DYNAMICS AND STABILITY OF SURFACTANT COATED THIN SPREADING FILMS

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ABSTRACT

Within lubrication theory, we investigate the hydrodynamic stability of a thin surfactant coated liquid film spreading strictly by Marangoni stresses. These stresses are generated along the air-liquid interface because of local variations in surfactant concentration. The evolution equations governing the unperturbed film thickness and surface surfactant concentration admit simple self-similar solutions for rectilinear geometry and global conservation of insoluble surfactant. A linear stability analysis of these self-similar flows within a quasi steady-state approximation (QSSA) yields an eigenvalue problem for a single third-order nonlinear differential equation. The analysis indicates that a thin film driven purely by Marangoni stresses is linearly stable to small perturbations of all wavenumbers. The insights gained from this calculation suggest a flow mechanism that *can* potentially destabilize the spreading process.

INTRODUCTION

The spontaneous spreading of surface active solutions along a liquid support of higher surface tension, so called Marangoni spreading, plays a significant role in processes from industry to daily life, including detergency, optical coating manufacture, lubrication, and aerosol delivery of bronchodilating drugs. As an example of a Marangoni spreading process, many premature infants develop a respiratory distress syndrome at birth if their lungs have not sufficiently matured to produce adequate quantities of pulmonary surfactant. This substance reduces the surface tension of the liquid which lines the alveoli and lung airways and its deficiency can give rise to respiratory difficulties associated with airway closure, decreased lung compliance and mechanical damage of the airway linings. An effective technique for the treatment of this condition is to deliver surfactant externally through inhalation of surfactant in aerosol form [1]. This process can accurately be modeled as surface active liquid droplets spreading along a thin water based film [2-5].

Marangoni driven spreading occurs spontaneously and rapidly. Variations in the concentration of surface active material produce surface tension gradients at the air-liquid interface. Such gradients create surface stresses which induce motion in the spreading film and liquid support in the direction of increasing surface tension. It has been shown experimentally and theoretically that such stresses lead to the formation of a thinned region near the surfactant deposition point and a subsequent film thickening at the advancing front [2-10]. Within the past few years, the description of the unperturbed uniform spreading process has been the subject of considerable interest. The base state equations have been expanded to include many of the forces affecting thin film flow including Marangoni stresses, surface diffusion, capillarity, gravity, solubility and van der Waals forces [2-5]. In addition, the spreading process has been extended to several geometries and to cases for which the surfactant reservoir can provide either a finite or infinite amount of material.

Experiments have revealed the existence of a new fingering instability near the point of deposition [6-10] and at the advancing front [11] of thin surfactant coated water films spreading on a thin water support. Though modeling efforts have concentrated on the uniform spread-

ing process, the stability of the system of equations describing spontaneous Marangoni driven spreading has received surprisingly little attention. We would like to determine whether linear stability analysis can uncover unstable flow and subsequent finger formation near the thinned region upstream of the initial advancing front. A much simplified linear stability analysis within a long wavelength approximation has suggested that Marangoni driven films are susceptible to perturbations in the thinned region [5]. In this work the unperturbed flow was modeled as a spherical cap of liquid coated with insoluble surfactant spreading on an uncontaminated layer of the same liquid. Allowing only concentration disturbances and assuming that the surfactant reservoir provided unlimited material, the flow was shown to be unstable to perturbations near the surfactant deposition point. Within this model, both Marangoni and capillary effects were included.

The work presented below provides a more complete and rigorous linear stability analysis without the approximations used previously. We investigate flows driven strictly by Marangoni stresses (with no capillary effects) in order to isolate the dominant source of unstable flow. The possibility of an instability arising solely from Marangoni flow and not capillary driven flow is studied by considering the spread of a surfactant monolayer. With only one mechanism present, the base flow profiles demonstrate simple and analytical self-similar form. The linear stability analysis of these profiles includes fluctuations in the film thickness *and* surfactant concentration, both of which are treated self-consistently. We show below that such self-similar profiles are stable to linear perturbations of all wavenumbers. With the insight gained from this analysis, we propose a mechanism which can enhance disturbances in the flow to destabilize the system.

PROBLEM FORMULATION

Base State

Consider a thin Newtonian liquid layer of viscosity μ^* and density ρ^* partially covered with surfactant and resting on a solid substrate. The asterisk denotes dimensional quantities. The aspect ratio of initial film thickness, H_o^*, to the horizontal extent of the initial surfactant distribution, L^*, is denoted by ε, the small parameter characteristic of the lubrication approximation. The difference in surface tension between the surfactant free, σ_o^*, and contaminated liquid surfaces, σ_m^*, is given by the spreading coefficient $\Pi^* = \sigma_o^* - \sigma_m^*$. Initial gradients in surface tension of order Π^*/L^* generate a shear stress at the interface of order $\mu^* U^*/L^*$ that drives the spreading. From the shear stress balance at the interface emerges the velocity scaling $U^* = \varepsilon \Pi^*/\mu^*$. The horizontal and transverse coordinates, x^* and z^*, are scaled by L^* while the vertical coordinate y^* is scaled by H_o^*. The axial and transverse velocities, u^* and w^*, are scaled by U^* and the vertical velocity, v^*, by εU^*. Time is rescaled by $\mu^* L^*/\varepsilon \Pi^*$ and pressure by Π^*/H_o^*. The lubrication approximation dictates that $\varepsilon \ll 1$ and $\varepsilon Re \ll 1$, where $Re \equiv \frac{\rho^* U^* H_o^*}{\mu^*} = \frac{\varepsilon \rho^* \Pi^*}{\mu^{*2}}$ is a modified Reynolds number. The dimensionless surface tension is taken to be $\sigma = (\sigma^* - \sigma_m^*)/(\sigma_o^* - \sigma_m^*)$.

Introduction of the above scalings into the equations of mass and momentum conservation yields the following dimensionless evolution equations to leading order in ε:

$$u_x + v_y + w_z = 0. \tag{1}$$

$$P_x = u_{yy} + O(\varepsilon Re, \varepsilon^2), \tag{2}$$

$$P_y = 0 + O(\varepsilon^2), \tag{3}$$

$$P_z = w_{yy} + O(\varepsilon Re, \varepsilon^2). \tag{4}$$

The no slip boundary condition at $y = 0$ demands that $u = v = w = 0$, while the tangential and normal stress conditions at the interface $y = H(x, z, t)$, demand that $u_y = \sigma_x$, $w_y = \sigma_z$, and $\vec{p} = 0 + O(\varepsilon^2)$. Integration of Eqs. (2) and (4) subject to the boundary conditions yields a simple Couette type velocity profile for the spreading film. Mass conservation for the liquid support and insoluble surfactant require $H_t + \nabla \cdot \vec{Q} = 0$ and $\Gamma_t + \nabla \cdot (\Gamma \vec{u}_s) = \frac{1}{Pe_s} \nabla^2 \Gamma$, where $\vec{Q}$ represents the dimensionless liquid flux, $\Gamma(x, z, t)$ is the surface surfactant concentration and $\vec{u}_s$ is the surface velocity vector. Substitution of the velocity profile into these equations yields the evolution equations for the film thickness, $H(x, z, t)$, and the surfactant concentration, $\Gamma(x, z, t)$ where $\sigma_\Gamma = \partial\sigma/\partial\Gamma$:

$$H_t + \frac{1}{2} \nabla \cdot (H^2 \sigma_\Gamma \Gamma_x) = 0, \tag{5}$$

$$\Gamma_t + \nabla \cdot (\Gamma H \sigma_\Gamma \Gamma_x) - \frac{1}{Pe_s} \nabla^2 \Gamma = 0. \tag{6}$$

The linear equation of state, $\sigma = 1 - \Gamma$, suitable for dilute concentrations couples the two equations. More complex equations of state can be introduced for concentrated solutions. The modified Peclet number, $Pe_s \equiv \frac{U^* \cdot L^*}{D_s^*} = \frac{\Pi^* H_o^*}{\mu^* D_s^*}$ represents the ratio of bulk Marangoni convection to surface diffusion. Since the convection process always dominates spreading by surface diffusion, we consider the limit $\frac{1}{Pe_s} \to 0$. For a finite surfactant reservoir, then, Eqs.(5) and (6) admit the following self-similar solutions for rectilinear geometry [4]:

$$H_o(x, t) = h(\xi) = 2\xi \quad \Gamma_o(x, t) = \frac{g(\xi)}{R(t)} = \frac{\lambda}{2R(t)}(1 - \xi) . \tag{7}$$

The self similar variable $\xi \equiv \frac{x}{R(t)}$ where $R(t) = (3\lambda t)^{\frac{1}{3}}$. The parameter $\lambda = 4M_o$ where M_o is the total mass of surfactant deposited on the liquid support. Inspection of this solution reveals that the rates of change of $h(\xi)$ and $g(\xi)$ decrease as $t^{-4/3}$. This observation justifies the use of the quasi steady-state approximation in the linear stability analysis.

Linear Stability Analysis and Quasi-Steady State Approximation (QSSA)

We appeal to linear stability analysis and propose a normal mode form for the applied perturbations. Since the base flow solutions change with position and time, the meaning of the stability of this system remains somewhat ambiguous. As is normally done with such flows, we first investigate the stability within the QSSA for which the perturbations are assumed to evolve on a faster time scale than the base state. The normal mode perturbations of wavenumber K, chosen as $\widetilde{H}(x, z, t) = \Psi(\xi, t) e^{iKz}$ and $\widetilde{G}(x, z, t) = \frac{\Phi(\xi, t)}{R(t)} e^{iKz}$, are substituted into Eqs.(5) and (6). The coupled pair of PDE's governing the disturbances therefore becomes

$$\Psi_t = \frac{\dot{R}}{R} \xi \Psi_\xi + \frac{1}{2R^3} \left(h^2 \Phi_\xi + 2hg_\xi \Psi \right)_\xi - \frac{K^2}{2R} h^2 \Phi, \tag{8}$$

$$\Phi_t = \frac{\dot{R}}{R} (\xi \Phi)_\xi + \frac{1}{R^3} (gg_\xi \Psi + hg_\xi \Phi + hg \Phi_\xi)_\xi - \frac{K^2}{R} hg \Phi. \tag{9}$$

In accordance with the assumptions of the QSSA, we choose a time t_{qs}, sufficiently far from $t = 0$ for memory of initial conditions to be lost, beyond which the base flows remain frozen in time. The time dependent coefficients in Eqs.(8) and (9) are therefore evaluated at $t = t_{qs}$.

The disturbances Ψ and Φ are therefore only spatially inhomogeneous and assume the form $(\Psi, \Phi)(\xi, t) = e^{\sigma(K, t_{qs})t}(\psi, \phi)(\xi, t_{qs})$ where σ is the quasi-static growth constant. Combination of this form with Eqs.(7), (8) and (9) and the variable transformations $\sigma \to \sigma R(t_{qs})^3$, $K \to (KR(t_{qs}))^2$, and $\psi \to \lambda\psi$, gives a single nonlinear third order equation for the rescaled dimensionless surfactant concentration:

$$\frac{1}{2}\xi^2(1 - \xi)\phi_{\xi\xi\xi} + \xi(2 - \frac{5}{2}\xi - (\sigma + 1)(1 - \xi))\phi_{\xi\xi} +$$

$$(1 - 2\xi - \frac{1}{2}K\xi^2(1 - \xi) - (\sigma + 1)(1 - 2\xi))\phi_\xi +$$

$$(\sigma(\sigma + 1) - K\xi(1 - \frac{3}{2}\xi - (\sigma + 1)(1 - \xi))\phi = 0 \tag{10}$$

Eq.(10), which has regular singular points at $\xi = 0$ and $\xi = 1$, must be solved numerically subject to regularity conditions at the boundaries [12]. Removing the singular point at the origin by substituting the transformation $\phi(\xi) = \xi^{2\sigma+1}Y(\xi)$ into Eq.(10) gives

$$a(\xi)Y_{\xi\xi\xi} + b(\xi)Y_{\xi\xi} + c(\xi)Y_\xi + d(\xi)Y = 0 \tag{11}$$

where the coefficients are defined by $a(\xi) = \xi^2(1 - \xi)$, $b(\xi) = \xi(5 - 6\xi + 4\sigma(1 - \xi))$, $c(\xi) = 4(\sigma + 1)^2 - 2(\sigma + 1)(2\sigma + 3)\xi - K\xi^2(1 - \xi)$ and $d(\xi) = 2\sigma(\sigma + 1) - K\xi(1 - 2\xi)$. The quantity $2\sigma + 1$ represents the so-called indicial exponent in Frobenius expansions. Numerical solutions of Eq.(11) are constructed for different values of K using a standard shooting method by shooting away from the boundaries to a fitting point within the domain. Continuity of Y, Y_ξ and $Y_{\xi\xi}$ at the fitting point yields the conditions which form the basis for iterative solutions to the eigenvalue σ.

RESULTS AND DISCUSSION

Fig. 1 shows the relation between the quasi-static growth rate, σ, and the wavenumber of the perturbation, K. Since $\sigma < 0$ always, the spreading process is stable to perturbations of all K within the approximations used. An interesting feature of these stable eigenfunctions is the complementary relation that develops between ψ and ϕ near the origin as shown in Fig. 2. In particular, as the disturbance film thickness increases, the disturbance surfactant concentration decreases. The physical reason for this inverse relation is that regions of greater film thickness experience a larger mobility thereby facilitating surfactant transport and decreasing the local surfactant concentration. Apparently the disturbances readjust so as to stabilize any perturbations in film thickness or surfactant concentration.

In order to visualize the three-dimensional flow, the perturbations are superimposed upon the base state and extended periodically in the z direction. The amplitude of the perturbations is exaggerated in order to emphasize the formations created by the disturbances. The corrugated flow profiles shown in Figs. 3, 4, 5 and 6 resemble fingering-like instabilities in other systems but for this situation, the flow is stable. As shown in Figs. 4 and 6, large wavenumber disturbances become increasingly localized near the origin. This is consistent with the transformation $\phi = \xi^{2\sigma+1}Y$ which requires that both ψ and ϕ become increasingly singular at the origin as σ becomes more negative. (The interested reader can find more details of this analysis in a forthcoming publication [12].)
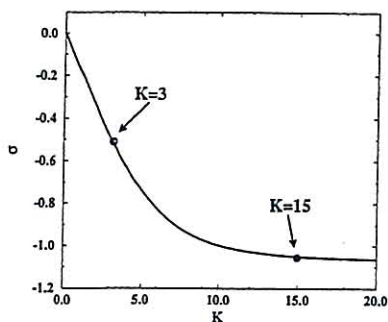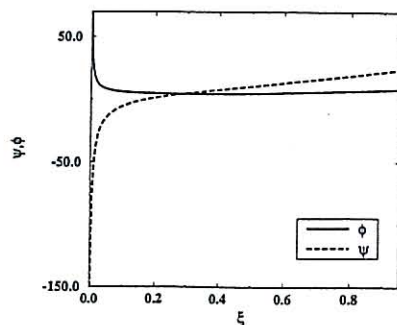
Fig. 1 Partial eigenvalue spectrum.

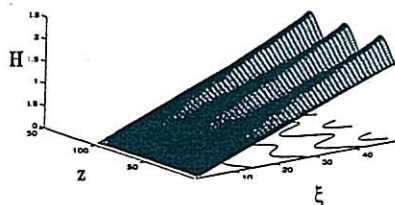Fig. 2 Illustration of the complementarity relation between ψ and ϕ near $K = 6$.
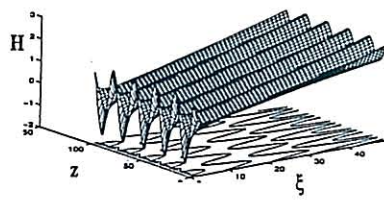

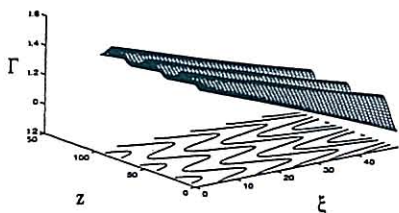Fig. 3 Total film thickness, H ($K=3$).

Fig. 4 Total film thickness, H ($K=15$).

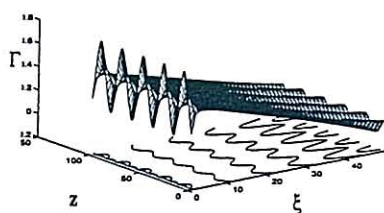Fig. 5 Total surfactant concentration, Γ ($K=3$).

Fig. 6 Total surfactant concentration, Γ ($K=15$).

It proves instructive to consider the average velocity of the disturbance flow, $\bar{u}(\xi) = \frac{\psi}{4} - \xi\phi_\xi$. Examination of this equation suggests a mechanism for destabilizing the flow profiles. Regions in which *both* $\psi > 0$ and $\phi_\xi < 0$ can enhance the local film velocity $\bar{u}$ thereby advancing any protrusions in the flow. Inspection of Fig. 2 reveals that the above condition is never satisfied. In particular, both $\phi_\xi < 0$ and $\psi < 0$ near the origin while both $\phi_\xi > 0$ and $\psi > 0$ downstream. The dominant terms, $\psi < 0$ near the origin, and $\phi_\xi > 0$ downstream, are therefore very effective in stabilizing the flow. We have also performed an energy analysis to determine which terms in the disturbance flux enhance perturbations and which terms retard them [12]. Not surprisingly, perhaps, Marangoni convection in the streamwise direction can destabilize the flow while Marangoni convection in the transverse flow direction always stabilizes the fluid redistribution. The energy analysis confirms the requirements cited above for conditions under which the flow will be unstable.

CONCLUSIONS

A linear stability of the self-similar profiles governing the long time spreading behavior of insoluble surfactant on a thin liquid support has been shown to be stable for all wavenumbers within a QSSA. The Couette-like velocity profiles studied here do not contain an appropriate mechanism for destabilizing the spreading process. The disturbance flow, nonetheless, produces surface corrugations resembling fingering instabilities in other flow phenomena. Flow profiles for which the disturbance film thickness is positive while the surfactant concentration gradient is negative could create unstable flow. We are investigating such a possibility by probing the stability characteristics at earlier times than those studied here and by including the effects of capillarity and surface diffusion.

ACKNOWLEDGMENTS

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