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Flow-controlled Phase Boundaries in Langmuir Monolayers

R. M. Muruganathan and Th. M. Fischer*

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306

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Flow-controlled fingering of the liquid expanded/liquid condensed phase boundary in a 2-d insoluble monolayer is investigated using a laser-induced thermocapillary pump. Spatially periodic perturbations of the initially smooth monolayer phase boundary between a liquid expanded and liquid condensed phase are shown to lead to the development of steady profile of one-dimensional fingers. The steady-state modulation wave vector and the transient growth rate increase with the flow velocity that drives the instability following power scaling laws consistent with a theory of Bruinsma, Rondelez, and Levine (Bruinsma, R.; Rondelez, F.; Levine, A. *Eur. Phys. J. E.* **2001**, *6*, 191) on flow rather than diffusion dominated instabilities in monolayers.

Introduction

Pattern formation occurs in a wide variety of natural contexts, from animal coat markings to convection cells in the Sun. Among a variety of patterns, a crystal dendrite is a type of pattern that develops with a typical multi-branching tree-like form. Dendritic crystal growth is very common and illustrated by snowflake formation and frost patterns on a window. Thus, dendritic crystallization forms a natural fractal pattern. Experimentally, such patterns have been studied in many different systems, including Rayleigh−Bénard convection, solidification, chemical reactions, and Faraday waves. Despite the physical differences between these systems, the patterns that appear display common features, indicating some kind of universal underlying structure. In analogy to 3-d patterns, various 2-d fractal patterns are observed in Langmuir monolayers (LMs).[1−8] In general the pattern formation on the Langmuir monolayers can be attributed to the transport of at least one conserved quantity, the solute material or the latent heat of solidification, which is transported via diffusion. This is a type of Stefan[9] or moving boundary problem, and it is one of the simplest pattern-forming processes conceivable under essentially homogeneous nonequilibrium conditions. Though the fractal patterns are mostly observed in the coexisting phases of islands of 2-d “liquid condensed” (LC) and supercooled “liquid expanded” (LE) phases, the heat build-up at the LC/LE interface can be neglected owing to the fact that the monolayer rests on a large body of water that would act as an isothermal reservoir and the heat liberated is very low (in the order of 1.49×10^{-19} J/molecule). An alternative and contentious conclusion was proposed based on the expulsion of the excess impurities,[6−8,10] such as fluorescent dye molecules, from the condensed phase. However, there are several experimental results that are in conflict with this conclusion.[11−14] If the surface tension is anisotropic, for example due to crystalline anisotropy, it is generally believed that a growing circular nucleus becomes unstable as its radius becomes bigger than a few times the critical radius that eventually deforms into a dendritic pattern. The limit of vanishing anisotropy, however, is still somewhat less clear, although substantial progress was made during the past decade. Very recently, a hydrodynamic mechanism has been proposed by Bruinsma et al.[15] based on Marangoni flow, which satisfactorily describes the growth instabilities in Langmuir monolayers. This kind of Marangoni instability is intrinsic to Langmuir monolayers and is not controlled by the expulsion of chemical impurities from the liquid condensed phase. The hydrodynamic transport of the insoluble surfactants overwhelms the passive diffusion and provides a mechanism for fingering instabilities. The hydrodynamic theory of Bruinsma et al. has not been tested experimentally so far. The intention of the present work is to experimentally substantiate the practical applicability of the Marangoni flow to describe growth instabilities of domains in Langmuir monolayers. Bruinsma et al.[15] develop their theory for a steady-state condition, where a permanently maintained level of supersaturation of a liquid expanded (LE) phase causes a hydrodynamic flow of the LE phase with velocity V onto the phase boundary to a quiescent liquid condensed (LC) region far away from the supersaturated region. At the LE/LC phase boundary the hydrodynamic flow converts the LE phase to LC phase, leading to a progression of the phase boundary with velocity $-U$ in the direction opposing the LE flow.

In our experiments we impose a hydrodynamic flow of the LE phase of a methyl-octadecanoate monolayer by using the thermocapillary flow induced by an IR laser (wavelength 1064 nm, $P = 10$ mW−4 W) locally heating the monolayer. Successive increase of the laser heating of the LC phase (surface pressure $\pi = 18$ mN/m, subphase temperature $T = 42$ °C) first leads to an increase of the temperature in the focus of the laser. Beyond a certain threshold power ($P > 1.2$ W) the LC phase will be converted into the LE phase in the focus of the laser.[16] The radius of this LE region increases with the laser power. Above a second threshold ($P > 1.5$ W) a two-dimensional cavitation bubble forms within the LE region,[17,18] such that one observes three phases (gaseous, LE, and LC) as one moves away from the laser focus. The line tension between the cavitation

* Author to whom correspondence should be addressed. E-mail: tfischer@chem.fsu.edu.

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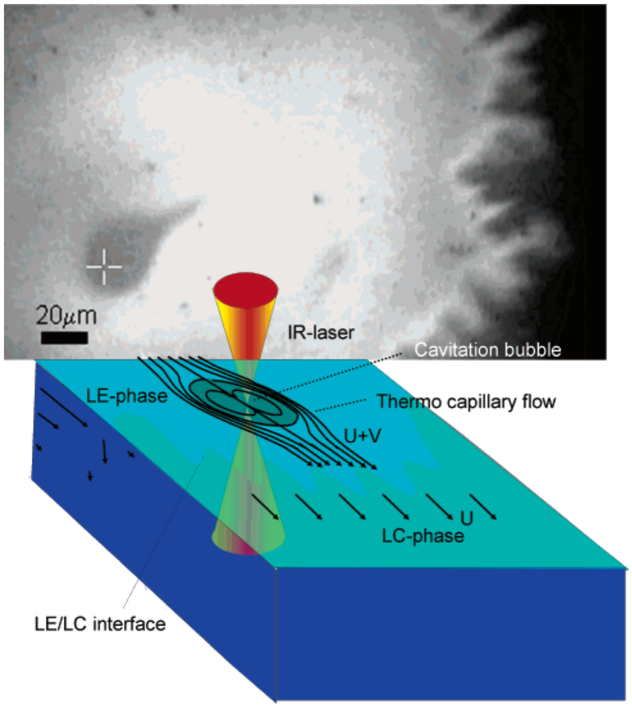

Figure 1. (top) Fluorescence microscope image of a methyloctadecanoate monolayer (π = 18 mN/m, T = 42 °C) heated with an IR laser (cross hair). The heating converts the original liquid condensed phase into a liquid expanded phase with a cavitation bubble in the laser focus. Thermocapillary flow around the cavitation bubble pumps the LE phase onto the LE/LC interface and a fingering instability is observed at the LE/LC interface. (bottom) The scheme illustrates the laser heating, the monolayer phases, the flow profile and the fingering instability. A movie of the stationary pattern can be viewed in the Supporting Information.

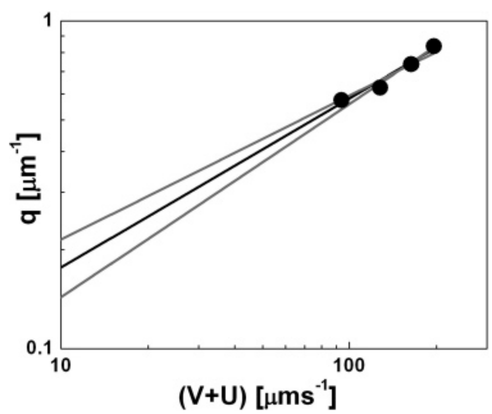

Figure 2. Wave vector of the fingering instability vs the monolayer velocity. The straight lines are fits according to a power law with exponent $\beta = 0.51 \pm 0.08$. The behavior is consistent with an advection-dominated instability.

bubble and the LE phase depends on temperature, and beyond a third threshold (P > 1.8W) line tension gradients cause a thermocapillary flow around the cavitation bubble[19] that pumps the LE phase onto the LC phase (Figure 1). The stationary thermocapillary flow is very similar to the stationary flow proposed by Bruinsma et al. in their theory. The situation is a little more complicated since in our experiments the temperature varies with the distance from the laser and we perform the experiments in the rest frame of the LE/LC boundary, not in the rest frame of the LC phase. As a result of the flow across the LE/LC interface, a modulated interface is formed with a typical wave vector $q = 2\pi/\lambda$ consisting of protrusions of the LC phase that extend into the LE phase. A movie of the stationary pattern can be viewed in the Supporting Information.

In their theory Bruinsma et al.[15] distinguish between the flow-dominated and diffusion-dominated fingering regimes and the wave vector q of the instability should scale differently with the level of supersaturation or with the monolayer velocity. They predict that most monolayers should be in the flow-dominated regime and the wave vector q should scale as

$$q \propto (V + U)^{1/2} \tag{1}$$

In Figure 2 we plot q as measured from the fluorescence images vs the monolayer velocity $V + U$ that we obtain by measuring the velocity of impurities in the monolayer that appear somewhat brighter than the LE phase. The range of monolayer velocity is limited to values between $V + U = 100 - 200$ μm s^{-1}. The lower limit is arising from the minimum thermocapillary flow velocity. Above $V + U > 200$ μm s^{-1}, the LE/LC boundary moves out of the field of view of the microscope. The data collected in this limited range is consistent with the predictions Bruinsma et al.[15] made for the flow-dominated regime. A fit of the data to a power law $q \propto (V + U)^\beta$ yields an exponent $\beta = 0.51 \pm 0.08$, shown in Figure 2 as a double logarithmic plot. The exponent is in good agreement with eq 1 and a linear behavior ($\beta = 1$) can be clearly excluded.

Bruinsma et al.[15] also treat the transient growth of the instability pattern that occurs before reaching a stationary pattern. It is difficult to measure the transient when switching on the thermocapillary flow. Hydrodynamic transients associated with the thermocapillary bubble interfere with the transients of the Marangoni instability at the LE/LC boundary since there is only a small spatial separation between the two at the onset of the thermocapillary flow.

We try to catch the essence of the transient by focusing the laser onto the LE/LC coexistence region (π = 27 mN/m, T = 37 °C) and converting the coexistence region around the focus into a single LE-phase region. Suddenly switching off the laser takes the monolayer back to the LE/LC coexistence with LC domains nucleating in the cooling single LE-phase region. The dendritic growth of the LC domains is shown in Figure 3.The supersaturation persists for a time of the order of a second as long as the temperature profile needs to equilibrate in the water. After the temperature has equilibrated, the dendritic shape does not persist but relaxes back to a circular equilibrium shape. In the initial growth regime we measure the length l of the dendritic arms as a function of time. A fit according to an exponentially

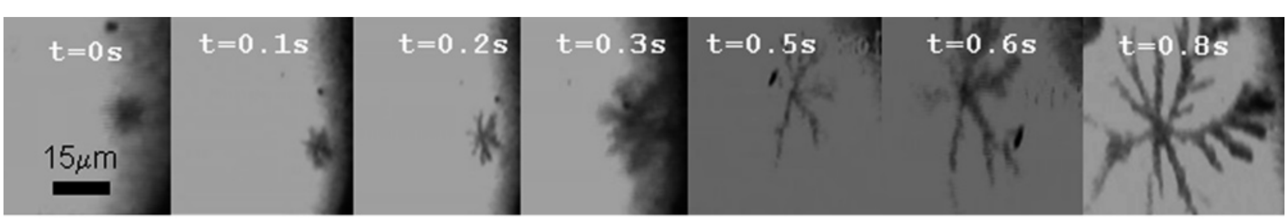

Figure 3. Sequence of fluorescence microscopy images of a methyloctadecanoate monolayer. T = 37 °C, π = 27mN/m right after switching off a laser P = 3 W that was focused on the region. The sequence shows the fractal growth of the LC domain as a function of time.

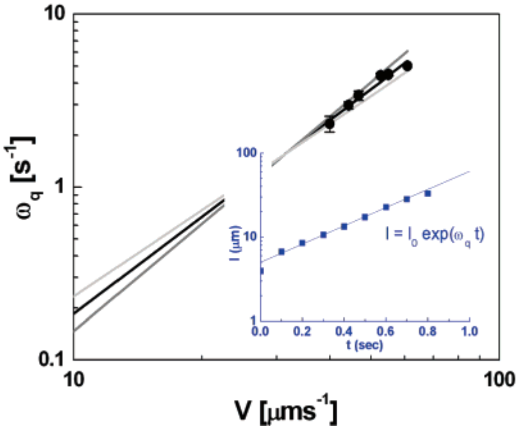

Figure 4. Growth rate ω_q of the dendritic arms as a function of the radial LE velocity V following a power law with exponent $\gamma = 1.86 \pm 0.2$. The inset shows the exponential growth of one arm together with a fit according to eq 2.

growth law

$$l = l_0 \exp(\omega_q t) \tag{2}$$

is shown as inset in Figure 4. The fitted growth rate ω_q is plotted versus the inward radial flow velocity V of the LE phase. All presented ω_q values are arithmetical means from three single experimental values. The sample standard deviations are shown as error bars in the figure. The slope in the double logarithmic plot presented in Figure 4 yields a power law $\omega_q \propto V^\gamma$ with an exponent $\gamma = 1.86 \pm 0.2$. In the range of monolayer velocities from 40 to 60 μm s^{-1}, the dependence of the growth rate of the dendrites is close to Bruinsma et al.'s prediction, i.e.,

$$\omega_q \propto V^{3/2} \tag{3}$$

Our measurements support the intrinsic flow-controlled mechanism suggested by Bruinsma et al. The transient growth as well as the stationary patterns here point toward a flow controlled fingering instability, an intrinsic mechanism, and does not depend on the fluorescence label concentration.

Supporting Information Available: A movie showing the stationary fingering pattern of the LE/LC interface and the thermocapillaey flow induced by the laser heating. This material is available free of charge via the Internet at http://pubs.acs.org.

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