Leveling of a Film with Stratified Viscosity and Insoluble Surfactant

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The evolution of a film with insoluble surfactant on a wavy horizontal wall differs from flow without surfactant (the way it usually is studied) in that the film passes through different stages. The first stage is as if the surfactant were absent. Once the surface tension gradient—induced by the nonuniform surfactant concentration adsorbed at the free surface—starts resisting the flow effectively, the evolution enters a transitional stage. A final stage is reached once the free surface becomes rigid due to the surface-tension gradient (high elasticity limit) or becomes virtually leveled before the surface-tension gradient is released (low elasticity limit). The velocity profile through the film changes with time, so fluid is depleted or accumulated at different strata in the film as the flow evolves. The velocity profile and resulting deformations throughout the film can be influenced significantly by the viscosity distribution or stratification, which occurs, for example, when multiple layers of different viscosity are coated simultaneously. A model and applications for the leveling of such a film are presented. The evolution is described in general terms for a film of uniform viscosity and for a film of two discrete layers of different viscosity. Then the three limiting cases are established. For two of these limits, the effect on the exponential decay rate of the flow and the deformation of the different strata or layers is examined when the viscosity is changed in an infinitesimally thin layer or stratum, and in a layer of finite thickness in films of two and three discrete layers.

Introduction

In the manufacture of photographic film, coated layers that are sensitive to light are applied to the paper or plastic backing or support of a photograph or roll of film. It is important that these layers be uniform in thickness; otherwise the variations in thickness can be transferred to the developed images as changes in intensity of colors that are foreign to the image taken, and therefore undesirable. Usually several of these layers are coated simultaneously on the support in liquid form, each layer having a different viscosity. Unless the support is completely flat, the coated film flows either until it is immobilized by a drying or setting process or until the free surface flattens or levels, which may occur if the support is placed horizontally. The flow induced by leveling affects each layer's thickness differently, depending on the layer's thickness, viscosity, and position within the coating. Furthermore, certain layers are more sensitive to variations of uniformity than others. Thus the importance of determining the effect that thickness and viscosity of different layers have on the uniformity of a coating that is leveling.

This article deals with the problem of leveling of films of stratified viscosity (including films with discrete layers of uniform viscosity) on a wavy horizontal wall with an insoluble surfactant adsorbed at the free surface. The film's thickness is initially uniform, so its free surface is wavy too and starts to flow under the influence of surface tension and gravity. The distribution of viscosity throughout the film is arbitrary except that it is stratified, so that all cross sections of the film contain infinitesimal layers or strata of the same viscosity arranged in the same order. This structure includes films of multiple layers of different viscosities applied to horizontal substrates. During the leveling process, the liquid will redistribute itself along the wall, thinning in areas where the free surface is high and thickening where it is low. The velocity profiles that develop early on through the film cause the free surface to extend in some areas and compress in others. This deformation of the free surface creates nonuniformities in surfactant's surface concentration, which, in turn, causes surface tension imbalances that modify the original velocity profiles. The rate of flow and the velocity profiles also depend on the stratification of the viscosity throughout the film. The velocity profile is not uniform throughout the film, so the flow is distributed unevenly among the strata. If the film consists of multiple layers, the thickness of some of the layers will be affected more by the leveling process than others.

Although the leveling of thin liquid films on a horizontal surface has been studied for more than three decades now, there have been no articles in the scientific literature addressing the leveling of films, in the presence of surface active materials, with stratified viscosity (or several layers of different viscosity). Early work was motivated by the flow due to brush marks in paint (Orchard, 1962; Dodge, 1972; Degani and Gutfinger, 1974), later by the flow caused by the irregularities in sprayed powder coatings (Anshus, 1973; Keunings and Bousfield, 1987), and more recently by the flow due to nonuniformities such as ribbing at the application point of industrial processes such as the coating of paper (Kheshgi and Scriven, 1983, 1988; Bousfield, 1991). All these papers have assumed that the film was of a single layer; all (except Keunings and Bousfield) have assumed the flow to be Newtonian; and most (except for Kheshgi and Scriven, and Keunings and Bousfield) have assumed that the free surface's disturbance is small compared to the film's thickness and that cross-convective inertia terms are negligible.

The effect of surface-active agents at the free surface of thin films has also been studied for over three decades. These have often been concerned with the instability of a film caused by surface tension gradients induced by diffusion of surfactants or conduction of temperature to the free surface (Pearson, 1958; Brian, 1971). Others have studied the damping of waves caused by surfactants and related it to the free surface dilational modulus (Garrett and Joos, 1976; Lucassen-Reynders, 1981). The surface dilational modulus measures the reaction of a free surface to being extended and compressed by creating a surface tension gradient induced by a surfactant concentration gradient. The modulus is a complex number with the real and imaginary parts called the *surface dilational elasticity* and *viscosity*, respectively. The surface dilational elasticity is the part of the modulus that is recoverable as it opposes the deformation of the surface even after the stresses promoting the surface's deformation have disappeared (like a spring), while the surface dilational viscosity merely resists the deformation of the surface as it occurs (like a dashpot). The comparative magnitudes of the surface dilational elasticity and viscosity depend on the ability of the surfactant to diffuse between the free surface and the liquid bulk in the time scale of the fluid motion (Miller and Neogi, 1985). As the diffusion rate decreases, elasticity increases over viscosity. When the surfactant is insoluble and no diffusion occurs, surface dilational viscosity is negligible compared to the surface dilational elasticity.

Leveling of films of uniform viscosity when surfactants are present has been studied before. Ruschak (1987) applies a surfactant model that includes diffusion of the surfactant between the free surface and the liquid bulk in a study of films excited by sinusoidally traveling pressure waves. Schwartz and Eley (1992) consider the interaction of leveling with soluble surfactant as one of the liquid's components is evaporating.

Films of uniform viscosity are studied by Wang (1981), Pozrikidis (1988), and Smith et al. (1990) as they flow down a slightly wavy incline. While the first two articles predict the steady-state condition, the latter examines the transient and compares theory with experiment. Films of multiple layers of different viscosity have also been investigated for their stability as they flow down an incline (Weinstein and Kurz, 1991) or for their evolution as they are extruded and coated (Anturkar et al., 1990).

A closely related problem to the one treated by this article is leveling of films on flat surfaces, such as occurs after ribbing or chatter waves form as a liquid film is coated onto a support. (The reviews by Ruschak (1985), and Gutoff (1992), describe these phenomena.) The evolution of the flow is identical, except for the deformation of the strata, as they are not initially uniform in this case. As is discussed at the end of the following section, the results of this article can be converted to account for this complication.

Although viscosity stratification has not been addressed in previous studies on leveling, it is experienced by many films (such as paint coatings) in the early parts of the drying process, when the film still can flow and the total fraction of solvent removed is small. During this stage, some solvent is removed by evaporation from the film's free surface without changing its thickness significantly. Within the film, solvent diffuses from the bulk to the free surface, thereby stratifying the concentration of solvent. Viscosity is usually a strong function of solvent concentration, so it is also stratified, and in this case varies continuously both in time and through the film. This article shows that the viscosity stratification can have a significant effect on the overall rate of leveling. Furthermore, while the equations defining solution and some of the applications in this article allow only for variable viscosity stratification, the governing differential equations can be applied when the viscosity also varies with time (and film thickness remains constant).

This problem can easily become very complicated and the competing mechanisms difficult to discern. For this reason, and so that the model's predictions can be readily explained, the approach taken here is to construct the simplest possible model that can account realistically for the combined effects of surfactants and viscosity stratification on leveling of films. First the governing equations and a closed-form solution are developed for the displacement of the free surface, the variation in surfactant surface concentration, and the local deformation of the different strata or layers. Since changes in thickness of individual strata or layers must be studied, the concept of relative deformation of strata or discrete layers is developed. Predictions are then developed for the leveling of films with different surface dilational elasticity formed by one or two discrete layers of uniform viscosity. Many of the observed trends are exploited to develop three limiting cases, two of which are independent of the precise magnitude of the dilational elasticity. When leveling starts, the flow proceeds as if there was no surface elasticity and the deformation of the strata increases with distance from the wall. Later, if the magnitude of the dilational elasticity is sufficiently high, the exponential decay rate is reduced substantially, and the deformation becomes the greatest for the strata near the middle of the film. If the magnitude of the elasticity is sufficiently low, the surface elastic effect becomes dominant only once the free surface is virtually flat, but the deformation of the strata eventually becomes the same as if the elasticity had been high. For the first two limiting cases, the decay rate of leveling and the deformation of the strata or layers are then studied in films or arbitrary viscosity stratification, and in films of two and three discrete layers of uniform but different viscosity. It is shown that, in these limiting cases, the distribution of viscosity throughout the strata determine the decay rate and deformation profile.

Theory

Following are the principal assumptions of the model.

- The thickness of the film and the amplitude of the wall's waviness are much smaller than its wavelength, so the assumptions of long wavelength and linear disturbance apply.
- The flow is sufficiently slow that inertial forces are negligible compared to viscous forces.
- The liquid in the film is at rest, except for the flow induced by the wall's waviness.
- The surfactant is insoluble, and the effect of its surface concentration on the surface tension is described by a constant dilational elasticity.
- The density is uniform and constant throughout the film.
- The viscosity is stratified throughout the film.
- The different strata or layers are miscible, so the interior interfaces do not support surface tension.
- There is no mass transfer between the strata of the film, across its free surface, or to the wall.
- The strata in the film and the surfactant surface concentration are initially uniform.

The irregularities of the substrate are assumed to be sinusoidal and two-dimensional. Less regular surface shapes can always be described as a Fourier series or transform. As Anshus (1973) shows, general three-dimensional disturbances of films can always be reduced to two dimensions. The interface between two layers is defined by an abrupt change in viscosity in the interior of a film. The model does allow for spatially gradual changes in viscosity with distance from the wall, which may be the situation when miscible, multiple layers have been in contact for some time as substances in them (mainly solvents) diffuse between layers. Furthermore, for the derivation of the governing differential equations, the assumption of no mass transfer between the strata is unnecessary as long as the history of the viscosity distribution can be established independently. However, the closed-form solution of the governing differential equations presented in this section requires that the viscosity be constant in time.

Figure 1 introduces the geometry and stratification of the film. Time is given by t, and the subscripts S and W refer to variables at the free surface and the wall, respectively. The wavy lines represent strata or material surfaces of constant viscosity; these are material surfaces along which the viscosity is constant. A stratum is shown inside the film, another at the wall, and a third at the free surface. The horizontal planes represent the average positions of the strata at the time the evolution of the flow is initiated. There are two coordinate systems. The first is a normal Cartesian coordinate system

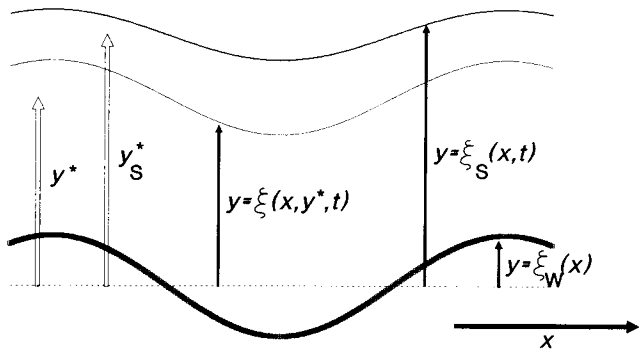

Figure 1. Definition of the coordinate systems.

(x,y) in which the field equations and boundary conditions are expressed. The second is the (x, y^*) pair relating the position of the strata to the first coordinate system: y^* represents the distance between the horizontal plane corresponding to a stratum and the plane at $y = 0$, and $\xi(x, y^*, t)$ is the y-coordinate of that stratum located at the x position along the wall. As $y = \xi(x, y^*, t)$, the differential relationship between y and y^* can be expressed as

$$\frac{\partial(y-y^*)}{\partial y^*} = \frac{\partial(\xi - y^*)}{\partial y^*}. \tag{1}$$

So $\partial(\xi - y^*)/\partial y^*$ represents the local change in distance between two adjacent strata and their average distance, per unit distance. This is similar to the concept of one-dimensional strain used in mechanics of deformable bodies (see, for example, Joos and Freeman, 1958). Thus $\partial(\xi - y^*)/\partial y^*$ defines the deformation of the different strata.

The equations of continuity and momentum in the x- and y-directions are

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{2}$$

$$0 = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right) \tag{3a}$$

$$0 = -\frac{\partial p}{\partial y} - \rho g. \tag{3b}$$

Gravity is included because its role in the leveling process can be more significant than capillarity if the wavelength of the disturbance is sufficiently long. The conservation equation for the surfactant concentration γ adsorbed to the free surface is

$$\frac{\partial \gamma}{\partial t} + \frac{\partial(\gamma u_S)}{\partial x} = 0 \quad \text{at} \quad y = \xi(x, y_S^*, t). \tag{4}$$

All strata are material surfaces, so they obey the following Eulerian kinematic relation (Batchelor, 1967; Melcher, 1981):

$$v = \frac{\partial \xi}{\partial t} + u\frac{\partial \xi}{\partial x}. \tag{5}$$

The boundary condition at the wall is no-slip, while at the free surface the normal and tangential shear stresses depend on surface tension and its surface gradient:

$$u = 0 \qquad \text{at } y = \xi(x, 0, t) \quad (6a)$$

$$p = p_a - \sigma \frac{\partial^2 \xi_S}{\partial x^2} \Bigg/ \left[1 + \left(\frac{\partial \xi_S}{\partial x} \right)^2 \right]^{3/2} \text{at } y = \xi(x, y_S^*, t) \quad (6b)$$

$$\mu \frac{\partial u}{\partial y} = \frac{\partial \sigma}{\partial x} \qquad \text{at } y = \xi(x, y_S^*, t). \quad (6c)$$

Matching conditions are not required at internal interfaces, even when there is an abrupt change in viscosity, because they are properly accounted for by the preceding continuum equations (see especially Eqs. 3a and 5). The surface tension gradient in Eq. 6c is caused by the surfactant concentration gradient; they are related by the surface dilational elasticity:

$$e \equiv \gamma \frac{\partial \sigma}{\partial \gamma}. \quad (7)$$

Because surface tension decreases with increasing surfactant surface concentration, surface dilational elasticity is negative. The initial conditions are:

$$\xi = y + \xi_{1W}(x) \quad \text{at} \quad t = 0 \quad (8a)$$

$$\gamma = \gamma_0 \quad \text{at} \quad t = 0, \quad (8b)$$

where $\xi_{1W}(x) \equiv \xi_W(x)$ is the displacement of the wavy wall from its average position. The subscript 1 indicates that the magnitude of the displacement is small compared to the thickness of the film.

The derivation of the governing differential equations and their solution is quite conventional but rather tedious, so only a detailed outline is given here. The base (or zeroth-order) case occurs when $\xi_{1W} = 0$ in Eq. 8a, so all strata are initially leveled. Then there is no motion ($u = v = 0$), the coordinates y and y^* coincide ($y = y^* = \xi$), the surfactant concentration is uniform ($\gamma = \gamma_0$), and the pressure is hydrostatic, ($p = p_0 + \rho g[y - \xi_S]$). In fact, there are no variations in the x-direction. The first-order approximation arises when the wall's waviness perturbs the flow. Assuming that the waviness $\xi_{1W}(x)$ is sinusoidal with wavelength λ, linear variations in the horizontal direction for all dependent variables are also sinusoidal and expressed by the multiplicand $e^{i2\pi x/\lambda}$.

Table 1 defines the dimensionless variables and parameters. In these definitions, the viscosity adjacent to the wall, μ_W, is used as the representative viscosity. Notice that the dimensionless time τ is the time t divided by the time scale characterizing the leveling process as Ruschak (1987) defines it. The dependent variables are decomposed into the base case (subscript 0) and a perturbation (subscript 0), with the sinusoidal behavior shown explicitly. The parameter Λ is a Bond number based on the sinusoidal wavelength.

Equations 2–8 are nondimensionalized using the preceding definitions and nonlinear terms eliminated. The X dependence is therefore eliminated from the set of equations. Furthermore, to zeroth order, partial differentiation in Y and Y^* are the same because the deformation relationship, Eq. 1, requires that $\partial Y/\partial Y^* = 1 + \partial \Xi/\partial Y^*$ and $\partial \Xi/\partial Y^* \ll 1$. From the momentum equations (Eqs. 3) and boundary conditions, Eqs. 6, relationships for pressure P_1 and velocity U_1 are obtained:

Table 1. Nondimensionalization of Variables

Independent Variables	
	$X \equiv \frac{2\pi}{\lambda} x \quad Y \equiv \frac{y}{y_S^*} \quad Y^* \equiv \frac{y^*}{y_S^*} \quad \tau \equiv \frac{(\rho g)^2 y_S^{*3}}{\sigma \mu_W} \frac{(1+\Lambda^2)}{\Lambda^4} t$
Dependent Variables	
Displacement	$\Xi = Y^* + \Xi_1(Y^*, \tau) e^{iX} \equiv \frac{\xi(x, y^*, t)}{y_S^*}$
Surfactant concentration	$\Gamma = 1 + \Gamma_1(\tau) e^{iX} \equiv \frac{\gamma(x,t)}{\gamma_0}$
x-velocity	$U = U_1(Y, \tau) e^{iX} \equiv \frac{\mu \lambda/2\pi}{\rho g y_S^{*3}} \frac{\Lambda^2}{1+\Lambda^2} u(x,y,t)$
y-velocity	$V = V_1(Y, \tau) e^{iX} \equiv \frac{\mu (\lambda/2\pi)^2}{\rho g y_S^{*4}} \frac{\Lambda^2}{1+\Lambda^2} v(x,y,t)$
Pressure	$P = P_0 + P_1(Y, \tau) e^{iX} \equiv \frac{1}{(\rho g y_S^*)} \frac{\Lambda^2}{1+\Lambda^2} p(x,y,t)$
Parameters	
	Wavelength $\Lambda \equiv \frac{\lambda}{2\pi} \sqrt{\frac{\rho g}{\sigma}}$ Elasticity $E \equiv \frac{e}{\rho g y_s^{*2}} \frac{\Lambda^2}{1+\Lambda^2}$
	Viscosity $M \equiv \frac{\mu}{\mu_W}$

$$P_1 = \Xi_{1S} \quad (9a)$$

$$U_1 = i(-I_1 \Xi_{1S} + I_0 E \Gamma_1), \quad (9b)$$

where the film structure coefficients I_n represent weightings of viscosity distribution from the wall to a point Y:

$$I_n \equiv \int_0^Y \frac{(1 - Y')^n}{M} dY' \quad (10)$$

and n is a positive integer. Notice that, as $0 \le Y \le 1$ and $M > 0$, the inequality $I_n \ge I_{n+1}$ is valid. It can be easily shown that, when the viscosity is uniform ($M = 1$), I_0 and I_1 represent, respectively, a straight line and half a parabola, both equal to zero at $Y = 0$. This coincides with the shape of the Couette and Nusselt velocity profiles. Thus, according to Eq. 9b, in a film with uniform viscosity the free surface disturbance contributes a Nusselt-like component to the velocity profile, and the surfactant disturbance contributes a Couette-like component.

Differentiating the kinematic relation, Eq. 5, with respect to Y, applying the continuity equation (Eq. 2) and the expressions for P_1 and U_1, Eqs. 9, an expression for the rate of change of the deformation, $\partial^2 \Xi/\partial Y \partial \tau$, is obtained.

$$\frac{\partial^2 \Xi_1}{\partial \tau \partial Y} + I_1 \Xi_{1S} - E I_0 \Gamma_1 = 0. \quad (11)$$

Integrating this expression through the film thickness yields the first of two governing differential equations for the evolution of the free surface:

$$\frac{\partial \Xi_{1S}}{\partial \tau} + I_{2S}\Xi_{1S} - EI_{1S}\Gamma_1 = 0. \tag{12a}$$

The second governing differential equation is obtained by inserting the velocity U_1 of Eq. 9b into the surfactant conservation equation (Eq. 4):

$$\frac{\partial \Gamma_1}{\partial \tau} + I_{1S}\Xi_{1S} - EI_{0S}\Gamma_1 = 0. \tag{12b}$$

Equations 12 are essentially those derived by Ruschak (1987) for the case of insoluble surfactant with no pressure excitation, except for the added complication of the stratified viscosity distribution expressed by the structural coefficients I_{nS}. These are the structural coefficients $I_n(Y)$ evaluated at the free surface:

$$I_{nS} \equiv I_n(1) = \int_0^1 \frac{(1-Y)^n}{M} dY = \int_0^1 I_{n-1} dY. \tag{13}$$

The film structure coefficients I_{nS} depend only on the distribution of the relative viscosity $M(Y) \equiv \mu(y)/\mu_W$ throughout the film. The last equality in Eq. 13 is a recursive relationship that is applied in the derivation of Eq. 12a. As is shown in the next section, the relative deformation and decay rate for leveling can be expressed exclusively as combinations of the structural coefficients I_n and I_{nS}. For later reference, therefore, note that if the viscosity in the film is uniform, $I_{nS} = 1/(n+1)$.

The initial conditions in Eqs. 8 become:

$$\Xi_1(Y,0) = \Xi_{1W} \tag{14a}$$

$$\Gamma_1(0) = 0. \tag{14b}$$

Using Eqs. 12, the undifferentiated variables Ξ_{1S} and Γ_1 can be eliminated from Eq. 11 and the resulting expression readily integrated in time τ. Applying the initial conditions, Eqs. 14, yields a relatively simple expression for the deformation of strata, $\partial \Xi_1/\partial Y$:

$$\frac{\partial \Xi_1}{\partial Y} = \frac{I_1 I_{0S} - I_0 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2}(\Xi_{1S} - \Xi_{1W}) + \frac{I_{2S}I_0 - I_1 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2}\Gamma_1. \tag{15}$$

An important property deduced from Eq. 15 is that the deformation depends on the instantaneous disturbances of the free surface and surfactant concentration, and the viscosity distribution through the film, but not on the surface elasticity nor the history of the disturbances.

A useful concept for describing the evolution of leveling throughout the film is relative deformation, which compares the deformation of an infinitesimal layer with the average deformation of the entire film:

$$R \equiv \frac{\partial \Xi_1/\partial Y}{(\Xi_{1S} - \Xi_{1W})/Y_S} = \frac{\partial \Xi_1/\partial Y}{\Xi_{1S} - \Xi_{1W}}. \tag{16}$$

Although R varies with time and stratum in the film, it is independent of the amplitude of the wall's disturbance, so it allows one to compare how strata deform in different portions of the film.

When the film consists of several discrete layers of different viscosity, it is useful to consider the deformation of strata averaged over each discrete layer. To discriminate between layer-averaged and local stratum values, symbols are subscripted with an additional number corresponding to the layer, starting at $i = 1$ for the layer adjacent to the wall, and increasing in number with distance from that wall. Thus the film structure coefficients and the relative deformation of the ith layer are I_{ni} and R_i, respectively.

$$I_{ni} \equiv \frac{1}{Y_i - Y_{i-1}} \int_{Y_{i-1}}^{Y_i} I_n \, dY \tag{17a}$$

$$R_i \equiv \frac{1}{Y_i - Y_{i-1}} \int_{Y_{i-1}}^{Y_i} R \, dY. \tag{17b}$$

The general solution for the free surface perturbations and the deformation of strata is obtained by integrating the differential equations (Eqs. 12), applying the initial conditions, Eqs. 14, and evaluating the deformation relationship, Eq. 15:

$$\Xi_{1S} = \frac{\Xi_{1W}}{2}\left[\left(1 - \frac{I_{2S} + EI_{0S}}{\Delta}\right)e^{-\kappa_1 \tau} + \left(1 + \frac{I_{2S} + EI_{0S}}{\Delta}\right)e^{-\kappa_2 \tau}\right] \tag{18a}$$

$$\Gamma_1 = -\Xi_{1W}\frac{I_{1S}}{\Delta}(e^{-\kappa_1 \tau} - e^{-\kappa_2 \tau}) \tag{18b}$$

$$\frac{\partial \Xi_1}{\partial Y} = \Xi_{1W}\left[-\frac{I_1 I_{0S} - I_0 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2} + \frac{(I_{2S} + EI_{0S} - \Delta)I_1 - 2EI_{1S}I_0}{\Delta(EI_{0S} - I_{2S} + \Delta)}e^{-\kappa_1 \tau} - \frac{(I_{2S} + EI_{0S} + \Delta)I_1 - 2EI_{1S}I_0}{\Delta(EI_{0S} - I_{2S} - \Delta)}e^{-\kappa_2 \tau}\right], \tag{18c}$$

where the following definitions have been used:

$$\Delta \equiv \sqrt{(EI_{0S} + I_{2S})^2 - 4EI_{1S}^2} \tag{19a}$$

$$\kappa_1 \equiv \frac{-EI_{0S} + I_{2S} - \Delta}{2} \tag{19b}$$

$$\kappa_2 \equiv \frac{-EI_{0S} + I_{2S} + \Delta}{2}. \tag{19c}$$

Leveling is a stable process when the film is spread on top of the wavy wall. To demonstrate this, one has to prove that $\kappa_i \tau > 0$ for $i = 1$ and 2. As $E \le 0$ (because $e \le 0$) and $I_{nS} > 0$ (by inspection of Eq. 13 and because $M > 0$), Eqs. 19 show that $\kappa_1 \le \kappa_2$. Thus stability is assured if κ_1 is positive, which can be demonstrated by manipulating Eqs. 19a–19b and applying the inequality $I_{0S}I_{2S} - I_{1S}^2 > 0$, which is a corollary of Eq. 23B in Table 2. Therefore, the free surface's displace-

Table 2. Limiting Solutions

Limit	A: Initial Stage	B: High Elasticity	C: Low Elasticity	Eq.
Term neglected in Eqs. 12	$E\Gamma_1$ in Eqs. 12	$\partial \Gamma_1/\partial \tau$ in Eq. 12b	$\partial \Xi_{1S}/\partial \tau$ in Eq. 12a	
Initial conditions	Eqs. 14	Eq. 18a as $\tau \to \infty$	Eq. 18b as $\tau \to \infty$	20
Simplified solutions				
Ξ_{1S}	$= \Xi_{1W} e^{-\kappa\tau}$	$= \Xi_{1W} e^{-\kappa\tau}$	$= -E\left(\frac{I_{1S}}{I_{2S}}\right)^2 \Xi_{1W} e^{-\kappa\tau}$	21a
Γ_1	$= -\Xi_{1W}\frac{I_{1S}}{I_{2S}}(1-e^{-\kappa\tau})$	$= \Xi_{1W}\frac{I_{1S}}{EI_{0S}}e^{-\kappa\tau}$	$= -\Xi_{1W}\frac{I_{1S}}{I_{2S}}e^{-\kappa\tau}$	21b
$\frac{\partial \Xi_1}{\partial Y}$	$= -\Xi_{1W}\frac{I_1}{I_{2S}}(1-e^{-\kappa\tau})$	$= -\Xi_{1W}\frac{I_1 I_{0S} - I_0 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2}(1-e^{-\kappa\tau})$	$= -\Xi_{1W}\frac{I_1 I_{0s} - I_0 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2}\left[1 + \alpha(Y)\frac{I_{1S}}{I_{2S}}e^{-\kappa\tau}\right]$	21c
Simplifying conditions	$\tau \ll 1/I_{2S}$ $E\tau \ll I_{2S}/I_{1S}^2$	$E\tau \gg 1/I_{0S}$ $E \gg (I_{2S}I_{0S} - I_{1S}^2)/I_{0S}^2$	$\tau \gg 1/I_{2S} =$ $E \ll I_{2S}^2/(I_{2S}I_{0S} - I_{1S}^2)$	22a 22b
Decay rate				
κ	$= I_{2S} = \int_0^1 \frac{(1-Y)^2}{M}dY$	$= \frac{I_{2S}I_{0S} - I_{1S}^2}{I_{0S}} = \int_0^1 \frac{(Y_M - Y)^2}{M}dY$	$= -\frac{(I_{2S}I_{0S} - I_{1S}^2)E}{I_{2S}}$	23
Relative deformation profile R	$= \frac{I_1}{I_{2S}} = \frac{\int_0^Y \left(\frac{1-Y'}{M}\right)dY'}{\int_0^1 \frac{(1-Y)^2}{M}dY}$	$= \frac{I_1 I_{0S} - I_0 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2} = \frac{\int_0^Y \left(\frac{Y_M - Y'}{M}\right)dY'}{\int_0^1 \frac{(Y_M - Y)^2}{M}dY}$	$\to \frac{I_1 I_{0S} - I_0 I_{1S}}{I_{2S}I_{0S} - I_{1S}^2}$ as $\tau \to \infty$	24

Notes: $\alpha(Y) \equiv \frac{I_{2S}I_0 - I_1 I_{1S}}{I_1 I_{0S} - I_0 I_{1S}}$; $Y_M \equiv \left(\int_0^1 \frac{Y}{M}dY\right) \Big/ \left(\int_0^1 \frac{dY}{M}\right)$.

ment and surfactant concentration disturbance eventually decay to zero with time. Another consequence is that, according to Eq. 18c, the deformation of a stratum $\partial \Xi_1/\partial Y$ eventually becomes constant and equal to $-\Xi_{1W}(I_1 I_{0S} - I_0 I_{1S})/(I_{2S}I_{0S} - I_{1S}^2)$. Aside from the amplitude of the wall's displacement, the final deformation $\partial \Xi_1/\partial Y$ in a stratum depends only on its position within the film and the distribution of relative viscosity throughout the film, but not on the elasticity.

Stability is not assured when the film is on the underside of the wavy wall (so $g < 0$). If the wavelength is sufficiently long, that is, if $(\lambda/2\pi)^2 > \sigma/\rho(-g)$, then $\Lambda^2 < -1$ so, by definition, $E > 0$ and $\tau < 0$. Furthermore, Eqs. 19a and 19c show that κ_2 remains positive, so $\kappa_2\tau < 0$, and the disturbance in Eqs. 18 grows. This represents the Rayleigh–Taylor instability for thin films.

As mentioned in the Introduction, the leveling of a film that is initially of variable thickness over a flat surface is closely related to the flow considered here. In fact, assuming that the surfactant surface concentration is initially uniform, the evolution of the free surface displacement, the surfactant surface concentration and the velocity profile are all the same, except that the initial disturbance of the free surface $\Xi_{1S}(0)$ induces the flow instead of the disturbance at the wall Ξ_{1W}. (Thus $\Xi_{1S}(0)$ replaces Ξ_{1W} in Eqs. 15, 16 and 18.) The expressions for deformation and relative deformation of the strata only account for the changes that have occurred in these properties since the evolution of the flow started. (Thus Eqs. 15, 16, and 18c must be modified by replacing $\partial \Xi_1/\partial Y$ with $\{\partial \Xi_1/\partial Y - \partial \Xi_1/\partial Y|_{\tau=0}\}$.) With these changes in mind, the model presented earlier and the applications presented in the next section apply to the problem of leveling on a flat surface.

Applications

The governing equations are applied to examine the evolution of two-layer films of the same and different viscosities. Certain patterns in the evolution are exploited to determine three limiting conditions, and these are applied to establish the effect of changing the viscosity of a stratum in a film and the relative thickness of a layer in films with two and three layers.

Evolution of two-layer films

Leveling of films of two layers of discrete viscosity present many of the characteristics of the flows studied in this article. The flow depends on four parameters: the dimensionless time τ, the dimensionless elasticity E, the relative viscosity $M_2 \equiv \mu_2/\mu_1$, and the bottom layer's relative thickness Y_1. The last two parameters define the relative structure of the film and, therefore, the coefficients I_n and I_{nS} of Eqs. 10 and 13. Here the main features of the evolution are explored by examining the effect of E, M_2 and Y_1 on the evolution of the flow. A film with two layers of equal viscosity is discussed first.

Films of Uniform Viscosity. The velocity in the liquid film is given by Eq. 9b. Figure 2 shows the velocity profile, nor-

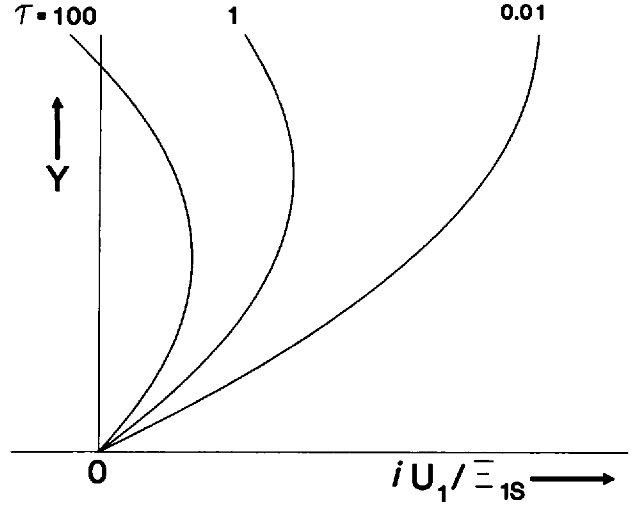

Figure 2. Velocity profiles at different times ($\tau = 0.01$, 1, 100) for a film with uniform viscosity and dimensionless elasticity $E = -1$.

malized by the free surface displacement amplitude Ξ_{1S}, for $E = -1$ at the times $\tau = 0.01$, 1, and 100. Initially, the velocity profile is approximately of the Nusselt-type of shape. As time increases, the profile remains parabolic but its average and free surface velocities (divided by the free surface displacement Ξ_{1S}) diminish. At $\tau = 100$, the velocity is roughly of the Poiseuille shape. The change in the profile's shape is caused by the competing effects of normal and shear stresses induced by the free surface displacement and surfactant concentration disturbance.

The velocity profile in films with discrete layers of uniform viscosity are also parabolic, but only within each layer; the slope at the interface between layers is discontinuous to match shear stress across it (Eq. 3a).

Figure 3 shows the evolution for a film of uniform viscosity that is split into two equal layers. The top chart represents the free surface relative displacement, Ξ_1/Ξ_{1W}. According to the preceding section, the free surface displacement is the sum of two decaying exponentials, so it is not surprising if this is its basic behavior. However, the log-log plot emphasizes more subtle features of the displacement.

The displacement chart shows that the films with higher magnitudes of elasticity ($E \leq -1$) evolve along a similar path, especially when compared with the films with lower magnitude of elasticity ($E \geq -0.1$). Early on in the evolution, the displacement decreases more rapidly in the latter, and then slows down to the point that the films with larger magnitude of elasticity overtake them. Furthermore, the evolution for films with lower magnitude of elasticity varies significantly with elasticity when the free surface is nearly flat. Other differences are more noticeable in Figure 4, which is discussed below.

The middle plot in Figure 3 represents the evolution of the disturbance to the surfactant surface concentration. Although not included in the log-log plot, the surfactant disturbance is zero when leveling starts. Over the range of four decades of elasticity shown here, the surfactant disturbance varies by only a factor of 2 when $\tau = 0.01$, so it can be inferred that the initial part of the evolution is insensitive to elasticity. At later times, however, the disturbance varies by several orders of magnitude for the films with different elasticities. As the surfactant is insoluble, changes of surfactant concentration can be directly related to the extension and compression of the free surface. Initially, the surfactant concentration is uniform and the driving force for leveling is greatest, so the flow is rapid and the free surface is extended over the crests on the wavy wall. At times shorter than $\tau \cong 0.01$, the flow is not sensitive to the magnitude of elasticity. As the driving force for leveling decreases and the surfactant concentration gradient increases, the free surface starts resisting the flow and eventually retracts. The surfactant-in-

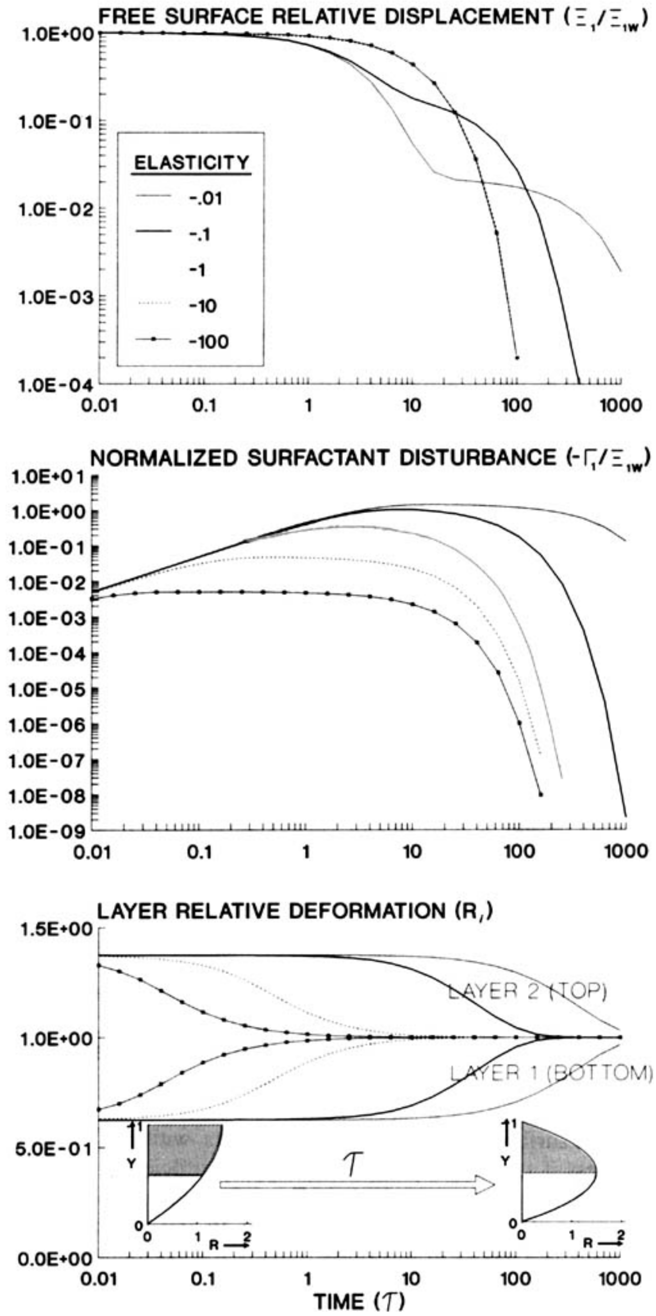

Figure 3. Evolution of a leveling film of uniform viscosity over a range of elasticities split into two layers ($M_2 = 1$, $Y_1 = 0.5$).

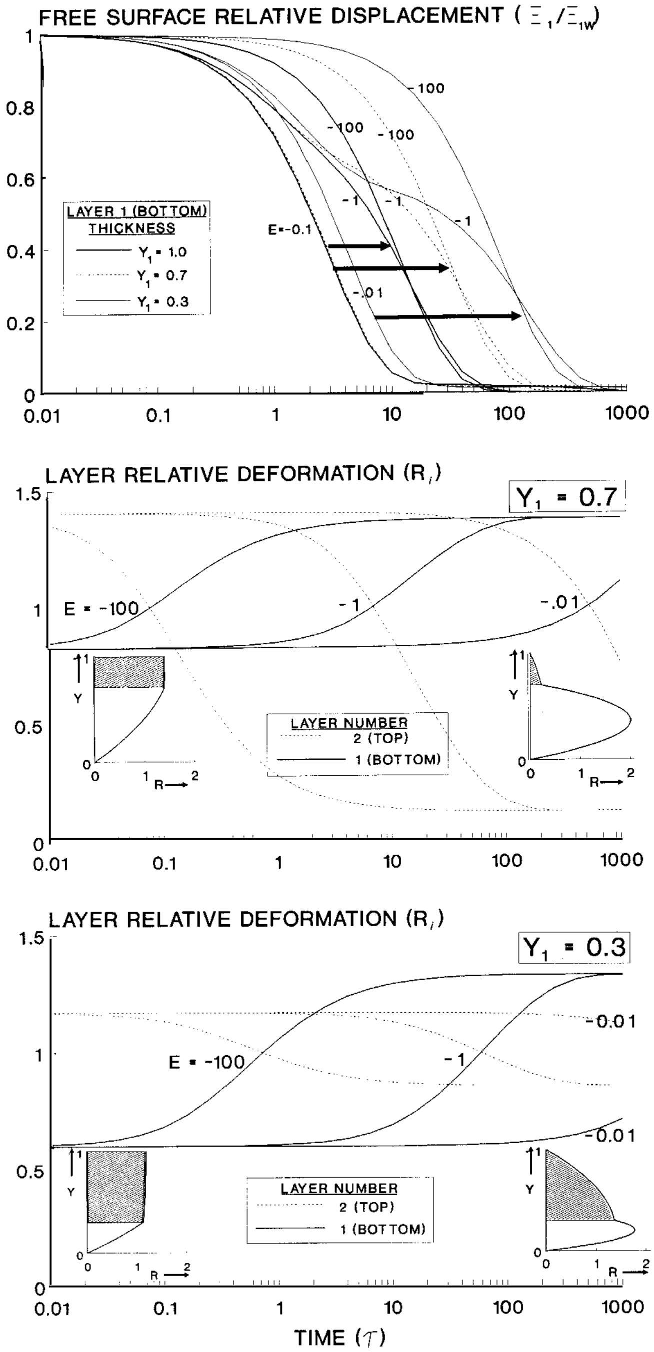

Figure 4. Evolution of a leveling film of two layers of unequal viscosity ($M_2 = 20$), for three elasticities ($E = -0.01, -1, -100$), and three bottom layer relative thicknesses ($Y_1 = 1, 0.7, 0.3$).

duced surface tension gradient interacts with the leveling process if the magnitude of elasticity is sufficiently large ($E \leq -1$). For lower magnitudes ($E \geq -0.1$), the retraction occurs after leveling is virtually complete. In any event, the free surface retracts until it returns to its initial position, which is of uniform surfactant concentration (zero disturbance). In the present context, the free surface with insoluble surfactant behaves similarly to a thin sheet of latex, that is, a membrane that deforms elastically and returns to its original shape of rest once all forces relax.

Additional information is extracted by splitting the film into two layers of equal thickness and examining their relative deformations. The bottom plot of Figure 3 shows curves of the evolution of relative deformation for the two layers, R_1 and R_2, and, as insets, the profiles of relative deformation for the infinitesimal strata, $R(Y)$, at the beginning and end of the evolution. The profiles are parabolic, and are transformed over time from the half- to full-parabola, similar to the Nusselt and Poiseuille velocity profiles. As expected, the relative deformation of the layers is independent of elasticity at the beginning and end of the evolution. However, the transition between these two extremes occurs earlier as the magnitude of elasticity increases. The transition coincides with the early part of the flat region of the evolution of the surfactant disturbance shown in the middle plot.

Films with Layers of Different Viscosity. In this example, the viscosity distribution through the film influences the evolution of the flow. The trends discussed for uniform viscosity films still apply, but differences arise in the magnitude of the changes.

At the top of Figure 4 is a semilog chart of the free surface displacement for the film of uniform viscosity and for two-layer films with top-to-bottom layer relative viscosity of $M_2 = 20$, and different bottom layer relative thicknesses, $Y_1 = 1, 0.7$, and 0.3 ($Y_1 = 1$ is actually the uniform viscosity case just studied). For each of these film structures, the evolution is plotted for three different elasticities, $E = -0.01, -1$, and -100. Two new features appear in this graph. First, as this is a semilog plot (instead of log-log, as in Figure 3), differences between the free surface displacements earlier in the evolution are more noticeable, so it is made clear here that the free surface displacement of the films of intermediate elasticity ($E = -1$) also undergo a transition. Second, early in the evolution, the higher viscosity in the upper layer reduces only slightly the rate at which the free surface displacement decreases but, after the transition has started, the reduction in the rate of change in the displacement is much more significant.

The lower two plots of Figure 4 show the evolution of relative deformations for the film structures with interfaces between the layers at $Y_1 = 0.7$ and 0.3. (The remaining case, $Y_1 = 1$, has no top layer and the relative deformation of its bottom layer is trivial, $R_1 = 1$.) Included in these charts as insets, are the relative deformation profiles for all the strata, at the beginning and end of the evolution. Two additional characteristics appear in these plots. First, the higher viscosity in the top layer reduces its relative deformation. This effect may not be significant in the early part of the evolution, but is very noticeable later on. Second, the thinner layer of the two is the most influenced by the increase in viscosity. Thus, when $Y_1 = 0.7$, the decrease in the relative deformation of the top layer is greater than the increase in the bottom layer, and conversely when $Y_1 = 0.3$.

Limiting cases

Equations 18 have three limiting solutions that are particularly simple that can be inferred from the preceding discussion and by examining Figures 3 and 4. This simplification arises when one or two terms in the governing differential equations (Eqs. 12) can be eliminated. The limits describe the evolution during the initial stage, and in the final stage when the magnitude of the elasticity is high or low. In two of these limits, the role of elasticity is secondary.

The limiting solutions are presented in Table 2, together with the corresponding simplifying assumptions, exponential decay rates and relative deformation profiles. The three middle columns relate to the simplifying limits, while the rows relate to their properties. As many of the equations are referred to below, the rows with equations have been assigned a number, from 20 to 24 (given in the last column), and the columns have been assigned a letter, from A to C (given in the first row).

The *initial stage limit* arises from the observation that, early in the evolution, the free surface displacement and surfactant disturbance are all the same. This is because the surfactant disturbance is initially zero but the displacement is not, so early on, the third term in Eqs. 12a and 12b is negligible. As the transient proceeds, the evolution toward complete leveling appears to follow one of two different paths. The first, called the *high elasticity limit*, arises when the magnitude of the dilational elasticity is large enough that surface tension gradients build up sufficiently to resist the flow before the free surface is virtually leveled. This limit applies to the three curves in Figure 3 with $E \leq -1$, when $\tau \geq 10$. In this case, as the middle plot of Figure 3 shows, the surfactant disturbance is nearly steady throughout this stage, so the unsteady surfactant surface concentration disturbance term, $\partial \Gamma_1/\partial \tau$, in Eq. 12b is neglected. The other case, named the *low elasticity limit*, arises when the film's free surface is virtually flat before surface tension gradients have built up sufficiently for the free surface to start retracting and the surfactant disturbance decreasing. This occurs in Figure 3 when $E \geq -0.1$ and $\tau \geq 10$. Then the unsteady free surface displacement term, $\partial \Xi_{1S}/\partial \tau$, is negligible in Eq. 12a.

Depending on the number of unsteady terms that are important, one or two conditions are needed to determine unspecified coefficient of the limiting solutions to the governing differential equations. For the initial stage limit, they are the initial conditions, Eqs. 14. However, the other two limits apply as $\tau \to \infty$, so the unspecified coefficient must be determined from expanding one component (Ξ_{1S} or Γ_1) of the closed-form solution in Eqs. 18 under condition of high or low elasticity and long time.

The simplified or limiting solutions are presented in Eqs. 21 of Table 2 for free surface displacement, Ξ_{1S}, surfactant surface concentration disturbance, Γ_1, and deformation of the strata in the film, $\partial \Xi_1/\partial Y$. (The coefficient κ in the exponentials is the decay rate given in Eqs. 23 and discussed below.) Comparing these solutions with the complete one of Eqs. 18, the reduction is drastic, and in these limits interactions are greatly simplified.

During the initial stage limit, the evolution is completely independent of elasticity, as shown by Eqs. 21A and 23A of Table 2. In dimensionless terms, the evolution depends only on the distribution of viscosity throughout the film. This important result has been anticipated in the previous subsection.

Less obvious but equally important is the conclusion that, in the high elasticity limit, the free surface displacement and film deformation are also independent of the actual magnitude of the elasticity. This is determined by inspecting Eqs. 21B and 23B. (The surfactant disturbance is inversely proportional to elasticity, but is small so does not affect the flow significantly.)

In the low elasticity limit, elasticity plays a dominant role. The decay rate (Eq. 23C) is proportional to the elasticity, so all components of this limiting solution (Eqs. 21C) are affected by elasticity. In addition, the free surface displacement is proportional to E. However, the displacement is actually very small in this limit.

For these limits to be valid, certain conditions must be satisfied and they are given in Eqs. 22 of Table 2. The first inequality compares the neglected term (see first row of Table 2) in the governing differing equations (Eq. 12) with one of the two other terms in the same equation applying some basic observations of the evolution and of the limiting situation to obtain an estimate of the time scale in which the limit is valid. The second condition is one of consistency, which is obtained by performing the same comparison, but after applying the predictions for the simplified solution to determine whether the neglected term is indeed negligible. Thus generally the first inequality refers to time, and the second one to the magnitude of the elasticity.

The inequalities of Eqs. 22 apply as long as the elasticity term is strictly negative. If $E = 0$, the entire evolution occurs as if the film were in the initial stage. This is the situation of no surfactant, which has been studied by others for films of uniform viscosity.

For a film of uniform viscosity, the inequalities of Eqs. 22 can be easily evaluated by applying $I_{nS} = 1/(n+1)$, which is determined in the paragraph below Eq. 13. Therefore, for the initial stage limit, $\tau \ll 3$ and $|E|\tau \ll 4/3$; for the high elasticity limit, $|E| \gg 1/12$ and $|E|\tau \gg 1$; and for the low elasticity limit $\tau \gg 3$ and $|E| \ll 4/3$. Referring to Figure 3, it is easy to confirm the validity of these inequalities. The evolution of the initial stage limit is followed most closely by the curve for $E = -0.01$; the curves for the elasticities of larger magnitude break off consistently with the condition $|E|\tau \ll 4/3$, except for $E = -0.1$, which breaks off sooner, consistent with the condition $\tau \ll 3$. During the final stage, the three films with greater magnitude of elasticity ($E \leq -1$) eventually follow the same trajectory for displacement and relative deformation, but their arrival at it is consistent with the inequality $E\tau \gg 4/3$. During their final stage, the other two films fall within the low elasticity limit, entering this range sometime after $\tau = 3$.

The exponential decay rate is given by Eqs. 23 of Table 2. Evaluating these equations for a film of uniform viscosity, one obtains $\kappa = 1/3$, $1/12$, and $-E/4$ for the initial stage, and high, and low elasticity limits, respectively. Although the decay rate is the lowest for the low elasticity limit (because $|E| \ll 4/3$), the film is virtually completely leveled by the time this limit applies. As the exponential decay rate is four times smaller for the high elasticity limit compared to the initial stage limit, and considering that the transition from the initial stage to the high elasticity limit occurs earlier when the magnitude of the elasticity is larger, the rate at which leveling is achieved is substantially decreased when the magnitude of E is large.

For the initial stage and high elasticity limits, Eqs. 23 provide a relationship for the exponential decay rate showing more explicitly its dependence on the viscosity distribution. Mathematically, the decay rate is the second moment of the inverse of the relative viscosity, taken around $Y=1$ and Y_M, respectively, for the initial stage and high elasticity limits. The note below Table 2 defines Y_M, which can be interpreted mathematically as the center of the first moment of the inverse of relative viscosity. More importantly, however, it can be shown by manipulating Eqs. 10, 13, 9b, and 21B that $Y = Y_M$ is where the velocity profile is maximum in the high elasticity limit. Therefore, in both limits, the second moment defining the decay rate is taken around the plane of maximum velocity.

The relative deformation profile is derived from Eqs. 16 and 21 and presented in Eqs. 24. The relative deformation in the initial stage and high elasticity limits are independent of time as well as elasticity, so they only depend on the distribution of viscosity. This dependence is shown explicitly by the second equality for these two limits, which is obtained by applying Eqs. 10 and 13. On the other hand, the relative deformation of the low elasticity limit is time-dependent.

For the final stage and high elasticity limits, the shape of the velocity and relative deformation profile coincides. The velocity profiles are determined by inserting Eqs. 21A or 21B, describing the evolution, into Eq. 9b, defining the velocity profile. As discussed earlier, the velocity profiles for the two limits are of the Nusselt and Poiseuille type. The next section examines more fully the effect the viscosity distribution has on the exponential decay rate and the relative deformation of the strata in films at these two limits.

Decay rates and relative deformations for the initial stage and high elasticity limits

If the viscosity is changed in a stratum or a layer, it affects the evolution of the free surface and relative deformation of all the strata in the film. In practice it is important to understand this effect because then one can improve the relative deformation of a stratum at the expense of some other strata in the film. An exhaustive survey is not feasible nor desirable. However, Figures 3 and 4 show that a broad portion of the evolution occurs in the initial stage or the high elasticity limit, so a survey limited to these ranges can be profitably made. This subsection presents the general trends due to changes in viscosity in an infinitesimal layer and then the results of changing the relative layer thickness of films with two and three layers.

Changing Viscosity in a Stratum. A great deal of the effect of changing viscosity in an infinitesimally thin stratum or layer can be learnt from examining in detail how the viscosity distribution is weighted in the formulas for the decay rate and relative deformation profile.

Exponential Decay Rate. As mentioned earlier, the decay rates for the initial and high elasticity limits, Eqs. 23A and 23B, are second moments of the inverse to the relative viscosity taken around the horizontal plane of zero shear stress (or maximum velocity). Therefore, the decay rate is least affected by the viscosity at the no-shear plane. In these two limits the decay rate is affected most heavily by:

- The strata of lower viscosity, as their contribution is proportional to large for the inverse of the relative viscosity; and
- The regions experiencing higher shear stress, that is, the layers near the wall and—in the high elasticity limit—the layers near the free surface.

The weighted function is always positive; therefore, increasing the relative viscosity of an infinitesimal layer decreases the exponential decay rate of the film.

Relative Deformation. Equations 24A and 24B give the relative deformation for films with continuously varying viscosity for the initial stage and high elasticity limits. The relative deformation at a certain stratum is the first moment of the inverse of the relative viscosity for the portion of the film between the wall and the stratum, normalized by the average of this moment for the entire film. The moment is taken around the no-shear plane, at $Y=1$ (the free surface) or $Y = Y_M$, for the initial stage and high elasticity limits, respectively. The following are rules common to the two limits.

- Relative deformation decreases as the relative viscosity at that position increases.
- Relative deformation is zero at the no-slip planes.
- Relative deformation increases with proximity to the plane around which the moments are taken.

A finite change in relative viscosity ΔM_j in a stratum of infinitesimal thickness δY_j, located at $Y = Y_j$, creates an infinitesimal change in the relative deformation throughout the film. In the initial stage limit, the infinitesimal change in relative deformation δR is obtained from Eq. 24A:

$$\delta R = \frac{(1-Y_j)\Delta M_j \delta Y_j}{M_j(M_j+\Delta M_j)\int_0^1 \frac{(1-Y)^2}{M+\Delta M} dY} [(1-Y_j)R(Y) - S(Y-Y_j)], \quad (25)$$

where M_j is the relative viscosity at $Y = Y_j$, ΔM in the integral's integrand is zero everywhere except at $Y = Y_j$, where it is equal to ΔM_j, and S is the unit step function. From Eq. 24B and the definition of Y_M in the note below Table 2, the same increase in viscosity in a stratum during the high elasticity limit shifts the no-shear plane by δY_M and changes the relative deformation throughout the film by δR:

$$\delta Y_M = \frac{(Y_M - Y_j)\Delta M_j \delta Y_j}{M_j(M_j+\Delta M_j)\int_0^1 \frac{dy}{M+\Delta M}} \quad (26a)$$

$$\delta R = \frac{(Y_M - Y_j)\Delta M_j \delta Y_j}{M_j(M_j+\Delta M_j)\int_0^1 \frac{(Y_M-Y)^2}{M+\Delta M} dY} \times \left[R(Y)(Y_M + \delta Y_M - Y_j) - S(Y-Y_j) + \frac{\int_0^Y \frac{dY}{M+\Delta M}}{\int_0^1 \frac{dY}{M+\Delta M}} \right]. \quad (26b)$$

Equation 26a shows that, in the high elasticity limit, an increase in viscosity at the strata $Y = Y_j$ shifts the no-shear plane $Y = Y_M$ away from that strata, as $\delta Y_M > 0$ and $Y_j < Y_M$. The magnitude of that shift is proportional to the distance between the layer and the no-shear plane.

Other trends can be derived from Eqs. 25 and 26. Figure 5 presents profiles of change in relative deformation δR in a

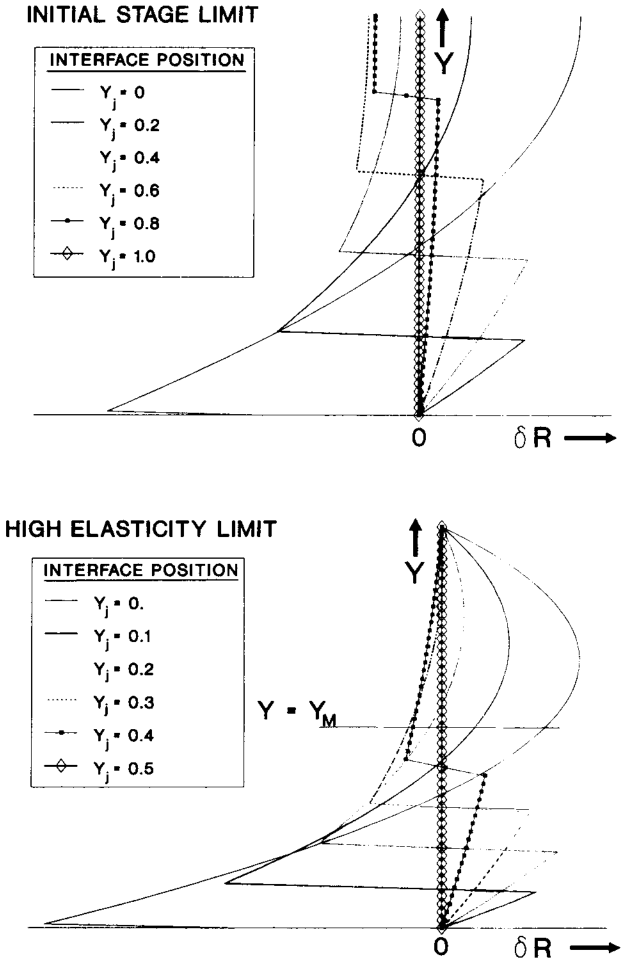

Figure 5. Change in the relative deformation profile caused by an infinitesimal change of viscosity in a stratum at different planes $Y = Y_j$, for the initial stage and high elasticity limits.

film of uniform viscosity caused by an infinitesimal increment of viscosity ($\Delta M_j/M_j \ll 1$) for a stratum at different heights, Y_j. For the high elasticity limit, the behavior of relative deformation is symmetric around the no-shear plane. Therefore, for the purpose of the following discussion it is assumed that, in the high elasticity limit, the stratum is below the no-shear plane. For both limits, the change in relative deformation

- Is most sensitive to changes in relative viscosity placed at the no-slip planes where the shear stress is highest.
- Is insensitive, at no-slip planes, to changes in relative viscosity located anywhere in the film.
- Experiences a discontinuity with change in sign at the layer where viscosity changes.
- Increases, in the region between the stratum and the no-slip plane, with increasing stratum viscosity.

The effect on the top portion of the film depends on its distance from the stratum: the further the layer is from the no-shear plane, the more it is deformed by the increase in viscosity. But as the stratum approaches the no-shear plane, the upper portion's relative deformation can actually decrease.

Changing Relative Thickness in Films of Two Layers. The properties of the decay rate and relative deformation of films with discrete layers of uniform viscosity can be derived, in principle, from the study given above for strata in films with arbitrary viscosity distribution. However, when the film is formed by only two or three discrete layers, it is easier to glean this information directly from Eqs. 23 and 24.

Exponential Decay Rates. The exponential decay rate κ for the two limits is given by Eqs. 23A and 23B. The top and bottom charts of Figure 6 show, respectively, the decay rates for the initial stage and high elasticity limits in terms of the bottom layer relative thickness, Y_1, at four different relative viscosities: $M_1 = 0.2$, 1, 5, and 20. In the initial stage, if the relative viscosity is unity, the decay rate is 1/3. The decay rate remains near 1/3 if the relative viscosity of the top layer is greater than unity and as long as the bottom layer relative thickness is at least half the thickness of the film. As the bottom layer relative thickness decreases below this value, the decay rate decreases slowly at first and, when the bottom layer becomes very thin, it steeply reaches the decay rate corresponding to a film at the upper layer's viscosity. As already indicated, the general insensitivity of the decay rate to changes in relative thickness is caused by shear stresses being small in the upper regions of the coating during the initial stage. Thus the viscosity in the upper half of a film is largely irrelevant to this stage's decay rate.

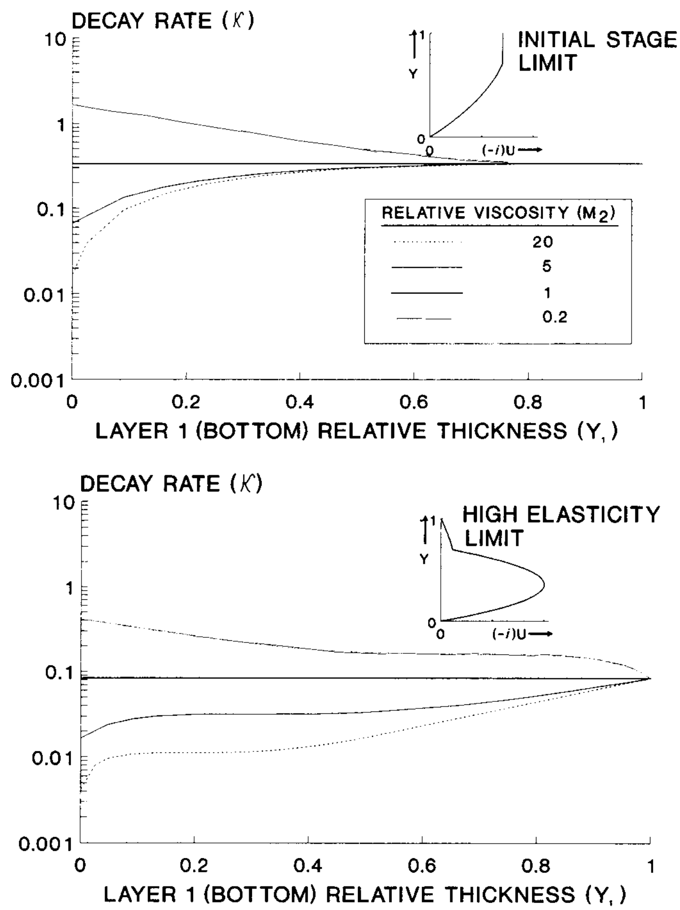

Figure 6. Exponential decay rates for films of two layers in the initial stage and high elasticity limits.

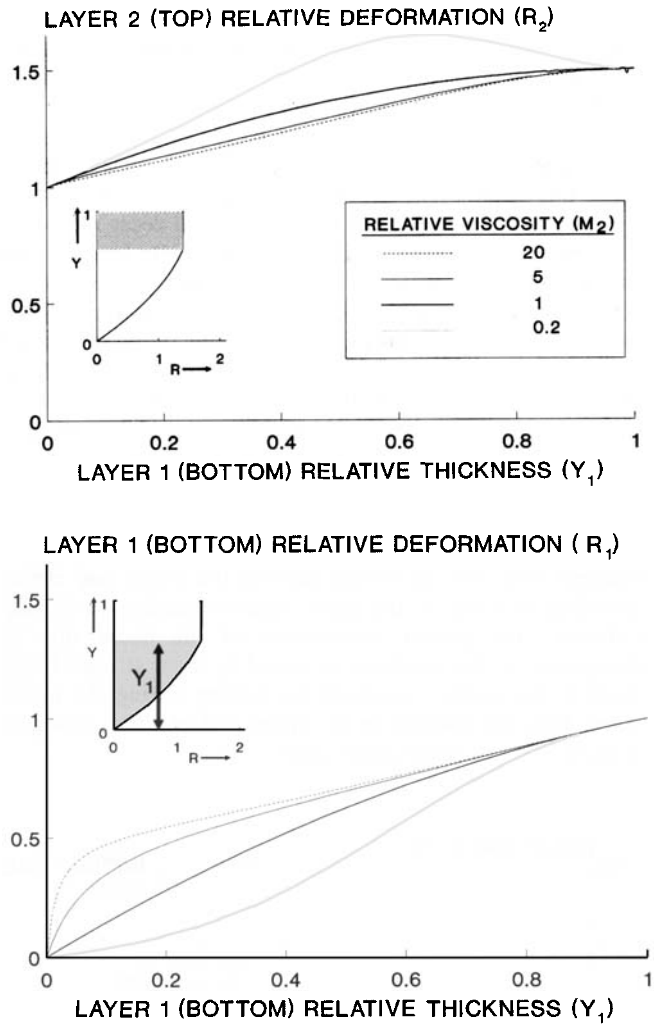

Figure 7. Relative deformation for films of two layers in the initial stage limit.

The upper and lower charts correspond to the top and bottom layers, respectively.

The decay rate for the high elasticity limit is 1/12 for a relative viscosity of unity, that is, it is one-fourth of the rate for the same film in the initial stage. This is shown in the bottom chart of Figure 6. For relative viscosities greater than unity and bottom layer relative thicknesses below 0.1, the decay rate increases fairly steeply with increasing bottom layer relative thickness. There is a broad middle region for which the decay rate is insensitive to bottom layer relative thickness. This is because the fluid is sheared both at the substrate and at the free surface, so the viscosity in the upper region is as important as in the lower regions of the film.

Relative Deformations. Figure 7 shows the relative deformations in the initial stage predicted for the top and bottom layers in terms of the bottom layer relative thickness for relative viscosities of $M_2 = 0.2$, 1, 5, and 20. The relative deformation of the ith layer is calculated by taking the average of Eq. 24A over that layer:

$$R_i = \frac{I_{1i}}{I_{2S}}, \tag{27}$$

where R_i and I_{1i} are, respectively defined by Eqs. 17. In this limit, the relative deformation of both layers increases with increasing bottom layer relative thickness and the relative deformation of the top layer is always greater compared to the bottom layer's. The bottom layer's relative deformation is near zero for a relatively thin bottom layer because the fluid in that layer is very near the wall and thus has very low mobility. One the other hand, a very thin upper layer will have the highest relative deformation because the mobility is highest at the free surface. The top layer's relative deformation is quite insensitive to the relative viscosity; this is because viscosity plays a minor role in the upper regions of the film as that region experiences the least shear stress.

For the high elasticity limit, Figure 8 shows bottom and top layer relative deformations that are predicted by taking the average of Eq. 24B throughout the layer:

$$R_i = \frac{I_{1i}I_{0S} - I_{0i}I_{1S}}{(I_{2S}I_{0S} - I_{1S}^2)}. \tag{28}$$

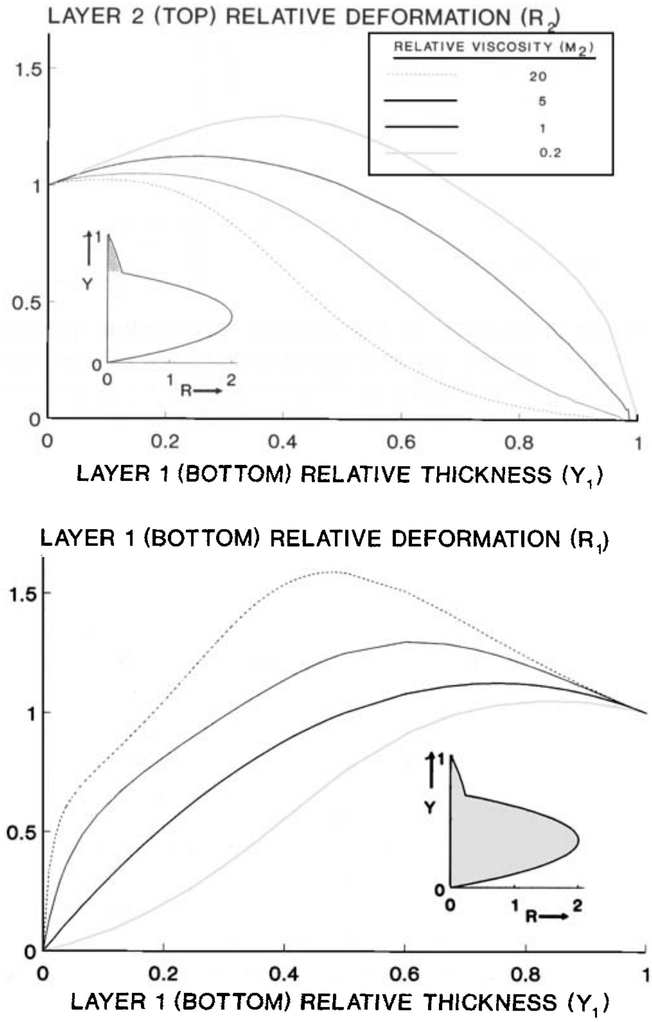

Figure 8. Relative deformation for films of two layers for the high elasticity limit.

The upper and lower charts correspond to the top and bottom layers, respectively.

The figure shows very different results compared to the initial stage limit's. In the high elasticity limit, the bottom layer's relative deformation passes through a maximum at an intermediate relative thickness. Furthermore, the bottom layer's relative deformation is sensitive to the relative viscosity at small to intermediate bottom layer relative thickness. Similarly, the top layer's relative deformation is sensitive to relative viscosity when the top layer's relative thickness is less than about half. The relative deformation is sensitive to the relative viscosity because shear stress is high near the wall and the free surface. When the relative viscosity M_2 increases, the top layer transfers more strain to the bottom layer, so the relative deformation of the top layer will decrease at the expense of the bottom layer's. Notice that when the film's viscosity is uniform ($M_2 = 1$), the relative deformation of the layers is symmetric to each other around the line of bottom layer relative thickness $Y_1 = 0.5$. This is because, in the uniform viscosity case, the velocity profile is symmetrical around the midplane of the film.

Changing relative thickness in films of three layers

A survey can be performed for three-layer films in much the same way. However, as many of the trends are close to those of two-layer films and much more space would be required, they are not presented here in detail. No new results are found for the exponential decay rate. Relative deformations are complicated by the presence of a middle layer, so what follows are the highlights of a survey on relative deformations for relative viscosities ranging between 0.2 and 20.

The main trends of Figure 7 for relative deformation of two-layer films in the initial stage represent well the case of three-layer films in that limit. For constant bottom layer relative thickness, the bottom layer is insensitive to changes in relative thickness of the upper layers. In fact, the minimum relative deformation for all the layers occurs simultaneously when the two lower layers are very thin and the top layer makes up virtually the whole film, and conversely, the maximum relative deformation of all the layers occurs simultaneously when the upper layer is very thin, and typically when the middle layer is also very thin. Therefore, the two-layer predictions typically bound those for three-layer films.

Figure 9 is an example of a three-layer film in the high elasticity limit, showing contours of relative deformation with the middle and top layer relative viscosities $M_2 = 5$ and $M_3 = 20$, respectively. At the diagonal boundary, the two lower layers make up the entire film. The abscissa and ordinate represent the relative thicknesses of the bottom and middle layers. The maximum relative deformation of a layer typically occurs in the interior of charts such as Figure 9, indicating that relative deformations of films with three layers can be higher than with two layers. In fact, often the middle layer is the most deformed by the flow. Joos and Jacobsmeyer (1992) have reported observing this effect experimentally in films of three layers of equal thickness and viscosity.

There are two situations, however, for which the relative deformation of layers is greatest at the boundaries of charts such as Figure 9, in which case the two-layer predictions can be used to locate the greatest relative deformation. The first is when the viscosity of the middle layer is greatest of the three layers; then the maximum relative deformation of all three layers occurs on different borders of the chart (effec-

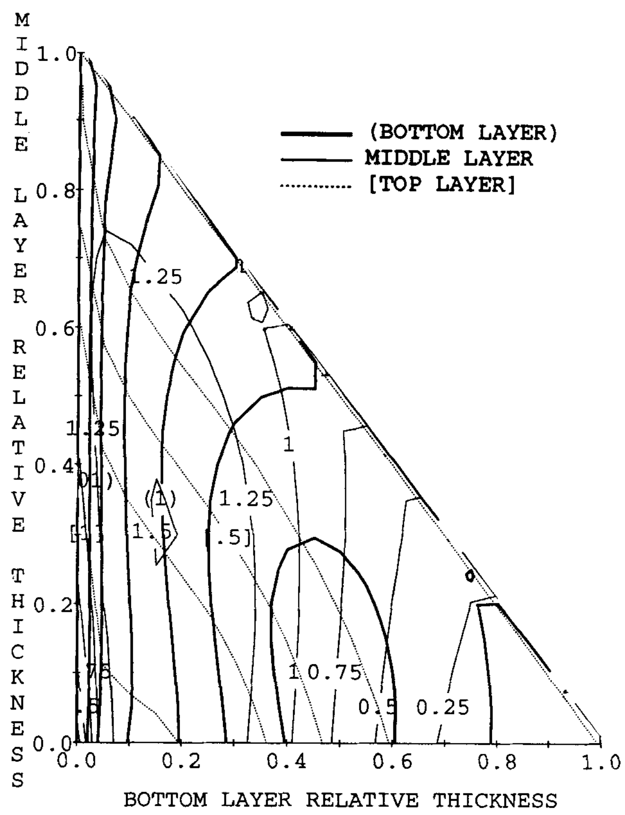

Figure 9. Contours of constant relative deformation for the three layers of a three-layer film in the high elasticity limit.

The top and middle layer relative viscosities are $M_2 = 5$ and $M_3 = 20$.

tively making it a two-layer film). For this arrangement, the middle layer's largest relative deformation occurs when it is infinitely thin and placed along the plane $Y = Y_M$ of maximum velocity. This annuls the effect of its higher viscosity; its deformation cannot be read from the chart for two layers, but can be easily computed from Eq. 24B. The largest deformation for the top layer is when the bottom layer is infinitely thin, and the middle layer has a finite thickness. Thus, Figure 7 can be used to establish the upper bound of relative deformation for the top layer. Similar procedures using the two-layer data determine the lower bound of relative deformation for the top layer, and both bounds for the bottom layer.

The second case is when the viscosity changes monotonically with layer height; then the maximum relative deformation of the layer with the highest viscosity lies on the boundary of the contour plot. Then the maximum relative deformation of the layer with the highest viscosity is that of a film with two layers, with the second layer corresponding to the middle one. Figure 9 is an example of this ordering of layer viscosities; it shows the maximum relative deformation for the top layer on the boundary, and the maxima for the bottom and middle layers are interior points.

Conclusion

The evolution of a film as it levels over a wavy horizontal wall has been examined for the case that the film is initially uniform along the wall. The free surface of the film has an insoluble surfactant adsorbed to it, and the viscosity is allowed to vary through the film in a stratified manner (which includes the particular case of discrete layers of different viscosity).

The velocity profile is parabolic when the viscosity is uniform throughout the film. This profile is a linear combination of the free surface displacement and the surfactant concentration disturbance. The free surface displacement and surfactant disturbance contribute profiles of the Nusselt and Couette type, respectively. Although, in principle, the relative deformation profile of the strata is caused by changes throughout the entire evolution of the flow, it can be expressed as a linear combination of the instantaneous free surface displacement and the surfactant concentration disturbance. At the end of the leveling process, the free surface displacement and surfactant concentration disturbance are zero, so the final deformation of the layers is independent of the elasticity parameter.

The free surface displacement and surfactant surface concentration of a film on a wavy horizontal wall decay exponentially to the condition of flat free surface and uniform surfactant concentration. The free surface is therefore unconditionally stable. If inertial effects are neglected, then there are no phase differences between the deformations of the layers. There is, however, a 180° phase shift between the wall's waviness and the deformations. On the other hand, the deformations of strata or average film are neutrally stable because a wall disturbance is invariably transmitted as a thickness disturbance in the film.

Leveling of a film with an initially wavy free surface spread over a flat wall is closely related to the problem considered here. The evolution of the free surface displacement and surfactant's surface concentration disturbance are, in fact, identical, but the relative deformation of strata and layers studied here refer only to the change in their deformations throughout the evolution.

Three limiting cases have been identified that, together, explain parts of the evolution in particularly simple ways. There is an initial stage where the exponential decay rate is the most rapid and the velocity and layer deformation profiles are of the Nusselt type, with one no-slip or zero condition at the wall and another no-shear or maximum condition at the free surface. There also is a final stage, with two limiting cases that depend on the magnitude of the dimensionless elasticity. When the elasticity's magnitude is high, the free surface starts to react relatively early against the extension and compression it has undergone because of the large surface tension gradient induced by the surfactant concentration gradient. The exponential decay rate is reduced to one quarter of the initial stage's, and the velocity and deformation profiles are of the Poiseuille type, with two no-slip or zero velocity conditions at the wall and free surface, and a no-shear or maximum at some interior stratum. When the elasticity's magnitude is low, the surface tension gradient plays a dominant role only after the free surface has virtually leveled. In this case the velocity profile is a linear combination of Poiseuille and Couette profiles, with the constraint that there is no net flow through the film. The relative deformation profile eventually coincides with that of the high elasticity limit.

The decay rates and profiles of velocity and deformation for initial stage and high elasticity limits are independent of the surfactant's elasticity. In both these limits, the exponential decay rate is decreased by increasing the viscosity in any part of the film. The layers of lowest viscosity have greater influence. Changes in viscosity are most effective near the no-slip planes and least effective near the no-shear plane. However, the relative deformation of a stratum is zero if it is at a no-slip plane and maximum if it coincides with the no-shear plane. Increasing the viscosity of an infinitesimally thin stratum increases, on the one hand, the deformation of the portion of the film between the stratum and the nearest no-slip plane, but decreases, on the other hand, the deformation of the portion just on the other side of the stratum.

When the relative layer thickness of a film of two layers is changed, it also affects the decay rate and relative deformations of both layers. In the initial stage limit, the top layer is ineffective at changing the decay rate or the relative deformation of either layer unless it becomes a large position of the entire film (60% or more for the range of viscosity surveyed), while in the high elasticity limit both layers are equally influential. Furthermore, the relative deformation is quite sensitive to relative viscosity, especially when the interface between layers is in the central region of the film.

The decay rate and deformation in films with three discrete layers of different viscosity are similar to those of two layers, especially in the initial stage limit. However, the relative deformation of the middle layer in the high elasticity limit is usually the largest of the three and can be significantly higher than the values obtained for two-layer films.

Acknowledgments

I am grateful to all who have contributed to this work, especially K. J. Ruschak, A. S. Platten, and A. Gros.

Notation

e = surface dilational elasticity, Eq. 7, N/m
g = gravitational acceleration, m/s^2
p = pressure in the liquid, Pa
u = liquid velocity in the horizontal direction, m/s
v = liquid velocity in the vertical direction, m/s
V = dimensionless liquid velocity in the vertical direction, Table 1, $v\mu(\lambda/2\pi)^2\Lambda^2/[\rho g y_S^{*4}(1+\Lambda^2)]$
Y = dimensionless normal coordinate, Table 1, y^*/y_S^*

Greek letters

α = coefficient in the relative deformation expression for the lower elasticity limit, in note below Table 2
ρ = liquid density, kg/m^3
σ = surface tension, N/m
ξ = position of material surface of constant viscosity, m
Ξ = dimensionless position of lines of constant viscosity, Table 1, ξ/y_S

Subscripts

i = associated with the ith layer or its upper interface (always the last subscript)
o = associated with the initial condition
1 = associated with disturbance from the initial condition

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Manuscript received Apr. 12, 1994, and revision received Mar. 30, 1995.