

SURFACTANT-INDUCED FINGERING PHENOMENA IN THIN LIQUID FILMS

M. R. E. Warner *, R. V. Craster *, Omar K. Matar*** *Department of Mathematics, Imperial College London, SW7 2AZ, UK*** *Department of Chemical Engineering, Imperial College London, SW7 2AZ, UK*

Summary The spreading of surfactant on thin liquid films is accompanied by a fingering instability. We have developed a model, based on lubrication theory, which provides an explanation for this phenomenon. The patterns obtained from our simulations, which undergo tip-splitting and shielding, are in good agreement with those observed experimentally.

INTRODUCTION

Experimental studies involving the spreading of surfactants on thin fluid films by Marangoni stresses have demonstrated that these flows are susceptible to fingering instabilities [1-4]; an example of the fingering patterns from [3] is shown in Fig. 1. Several modeling studies, which have examined the stability of a surfactant monolayer spreading on a film of initially uniform thickness have shown that in the absence of van der Waals forces, growth could not be sustained [5] except in the presence of artificial constant feeding at the origin [6]. More recently, however, Warner *et al.* [7], focused on the dynamics of an insoluble surfactant deposition of order one thickness spreading over a much thinner liquid film; here the surfactant was present in dilute concentrations. These authors showed [7], that for a sufficiently large disparity in film thickness between the deposition and underlying film thickness, transverse perturbations of intermediate wavenumber grow exponentially targetting the leading edge of the droplet deposition behind the advancing front, in agreement with experimental observations.

Here, we extend the work of Warner *et al.* [7] in an attempt to capture trends associated with solubility and large concentrations observed experimentally [3], which show them to be destabilizing. We use lubrication theory to derive a coupled system of equations for the film thickness and surfactant bulk and surface concentrations in the limit of rapid vertical diffusion. Results from a transient growth analysis and direct numerical simulations show that a combination of surfactant solubility with high surfactant concentrations is in fact destabilizing in agreement with experimental trends. Here, we summarize the results of the numerical simulations only.

FORMULATION

We consider an initially stationary drop of soluble surfactant of constant viscosity μ^* and density ρ^* and of initial thickness \mathcal{H}^* and extent \mathcal{L}^* on a thinner uncontaminated fluid film of thickness \mathcal{H}_b^* and the same physical properties; here, dimensional variables are decorated with an asterisk. The solid substrate underlying the thin film is rigid, horizontal and impermeable and the dynamics of the overlying essentially inviscid gas are neglected. The initially uniform surface and bulk concentrations of the surfactant are denoted by Γ_m^* and C_m^* , respectively; we introduce the ratio $b \equiv \mathcal{H}_b^*/\mathcal{H}^*$: $b \rightarrow \infty$ corresponds to a monolayer spreading on an initially uniform film. The system dynamics are described by the following dimensionless evolution equations for the film thickness and surfactant surface and bulk concentrations, h , Γ and c , in the lubrication approximation [8]:

$$h_t = -\nabla \cdot \left[\frac{\mathcal{C}}{3} h^3 \nabla \kappa + \frac{1}{2} h^2 \nabla \sigma \right], \quad \Gamma_t = -\nabla \cdot \left[\frac{\mathcal{C}}{2} h^2 \Gamma \nabla \kappa + h \Gamma \nabla \sigma \right] + \frac{1}{\text{Pe}_s} \nabla^2 \Gamma + K(c - \Gamma), \quad (1)$$

$$c_t = - \left[\frac{\mathcal{C}}{3} h^2 \nabla \kappa + \frac{1}{2} h \nabla \sigma \right] \cdot \nabla c + \frac{1}{\text{Pe}_b} \frac{1}{h} \nabla \cdot (h \nabla c) - \frac{\beta K}{h} (c - \Gamma). \quad (2)$$

Here, the surface curvature, is given by $\kappa = \nabla^2 h$ and we have assumed that $\epsilon \ll 1$ and $\epsilon^2 \text{Pe}_b \ll 1$ (rapid vertical diffusion). In Eqs. (1) and (2), $\beta \equiv \frac{k_1^*}{\mathcal{H}^* k_2^*}$, $K \equiv \frac{k_2^* \mathcal{L}^*}{U^*}$, $\text{Pe}_b \equiv \frac{U^* \mathcal{L}^*}{\mathcal{D}_b^*}$, $\text{Pe}_s \equiv \frac{U^* \mathcal{L}^*}{\mathcal{D}_s^*}$, $\mathcal{C} \equiv \frac{\epsilon^2 \sigma_m}{\mathcal{S}}$, where k_1^* and k_2^* are adsorption and desorption rate constants, respectively; \mathcal{D}_s and \mathcal{D}_b denote the surfactant surface and bulk diffusion coefficients; $U^* = \mathcal{S} \mathcal{H}^* / \mu^* \mathcal{L}^*$ where $\mathcal{S} = \sigma_0 - \sigma_m$, the surface tension difference between the clean and contaminated interfaces. Note that small values of β represent highly soluble surfactants whilst $\beta \rightarrow \infty$ represents the insoluble surfactant limit. A dimensionless nonlinear equation of state, is used for closure: $\sigma(\Gamma) = \frac{\alpha+1}{[1+\Theta(\alpha)\Gamma]^\alpha} - \alpha$; $\Theta(\alpha) = \left(\frac{\alpha+1}{\alpha}\right)^{1/3} - 1$. In the limit $\alpha \rightarrow \infty$, $\sigma = 1 - \Gamma$.

RESULTS

We utilize an ADI scheme [7], which is based on operator splitting methods, to perform two-dimensional simulations of Eqs. (1)-(2) on a grid $0 < x < L_x$, $0 < y < L_y$, starting from $h(x, y, 0) = (1 - x^2 + b)H(1 - x) + bH(x - 1) + A(y) \exp(-5(x - 1)^2)$, $\Gamma(x, y, 0) = H(1 - x)$. Here, $A(y)$ comprises random values chosen from a uniform distribution on $[-0.01, 0.01]$ and $H(x)$ is a smoothed Heaviside function. These solutions are subject to the following boundary conditions: $h_x(0, y, t) = h_{xxx}(0, y, t) = 0$, and $h(L_x, y, t) = b$, $h_x(L_x, y, t) = 0$,

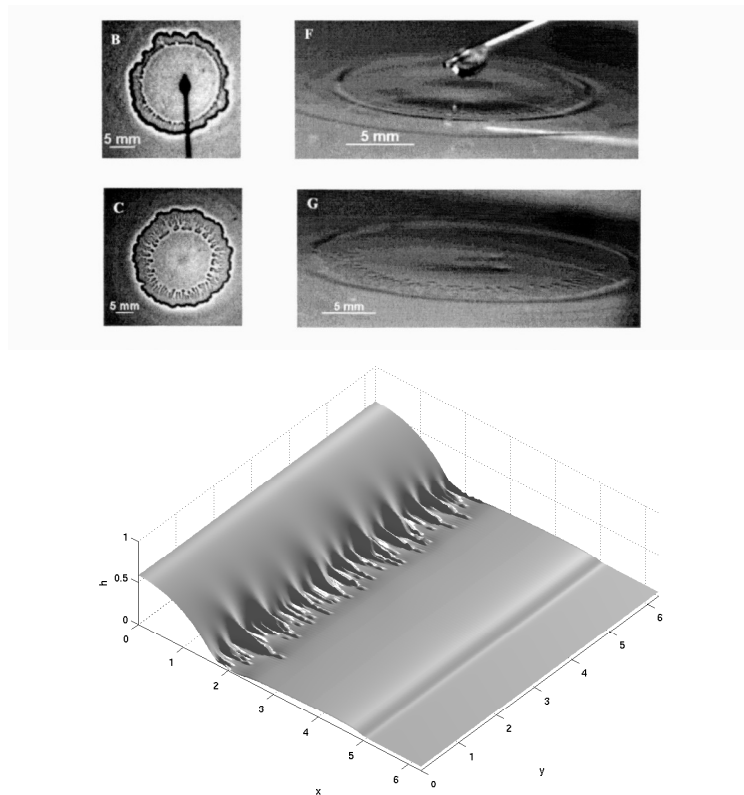


Figure 1. (Top): Fingering patterns at $t = 0.067$ sec ('B') and 0.31 sec ('C') during the spreading of a $9 \mu\text{l}$ droplet of 1.2 CMC SDS solution on a $25 \mu\text{m}$ water film [3]; side-views are shown in 'F' and 'G'. (Bottom): Surface plot of h with $\alpha = 0.1$, $\beta = 1$, $b = 0.1$, $K = 1$, $Pe_b = 100$, $Pe_s = 10^4$, $C = 10^{-3}$ and $t = 125$.

$\Gamma_x(0, y, t) = c_x(0, y, t) = 0$ and $\Gamma(L_x, y, t) = c(L_x, y, t) = 0$. Periodic boundary conditions are imposed at $y = 0, L_y$. Typically we utilize a 2π square grid and have a 200×200 mesh. As shown in Fig. 1, the initially noisy disturbances have self-organised into coherent fingering structures, which exhibit splitting and shielding events. The results shown in Fig. 1 demonstrate that the emerging fingering patterns, which are associated with a soluble surfactant are in qualitative agreement with the observed finger formation in many experiments [2,3]. We have also shown [8] that increasing the degree of solubility is destabilizing (except for very small β , for which the Marangoni stresses that drive the instability are very weak).

CONCLUSIONS

We have considered the stability of a drop laden with soluble surfactant spreading on the surface of a thin liquid film within the framework of lubrication theory and rapid vertical diffusion. The results of our numerical simulations of the fully nonlinear governing equations summarised here [8] show the appearance of fingering patterns, which localize at the drop leading edge accompanied by tip-splitting, coalescence and shielding.

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