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Phase diagram of a lattice model for ternary mixtures of water, oil, and surfactants

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We study a lattice model for a three-component system of water, oil, and surfactants in two dimensions. Large-scale Monte Carlo simulations were performed to obtain the phase equilibria for a wide range of temperatures and surfactant concentrations. We show that this model has a rich phase behavior, and both microemulsion and liquid crystalline phases were found. The phase behavior is consistent with that of a real system, and is in qualitative agreement with the model of Gompper and Schick [Phys. Rev. Lett. **62**, 1647 (1989)], which is based on three-body interactions.

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Liquid mixtures of oil, water, and amphiphilic surfactants have a rich phase behavior. This is due to the molecular structure of the surfactants, which have a hydrophilic or polar head plus a hydrophobic tail. The surfactants can therefore reduce the interfacial tension by positioning themselves preferentially at oil-water interfaces. The resulting phases can be identified as structured fluids [1], which are homogeneous on large length scales but remain heterogeneous over small length scales. The detailed structure of these phases depends on factors such as the concentration and molecular structure of the amphiphiles and the relative concentration of water and oil. Since water and oil are immiscible, phase coexistence occurs at sufficiently low surfactant concentrations. On increasing the concentration, the system breaks up into microdomains of water and oil separated by fluctuating and flexible interfaces. This structure is known as a microemulsion, and the microdomain size is of the order of several hundred angstroms. The microdomains are often globular in shape, if, say, the concentration of water is much larger than that of the oil, and they can form a bicontinuous phase when the concentrations of water and oil are comparable. Experiments on bicontinuous microemulsions show that there is a peak at a wave number $q > 0$ in the water-water scattering intensity [2, 3] and that the position of the peak moves to higher wave numbers as the surfactant concentration increases. At sufficiently high surfactant concentrations, the interfaces become very stiff, leading to a variety of phases with relatively long-range order, such as lamellar, hexagonal, cubic, and other liquid-crystalline phases [4].

In this paper we present a detailed Monte Carlo study of the phase diagram of a lattice model for water-oil-surfactant mixtures in two dimensions. Previous theoretical work was based on both phenomenological models [5–9] and lattice models [13,21–23,33,34] where the mean-field approximation was used to study the equilibrium phase behavior of 3D ternary water-oil-surfactant systems. Some Monte Carlo simulations have also been used for studies [10–12] of the phase diagram of the Wheeler-Widom model [13]. The first extensive analysis of the effect of fluctuations on the phase behavior of two-dimensional ternary mixtures was due to Gompper and Schick [14] using a transfer-matrix method on a model with three-body oil-surfactant-water interactions. They found significant deviations from mean-field behavior. Recently Chowdhury and Stauffer used the Wheeler-Widom model for Monte Carlo studies of the stability of bilayers [15] and of microemulsions in a restricted geometry [16].

We have made use of a simple two-dimensional lattice-gas Hamiltonian, defined below, into which we expect to incorporate much of the essential physics of the mixture. To determine the phase boundaries as accurately as possible, we combined the Metropolis Monte Carlo method with the finite-size analysis recently developed by Ferrenberg and Swendsen [17], and by Lee and Kosterlitz [18]. This led to the following phase diagram as a function of surfactant concentration: the phase coexistence of water and oil, followed by a microemulsion region of the disordered phase, a lamellar phase, and a square phase, which is the two-dimensional analog of the experimentally observed cubic phase. Structure functions were calculated in the microemulsion region and qualitative agreement with experimental results was found. Finally, we calculated the phase diagram in the mean-field approximation using a local-mean-field method that involves the Monte Carlo algorithm. This allowed us to examine the role of fluctuations particularly in the microemulsion region where the interfacial tension approaches zero.

In the model studied in this work, each water, oil, or surfactant molecule occupies a single site on a two-dimensional square lattice. This is represented by a three-component spin variable S_i that takes values of $+1$, -1, and 0, respectively. Since amphiphilic surfactants are anisotropic molecules, we represent them in terms of a vector operator, $\mathbf{m}_i$, at site i. We allow $\mathbf{m}_i$ to have four possible directions along the bonds of a square lattice. $\mathbf{m}_i$ equals 0 whenever the site i is occupied by a water or an oil molecule. The Hamiltonian is written as follows:

$$\mathcal{H} = -J_1 \sum_{<i,j>} S_i S_j - J_2 \sum_{<i,j>} (S_j \mathbf{m}_i \cdot \mathbf{r}_{ij} + S_i \mathbf{m}_j \cdot \mathbf{r}_{ji}) \\ -\mu_s \sum_i \mid \mathbf{m}_i \mid^2 - (\mu_w - \mu_o) \sum_i S_i . \qquad (1)$$

The first term of $\mathcal{H}$ corresponds to the usual Blume-Capel spin-1 model for a tricritical system [19, 20]. The second term is crucial since it mimics the two-body interaction between a surfactant and water or oil molecules. This term reflects the fact that the tail of a surfactant prefers a hydrophobic environment such as oil, and the polar head interacts preferentially with water molecules. For simplicity, we consider a Hamiltonian that is symmetric between water and oil. This corresponds to the case where surfactants do not induce a spontaneous curvature in the interfaces. The last two terms of Eq. (1) represent the chemical potentials of the three species. In this work we are interested in systems with equal amounts of water and oil and therefore $\mu_w = \mu_o$. Defining

$$\Delta = \mu_s - \tfrac{1}{2}(\mu_w + \mu_o), \qquad (2)$$

the Hamiltonian is rewritten as

$$\mathcal{H} = -J_1 \sum_{i,j} S_i S_j - J_2 \sum_{i,j} (S_j \mathbf{m}_i \cdot \mathbf{r}_{ij} + S_i \mathbf{m}_j \cdot \mathbf{r}_{ji}) \\ +\Delta \sum_i {S_i}^2 . \qquad (3)$$

This model contains the essential physics of the three-component system, while remaining relatively uncomplicated. The only free parameter is the interaction ratio J_2/J_1, in contrast to other models in the literature where more interactions are usually included [9, 14, 21, 22]. A related model was studied within the mean-field approximation for small temperatures by Ciah *et al.* [23]. More recently, Matsen and Sullivan [21] proposed a lattice-gas model that included interactions between surfactants, and used it to calculate phase diagrams using mean-field and Bethe approximations. They found that the microemulsion region was characterized by large values of the surfactant concentration (> 68%). This is most probably due to the use of the mean-field approximation and they indicate that a treatment that includes fluctuations is required.

An exact evaluation of the ground state of the present model shows that for $J_2/J_1 < 0.5$ the model reduces to the usual Blume-Capel model, which has a region of two-phase coexistence followed by a disordered phase [19, 20]. This corresponds to the case of weak surfactants. Since both lamellar and square phases are found for $J_2/J_1 > 0.5$, a value of $J_2/J_1 = 3$ was used in our simulations. Our Monte Carlo work consisted of two parts. First, extensive Monte Carlo simulations were performed using the usual Metropolis Monte Carlo algorithm at many points of the phase diagram for system sizes ranging from $L = 4$ to 40. We then used the extrapolation method of Ferrenberg and Swendsen [17], which requires extremely good statistics ($\sim 10^6$ Monte Carlo steps/spin) at a point (Δ, T) in the phase diagram very close to the transition line. This run is used to calculate the equilibrium probability distribution of energy and surfactant concentration, which is then used to extrapolate to the probability distribution at a neighboring point (Δ', T'). This allows us to obtain thermodynamic functions such as the specific heat and the compressibility at the neighboring point in terms of (Δ, T). The transition can then be located from the position of the peak in the specific heat or the compressibility. Finite-size scaling was then performed on the data. For a first-order phase transition, the heat capacity scales as L^d [24], whereas it scales as $L^{\alpha/\nu}$ for second-order transitions where α and ν are the usual critical exponents [25]. The order of the transition lines were checked using the method of Lee and Kosterlitz mentioned above, which consists of calculating the free energy as a function of the order parameter at the transition from the probability distribution at the specific-heat peak. Good agreement with the extrapolation results was found. Details of these calculations are planned to be presented elsewhere [26].

The resultant phase diagram is shown in Fig. 1. The transition from the phase coexistence of water and oil to the disordered region is initially second order with a region that we believe to be first order, as we shall discuss below. There is no phase transition between the region of two-phase coexistence and the lamellar phase except at $T = 0$. Thus the disordered phase essentially extends to $T = 0$. The same behavior has been observed by Gompper and Schick [14]. The lamellar phase consists of domains of water and oil in the [10] or [01] directions, separated by surfactant monolayers. These domains can have different widths depending on temperature and chemical potential, but the width is generally of the order of a few lattice spacings. A typical configuration for the lamellar phase is shown in Fig. 2(a). The transition from the disordered phase to the lamellar phase is first order, as found from the finite-size analysis. A first-order phase boundary separates the lamellar phase from the square phase, which corresponds to alternating regions of water and oil in the "checkerboard" pattern, as shown in Fig. 2(b). The transition from the square phase to the disordered phase is also first order. In contrast to previous lattice models [22], we found that the lamellar and square phases have quasi-long-range order.

The disordered phase has a different behavior depending on the values of T and Δ. To the left of the dotted

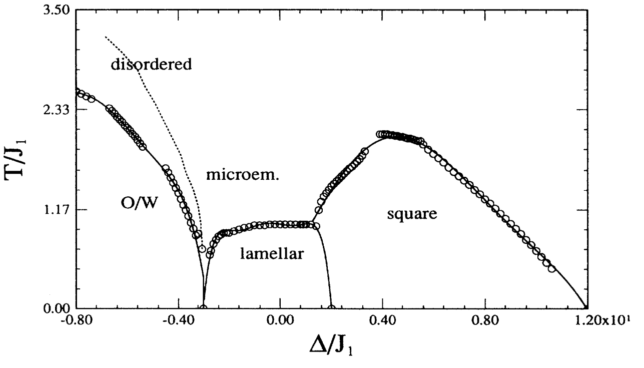

FIG. 1. Phase diagram of model of Eq. (3) with $J_2/J_1 = 3$ from Monte Carlo simulations. See text for details. The dotted line is the Lifshitz line.

line in Fig. 1, the water-water structure function shows the same monotonic decay plus a peak at $q = 0$, as found for simple fluids. However, to the right of the dotted line, there is a peak at $q > 0$. This implies that the disordered phase in this region is characterized by the presence of short-range order. This region can then be identified as the microemulsion region. The configurations are given in Fig. 3 and clearly show interconnected domains of water and oil separated by surfactant monolayers. This should be compared with the three-dimensional bicontinuous microemulsions [2, 3]. It is also clear from Fig. 3 that the average domain size decreases as the surfactant chemical potential Δ increases (i.e., as the surfactant concentration increases). Note that the domains are well segregated and most surfactants are positioned at the oil-water interfaces. The dotted line of Fig. 1 that separates the two regimes of the disordered phase is a Lifshitz line [27], and not a phase boundary, since no singularities were detected in any thermodynamic quantity.

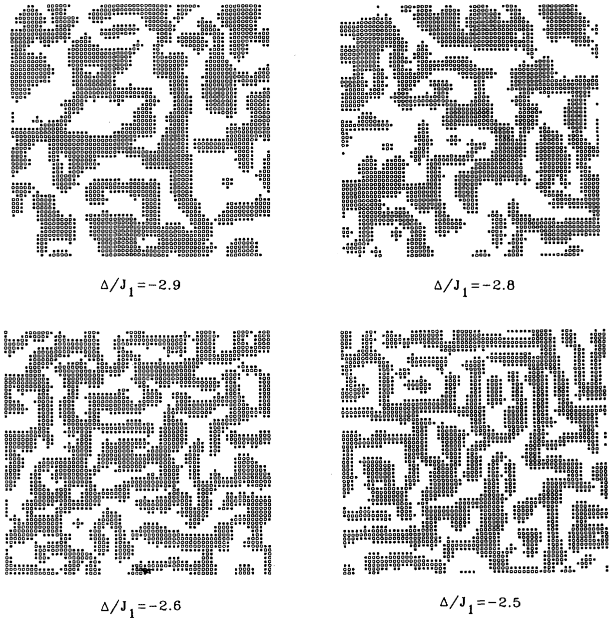

FIG. 3. Configurations in the microemulsion regime of the disordered phase at $T/J_1 = 0.8$. The values of Δ are -2.9, -2.8, -2.6, and -2.5 for (a), (b), (c), and (d), respectively . Closed squares represent surfactants, open squares represent water, and white regions represent oil.

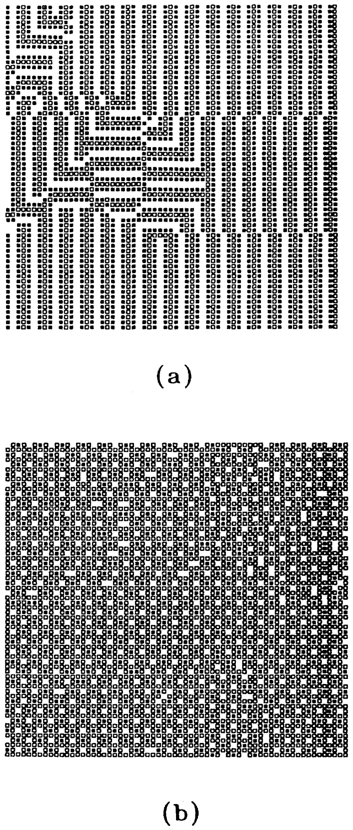

FIG. 2. (a) A typical configuration in the lamellar phase $(\Delta/J_1, T/J_1) = (-0.5, 0.55)$, the closed squares represent surfactants, open squares represent water, and white regions represent oil. (b) shows a typical configuration in the square phase $(\Delta/J_1, T/J_1) = (4, 1)$. In this case open squares represent surfactants.

In order to examine the effect of fluctuations on the phase diagram, we adapted a local mean-field theory method, which was used by Soukoulis and co-workers [28] to examine spin-glass systems. This method uses the Metropolis Monte Carlo algorithm in conjunction with the mean-field approximation. The role of fluctuations is particularly important when the interfacial tension is small since this leads to the creation of many fluctuating interfaces. The mean-field phase diagram for our model is shown in Fig. 4. This figure shows that the same phases as those in Monte Carlo simulation are found, but the phase boundaries are shifted. In particular the microemulsion region no longer extends to very small temperatures. This is due to the lack of fluctuations, which makes the lamellar phase unstable against the microemulsion. Furthermore, the microemulsion, the disordered phase, the lamellar phase, and the water- and oil-rich phases all meet at a single tricritical point. We

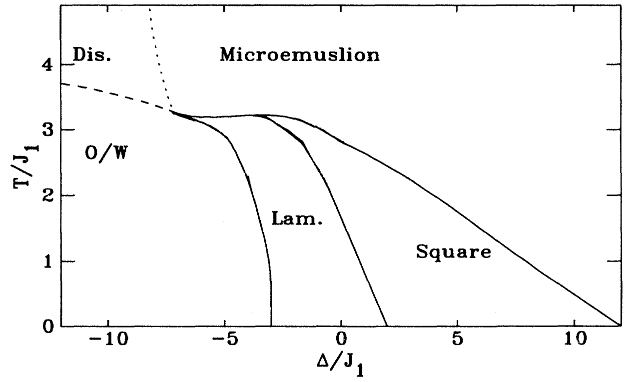

FIG. 4. Phase diagram of model of Eq. (3) with $J_2/J_1 = 3$ from the local mean-field technique. Solid lines are first-order lines, the dashed line is a second-order line, and the dotted line is the Lifshitz line.

also found that the lamellar-phase domains are not only oriented in the [10] or [01] directions, but also in the [11] direction. Details of our version of the local mean-field technique are planned to be presented elsewhere [26].

We were not able to determine the order of the transition between the two-phase water-oil region and the disordered phase at low temperature in the simulations. This is probably due to the extremely small interfacial tension between water-rich, or oil-rich, and microemulsion phases. It is observed experimentally that, when the microemulsion coexists simultaneously with water- and oil-rich phases, the interfacial tension between any two of the three phases is usually very small [29]. Thus if the transition is indeed first order, it should be rather weak. Indeed, our numerical calculation of the interfacial tension in this regime has given a value which is about 5% of the bare water-oil interfacial tension. Therefore the usual finite-size scaling behavior in this region will not be observed unless extremely large systems are studied. We can, however, give some arguments suggesting that the line separating the two-phase water-oil region and the disordered phases is first order at low temperatures. First, the ground-state calculation shows that the transition at $T = 0$ is first order. Second, we found that the Lifshitz line intersects the transition line, again implying the existence of a first-order line [30] and therefore a tricritical point separating the second- and first-order lines. Finally the local mean-field theory discussed above does indeed give such a tricritical point.

The water-water structure factor on a system of $L = 64$ in the microemulsion region is shown in Fig. 5. This was obtained by Monte Carlo calculations for $T/J_1 = 0.8$ in the region between the water-oil coexistence and the lamellar phase, and a peak at $q > 0$ is observed. As the chemical potential increases, the position of this peak shifts to higher wave numbers. This corresponds to a decrease in the average size of the water and oil domains consistent with Fig. 3. The inset of Fig. 3 shows that $q_{\max} \sim \rho_s$, where ρ_s is the surfactant concentration. This can be explained as follows. Since most surfactants are adsorbed at the interfaces, the total length of the interface $l \sim \rho_s$. But the average domain size $R \sim 1/l$, and therefore $q_m \sim \rho_s$. We note that a similar behavior has been observed experimentally [31]. The tail of the structure factor decays as a power law, $q^{-3} = q^{-(d+1)}$, which is equivalent to Porod's law found experimentally for three-dimensional microemulsions [32]. Finally, we have also obtained the surfactant-surfactant structure factor and observed a peak at nonzero q.

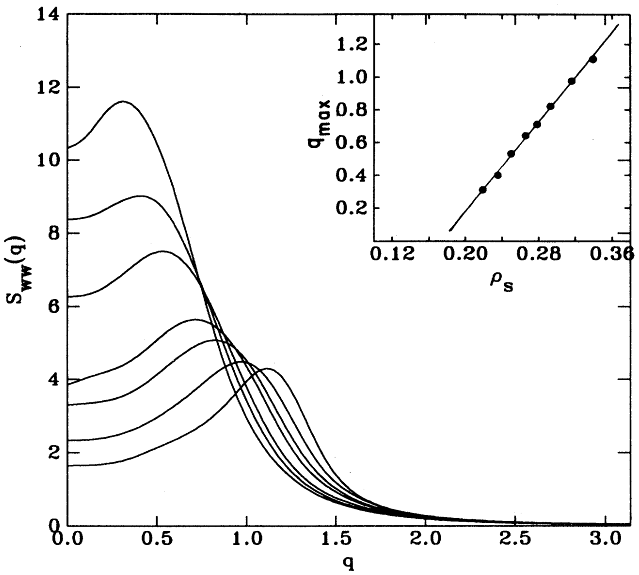

FIG. 5. The water-water structure factor in the microemulsion regime of the disordered phase at $T/J_1 = 0.8$. Inset shows the position of the maximum of structure factor $q_{\max}$ as a function of surfactant concentration. Curves from top to bottom correspond to the following values of the chemical potential: $\Delta/J_1 = -2.85$, -2.8, -2.75, -2.6, -2.5, and -2.4.

In conclusion, we have studied a model that captures the essential phase equilibria of a ternary surfactant mixture in two dimensions. An extensive Monte Carlo simulation has been performed revealing the phase diagram in such a system, with the transition lines obtained via detailed finite-size analysis. Using only one free parameter, the phase behavior of our model is qualitatively consistent with experimental results. We are currently extending our studies to three dimensions. These and other results are planned to be reported in future publications.

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