Anomalous phase separation dynamics in the presence of surfactants

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We study the phase separation of water and oil in a water-oil-surfactant microemulsion, from a totally disordered phase in both two and three dimensions using extensive Monte Carlo simulations of a spin model of microemulsions. The evolution of the characteristic length scale and the structure factor are measured and compared with recent experiments and theoretical work. At relatively high surfactant concentrations and off-critical quenches, we obtain results in agreement with earlier theoretical approaches. For critical quenches at *very* low surfactant concentrations, we observe the surprising result that it is easier to get to the scaling regime than in the pure binary case. [S1063-651X(96)50809-3]

The kinetics of phase separation of two immiscible phases, such as a binary mixture of water and oil, from a totally disordered initial state has been the subject of considerable study in recent years [1,2]. The essential behavior of such systems is the separation, immediately after the quench, of the two phases into small domains that grow in time. The morphology of these domains may be an interconnected structure or isolated clusters, depending on the relative fractions of the two phases and on whether or not the order parameter $\phi(\mathbf{r})$, a measure of the *local* relative fractions of the phases, is conserved.

While there is as yet no full scaling theory describing the evolution of the domains, a good number of experimental results may be understood within the framework of the "dynamic scaling hypothesis" [3]. This proposes that at late times, there is one characteristic length scale of the system, L, which grows as a function of time according to the asymptotic power law,

$$L(t) \sim t^{1/z}, \tag{1}$$

where for conserved order parameter, *without hydrodynamics*, a theoretical value of $z=3$ is generally agreed on. This means that the domain structure remains statistically invariant in time if at time t all lengths are rescaled by $L(t)$. Within this formalism, the equal-time pair correlation function, $C(\mathbf{r},\mathbf{r}',t) = \langle \phi(\mathbf{r})\phi(\mathbf{r}') \rangle$, which is the probability of finding regions of the same phase at points $\mathbf{r}$ and $\mathbf{r}'$, is given by

$$C(\mathbf{r},\mathbf{r}',t) = h\left(\frac{|\mathbf{r}-\mathbf{r}'|}{L(t)} \right), \tag{2}$$

where h is an (unknown) scaling function.

A related problem of which relatively little is known is the phase separation of two immiscible phases in the presence of surfactants, which tend to position themselves at the interface between the two phases [4]. Typical surfactants are amphiphiles which are chain molecules consisting of two parts, each of which finds it energetically favorable to be near one of the two phases: a polar "head," which likes to be near water and a hydrocarbon "tail," which prefers to be near oil. Ternary mixtures of oil, water, and amphiphile are known to form a large variety of complex phases [5]. Consequently, there has been extensive research, both experimental and theoretical, on the static behavior of amphiphiles in ternary mixtures [6]. At high concentrations of amphiphile, they are known to form complex liquid crystalline phases with long-range order, while at low concentrations a homogenous, transparent disordered phase with structure on the scale of 100 Å called a microemulsion is formed [5]. There are several models used to study the static behavior of ternary mixtures of amphiphiles, which fall into three main groups: microscopic approaches typified by the Widom model [7] or Larson-type models [8,9], coarse-grained Ginzburg-Landau models [10,5], and membrane models [11].

The dynamic behavior of these systems has not been so extensively studied and consequently, compared to statics, not too much is known. The kinetics of ternary systems has been studied recently using numerical integration of time-dependent Ginzburg-Landau models [12], molecular dynamics simulations [13], and hybrid lattice-continuum models [14]. In all these models, amphiphile, oil, and water are all represented by coarse-grained position-dependent fields whose evolution is followed in time. They therefore do not include the chainlike nature of the amphiphiles and the effects of amphiphile conformations. Experimentally, there have been recent studies of the spinodal decomposition of ternary mixtures of water-oil-amphiphile [15] and $A/B/A$-B block copolymer mixtures [16].

In this paper, a number of different but related problems are considered. We study the scaling properties of the growth of the average domain size of the three components with time when the relative concentrations are varied. We show that for relatively high concentrations of surfactant, our results agree with those of experiment and the earlier numerical studies. The evolution of the structure factor is calculated

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for several different temperatures and the effect of changing the structure of the amphiphiles is discussed.

We study the dynamics of phase separation using a Larson-type model [8,9] of amphiphiles in ternary mixtures. The simulations were performed on a $L \times L$ square lattice of spins in two dimensions and $L \times L \times L$ simple-cubic lattice of spins in three dimensions. Helical boundary conditions in one direction and periodic boundary conditions in the rest were used. A certain fraction of the sites ϕ_a was occupied by amphiphile molecules and the rest was occupied by either water with spin up or oil with spin down. The amphiphile is a *connected*, nonoverlapping chain of ℓ sites which we denote by $H_n N_m T_p$ with n ''head'' sites with positive spin, m neutral sites (zero spin), and p ''tail'' sites with negative spins so that $\ell = n + m + p$. The interaction energy for *all* the sites is given by

$$E = -J \sum_{\langle ij \rangle} S_i S_j, \quad (J > 0), \tag{3}$$

where S_i is the spin at site i and the sum $\langle ij \rangle$ is only over nearest neighbors. The temperature is defined in units of the interaction parameter, $\tau = k_B T / J$. The model is thus similar to the dilute Ising model with ''moving'' defects at chain sites. The ''free'' sites (oil or water) move via Kawasaki spin exchange with one of their neighbors while an amphiphile chain moves by *reptation*, where it slithers along its length like a snake, by *kink jump*, where a kink (right angle) on the amphiphile flips, or by spontaneous *buckling and unbuckling*, where two sites in the middle of the chain move one lattice spacing perpendicular to the bond joining them. Detailed descriptions of the dynamics can be found elsewhere [17]. With these moves, we have explicitly not included hydrodynamics. The system evolves via a Glauber algorithm in which the change in energy of a move ΔE is calculated using Eq. (3) and moves are accepted with probability $p = 1/(1 + e^{+\Delta E/k_B T})$. A Monte Carlo (MC) step refers to one attempt to flip all free sites and one attempt at all three chain moves for each amphiphile. A detailed analysis of the cluster distribution of water, oil, and amphiphile is performed. A site belongs to a cluster if any of its nearest neighbors are of the same type and are already counted as part of the cluster. The mean cluster size of component A is estimated as

$$\chi_A = \sum_{s=1}^{s_{max}-1} s^2 n(s) \bigg/ \sum_{s=1}^{s_{max}} s n(s), \tag{4}$$

where A can be water, oil, or amphiphile, s_{max} is the largest cluster of type A, and $n(s)$ is the number of clusters of type A with s sites. In two dimensions $\chi_A \sim R_A^2$ and in three dimensions $\chi_A \sim R_A^3$, where R_A refers to the mean cluster radius. We calculated the equal-time structure factor $S(k,t)$, which is the Fourier transform of the equal-time pair correlation function [1], in d dimensions defined as

$$S(k,t) = \int d^d r C(\mathbf{r},t) e^{i\mathbf{k} \cdot \mathbf{r}} \tag{5}$$

using fast Fourier transforms. For example, the equal-time pair correlation for water, $C_{ww}(\mathbf{r},t)$ is calculated by drawing shells of radius r and $r+1$ around each water molecule and counting the number of water molecules between the two shells and finally normalizing by dividing by r. The structure factor is what is measured in x-ray and neutron scattering experiments [15,16].

Simulations were begun from a random initial condition of water, oil, and amphiphile for up to 200 000 MC steps. Most of the simulations were performed with amphiphile $H_3 T_3$ with structure $+1, +1, +1, -1, -1, -1$ but amphiphiles of type $H_2 N_1 T_3$ with spin distribution $+2, +1, 0, -1, -1, -1$ were also studied for comparison. The simulations were performed on a Silicon Graphics Machine with 16 processors, a Dec Alpha, and on an Intel Paragon with 136 processors. A small section of a 1000×1000 lattice with a surfactant concentration of $\phi_a = 0.1$ and equal concentrations of oil and water, $\phi_o = \phi_w = 0.45$ is shown at different times in Fig. 1, showing the change of the length scale with time.

The exponent $1/z$ was calculated in two dimensions by studying the evolution of the average cluster radius $\langle R \rangle$ with time. The average cluster radius was defined as $\langle R \rangle = [\frac{1}{2}(\chi_o + \chi_w)]^{1/3}$. We calculated the average cluster radius for a system of size 1000×1000 at $\tau = 1.5$ using amphiphile type $H_3 T_3$ for amphiphile concentrations of $\phi_a = 0.1$, 0.15, 0.2, and 0.5 and equal concentrations of water and oil. The evolution is shown in Fig. 2. At $\phi_a = 0.1$ and $\phi_a = 0.15$, we see that $\langle R \rangle \sim t^{0.33 \pm 0.01}$ which is in very good agreement with the theoretical estimates for phase separation in binary mixtures. This is in contrast to similar lattice simulations of *binary* mixtures *without amphiphiles*, using Kawasaki spin dynamics [18] where the value of 1/3 has not been directly observed and it is assumed that due to interface effects, it is extremely hard to get to the late stage. About $z = 4$ is typically obtained [18]. The effect of a small amount of amphiphile seems to make the late stage more easily accessible. The amphiphiles increase the roughness of the interface. This we believe to be the advantage of using a model that includes the polymerlike nature of the amphiphiles. As the concentration is increased to $\phi_a = 0.2$, there is a decrease in the growth rate of $\langle R \rangle$ and at $\phi_a = 0.5$, there is hardly any growth after the initial stage. This is in agreement with other numerical studies [12] and may be understood from the equilibrium phase diagram as the formation of a microemulsion or ordered phase and phase separation slows down as the characteristic domain size approaches that of the equilibrium system.

Simulations were also performed on smaller 200×200 systems with off-critical quenches, where the concentration of water and oil were not equal, e.g., $\phi_a = 0.1$, $\phi_o = 0.6$, $\phi_w = 0.3$. In this case we were not able to observe augmented cluster growth at low amphiphile concentration.

The equal-time structure factors in two dimensions, $S(k,t)$, for amphiphile type $H_3 T_3$ was also studied as a function of time and temperature. The structure factors for temperatures, $\tau = 1.1$, 1.5, and 2.5 are shown in Fig. 3. At temperatures below the demixing temperature, $\tau = 1.1$, 1.5, the structure factor develops a peak at nonzero wave number that grows in time and the position of the peak moves to lower k as t increases. It was also observed that the rate of growth of the peak was higher for $\tau = 1.5$ than for $\tau = 1.1$. At tem-
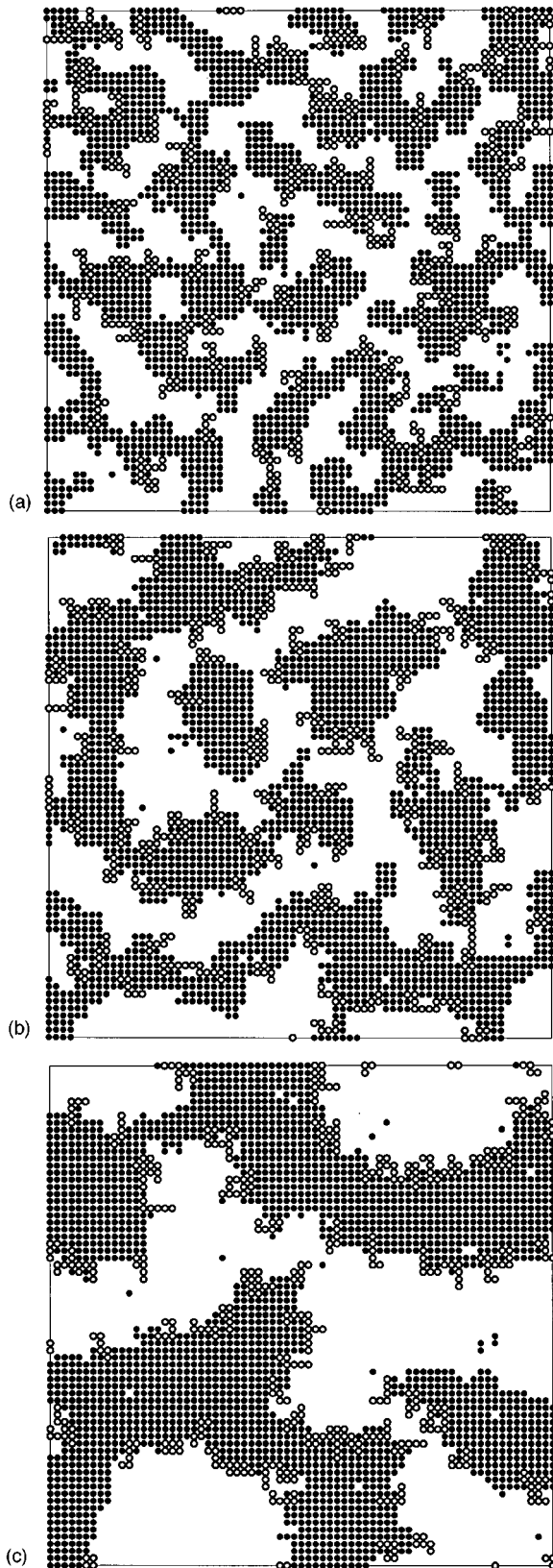
(a)

(b)

(c)

FIG. 1. A 70×70 section of a 1000×1000 system with $\phi_a = 0.1$, $\phi_o = \phi_w = 0.45$ after (a) 1000 MC steps, (b) 10 000 MC steps, and (c) 100 000 MC steps. Oil is represented by ($\bullet$) and amphiphiles by a string of ($\bigcirc$) and water is left blank. Notice that the amphiphiles are concentrated at the interface.
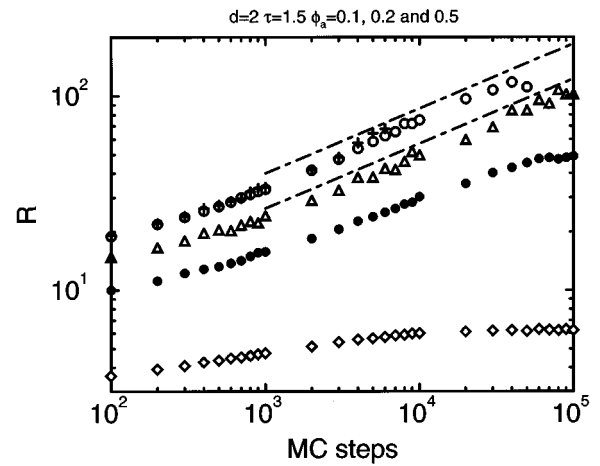

FIG. 2. The evolution of $\langle R \rangle$ with t for a 1000×1000 system at $\tau = 1.5$ with equal fractions of water and oil as the fraction of amphiphile is varied. $\bigcirc$ is $\phi_a = 0.1$ averaged over 20 samples, $\triangle$ is $\phi_a = 0.15$ averaged over 4 samples. $\bullet$ is $\phi_a = 0.2$ and $\diamondsuit$ is $\phi_a = 0.5$. We also show a single 2000×2000 system with $\phi_a = 0.1$ represented by $+$. The dashed line has slope 1/3.

peratures above the demixing temperature, $\tau = 2.5$, the structure factor does not show any structure. This is in perfect agreement with experiment [5,15,16]. We also measured $S(k,t)$ for asymmetric surfactant $H_2N_1T_3$ and observed that the height of the peak increased faster than for the symmetric case.

The evolution of the mean cluster size was also studied in three dimensions using systems of size $150 \times 150 \times 150$. Here we used the Coniglio-Klein [19] definition of clusters where the bonds within the clusters were only accepted with
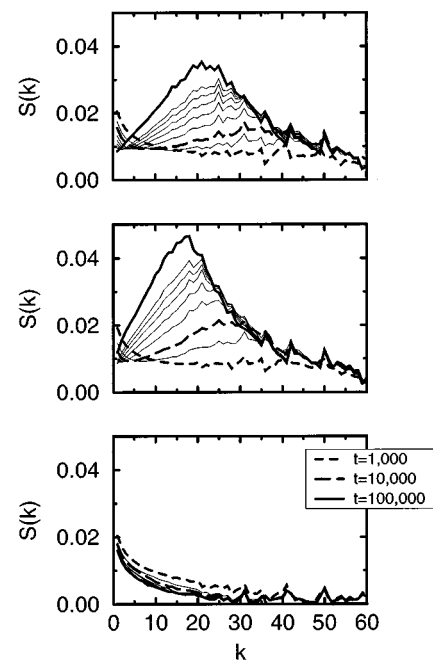

FIG. 3. The equal-time water-water structure factor for a 1000×1000 system with $\phi_a = 0.1$ for temperature (from top to bottom), $\tau = 1.1$, 1.5, 2.5. $S(k,t)$ is shown at times $t = 10^3$; $t = 1$, 3, 4, 5, 6, 7×10^4 and $t = 10^5$.
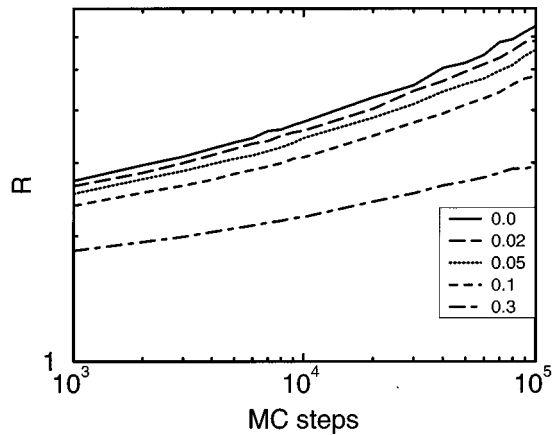
FIG. 4. The evolution of $\langle R \rangle$ with t for a $150 \times 150 \times 150$ system at $\tau = 1.5$ with equal fractions of water and oil as the fraction of amphiphile is varied, $\phi_a = 0.00, 0.02, 0.05, 0.10, 0.30$.

probability $p_b = 1 - e^{-2/\tau}$. This was because unlike the two-dimensional case, we are above the percolation threshold in three dimensions for the relevant concentrations of water and oil. Here the mean cluster size is defined as $\langle R \rangle = [\frac{1}{2}(\chi_o + \chi_w)]^{1/3}$. In Fig. 4, the evolution of mean clus-

ter size with time is shown for surfactant concentration $\phi_a = 0.00, 0.02, 0.05, 0.10,$ and 0.30. We were unable to get the theoretical values of $z = 3$ for *all* concentrations of amphiphile. We assume that this is a reflection of the fact that it is harder to get to the late stage in three dimensions. It was observed that the value of $1/z$ was constant near 0.26 ± 0.01 at low concentrations of amphiphiles and $1/z$ decreased as the amphiphile concentration increased.

In conclusion, we have performed extensive simulations of the phase separation of a ternary mixture of water-oil-amphiphile using a realistic microscopic model of surfactants. Our results are generally in agreement with experiment and also with other numerical approaches. The behavior when the concentrations of the components and the temperature are varied has been studied. At relatively high concentrations we observe behavior in agreement with coarse-grained theories. The behavior at low concentrations suggests that a small concentration of amphiphiles makes the phase separation faster. We suggest that phase separation at low amphiphile concentrations is an area that merits particular attention.

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