From: PHASE TRANSITIONS IN SOFT CONDENSED MATTER
Edited by Tormod Riste and David Sherrington
(Plenum Publishing Corporation, 1989)

FINGERING INSTABILITY OF A SPREADING DROP

S.M. Troian, X.L. Wu., E. Herbolzheimer and S.A. Safran

Exxon Research and Engineering Co.

Clinton Twp., Rt. 22E, Annandale, New Jersey 08801

Most studies of the dynamics of wetting have focused on the spreading of *pure* non-volatile drops on smooth and *dry* surfaces. For the most part, such spreading processes are well understood, with good agreement between experiment [1,2] and theory [3,4]. In all such studies of spreading on smooth substrates, the macroscopic wetting process, whether spontaneous or forced, proceeds by the movement of a uniform and circular contact line (the boundary where the air, liquid and solid meet). As first discovered by Marmur and Lelah [5], some unusual wetting behavior can result from the addition of surfactant to the spreading liquid. Anionic and non-ionic aqueous surfactant solutions spread on smooth glass by developing fingers, which branch as they grow and leave behind a dendritic-like pattern. The wetting process with surfactant proceeds at a rate which is approximately an order of magnitude faster than the spreading of a pure liquid, although the surface coverage is quite non-uniform. We summarize below some results of an experimental [6] and theoretical study [7] of the effect of adding surfactant to a spreading drop. The interested reader is referred to refs. 6 and 7 for all further details.

Contrary to earlier reports [5], we have confirmed that this novel hydrodynamic instability only occurs for a drop of surfactant solution spreading over a pre-exising film of pure water coating the glass surface. The instability disappears for spreading onto a dry surface. The dependence of the rapid spreading and fingering on the presence of the initial water film (and on the drop surfactant concentration) strongly suggests that the instability is driven by the Marangoni effect [8], which describes flow produced by variations in surface tension. Surface tension gradients, which can be established by gradients in surfactant concentration (as in our experiments) or temperature, cause traction along the air-liquid interface which must be balanced by a shear stress in the fluid. The surface traction induces flow in the interface and adjoining liquid layers in the direction of increasing surface tension.

In our experiments, for example, a 1mM aqueous Aerosol OT (sodium bis(2-ethylhexyl sulfosuccinate) drop has a surface tension of 40 dynes/cm, significantly lower than the surface tension, 73 dynes/cm, of the pre-existing water film. Therefore, upon deposition of the surfactant drop on the pure water film, the Marangoni force draws a layer of liquid out from the drop edge which thins the pre-existing water film as it quickly spreads radially outward. This initial "sheet" of spreading liquid appears to establish a surface tension gradient over a fairly long region ahead of the macroscopic drop. (For low surfactant concentrations, the surface tension is linearly and negatively proportional to the surfactant concentration.) The remainder of the drop then spreads over this thinned film. The velocity of the fingering front is strongly dependent on the

initial drop surfactant concentration and weakly dependent on the thickness of the pre-existing water film.

We discuss here only the patterns observed as the thickness of the pre-existing water film is varied and the AOT concentration is held fixed. Fig. 1 shows two typical patterns obtained for spreading of a 1mM drop of aqueous AOT on films of thickness estimated to be (a) $0.1\mu m$ and (b) $1\mu m$. Spreading on the thicker film leads to broader, rounded fingers, while spreading on the thinner film leads to narrow, sharply tipped, more ramified fingers. In all the cases using surfactants we have studied, the fingers undergo tip-splitting, implying there is a preferred finger width in this system. We are investigating whether this width might be set by the competition between the (destabilizing) Marangoni force and the (stabilizing) force of surface tension associated with the curvature of the three-dimensional air-liquid surface.

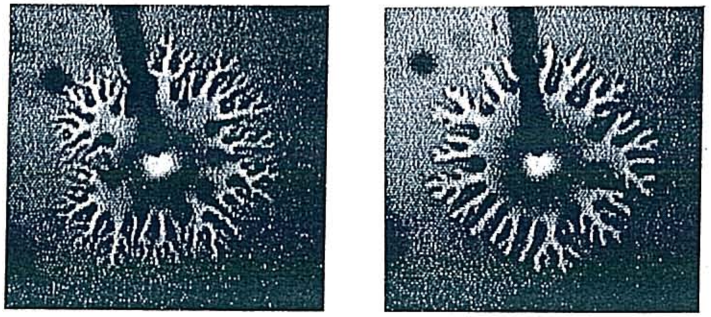
In addition to tip-splitting, the fingers also undergo shielding and spreading, processes also observed in other fluid flow instabilities [9]. We note, however, that the miscible fluids used (pure water and aqueous surfactant solution with less than 0.1% surfactant by weight) have negligible viscosity difference. In addition, the experiments are performed in an *open cell* geometry with no external pressure gradient forcing movement of the spreading front. These two features rule out the presence of a Saffman-Taylor instability as seen in viscous fingering experiments [10].

To characterize the patterns, we have measured the growth rate of the fingers by defining the radius R(t) of the circular envelope circumscribing the fingers minus the initial radius of the drop. Fig. 2 is a plot of the radius as a function of time. The fingers follow a power law growth in time, whether spreading on a thick or thin film. The proportionality constant is larger for spreading on the thicker water film since viscous dissipation effects are smaller. We have begun to study the fractal dimension of the fingering contours. Preliminary results indicate a perimeter fractal dimension consistent with $D_F \approx 1.7$ for spreading on different thickness films and for all fairly developed patterns.

The Marangoni effect is well understood but most studies have focused on an explanation of the uniform (unperturbed) front flow [11] in the absence of capillary terms or on the instability which gives rise to roll cells when a fluid is heated from above or below [12]. The instability we have modelled occurs at the *moving front* of the spreading drop. Before attempting the stability analysis, the unperturbed (base) flow profile is required of a drop spreading due to a surface tension gradient, including capillary terms. Although the fingering patterns we have seen have features in common with viscous fingers, this system differs from Hele-Shaw flow in two important ways. First, the spreading front is a real free surface and perturbations at the moving edge can cause corresponding changes in the local fluid height. Second, the motion and height of the fluid are strongly coupled to the local concentration distribution of surfactant.

The steady state solution of the two flow equations (in a lubrication approximation) coupling the local fluid height to the local surface tension reveals the presence of three distinct regions in the flow. There exists a region (1) extending across the radius of the macroscopic drop where the capillary term leads to an almost spherical cap shape and a small region (2) near the drop edge in which the droplet shape is smoothly matched to a long region (3) of constant height ahead of the drop. In this third region the surface tension changes from the value of the pure water to the value of the surfactant drop, a change in our experiments of over 30 dynes/cm. Region (1) proves uninteresting since the average flow essentially proceeds as in normal wetting. Region (2) is small in extent and hence accounts for a small fraction of the total change in surface tension. In the stability analysis, this region is collapsed onto an interface separating regions (1) from (3).

In an approximation which ignores height fluctuations in region (3), a simple linear stability analysis about the interface separating regions (1) and (3) indicates that the flow is unstable to perturbations in the position of the interface or in the local surface tension. The stability analysis does not include the



(a) (b)

Fig. 1 Fingering of a drop of 1mM aqueous AOT spreading on an (a) thin ($\approx$ 0.1 μm) and (b) thick ($\approx$ 1 μm) water film. The outer radius of the drops is $\approx$ 0.9 cm. The dark needle corresponds to the syringe tip used for depositing the drops on the water film.

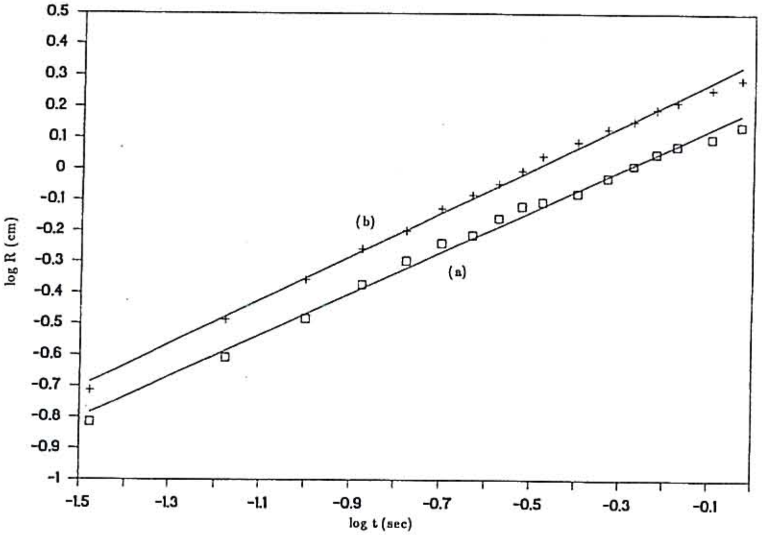


Fig. 2 Log-log plot of the fingering drop radius as a function of time. The squares and crosses correspond to the spreading of the drops in Fig. 1a and 1b, respectively. The solid line is a linear fit to the experimental data. The slopes obtained from the fits are (a) 0.66 and (b) 0.70.

presence of a stabilizing mechanism and, therefore, unrealistically predicts that the smallest wavelength disturbances are most unstable. Whether the stabilizing mechanism is the surface tension associated with the curvature of the air-liquid interface needs to be studied in more detail.

The onset of the instability is intimately connected to the presence of the long flat region ahead of the macroscopic drop which sustains a gradient in surface tension. Within the approximations stated above, the local surface tension satisfies Laplace's equation everywhere. In analogy to the Saffman-Taylor instability, a protrusion in the interface experiences a larger surface tension gradient at the tip. Since the Marangoni flow velocity is directly proportional to the gradient in surface tension, the tips move faster than the surrounding environment, and this should lead to fingering at the moving front. This type of instability is not peculiar to surfactant systems and we expect it to occur in many other thin film systems able to sustain surface tension gradients.

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