Marangoni flows during drying of colloidal films

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In this study we consider the drying of a thin film that contains a stable dispersion of colloidal particles so that a coating of these particles is formed after the liquid is driven off by evaporation. For sufficiently thin films, we show that evaporative cooling can drive a Marangoni flow that results in surface deformation of the drying film. A thin-film approximation is used to describe the velocity and temperature fields, and the particle transport equation with convective terms retained is used to describe the concentration field. A coupled finite difference/spectral element scheme is implemented numerically to solve the particle transport equation, where high accuracy is required to resolve sharp gradients within the film and to ensure particle conservation during drying. The model employed is capable of describing the evolution of film thickness and concentration field up to the time when maximum packing is nearly reached at some point in the domain. Three types of film structures are observed, all characterized by a final non-uniform thickness. In the first type, observed at low Peclet numbers, the maximum concentration is reached at the thinnest points in the film, which surround elevations with lower particle concentrations. This mode of instability suggests that dried coatings will have pronounced non-uniformities, resulting in the formation of craters or pinholes. In the second type, observed at high Peclet numbers, a closely packed skin of non-uniform thickness is formed, with low concentration fluid remaining beneath the elevations. In the final stages of drying one would expect capillary pressure to pull particles in the underlying fluid toward the skin, thus creating voids under a seemingly homogeneously applied coating. Finally, still at relatively large particle Peclet numbers and when the destabilizing Marangoni stresses are sufficiently strong, floating lumps of closely packed particles may form in the vicinity of film elevations.

1. INTRODUCTION

The solution coating of colloidal particles is frequently used in the production of displays and other optical films. A crucial step in these manufacturing processes is the drying of the coated film by evaporation to yield a particulate film of uniform thickness. The main motivation behind the present work is to model the effect of evaporation induced Marangoni instabilities on coated film quality and integrity. Non-uniformities in colloidal particle deposits have been extensively analyzed in the context of evaporating droplets because of enhanced evaporation at the contact lines[1,2]. However, in coated products which are essentially two-dimensional in lateral extent, other factors rather than edge effects may be important.

Routh and Russel[3] and Tirumkudulu and Russel[4] have studied drying colloidal dispersions, both experimentally and theoretically. In their analysis the Brownian diffusion of the particles was assumed large enough so that it effectively homogenizes the particle concentration across the liquid film. Routh and Zimmerman[5] analyzed the effect of non-zero particle Peclet number on film vertical uniformity but assumed that deformation and convective motion were absent. The present work focuses precisely on those two aspects, which may be driven by thermocapillary phenomena[6-8] or other effects giving rise to

surface tension gradients[9]. We focus here on the long wavelength surface deformation mode[10] that can ultimately lead to the formation of dry patches or elevated spots. This mode is more likely to be observed in evaporating rather than in non-volatile films heated from below because essentially higher temperature gradients may be established more easily.

II. PROBLEM FORMULATION

We consider a colloidal film on a solid substrate with initial thickness h_0, evaporating at a constant rate, E. The temperature at the interface relative to that of the substrate may be obtained from a balance of heat flux through the film and enthalpy of vaporization, i.e. $-k(T_i-T_0)/h_0=\lambda\rho E$. Here k is the film thermal conductivity, ρ is the density and λ is the heat of vaporization. When perturbations in the film thickness exist they are accompanied by variations of the interfacial temperature, i.e. elevations become colder and vice versa. As a result, surface tension varies also according to the relation $\sigma=\sigma_0 -\sigma_T(T_i-T_0)$. Surface tension tends to smooth out such perturbations but its variation induces shear stresses that tend to pull fluid from the hotter depressions towards the colder elevations. Two dimensionless parameters are defined: a capillary number, $C=\mu_0 E/\sigma_0$, and a Marangoni number, $M = \sigma_T\lambda\rho h_0/\mu_0 k$. In the context of the thin-film approximation[7], which requires that $CM<<1$, simplified expressions of the momentum equations may be used. The equation describing the motion of the free surface becomes

$$h_t + uh_x = v - (CM^2)^{-1} \qquad (1)$$

Thus, if CM^2 is a small number, liquid evaporation is fast compared to any convection due to Marangoni effects. On the other hand convective effects may play a role if $CM^2>>1$.

To obtain the velocities at the film surface in Eq. (1), the local and instantaneous value of viscosity is needed. For hard-sphere colloids the viscosity relative to that of the pure liquid is a function of particle concentration[11], i.e. $\mu=(1-\phi/0.64)^{-2}$. Thus, the convection-diffusion equation for the particles needs to be solved simultaneously. The dimensionless particle diffusivity, scaled by the Einstein diffusivity, D_0, is given by $D(\phi)=K(\phi)d[\phi Z(\phi)]/d\phi$, where $K(\phi)=(1-\phi)^{6.55}$ is the particle sedimentation coefficient and $Z(\phi)=1.85/(0.64-\phi)$ is the compressibility factor[11]. The relative effects of particle convection and diffusion define the dimensionless parameter $\hat{Pe}=CM^2(Eh_0/D_0)=CM^2 Pe$, where Pe is a Peclet number based on the evaporation velocity. Therefore, given the constraint $CM^2>>1$, so that Marangoni effects may be important, it is clear that particle convection is dominant. Thus, no simplification may be made other than neglecting the longitudinal diffusion terms in the particle transport equation. The latter, which is supplemented with the conditions of no particle flux at the substrate and the interface, takes the form

$$\frac{\partial\phi}{\partial t} + \nabla\cdot\boldsymbol{u}\phi = \frac{1}{CM^2 Pe}\frac{\partial}{\partial y}\left[D(\phi)\frac{\partial\phi}{\partial y}\right]. \qquad (2)$$

In the numerical formulation[12] the film thickness was discretized into equally-spaced segments and its spatial derivatives were expressed in terms of central finite differences. Eq. (1) was advanced in time by an explicit fourth-order Runge-Kutta procedure. To obtain the viscosity, a highly accurate spectral element representation of the concentration field in the y-direction was employed. The Arbitrary Lagrangian-Eulerian technique was implemented for particle transport equation in the moving domain.

III. RESULTS AND DISCUSSION

Two-dimensional simulations were performed in simple domains containing one unstable wavelength in the lateral direction. Periodic conditions for the film thickness, the velocities and particle concentration were assumed. In all the simulations a simple sinusoidal perturbation in the film thickness of amplitude

0.01 was applied as an initial condition. The simulations proceeded up to the time when the particle concentration approached the maximum packing limit to within 10^{-4} at some point in the domain.

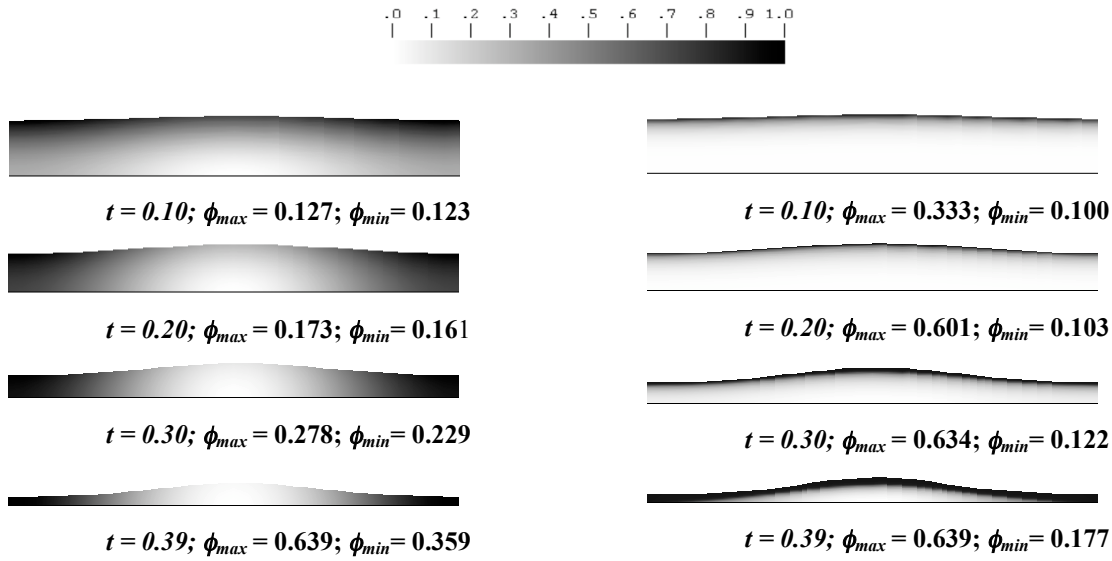

Fig. **1.** Particle concentration fields at various times during the evolution of film drying for Pe = 0.1 (left) and Pe = 10 (right). CM^2 = 50, ϕ_0 = 0.1. In each plot the grey scale is normalized so that zero and one correspond to the instantaneous minimum and maximum particle concentrations.

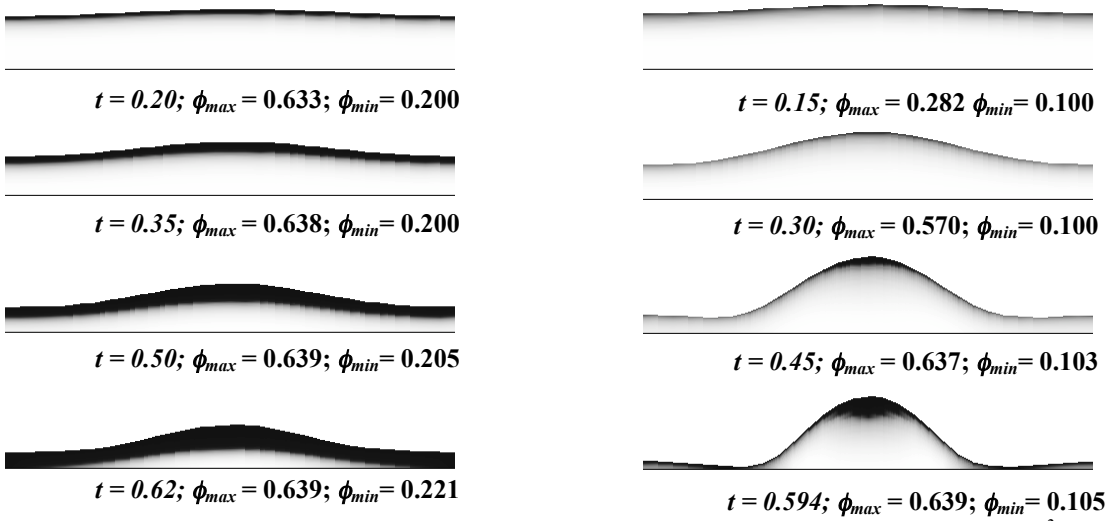

Fig. **2.** Particle concentration fields (left) at various times during the evolution of film drying, for CM^2 = 100, Pe =10, ϕ_0 = 0.2 (left) andϕ_0 = 0.1 (right).

At relatively low Peclet numbers vertical concentration gradients are effectively smoothed by diffusion (Fig. 1). Thus, the instability, which induces non-uniform thinning, results in a film more concentrated at the depressions and reaching the maximum packing limit first at the thinnest points. When the Peclet number is increased a relatively closely packed particle front is formed near the free surface. This front propagates downward eventually leaving less concentrated fluid only underneath the film elevations.

When the intensity of the destabilizing Marangoni stresses is further increased, and still at relatively high Peclet numbers, convective forces tend to collect particles more effectively near the film elevations and to create a skin of maximum local thickness there (Fig. 2). This effect is more pronounced for a more dilute initial dispersion under the same conditions due to the lower overall film viscosity. The nonlinear growth of disturbances leads to a balance between Marangoni and capillary forces and the formation of a sessile drop in quasi-equilibrium, which concurrently thins due to evaporation. Near the peak of such drops floating lumps of closely packed particles tend to form.

IV. CONCLUDING REMARKS

The Marangoni instability of an evaporating film of a colloidal dispersion has been considered in this study. Attention was restricted to thin films such that a deformational mode of instability may be operating. Two parameters control the stability characteristics, namely a capillary number, C, a Marangoni number, M. The long-wavelength approximation requires that the product CM be much smaller than unity, but in order for the instability phenomena to be faster than evaporation the product CM^2 must be much larger than unity. Gravity, which suppresses disturbance growth, introduces a third parameter, $G=gh_0k/\sigma_T\lambda E$, which must be less than 3/2 for the instability to exist. Gravity is assumed to be negligible in the present work.

Three types of film structures were observed, all characterized by a final non-uniform thickness. In the first type, observed at low Peclet numbers, the maximum particle concentration is reached at the thinnest points which surround elevations with lower concentration. In the second, a closely packed skin of non-uniform thickness is formed and low concentration fluid remains only underneath the elevations. Finally, still at relatively large particle Peclet numbers and when the destabilizing Marangoni stresses are sufficiently strong, floating lumps of closely packed particles may form in the vicinity of film elevations. Beyond this stage a different type of modeling would be necessary to pursue the evolution of the film characteristics up to complete drying. However, it is perhaps plausible to suggest that for the first type of behavior dried coatings with pronounced non-uniformities may be observed. Moreover, capillary pressure would tend to pull the fluid and particles towards the closely packed regions and in this way induce the formation of craters or pinholes. Profiles of dried coatings exhibiting similar forms of localized depressions at the center of 2-D films of finite extent were predicted in [4]. On the other hand, if a closely packed skin is formed it is likely that capillary pressure would tend to pull the particles of the underlying more dilute fluid toward this skin, thus creating voids under a seemingly homogeneously applied coating.

REFERENCES

1. R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, and T.A. Witten, , Nature **389,** 827 (1997).
2. H. Hu and R.G. Larson, Langmuir **21**, 3972 (2005).
3. A.F. Routh, and W.B. Russel, AIChE J. **44**, 2088 (1998).
4. M.S. Tirumkudulu and W.B. Russel,, Langmuir **20**, 2947 (2004).
5. A.F. Routh, and W.B. Zimmerman, Chem. Eng. Sci. **59**, 2961 (2004).
6. S.H. Davis, Ann. Rev. Fluid Mech. **19**, 403 (1987).
7. A. Oron, S.H. Davis, and S.G. Bankoff, Rev. Mod. Phys. **69**, 931 (1997).
8. S.J. VanHook, M.F. Schatz, J.B. Swift, W.D. McCormick, and H.L. Swinney, J. Fluid Mech. **345**, 45 (1997).
9. T. J. Rehg, "Spin coating of monodispersed colloidal suspensions: evidence of evaporative convection", PhD Thesis, University of California, Davis (1992).
10. L.E. Scriven and C.V. Sterling, J. Fluid Mech. **19**, 321 (1964).
11. W.B. Russel, D.A. Saville, and W.R. Schowalter, *Colloidal Dispersions*, Cambridge, 1989.
12. S.G. Yiantsios and B.G. Higgins, Phys. Fluids, submitted (2006).