



Rapid Communication

Switching the Roles of Wettability-based Patterns Through Solutal Marangoni Effect



Shantharama, Sreeram K. Kalpathy*

Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Madras, Chennai 600036, India

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ABSTRACT

Controlling the dynamics of thin liquid films on solid surfaces is illustrated by a combination of substrate patterning and solutal Marangoni effect. A solid surface, patterned based on wettability differences, can trigger film instability due to wettability gradient-driven flows. Additionally, if insoluble surfactants are introduced at the liquid film surface, the surfactant transport can cause surface-tension gradients across the film, and a solutal Marangoni flow results. By using suitable non-uniform initial surfactant concentration distributions, the rate and direction of Marangoni flow can be manipulated to compete with the wettability gradient-driven flows. It is found that film dewetting can be reversed in selected problem parameter space. Dewetting can be engendered on more wettable patches of the bounding solid, with a consequent accumulation of the liquid on less wettable regions. The importance of length scales of the less and more wettable patches on switching the roles of wetting behaviour is also investigated.

Liquid film dewetting on chemically patterned surfaces is a promising approach for templating, and fabrication of meso- and nano-structures [1]. If a flat liquid film is deposited on a solid consisting patches of less and more wettable regions, the wettability gradients will render the film unstable by driving a flow from the less to more wettable regions of the solid [2,3]. Consequently, the film dewets, with possible formation of various complex morphologies or droplet structures [4], depending on the length scale of the patterns present. This principle is potentially useful in several coating and printing processes, however, they are often conducted in environments which could contain surface-active contaminants. Besides, surfactants may be deliberately introduced in liquid film-based templating processes for patterning colloids and polymers [5–7]. Local concentration variations of surface-active particles cause gradients in surface tension in a liquid film, and induce a tangential flow by the solutal Marangoni effect [8]. The resulting nonlinear interplays between solutal Marangoni flows and the wettability gradients is the subject of the present work.

To the best of our knowledge, the present work is the first to address the combined effects of the two physics on liquid film behaviour: Wettability-based chemical patterning, and solutal Marangoni effect. We propose that, by suitably modifying the initial distribution of surface-active particles, Marangoni flow can be directed in such a way as to oppose the wettability gradient-driven flows. This competition can be exploited to make the liquid film dewet a potentially wettable patch, and collect itself largely on a non-wettable patch. A discussion of the

mechanisms by which this switching of roles of wettability may occur, and the role of pattern sizes on the same is presented here.

A schematic of the model 1-D problem setup is shown in Fig. 1. A thin film of a Newtonian liquid rests on a solid substrate, chemically patterned with alternate patches of less and more wettable regions. The film has a non-dimensional local film thickness $H(X, T)$, where X and T refer to the dimensionless spatial coordinate and time. The surface of the liquid film is covered with insoluble surfactants with local concentration $\Gamma(X, T)$. The governing equations and boundary conditions can be written in the lubrication limit [8,9], considering the small aspect ratio of the film. The following set of coupled non-dimensional equations govern the spatio-temporal evolution of the film thickness and the surfactant concentration [9]:

$$\frac{\partial H}{\partial T} - \frac{1}{2} M \frac{\partial}{\partial X} \left[H^2 \frac{\partial \Gamma}{\partial X} \right] - \frac{1}{3} \frac{\partial}{\partial X} \left\{ H^3 \left[\frac{\partial(AH^{-3})}{\partial X} \right] \right\} + \frac{1}{3} \bar{C}^{-1} \frac{\partial}{\partial X} \left[H^3 \frac{\partial^3 H}{\partial X^3} \right] = 0 \quad (1)$$

$$\frac{\partial \Gamma}{\partial T} - M \frac{\partial}{\partial X} \left[\Gamma H \frac{\partial \Gamma}{\partial X} \right] - \frac{1}{2} \frac{\partial}{\partial X} \left\{ \Gamma H^2 \left[\frac{\partial(AH^{-3})}{\partial X} \right] \right\} + \frac{1}{2} \bar{C}^{-1} \frac{\partial}{\partial X} \left[\Gamma H^2 \frac{\partial^3 H}{\partial X^3} \right] - \frac{1}{Pe} \frac{\partial^2 \Gamma}{\partial X^2} = 0 \quad (2)$$

Here M is the solutal Marangoni number, \bar{C} is the capillary number, and Pe is the Peclet number, all rescaled appropriately to account for

* Corresponding author.

E-mail address: sreeram@iitm.ac.in (S.K. Kalpathy).

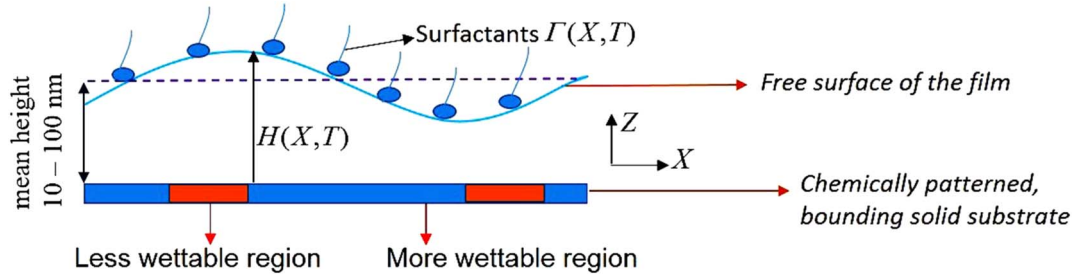


Fig. 1. Schematic of the problem setup with labelled symbols in dimensionless form.

the small aspect ratio of the film. The presence of van der Waals type intermolecular forces is incorporated through a disjoining pressure potential [8,9], expressed as AH^{-3} in Eqs. (1) and (2). Here A is a dimensionless Hamaker parameter that measures the van der Waals attraction between the solid and the free surface of the liquid [10]. The spatial variation in wettability of the bounding solid substrate is modelled using an analytical expression [11] for $A(X)$ that resembles a step function, with a provision for a smooth transition zone of adjustable width. The function is such that it approaches a constant, positive value all across the less wettable patches on the solid (higher attraction, leading to film dewetting or break-up), and approaches 0 over the more wettable or neutral patches on the solid (lesser attraction, maintaining a stable liquid film). Throughout the results in this paper, we have used a narrow transition zone between the more and less wettable patches, whose width is of the order of 0.2% of the total domain length.

If the spatial variation of A be temporarily ignored, a standard linear stability analysis of the coupled Eqs. (1) and (2) yields the following expression for the growth rate of small amplitude perturbations at the air-liquid interface, ω , as function of the perturbation wavenumber k :

$$\omega^2 + \omega \left(\frac{k^2}{3} \right) \left[\bar{C}^{-1} k^2 - 3A + 3M + \frac{3}{Pe} \right] + \frac{k^4}{3} \left[\bar{C}^{-1} k^2 - 3A \right] \left[\frac{M}{4} + \frac{1}{Pe} \right] = 0 \quad (3)$$

Fig. 2a shows plot of the maximum growth rate ω_{\max} as predicted by Eq. (3), which suggests that ω_{\max} decreases with increasing Marangoni number (M), and eventually plateaus to a saturation value. Since the maximum growth rate can be interpreted as an inverse of the break-up time scale (T_r) of the film, this means the film will be more stable for higher values of M . In the derivation of Eqs. (1) and (2), M has the mathematical definition $\frac{c_0}{\sigma_0} \frac{\partial \sigma}{\partial c} \Big|_{c=c_0}$, where c_0 is the mean, dimensionless, surfactant concentration in the film, and $\frac{\partial \sigma}{\partial c}$ measures the effectiveness of the surfactant, through the rate of decrease in surface tension from its pure liquid value σ_0 with concentration c . As M is seen to be a stabilizing parameter from Fig. 2a, the film can be stabilized either by adding more surfactants, or by using surfactants with greater surface-active tendency. On the other hand, Fig. 2b suggests that the maximum growth rate increases as a function of the Hamaker parameter A , with a power-law fit. This means, for a greater attraction between the liquid free surface and the solid, the maximum growth rate will be higher, and the break-up time (T_r) will be correspondingly lower. Such van der Waals-driven film rupture is a well-known mechanism for instability of thin liquid films [8]. Here we have established that the quantitative relationship is a power-law fit between ω_{\max} (or, $1/T_r$) and A .

Although Fig. 2b only models the situation of a solid surface with uniform wettability (for which A is constant), the important idea to be extracted is that the van der Waals attraction and solutal Marangoni effect counteract each other with respect to film stability. Therefore, when spatial variations in wettability are present, spatially non-uniform surfactant distributions could be used to manipulate the film dynamics. Fig. 2c shows a schematic of how the natural dewetting dynamics can be altered. In this schematic, surfactants are initially confined to certain locations along the film surface. Therefore, Marangoni flows would

result towards the surfactant-depleted zone. If the solid is patterned such that the flow driven by wettability patterns is in a direction opposite to the Marangoni flow, then the net flow rate leading to film break-up is reduced, and film rupture could be delayed significantly. Additionally, if either the initial mean surfactant concentration, or its surface-active tendency is high enough, it could as well suppress the dewetting of liquid at the less wettable patches.

The film dynamics at late stages of its evolution, and the role of varying wettability with different pattern widths, were studied by numerically solving the nonlinear evolution Eqs. (1) and (2). The centered finite difference scheme of fourth order accuracy was used for spatial discretization, with approximately 1500 nodes in a domain of size 3λ , where λ is the fastest growing wavelength as predicted by linear stability analysis. Numerical integration in time was performed using the DASSL package with a dimensionless time step of 10^{-6} . Periodic boundary conditions were implemented, and the initial condition for H was a random perturbation around the base state $H = 1$. The random perturbation consisted of a series of wavelengths ranging between λ and $\lambda/100$, and different amplitudes, with the mean amplitude being 0.01. For the surfactant concentration Γ , the initial condition was either a uniform concentration ($\Gamma = \Gamma_0$), or variable through an exponential distribution function of the following type:

$$\Gamma(X, T = 0) = Z \left[1 + \alpha \exp\left(\frac{(X - L/2)^2}{\delta}\right) + \alpha \exp\left(\frac{(X + L/2)^2}{\delta}\right) \right] \quad (4)$$

where L is the domain length, α , δ control the height and smoothness of the spike in concentration, and Z is a normalization factor to maintain a mean concentration.

Fig. 3a-c shows film height profiles at rupture for three different pattern sizes when the initial condition is a uniform surfactant concentration $\Gamma = 1$. In order, the central, less wettable patch (where $A(X)$ has a constant positive value) has widths of (a) 0.3λ , (b) 1.2λ , and (c) 2.0λ . These profiles resemble the ones in Ref. [12,13], which explain rupture behaviour of a pure liquid film in the absence of any surfactants. The occurrence of a single rupture at the center for a small pattern, and the tendency for multiple ruptures for larger patterns is a consequence of the balance between capillarity and wettability gradients [14]. Nevertheless, the rupture itself is initiated by the wettability gradients at the transition between less and more wettable patches. As observed by Karakashev et al., [15] the film evolution in the initial phase would not be affected by patterning on the bounding substrate. The dewetting kinetics would be similar until an equilibrium thickness is reached. As the strength of the Van der Waals attraction becomes more at a sufficiently thinned region, the dynamics is accelerated. The eventual rupture of the film inside the less wettable region at the center is because of the greater driving force there, in the form of van der Waals attraction ($A(X) > 0$) between the solid and the liquid free surface. The ruptured configuration would ultimately depend on the pattern size, as also noted in the experiments of Karakashev et al. [15] for surfactant-free wetting films. Therefore, it is intuitive from our results that an initially uniform distribution of surfactants does not alter the dewetting mechanism and the ruptured film profiles. It does, however, affect the rupture time, due to Marangoni flow-driven

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