]

We consider the leveling history of an initial sinusoidal free surface of wavenumber k bounding a two-dimensional thin liquid layer. The characteristic thickness is the average thickness h_0 and $1/k$ is the characteristic substrate length. The reference time is $T^* = 3\mu/(\sigma_0 h_0^3 k^4)$ which is the characteristic leveling time for a thin liquid layer with a slightly-perturbed clean surface.

The lubrication approximation is obtained by a systematic expansion in the assumed small parameter $h_0 k$. Using the characteristic quantities to form dimensionless variables, the resulting equations for surface concentration c, layer thickness h, and surface velocity $u^{(s)}$ become

$$c_t + (u^{(s)}c)_x = \Delta\, c_{xx} + O(h_0 k)^2, \tag{1}$$

$$h_t = -\left(h^3 h_{xxx}\right)_x + \frac{R}{2}\,\left(h^2 c_x\right)_x, \tag{2}$$

$$u^{(s)} = \frac{3}{2} h^2 h_{xxx} - Rhc_x. \tag{3}$$

The two parameters that appear in the model are

$$R = \frac{3\Gamma}{\sigma_0 h_0^2 k^2}, \qquad \Delta = k^2 D T^*. \tag{4}$$

where D is the surfactant diffusion coefficient and $\Gamma = -d\sigma/dc$.

The lubrication model may be further simplified by ignoring diffusion and by assuming that the thickness and concentration variations are small and sinusoidal with amplitudes $\alpha(t)$ and $\gamma(t)$ which may be found in closed form. For the initial conditions $\alpha(0) = a_0/h_0,\ \gamma(0) = 0$, All sinusoidal ripples will ultimately decay. For small surfactant effect $R \ll 1$, an approximate ripple amplitude expression is

$$\alpha/(a_0/h_0) = (3/4)R + O(R^2 t) + \ldots + \exp(-t) + \ldots. \tag{5}$$

Thus $(3/4)R$ is a residual amplitude that persists for long times. For large amounts of surfactant $R \gg 1$,

$$\alpha/(a_0/h_0) = \exp(-t/4)\left[1 - 3/(4R) + O(1/R^2)\right]. \tag{6}$$

Because of the residual amplitude, the two curves will cross, indicating that more surfactant will yield a smaller amplitude for a long period during drying. When R is small, the decay history is initially similar to the clean surface result at small times. However, leveling is always slower than if the surface were clean because surfactant is carried away from the crest by the pressure-driven flow. The lower concentration near the crest results in a surface traction that opposes leveling. As can be seen from (5), this effect is compounded until, at larger times, the amplitude decays to a plateau value that can be expected to persist until times t/T^* that are order $1/R$. On the other hard, if R is very large, the decay rate is seen to be one-quarter of the clean surface value, to leading order. This is exactly the result that would have been expected had the no-slip condition been imposed on the free surface. The surfactant-induced surface traction quickly reduces the surface velocity to small values. This phenomenon has been observed experimentally and is sometimes referred to as surface "hardening."

2. Draining flow in soap films

Soap films, because of their relative simplicity since substrate influence is absent, represent a good "test bed" to ascertain fundamental mechanisms of surfactant efficacy.

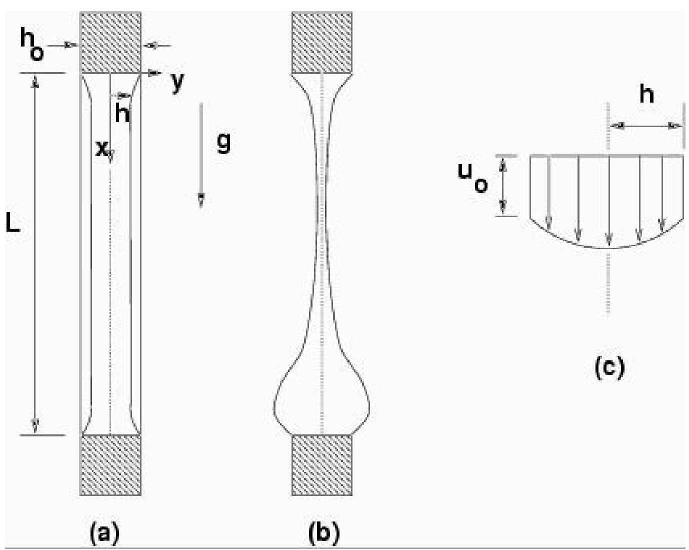

Figure 1: Definition sketch for (a) the initial state of a soap film held vertically between upper and lower supports for two different initial profile shapes. (b) Sketch of the soap film at a later time showing gravity drainage. (c). The downward velocity profile is a linear combination of a slug flow at the interface slip velocity U_0 and a parabolic shear flow.

Using a rigorous asymptotic analysis, we have derived a mathematical model to describe the flow in a vertical soap film that is draining under gravity, assuming two-dimensional motion.[3] A schematic diagram of the flow problem is shown in Fig. 1. The model yields three coupled partial differential equations for the film half-thickness $h(x,t)$, the surface concentration $G(x,t)$ of an assumed insoluble surfactant, and the slip or surface velocity $U_0(x,t)$. In dimensionless form these equations are

$$h_t = -\left[U_0 h + h^3(B_1 + h_{xxx} + A\,\Pi_x)\right]_x \quad , \tag{7}$$

$$G_t = -(U_0 G)_x + D G_{xx} \quad , \tag{8}$$

$$(hU_{0x})_x = C\left[G_x - h(B_1 + h_{xxx} + A\,\Pi_x)\right] \quad . \tag{9}$$

Here U_0 is a surface slip velocity, B_1 is a scaled Bond number representing the gravitational driving force and $\Pi[h(x,t)]$ is a disjoining-conjoining pressure functional that admits very thin stable "black" films. Unlike the leveling problem treated above, the surface velocity must be found as the simultaneous solution of the additional coupled equation (9).

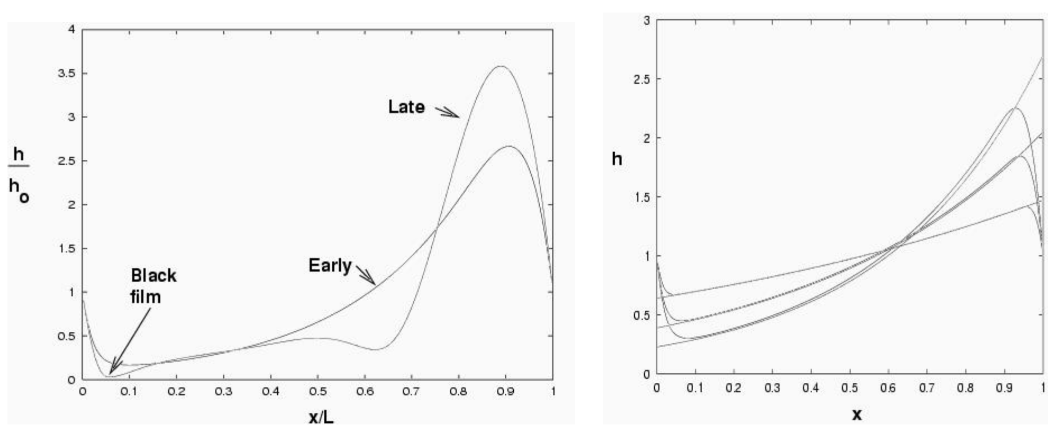

Figure 2: (Left) Computed dimensionless film profiles at early and late times for an initially uniform soap film $h(x,0) = h_0$. Gravity acts in the positive x direction. The early time profile shows a characteristic "hollow ground" shape. The late profile shows a "black" film region, followed by a parabolic profile and a growing blob near the bottom support. (Right) The same calculation without surfactant. Calculated profiles (solid) are compared with the extensional-flow similarity solution (10) (dashed) at early times.

While the model uses a simplified picture of the relevant physics, it appears to capture observed soap film shape evolution over a large range of surfactant concentrations. The model predicts that, depending on the amount of surfactant that is present, the film profile will pass through several distinct phases. These are (i) rapid initial draining with surfactant transport and characterized by a concave-out profile, (ii) slower draining with an almost immobile interface due to surface tension gradient effect, and (iii) eventual formation of black spots at various locations on the film. These features are all observed in the experiments of Mysels *et al.*[4] This work is relevant to basic questions concerning surfactant efficacy as well as specific questions concerning film and foam draining due to gravity. These issues arise, for example, in process modeling for the manufacture of dry foam products.

A time-dependent calculation showing transition from a mobile to a hard soap film, using the model, is shown in Fig. 2. A small black film is seem to develop near the top. At early times, the concave-out profile corresponds to pure extensional flow before surface tension gradients become operative. Using a Lagrangian description of the motion, we have found a similarity solution for this case of the form

$$\frac{h}{h_0} = \left(\frac{kL_0t}{e^{kL_0t} - 1} \right) \, e^{ktx} \, . \tag{10}$$

Here L_0 is the length of the film between supports and $k = \rho g/(4\mu)$. Aside from "boundary layers" near the end supports, (10) is a good model at early times, as shown in the figure.

3. Wetting and spreading behavior with concentrated surfactant

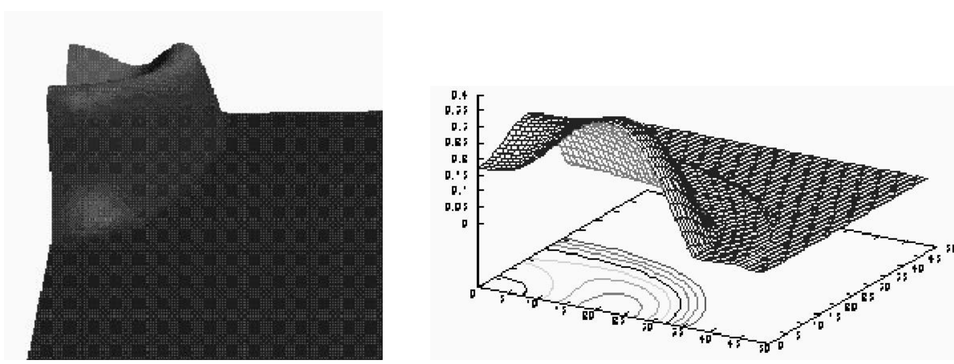

Figure 3: Frames from an unsteady simulation where a bolus of concentrated surfactant is placed near the center of a drop that is spreading on a thin layer of the same liquid. Strong surface tension gradients cause the drop to spread much more quickly that it would without the bolus. Early time ridge development (left). Shape at a later time (right) shows development of a precursor layer.

This study is relevant to wetting agents and detergency. We believe the static viewpoint, wherein surfactants are thought to aid spreading simply by lowering the equilibrium surface tension, is, at best, an incomplete explanation. We consider the fluid dynamical mechanisms by which surfactants influence wetting and spreading behavior on a solid substrate.

We model droplet motion, with insoluble surfactant, on a thin wetting layer of the same liquid. The simulation is quasi-three dimensional in space and the previous equations can be generalized to yield equations for $h(x, y, t)$ and the other dependent variables.[5] Efficient numerical algorithms, of alternating direction implicit type,[6] can be constructed for these thin-layer flows. We consider the time-dependent three-dimensional motion of an initially ellipsoidal drop. A concentrated spot or *bolus* of surfactant is placed at the drop center. Virtually instantaneously a ridge is formed (Fig. 3), due to strong Marangoni effect, at the edge of the surfactant bolus. At a later time a precursor layer is visible ahead of the apparent contact line. This precursor has been observed experimentally. The developed indentation in the drop is analogous, we believe, to the craters that are formed in drying paint layers due to contamination.

Strong surface tension gradients can also result from other causes including compositional changes during drying and spatial temperature gradients. A companion paper in this volume, *Theoretical and Numerical Modeling of Coating Flow on Simple and Complex Substrates including Rheology, Drying and Marangoni Effects*, treats these effects and gives results of other three-dimensional calculations.

This work is supported by the ICI Strategic Research Fund, The State of Delaware, and the NASA Microgravity Program.

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