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LETTER TO THE EDITOR

Dynamics of phase separation in the presence of surfactants

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Abstract. The dynamics of phase separation in two-dimensional binary systems containing surfactants is investigated by means of a time-dependent Ginzburg-Landau model. We study the Langevin dynamics of two scalar fields representing the local order parameter and the local surfactant concentration. In the intermediate time regime, domain growth is characterized by anomalously slow dynamics. Dynamic scaling of the pair-correlation function and structure factor are observed.

In colloidal dispersions, surfactants are adsorbed on the interfaces separating the dispersed phase from the dispersion medium. These systems exhibit a large area-to-volume ratio, given a relatively small amount of surfactant [1]. The common physical systems where these features are present include liquid and solid aerosols, foams, sols, pastes, suspensions, emulsions and microemulsions. For example, microemulsions are ternary mixtures of, say, water, oil and surfactants, where the surfactant makes the mixture homogeneous [2, 3]. The emulsion can therefore be thought of in terms of microphase separation, where small domains of water and oil exhibiting short-range order are separated by thin layers of surfactants. In contrast, on large length scales they are similar to disordered fluids, being isotropic, transparent and homogenous. These features are common to other colloidal suspensions.

We present the first study of the dynamics of microphase separation due to surfactants in a bicontinuous system using a simple coarse-grained model. Our model combines the physics of bulk phase separation with the fact that surfactants reduce the interfacial tension between domains of different phases. We concentrate on the transient dynamics of the growth of the microdomains, following a quench from high to low temperature, and the scaling properties of the dynamics in two dimensions. This could correspond experimentally to a thin layer of fluid constrained between two plates. It is worth noting that extensive experimental and theoretical studies have been performed on these systems. However, very little is known about the dynamics of formation of micellar and bicontinuous microemulsions or other colloidal systems starting from a completely disordered state. In particular we examine the effects of conservation laws on the dynamics, the morphology of the microdomains and the effects of surfactant concentration.

The growth of order during a first-order phase transition, such as for a binary alloy or fluid, has been examined by many authors [4]. There one studies the dynamics of a system which has been prepared by quenching from a high temperature, where the system is disordered, to a low temperature where the system is ordered in equilibrium. Usually the average domain size of one phase, $R(t)$, grows to macroscopic size

according to a power law, $R(t) \sim t^n$. The growth is to minimize surface energy following a quench, where the driving force is proportional to the product of surface tension and local curvature. In the present study, we examine domain growth when the surface tension becomes vanishingly small *due to the presence of surfactants* and the domains remain on small length scales [5]. We further investigate possible analogies between the effects of surfactants and those of quenched impurities. Quenched impurities can pin interfaces, thus limiting the growth to logarithmically slow activated processes [6], and indeed the surface tension itself can vanish in, for example, the two-dimensional random-field Ising model. We find the dynamics of domain growth for the system with surfactants to be similar to that seen in systems with quenched impurities.

We have constructed the most simple Landau-Ginzburg free-energy functional which incorporates the above considerations. The free energy is a functional of two local fields dependent on field point x : $\psi(x)$ and $\rho(x)$, where ψ is the local order parameter corresponding to the difference in the local densities of, say, water and oil, and ρ represents the local concentration of surfactants. Our model is based on the coupled-variable model of Hohenberg, Halperin and Ma, introduced to study critical dynamics [7]. Their free energy functional is [8]

$$\mathcal{F}[\psi, \rho] = \int dx [c(\nabla\psi)^2 - r\psi^2 + u\psi^4 + g\rho^2\psi^2 + a\rho^2 - \mu\rho] \quad (1)$$

where c , r , u , g , a and μ are positive constants for temperatures below the critical temperature T_c . This is in the equilibrium universality class of the Ising model, which can be easily found on integrating away the variable ρ . The double-well structure below T_c ensures phase separation to the two bulk phases given by $\psi = \pm 1$, for example. The novelty of the mode-coupling contribution of the ρ variable arises from the time t dependence. The equations of motion are

$$\frac{\partial\psi}{\partial t} = -M_\psi \frac{\delta\mathcal{F}}{\delta\psi} + \eta_\psi(x, t) \quad (2)$$

and

$$\frac{\partial\rho}{\partial t} = -M_\rho \frac{\delta\mathcal{F}}{\delta\rho} + \eta_\rho(x, t) \quad (3)$$

where for either variable the average noise satisfies

$$\langle \eta(x, t) \eta(x', t') \rangle = 2TM\delta(x - x')\delta(t - t') \quad (4)$$

and Boltzmann's constant has been set to unity. Following Hohenberg *et al.*, we consider models A, B, C and D, which are defined by the presence or absence of conservation laws: the kinetic coefficients M_ψ and M_ρ are constants (implying no conservation laws) except in model B where $M_\psi \propto -\nabla^2$ (implying a conservation law); in model C where $M_\rho \propto -\nabla^2$; and model D where both $M_\psi \propto -\nabla^2$ and $M_\rho \propto -\nabla^2$.

To this we add the most simple term which preferentially forces a concentration of ρ to the interface between different values of ψ :

$$\mathcal{F}_{\text{surfactant}} = -s \int dx \rho (\nabla\psi)^2 \quad (5)$$

where s is a constant. We expect that many colloidal dispersions are described by more complicated modifications to the free energy [9-13], but here we wish to show

the dramatic effects of only a simple change. Indeed, this term causes the surface tension between two bulk phases of ψ to vanish, if there is a non-zero average concentration of surfactant, ρ_0 , thus forbidding phase separation. Thus the dynamics of this system and its short-range order are different in important respects from a simple disordered system.

The Langevin equations were solved numerically using Euler's method on a two-dimensional grid of linear size $L=128$ with a finite difference scheme. Periodic boundary conditions were used throughout. The spatial mesh size was taken to be $\Delta x=0.7$, and the time mesh size is chosen as $\Delta t=0.02$. Further reduction of the mesh sizes gave essentially the same results. Large numbers of runs were needed to obtain reasonable statistics and we therefore performed over 50 independent runs for each system considered. The equations were iterated over a time corresponding to 100 000 iterations. Typical parameters used in the simulations were $c=\frac{1}{4}$, $r=\frac{1}{2}$, $u=\frac{1}{4}$, $g=\frac{5}{2}$, $a=\frac{1}{4}$ and $s=\frac{1}{4}$. Our results were not sensitive to these particular values. The chemical potential μ drops out from the Langevin equations in models C and D; its effect is determined by initial values of the surfactant concentration ρ_0 . μ is an input parameter for the other two models. The mobilities M_ψ and M_ρ were set to $\frac{1}{2}$ in the non-conserved case (the proportionality constants were set to this value in the conserved case). We furthermore set η_ψ and η_ρ to zero, since we do not expect the inclusion of a finite noise to change the dynamics significantly, as shown in the studies of spinodal decomposition [14]. We used random initial conditions for the simulation, i.e. to each grid point, $\psi(x)$ and $\rho(x)$ were assigned small random values around their initial average values at $t=0$, see below. We calculated the structure factor, which is the Fourier transform of the real space pair-correlation function

$$S(\mathbf{k}, t) = \left\langle \frac{1}{L^2} \left| \sum_{x_i} \psi(x_i, t) e^{i\mathbf{k} \cdot x_i} \right|^2 \right\rangle \quad (6)$$

The wavenumber k is defined as follows:

$$k^2 = \frac{2}{\Delta x^2} [2 - \cos(k_x \Delta x) - \cos(k_y \Delta x)] \quad (7)$$

where $k_x = (2\pi/L)m$, $k_y = (2\pi/L)n$, in units Δx , and $m, n = 0, 1, 2, \dots, L$. This definition of the wavenumber arises from the Fourier transform of the discrete Laplacian in two dimensions. We present results for the circularly averaged structure factor $S(k, t) = \Sigma' S(\mathbf{k}, t) / \Sigma' 1$, where Σ' denotes a sum over a circular shell defined by $n - \frac{1}{2} \leq kL / (2\pi) \leq n + \frac{1}{2}$. The average domain size is monitored as a function of time from the second moment of the circularly averaged structure factor:

$$R(t) = 2\pi \sqrt{\frac{\sum_{k=0}^k S(k, t)}{\sum_{k=0}^k k^2 S(k, t)}} \quad (8)$$

We present results mainly for model D, since this corresponds to the common experimental situation for colloidal dispersions; we shall simply mention the differences we have found between these results and models A, B and C, and present a more detailed comparison in a future paper. In model D, the surfactant concentration is conveniently fixed to its initial value, ρ_0 . Figure 1 shows the spatial configurations of the system after 100 000 iterations, for $\rho_0 = 0.1, 0.15, 0.17, 0.2$. The left column of snapshots illustrates the ordering field $\psi(x)$, the right column displays the surfactant field $\rho(x)$. It is clear that the surfactants accumulate at the interfaces, as expected. We also observe that the domain sizes decrease considerably as ρ_0 is increased.

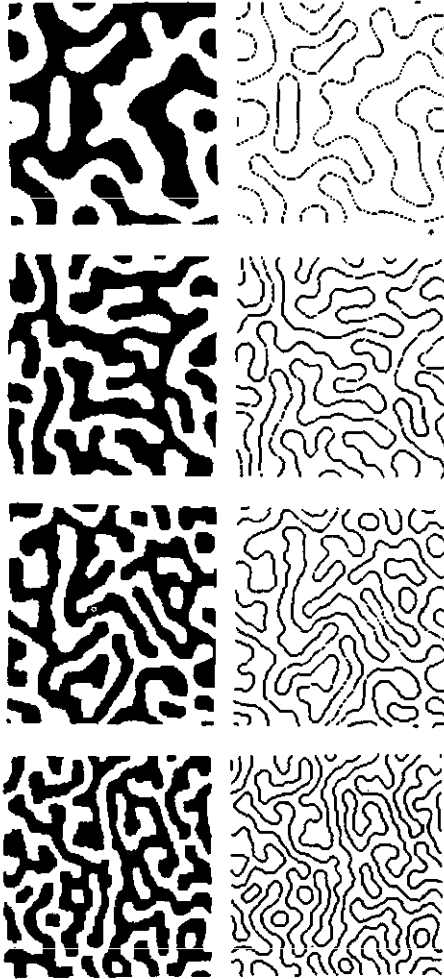


Figure 1. Final configurations (after 100 000 iterations) for the values of $\rho_0 = 0.1, 0.15, 0.17$ and 0.2 , from top to bottom. The left column of snapshots shows the spatial distribution of the ψ field, in which black regions correspond to positive ψ and white regions to negative ψ . The right column shows the spatial distribution of the ρ field. White regions correspond to small values of ρ (smaller than 0.04) and black regions correspond to positive values (about 1).

The process of microphase separation was found to be exceedingly slow, in contrast to the more familiar case of the phase separation in a first-order transition, where one often finds power law growth in the domain size. Figure 2 shows $R(t)$ as a function of $\ln t$ for different values of ρ_0 . We observe that, for values $\rho_0 \geq 0.1$, the growth appears logarithmic in time, and often becomes even slower for very late times. We have not attempted to estimate an exponent ϕ in $R \sim (\ln t)^\phi$. It is worth noting that the final domain size decreases as ρ_0 increases, in agreement with the configurations shown in figure 1. No power-law growth was observed for any of the surfactant concentrations considered in this study. The reason of such a slow growth is due to the accumulation of surfactants at the interfaces which reduces the interfacial tension. This results in a dramatic decrease of the driving force for the growth which is proportional to the

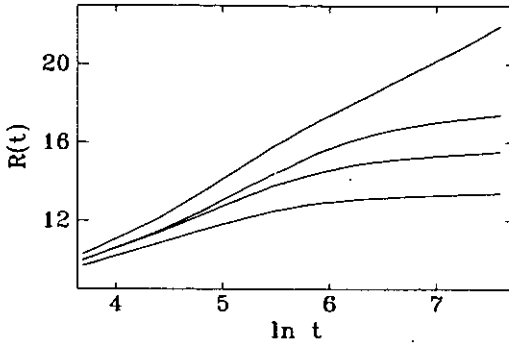


Figure 2. Time evolution of the domain size for the different values of ρ_0 . The domain sizes are plotted against $\ln t$ curves from top to bottom correspond to $\rho_0 = 0.1, 0.15, 0.17$ and 0.2 .

product of interfacial tension and the local curvature. In some sense, the surfactants play the role of the quenched impurities in a random system which are known to pin the domain walls leading to slow dynamics [6]. However, note that the surfactants are annealed and fluctuate in time: it is the fact that they accumulate at interfaces, stopping phase separation, which leads to the anomalously slow domain growth here. We observed similarly slow dynamics in models A, B and C.

The structure factor shows a peak at a non-zero wavenumber k for either ψ or ρ in model D. This peak moves to smaller values of k as time increases indicating coarsening. At very late times the system no longer coarsens and the peak stays at a fixed value of $k = k_e$, which corresponds to the inverse of the equilibrium domain size. Our calculation shows that k_e increases its value as ρ_0 increases, consistent with the behaviour of the domain size mentioned above. This behaviour is due to the conservation law; from the study of models A, B and C, we have found that if a field is non-conserved, the structure factor only peaks at $k = 0$.

Systems undergoing phase separation often exhibit self-similar behaviour which is reflected in the dynamic scaling of the structure factor [4]. This occurs when the average domain size becomes the only relevant length scale. Although the domain size saturates at late times in our case, implying that the width of the interface can play a role as a second length scale, this width is still much smaller than the domain size. It is therefore natural to make the usual scaling ansatz [4] $S(k, t) = R(t)^d F(\kappa)$ where $\kappa = kR(t)$, and $d = 2$ is the dimension of the system. The function $F(\kappa)$ is shown in figure 3 for $\rho_0 = 0.15$ and good scaling is observed. Similar results were obtained for other non-zero values of ρ_0 . We have also made a direct calculation of the real space two-point correlation function for the ψ field and observed the same dynamic scaling.

While non-zero ρ_0 leads to the slow dynamics mentioned above, we obtain the usual $t^{1/3}$ growth law for $\rho_0 = 0$. A crossover between the two distinct dynamic behaviours is therefore expected. We also expect the equilibrium domain size to be proportional to $1/\rho_0$ for non-zero ρ_0 since the surfactants mostly accumulate at the interfaces. This implies that the total length of the interface is proportional to ρ_0 . These considerations suggest the following crossover form

$$R(t)t^{-1/3} = f(\rho_0^3 t). \quad (9)$$

The function $f(\tau)$ is equal to a constant for $\tau = 0$ and is proportional to $\tau^{-1/3}$ for large τ . Our data for ρ_0 ranging from 0.15 to 0.20 are consistent with this form, as shown

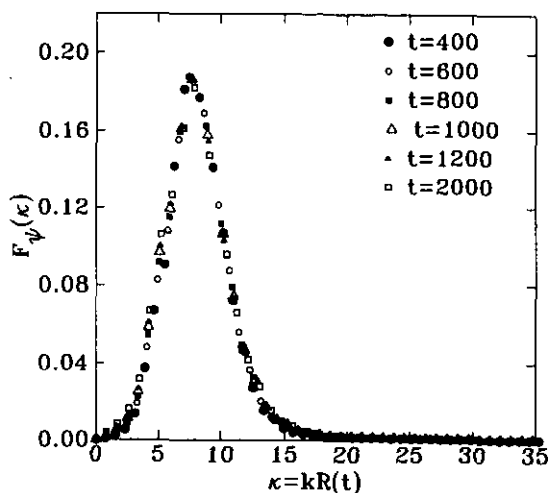


Figure 3. Dynamic scaling of model *D* in the intermediate to late times for $\rho_0 = 0.15$. Data for $t = 400$ to $t = 2000$ and wavevector values from $k = 0$ to $k = \pi$ are collapsed on to a single curve.

in figure 4. However, a detailed confirmation of this crossover form requires data for smaller values of ρ_0 , and longer time regimes, than we have studied so far.

In conclusion, a Ginzburg-Landau model based on two local fields for a ternary mixture of two phase separating variables and surfactants was introduced to study the dynamics of microphase separation. The domain growth was studied by monitoring the correlation function and the structure factor. We observe a slow growth in the domain structures characterized by a logarithmic time dependence. This can be attributed to the accumulation of the surfactants at the interfaces after their migration from the bulk, which drastically reduces interfacial tension leading to the diminishing of the driving force. The microdomain size decreases with increasing surfactant concentration. A dynamical scaling is observed in the pair correlation function and structure factor of the system. Although finite, the microdomain size always remains much larger than the width of the interface and plays the role of a dominant length scale. Finally, we do not expect the results to be qualitatively different in three dimensions. That is,

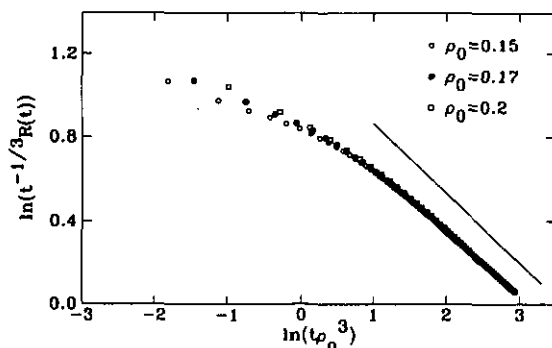


Figure 4. Crossover scaling function for the average domain size of model *D* for different ρ_0 . The straight line has a slope of $-\frac{1}{3}$.

we expect approximate scaling and anomalously slow growth to be general features of the dynamics. This is in the process of being tested.

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