

Marangoni Instabilities in Transient Coating Flows:

The Role of Multiple Time Scales

Stergios G. Yiantsios (*) and Brian G. Higgins (**)

(*)Department of Chemical Engineering
Aristotle University of Thessaloniki,
Thessaloniki, Greece

(**)Department of Chemical Engineering and Materials Science
University of California
Davis CA 95616, USA

Presented at the 15th International Coating Science and Technology Symposium,
September 13-15, 2010, St. Paul, MN¹

Introduction

When a coating film thins and dries through solvent evaporation, unwanted perturbations can lead to thickness imperfections in the dried film, or even worse, film de-wetting. Sources of unwanted perturbations are the thermocapillary or solutocapillary flows that arise due to surface tension gradients, the so-called Marangoni instability. In most circumstances film flow and drying are coupled, such that disparate time scales dictate the fate of film dynamics associated with solvent mass flux from the drying film, versus the various diffusion processes within the thinning film (momentum, thermal and molecular). A limiting case that has been studied frequently is the quasi - static limit. In this limit the evolution of the liquid film (due to solvent evaporation) is sufficiently slow that its variation with time can be neglected relative to exponentially growing perturbations superimposed on the base state. In this presentation we investigate circumstances in which the quasi-static limit is not valid. A thin film analysis is outlined and evolution equations for the film thickness and the surfactant/polymer concentration are derived and analyzed by the techniques of linear stability and numerical simulation. The developed theory describes the competition among the various instabilities (thermocapillary and solutocapillary) and their coupling. We consider two example problems: (i) the mechanism for instability due to soluble surfactants, and (ii) the thermocapillary instability when flow and drying are intimately coupled (as occurs in spin coating). Criteria for the onset of Marangoni instability are presented and where possible theoretical predictions are compared with experimental data. We conclude our presentation with overview of other coating scenarios where such instabilities might be important.

¹ Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

Analysis

We consider a thin liquid film of initial thickness h_0 , resting on a flat solid substrate. The liquid is a simple fluid with constant properties and is evaporating slowly at a constant rate E determined by a mass transfer process in the overlying gaseous phase. The film is thin enough to neglect the effects of gravity, yet thick enough so that molecular forces and disjoining pressure can also be ignored. It is further assumed that temperature differences developed due to the evaporation are insignificant and can be also ignored.

What we consider in detail and place emphasis upon are the effects of a surfactant which is soluble in the liquid. So part of it remains in the bulk and part of it is distributed along the liquid/gas interface. As the liquid is lost by evaporation, the surfactant concentration increases both in the bulk and at the interface. The relative rates of increase depend on surfactant solubility and on the kinetics of exchange. To make matters simple, it is assumed that the kinetics of this exchange is fast so that equilibrium between the two concentrations prevails at all times. Moreover, we consider the dilute limit so that a linear isotherm can be assumed. Finally, we assume that surfactant diffusion across the thin film is fast enough so that it is essentially uniform in the thin film dimension. Our analysis for the flow and surfactant transport is in the context of the lubrication approximation. Details are provided elsewhere, see Yiantsios and Higgins (2010). The analysis leads to a nonlinear evolution equation for the film thickness, that is non-autonomous in time. A linear stability analysis reveals that the evaporating film can become unstable. The instability is confirmed by a numerical simulation of the nonlinear evolution equation.

Sample Results

Figure 1 shows the largest eigenvalue ω as a function of wavenumber α for various values of Marangoni number M and the dimensionless surface viscosity S . We verify analytically that the eigenvalue asymptotes to $1/(1+\beta)$ for very small wavenumbers, which implies a neutral state according to linear theory (β is the dimensionless partition coefficient for the surfactant). However, for small β there is a range of wavenumbers where the eigenvalue exceeds the rate of change of the base concentration. The maximum eigenvalues increase as M increases but much less than proportionally to it. When the parameter S is one (dashed lines) the rates of change decrease in absolute value, indicating that surface viscosity slows down the dynamics. In Figure 2 the shape of the interface as evaporation proceeds is shown together with the corresponding bulk surfactant concentration distribution along the film for $M=10$. As may be observed, short wavelength initial perturbations in the thickness are quickly leveled out due to the action of capillarity and diffusion. However, longer wavelength perturbations persist and gradually increase in size as evaporation proceeds. Concentration non-uniformities develop and the maxima correspond to the points of minimum film thickness. For M equal to 10 the film thickness non-uniformities increase only imperceptibly. However, calculations for M equal to 100 the thickness non-uniformities increase significantly and for $M=1000$ the instability is strong enough so that at some points the thickness eventually increases despite the overall thinning due to evaporation.

In the presentation we will also discuss the thermocapillary instability when flow, drying and chemical reaction are intimately coupled (as occurs in spin coating and photopolymerization). In

these examples the base state is time dependent and the competition between various time scales determines the fate of the instability.

Conclusions

A new mechanism of Marangoni instability in evaporating thin films due to soluble surfactant has been presented and analyzed in this study. As the films thin due to evaporation, thickness perturbations lead to surfactant concentration and, hence, surface tension perturbations, which in turn drive the instability and tend to enhance uneven film drying. According to the present analysis, for the instability to be observed an appropriate Marangoni number has to be relatively large and the surfactant solubility in the bulk to be large as well. Estimates of the relevant parameters suggest that such conditions may be met in relatively thick films, on the order of tens of microns, for which the effects of molecular forces and disjoining pressure are not dominant. Diffusion of the surfactant and its effect on interfacial mobility tend to suppress disturbance growth, although their effects are not likely to become significant, unless the films are much thinner, i.e. on the order of one micron or below. Three-dimensional simulations showed that the surface irregularities induced by the instability are not correlated. This suggests that the instability might be a way to induce surface roughness onto a film. Such surface roughness may have implications for light scattering features of the film, wetting and adhesion properties of the film.

References

S.G. Yiantsios and B.G. Higgins, “A mechanism of Marangoni instability in evaporating thin liquid films due to soluble surfactant” *Phys. Fluids* **22**, 022102 (2010).

Figures

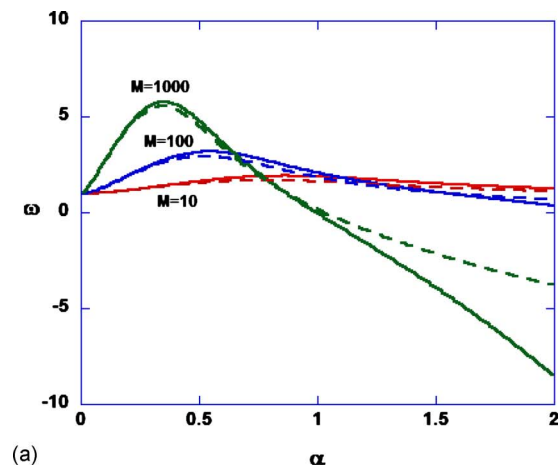


Figure 1: The largest eigenvalue as a function of wavenumber, for $M=10$, 100 and 1000 . (a) $\beta = 0.01$ Solid lines are for $S = 0$ and dashed lines for $S = 1$.

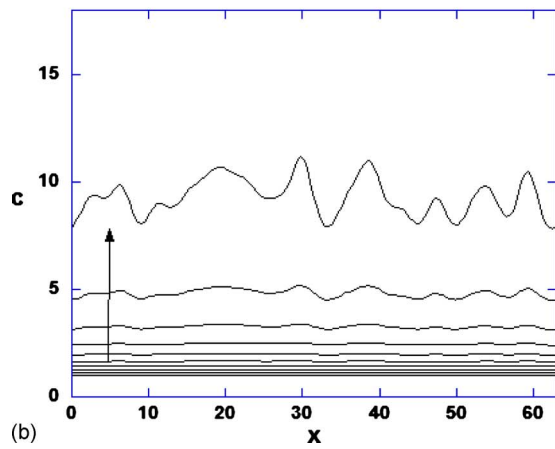
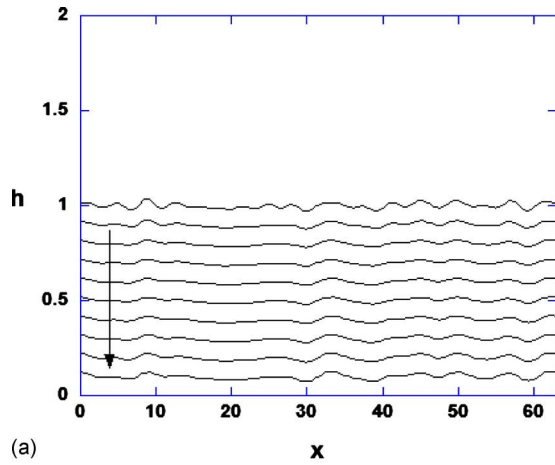


Figure 2: Contours of film thickness (a) and concentration (b) at successive time intervals of 0.1 dimensionless units. $M = 10$, $\beta = 0.01$, $S = 1$, $Pe_b = 1$, $Pe_s = 1$. Time progresses in the direction of the arrow.