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An Analysis of the Effect of Surfactant on the Leveling Behavior of a Thin Liquid Coating Layer

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A linear analysis, employing the lubrication approximation, is presented for the leveling history of a thin layer of Newtonian liquid. When the surface tension is taken to be constant, the classic result of Orchard is reproduced. As expected, the presence of surfactant, with resulting surface-tension-gradient forces, slows the rate of leveling of an initial train of periodic ripples. For very weak surfactants, initial leveling rates are unaffected, but ripple amplitude can be lowered only to a "plateau" level which persists for long times. Surprisingly, critical surfactant concentrations exist, depending on other system parameters such as the coating thickness and ripple wavelength, for which leveling is maximally retarded. To the extent that this retardation is generally undesirable, it is suggested that these critical values be avoided, even by increasing the amount of surfactant present. This anomalous effect is maximized for an assumed nondiffusing, insoluble surfactant and is mitigated by either surface or bulk diffusion of surfactant.

1. Introduction

Thin-film fluid flows are important to a wide range of industrial processes and products as well as to phenomena in the natural world. The coating industry, for example, is a multibillion dollar activity, worldwide. Commonly, it is desirable for a multicomponent liquid film to achieve a spatially uniform coating thickness as it dries. Thus the theoretical prediction of the leveling history of an initially rippled liquid surface is a problem of significant interest.

Surface tension is the principal agent responsible for the leveling of short-wavelength undulations (for example, see Landau and Lifshitz¹). A freshly applied liquid film normally has an uneven surface. When surface tension can be considered to be uniform, capillary forces tend to reduce surface irregularities to produce a level film. A linear theory involving the use of the lubrication assumption, proposed by Orchard,² predicts the rate of leveling and has met with considerable practical success. However, the condition of uniform surface tension may not be met during the course of film formation, due to several causes: (i) differential evaporation of solvent or cosolvent, (ii) thermal gradients, (iii) diffusion to the surface of low surface energy material, (iv) deposition of contaminants, or (v) dissolution of entrapped gas bubbles. Under such circumstance, surface flow from regions of low surface tension toward regions of high will occur. This creates a shear stress tangential to the liquid surface, producing a subsurface flow.

Flows with surface-tension-gradient effects are often termed "Marangoni flows." Kornum and Nielsen³ attribute a number of observed defects in dry coating layers to Marangoni effects. Overdiep⁴ and others considered surface-tension-gradient effects which arise from com-

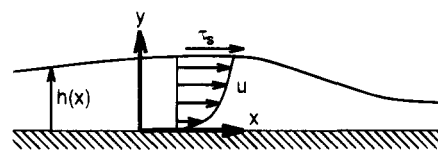


Figure 1. Nomenclature and coordinate system.

positional changes in the bulk liquid as it dries. They demonstrate that such compositional changes can result in both enhanced leveling and deleveling of the coating layer. In this paper, we analyze the time history of a two-dimensional coating layer of nonevaporating Newtonian liquid of constant viscosity. There is an assumed surface layer of contamination which convects, diffuses, and is also subject to material transfer to and from the bulk coating layer. The local surface tension is a function of the surface concentration of contaminant. Both capillary pressure due to surface curvature and the local surface tension gradient contribute to the fluid motion. The output quantities of interest are the layer thickness $h(x,t)$ (here x is the spatial coordinate and t is time), the surface tension $\sigma(x,t)$, and the surface concentration $c(x,t)$.

Section 2 presents the mathematical model, written in standard physical units, with a brief discussion of its origin. A linearized model is developed in section 3. By assuming that surface irregularities are small, it is possible to represent the unknown quantities as the solution of a coupled system of linear partial differential equations in space and time. This simplified system is solved in closed form, and results are presented graphically in terms of dimensionless quantities. For clarity, a set of physically realistic parameter values is suggested to lead to typical values of these dimensionless quantities.

2. The Mathematical Model

Figure 1 shows a thin layer of liquid on an impermeable horizontal substrate and the orientation of the (x,y) coordinate system. $h(x,t)$ is the layer thickness to be determined. A typical velocity profile $u(x,y)$ is also shown obeying the no-slip condition on the substrate.

The flow of Newtonian liquids is governed by the vector Navier-Stokes equation. Under the assumptions that the

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† Abstract published in *Advance ACS Abstracts*, September 1, 1995.

(1) Landau, L.; Lifshitz, E. M. *Fluid Mechanics*; Pergamon: Oxford, 1959.

(2) Orchard, S. E. *Appl. Sci. Res. A* **1962**, 11, 451.

(3) Kornum, L. O.; Raashou Nielsen, H. K. *Prog. Org. Coat.* **1980**, 8, 275.

(4) Overdiep, W. S. *Prog. Org. Coat.* **1986**, 14, 159.

fluid layer is thin, the motion is slow, and the free-surface is almost parallel to the substrate, the governing equation may be approximated as

$$-p_x + \mu u_{yy} = 0 \quad (1)$$

Here subscripts signify partial differentiation, μ is the viscosity, and p is the pressure. Equation 1 is the basis of the so-called lubrication theory. Because of the thinness of the liquid layer, $p = p(x, t)$ only, and, assuming μ is also independent of y , (1) can be integrated immediately to give a parabolic velocity profile in y . The stress at the free surface is equal to the surface tension gradient,¹

$$\tau_s = \sigma_x \quad (2)$$

The total flux at any x position is given by

$$Q = \int_0^h u \, dy$$

and, using (1), (2), and the relation $\tau = \mu u_y$, it can be written as

$$Q = \sigma_x h^2/(2\mu) - p_x h^3/(3\mu) \quad (3)$$

The pressure in the layer, relative to the air above, may be written as

$$p = \rho g(h - y) - \sigma h_{xx} \quad (4)$$

where ρ is the liquid density and g is the acceleration of gravity. The free-surface curvature has been approximated by h_{xx} , which is consistent with the small-slope assumption. The presence or absence of the gravity force is irrelevant to the phenomena considered here, because the ripple wavelength will be considered small, and will henceforth be neglected. Thus the orientation of the substrate relative to the direction of gravity is also irrelevant. Eliminating p by differentiation of (4) and substitution in (3) yields

$$Q = \sigma_x h^2/(2\mu) + \sigma h^3 h_{xxx}/(3\mu) + \sigma_x h_{xx} h^3/(3\mu) \quad (5)$$

The flux Q is related to the surface height h , for the assumed nonevaporating liquid, by

$$h_t = -Q_x \quad (6)$$

which is the mass conservation law.

We assume a surface concentration of surfactant c . The quantity c is considered to be dimensionless. The surfactant concentration changes by surface stretching, convection, and diffusion. Thus

$$c_t + (u^{(s)}c)_x = Dc_{xx} + D_b(c_b - c) \quad (7)$$

Here D is the surface diffusion coefficient while the bulk diffusion coefficient D_b controls transfer of surfactant to and from the bulk liquid when the local surfactant concentration differs from the reference value c_b . Since movement of surfactant to and from the bulk liquid is assumed to be small, c_b , which is proportional to the bulk concentration of surfactant, is taken to be constant. [A more complicated model, including diffusional motion of surfactant within the bulk of the liquid, is discussed by Levich.⁵] c_b and the initially uniform value of c may each be taken equal to 1, without loss of generality, since surface

motion depends only on relative values of c . In general the velocity distribution within the layer is given by

$$u(x, y, t) = (\sigma_x/\mu)y + p_x/(2\mu)(y^2 - 2hy)$$

Thus the surface velocity $u^{(s)} = u(y=h)$ is

$$u^{(s)} = -p_x h^2/(2\mu) + \sigma_x h/\mu \quad (8)$$

The surface tension variation is due to changes in surface concentration c according to the linear law

$$\sigma = \sigma_0 + \Gamma(1 - c) \quad (9)$$

Thus initially the surface tension is σ_0 . In general Γ will be a positive number. If the liquid surface had been completely clean, i.e. $c = 0$, the surface tension would have been equal to $\sigma_0 + \Gamma$; thus Γ , measured in the same units as σ , is the reduction in surface tension due to the presence of an assumed uniform layer of surfactant.

Combining (4), (5), (6), and (9) gives the evolution equation for the profile

$$h_t = -1/(3\mu)[h^3(\sigma h_{xx})_x] + \Gamma/(2\mu)(h^2 c_x)_x \quad (10)$$

while the equation for surfactant concentration is

$$c_t = -1/(2\mu)[ch^2(\sigma h_{xx})_x] + (\Gamma/\mu)(hcc_x)_x + Dc_{xx} + D_b(1 - c) \quad (11)$$

Equations (9)–(11), subject to appropriate initial and boundary conditions, constitute the full mathematical problem.

3. A Linearized Theory

Physical insight into the basic interactions can be obtained from a simplified theory, based on the assumption that the coating layer is almost flat, with the average value $h = h_0$, and the surfactant concentration differs only slightly from one; thus,

$$c = 1 + C$$

$$h = h_0(1 + H)$$

We will neglect terms of quadratic order C^2 , H^2 , and CH . The simplified evolution equations become

$$H_t = -\left(\frac{\sigma_0 h_0^3}{3\mu}\right)H_{xxxx} + \left(\frac{\Gamma h_0^2}{2\mu}\right)C_{xx} \quad (12)$$

$$C_t = -\left(\frac{\sigma_0 h_0^3}{2\mu}\right)H_{xxxx} + \left(\frac{\Gamma h_0^2}{2\mu}\right)C_{xx} + DC_{xx} - D_b C \quad (13)$$

For assumed initial sinusoidal ripples of wavenumber k , we separate variables according to

$$H = \alpha(\tau) \cos kx$$

$$C = \gamma(\tau) \cos kx$$

and introduce a dimensionless time variable by the substitution

$$t = T^* \tau$$

where the characteristic time T^* is

(5) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, N.J., 1962.

$$T^* = \frac{3\mu}{\sigma_0 h_0^3 k^4} \quad (14)$$

The resulting coupled system is

$$\alpha_\tau = -\alpha - (R/2)\gamma \quad (15a)$$

$$\gamma_\tau = -(3/2)\alpha - (R + \Delta)\gamma \quad (15b)$$

where

$$R = \frac{3\Gamma}{\sigma_0 h_0^2 k^2} \quad (15c)$$

and

$$\Delta = k^2 D T^* + D_b T^* \quad (15d)$$

The dimensionless parameters R and Δ represent the "strength" of the surfactant and its effective diffusivity, respectively. Also apparent from (15d) is the relative importance of surface diffusion versus diffusion from the bulk, D_b . For longer waves, i.e. small k , bulk diffusion dominates, while surface diffusion is most importance for short-wavelength undulations. The initial conditions are

$$\alpha(0) = a_0/h_0 \quad \gamma(0) = 0 \quad (16)$$

where a_0 is the semiwave amplitude of the initial sinusoidal undulation. The system (15) is treated by assuming a solution of the form $\exp(\omega t)$ for each unknown. The two eigenvalues $\omega_{1,2}$ satisfy the quadratic equation

$$4(\omega + 1)(\omega + R + \Delta) - 3R = 0$$

and are given explicitly as

$$2\omega_{1,2} = -(1 + R + \Delta) \pm [(1 + R + \Delta)^2 - R - 4\Delta]^{1/2} \quad (17)$$

where, for definiteness, ω_1 corresponds to the negative root. For physically realizable cases, R and D are non-negative and the two roots are negative, real, or zero. Thus all sinusoidal ripples will ultimately decay. Applying the initial conditions (16), the full solution is

$$\alpha/(a_0/h_0) = \exp(\omega_2 \tau) + [(\omega_2 + 1)/(\omega_2 - \omega_1)][\exp(\omega_1 \tau) - \exp(\omega_2 \tau)] \quad (18a)$$

$$\gamma/(a_0/h_0) = [(3/2)/(\omega_2 - \omega_1)][\exp(\omega_1 \tau) - \exp(\omega_2 \tau)] \quad (18b)$$

4. Graphical Results

A typical set of values for liquid coatings is

$$\begin{aligned} \mu &= 10 \text{ poise} \\ \sigma_0 &= 30 \text{ dyn/cm} \\ h_0 &= 0.2 \text{ mm} \\ \lambda &= 2\pi/k = 1.0 \text{ cm} \end{aligned} \quad (19)$$

For these values, we then have characteristic time

$$T^* = 80.4 \text{ s}$$

and surfactant strength parameter

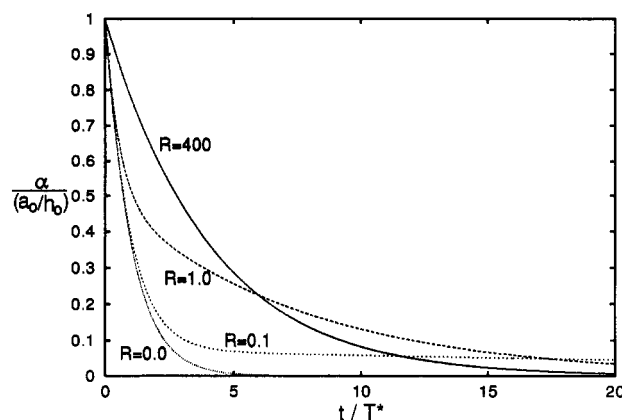


Figure 2. Dimensionless ripple amplitude versus time $\tau = t/T^*$ for various values of surfactant strength R . Here diffusion is ignored corresponding to $\Delta = 0$.

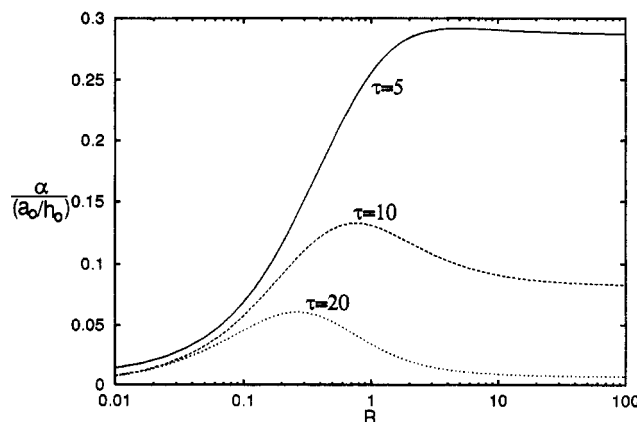


Figure 3. Dimensionless ripple amplitude versus surfactant strength at various times $\tau = t/T^*$. Diffusion is ignored.

$$R = 190(\Gamma/\sigma_0)$$

For relatively weak surfactants, R may be expected, therefore, to take on values perhaps in the range between 0.2 and 20. In order to satisfy the linearization criterion used here, a_0/h_0 must also be small, restricted perhaps to values less than 0.25.

A gross approximation for an actual liquid coating that dries is to ignore compositional changes, with consequent increase in viscosity, and loss of material by evaporation. Qualitative estimates of leveling behavior are given by simply identifying a "drying time" and inferring the extent of leveling from the values of α shown below. It is, in fact, possible to remove many of the restrictions inherent in the present linearized analysis by use of the numerical approach given in Schwartz and Eley.⁶ There a two-component liquid, with one phase volatile, is considered with viscosities that depend on local composition. Neither the shape nor the amplitude of the initial surface is constrained in that approach, except for the small-slope approximation inherent to lubrication theory. We are confident, however, in the robustness of the phenomena presented here and expect similar effects in the more complete model.

The figures below are calculated using (18). Figure 2 shows ripple amplitude $\alpha/(a_0/h_0)$ versus time t/T^* for a range of values of R . For this figure, as well as Figures 3 and 4, diffusional effects are ignored, i.e. $\Delta = 0$. The curve for $R = 0$ is simply given by $\exp(-t/T^*)$ which is Orchard's solution in the present notation. Two interesting features are apparent for the other cases:

(6) Schwartz, L. W.; Eley, R. R. *Prog. Org. Coat.*, in press.

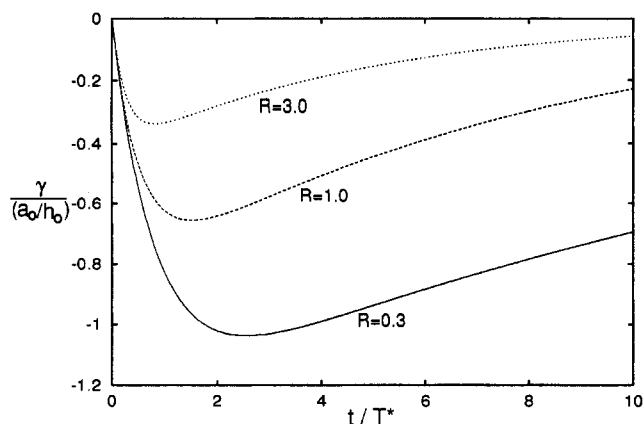


Figure 4. Fractional change in surfactant concentration at crest, $\gamma/(a_0/h_0)$, versus time $\tau = t/T^*$. Diffusion is ignored.

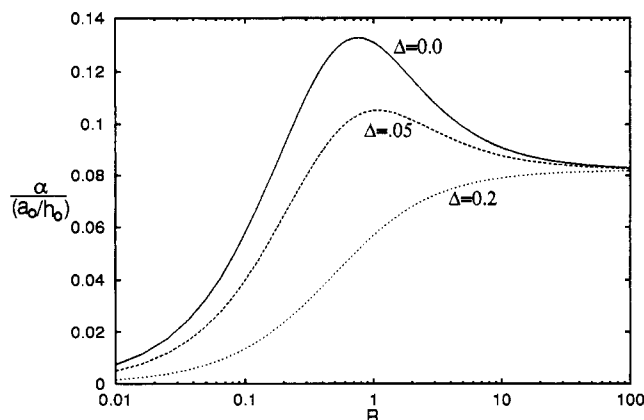


Figure 5. Dimensionless ripple amplitude versus surfactant strength at $\tau = 10$ for various values of the diffusion parameter Δ .

(i) For $R = 0.1$ we note that early leveling behavior is similar to the $R = 0$ case. However at later times, the ripple amplitude appears to plateau at a small nonzero value. This effect is easily seen analytically by expanding (18a) for $R \ll 1$ to yield

$$\alpha/(a_0/h_0) = (3/4)R + O(R^2\tau) + \dots + \exp(-\tau) + \dots \quad (20)$$

Thus the plateau value may be expected to persist until times t/T^* that are order $(1/R)$.

(ii) Note that the curves for nonzero values of R cross one another. Thus, at a given time, the expected ripple height is not a monotonic function of R . Therefore decreasing the strength of the surfactant will not necessarily cause a reduction in ripple amplitude. For large values of R , in fact, the actual value of R becomes unimportant, as is evident by expanding (18a) for $R \gg 1$,

i.e.

$$\alpha/(a_0/h_0) = \exp(-\tau/4)[1 - 3/(4R) + O(1/R^2)] \quad (21)$$

In the large R limit, the decay time is seen to be 4 times the Orchard value.

The second effect is illustrated more clearly in Figure 3, where $\alpha/(a_0/h_0)$ is plotted versus R for several values of the time. For $\tau = 10$, for example, a maximum ripple height occurs near $R = 1$. For $\tau = 20$, the ripple maximum is found at a smaller value of R . Note that, compared to this amplitude, the amplitude can be reduced by a large factor by increasing, rather than reducing, the surfactant strength.

The reason for the anomalous role of surfactant becomes apparent in Figure 4. The reduction in relative concentration at the crest, $\gamma/(a_0/h_0)$ from (18b), is plotted versus time for three values of R . For the larger values of R , the maximum reduction in γ occurs at earlier times, after which the magnitude of γ decreases. The cumulative counterflow, up to a given time, produced by the developed surface tension gradient, may thus be greater for smaller values of R .

The final figure considers the role of diffusion. Here $\alpha/(a_0/h_0)$ is plotted versus R for $\tau = 10$ and three different values of Δ . The curve for $\Delta = 0$ is identical to the one shown in Figure 3. The other two curves for $\Delta = 0.05$ and 0.2 correspond to characteristic diffusion times equal to $20T^*$ and $5T^*$, respectively. For $\Delta = 0.05$, the anomalous effect is reduced, while for $\Delta = 0.2$, it is effectively eliminated. Diffusion times for actual surfactants may be expected to include a wide range of values (see, for example, Sakata and Berg⁷).

5. Conclusion

Using a simple model, it has been demonstrated that ripple leveling is minimized for certain critical values of surfactant. This retardation is generally undesirable and it is suggested that these critical values be avoided, even by increasing the amount of surfactant present. In other cases, surface-tension-driven flow phenomena are themselves undesirable. One example is the tendency for a coating on an object with sharp outside corners to flow away from these corners, leaving unacceptably thin final layers at these places. In situations such as the latter, maintaining the surfactant at critical values that are compatible with the drying time may be expected to cause some desirable thickening of the final dry coating.

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LA950254B

(7) Sakata, E. K.; Berg, J. C. *Ind. Eng. Chem. Fund.* **1969**, 8 (3), 570.