

Failure of microemulsion models to exhibit a triple line in two dimensions

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Evidence has recently been presented [P. A. Slotte, *Phys. Rev. A* **46**, 6469 (1992)] showing that a two-dimensional lattice model for water-oil-surfactant mixtures exhibits a triple line along which water-rich, oil-rich, and microemulsion phases coexist. We present an argument and numerical evidence that such a triple line will not exist if the efficiency of the surfactant is sufficient to produce a lamellar phase. The failure of the model to produce a triple line for an efficient surfactant can be linked to the fact that the surfactant monolayers separating regions of water and oil are only one dimensional. The implication is that two-dimensional models are somewhat inappropriate for modeling the amphiphilic behavior of real three-dimensional ternary mixtures.

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Lattice models have been successful in modeling behavior of water-oil-surfactant mixtures [1–3]. These models employ a lattice where molecules are typically restricted to occupy only the sites of the lattice rather than any point in space. Although three-dimensional lattices are more realistic, it is advantageous when applying Monte Carlo methods to use two-dimensional lattices. Previous work [5–7] has indicated that a two-dimensional lattice may be sufficient for obtaining a triple line along which water-rich (W), oil-rich (O), and microemulsion phases coexist as observed experimentally in three dimensions [4]. (A microemulsion is generally defined as the portion of the disordered (D) phase that has sufficient structure to produce a peak at small, nonzero wave vectors in the water-water structure function, or alternatively, produce long-wavelength oscillation in the related correlation function [1,2,5–11].) In the context of these models, this means a second-order line separating the $W + O$ coexistence region from the D phase exhibits a tricritical point past which the transition is first order. Matsen and Sullivan [8] addressed the evidence in Refs. [5] and [6] and instead suggested that such a transition should always be second order when the lamellar phase is present. Hence, there would be no $W + O + D$ three-phase coexistence once the efficiency of the surfactant is great enough to produce a lamellar phase. Contrary to this conclusion, Slotte [7] has claimed to have found a tricritical point implying the existence of a triple line in the presence of a lamellar phase.

This Brief Report starts by first establishing that the evidence presented by Slotte does not necessarily imply the existence of a tricritical point. Then we describe the scenario presented by Matsen and Sullivan [8], which suggests how the phase diagram evolves with increasing efficiency of the surfactant and conflicts with the existence of the above tricritical point. Next, the argument given for this scenario in Ref. [8] is elaborated on. This argument does hinge on one important assumption. We provide motivation for this assumption and quote several previous works that support it, but admittedly it is a weakness in the argument. For that reason, numerical

evidence is also provided to support this point of view. Although this evidence is not sufficient to prove that point of view, the evidence is consistent with it, whereas it is not consistent with the tricritical point claimed by Slotte. When combined, the evidence presented here strongly favors the Matsen-Sullivan scenario over the tricritical point proposed by Slotte. Although this paper concerns a specific model, it does in the end provide a warning about modeling three-dimensional amphiphilic systems with two-dimensional models.

Slotte uses the standard Metropolis Monte Carlo method with single-site flips together with finite-size scaling to locate the second-order line. At high temperatures, this approach works well; however, as the temperature is decreased, it is bound to become less effective. For instance, critical slowing down would become a problem at low temperatures. This alone can produce a hysteresis [12], and so the hysteresis observed by Slotte is not necessarily due to the presence of a first-order transition. However, his claim that a tricritical point exists does not just rest on this, but also on the apparent finite-size scaling of the surfactant susceptibility with tricritical exponents. This might be convincing, except for a number of weaknesses in his finite-size-scaling plots (one for temperature and another for chemical potential). First, these plots only have points to one side of the alleged tricritical point. Secondly, the curves for different system sizes have relatively little overlap, making it unclear whether they all follow the same universal curve. It is also not clear that the simulations were done close enough to the tricritical point for scaling to occur. Finally, the use of logarithmic scales could reduce the sensitivity to true scaling behavior, making data that do not really scale appear to do so. In conclusion, it is felt that the scaling plots cannot be considered compelling evidence for the existence of a tricritical point.

Contrary to these scaling plots for the tricritical point, Slotte presents sample scaling plots for the second-order line that are convincing. This clears up a problem noticed earlier [8] with the location of this transition in Ref. [5]. With these new results of Slotte, it seems certain that

the location of this transition in Ref. [5] is incorrect. It is unclear what would cause such an error and to what extent it might effect other results in Ref. [5]. This is mentioned here primarily to alert the reader that a certain degree of caution should be taken in quoting results from this earlier work.

The lattice models used in Refs. [5], [7], and [8] employ a two-dimensional square lattice. The i th lattice site is assigned a state variable σ_i that takes on the values $+1$, 0 , and -1 , representing water, surfactant, and oil, respectively. A second state variable s_i is zero when the i th site is not occupied by surfactant, and, otherwise, it is a unit vector pointing towards one of the four nearest-neighbor sites specifying the orientation of the surfactant molecule. In terms of these state variables, the Hamiltonian used in Ref. [5] is

$$H = - \sum_{\langle i,j \rangle} \{ J_1 \sigma_i \sigma_j + J_2 [\sigma_i (s_j \cdot r_{ji}) + \sigma_j (s_i \cdot r_{ij})] \} + \mu_s \sum_i \sigma_i^2. \quad (1)$$

The symbol $\langle i,j \rangle$ denotes that the sum is over all distinct pairs of nearest-neighbor sites i and j . The vector r_{ij} , measured in units of the lattice spacing, is the displacement of lattice site j relative to lattice site i . The concentration of surfactant, ρ_s , is controlled by the chemical potential μ_s , and the ratio J_2/J_1 determines the efficiency of the surfactant (J_1 and J_2 are both positive). References [7] and [8] introduced more general Hamiltonians, but much of the work in these papers is done with the parameters of the additional terms set to zero. The model in Refs. [6] and [9] uses a somewhat different Hamiltonian, but it is still closely related to the present model [7] and is thus expected to behave similarly.

When $J_2=0$, the present model reduces to the Blume-Capel (BC) model [13], for which there is a tricritical point in two dimensions [14,15]. The suggestion by Matsen and Sullivan [8] was that as J_2 increased, this tricritical point would move towards zero temperature. Specifically, it would reach $T=0$ at $J_2/J_1 = \frac{1}{2}$ just as the lamellar (L) and square (S) phases appear [5]. Figures 1(a) and 1(b) show the expected topology of the phase diagram for $J_2/J_1 < \frac{1}{2}$ and $J_2/J_1 > \frac{1}{2}$, respectively, in the temperature-chemical-potential plane. Figures 2(a) and 2(b) show the corresponding plots in the temperature-density plane. We stress that the topology of the phase diagrams for $J_2/J_1 > \frac{1}{2}$ are not consistent with mean-field theory, but that those for $J_2/J_1 < \frac{1}{2}$ are.

In this paper, we are not concerned with the transitions that bound the L and S phases in Figs. 1(b) and 2(b). They are drawn as first-order transitions in agreement with the work of Laradji *et al.* [5]. We do not speculate how these first-order transitions extend to zero temperature in Fig. 2(b), but we think the second-order line terminates at $\rho_s=0$ based on our numerical results, as well as those of Ref. [8]. As the evidence in Refs. [5] and [6] suggests, we do believe the D phase extends between the $W+O$ and L regions down to zero temperature, as shown in Fig. 1(b). It is this belief that leads us to conclude that the transition from $W+O$ to D is second order

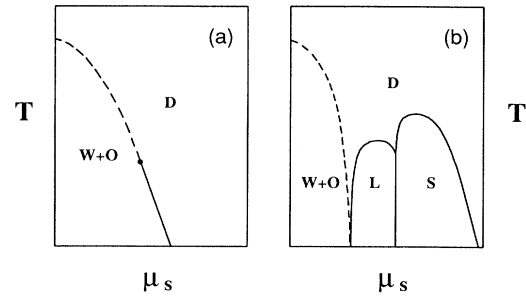


FIG. 1. The expected topologies of the phase diagram in the temperature-chemical-potential plane for (a) $J_2/J_1 < 0.5$ and (b) $J_2/J_1 > 0.5$. Solid and dashed lines represent first- and second-order transitions, respectively. The dot in case (a) indicates the location of the tricritical point.

for all temperatures when $J_2/J_1 > \frac{1}{2}$. In three dimensions, the D phase is not expected to separate the $W+O$ and L regions down to $T=0$, and, consequently, a triple line is possible in this case. We note that the disorder phase in the axial next-nearest-neighbor Ising (ANNNI) model similarly extends to zero temperature in two dimensions, but does not in three dimensions [16].

A simple argument explains why the D phase separates the $W+O$ and L regions in two dimensions but not in three dimensions. Imagine placing an $m \times n$ block of oil in the W phase when W and O are in coexistence. There would be two unfavorable contributions to the energy for such a defect: one due to the four edges and another due to the four corners. As μ_s is increased and the L phase is approached, the W/O surface tension becomes ultra low and the energy of the edges becomes negligible. This leaves only the energy of the corners, which is independent of the actual size of the defect. Although there may be a very small population of such defects at low temperatures, they may become macroscopic in size as the L phase is approached and still disorder the $W+O$ region, preempting a transition to the L phase. In three dimensions things are different. Here an $l \times m \times n$ defect has three contributions to the energy—the six faces, the

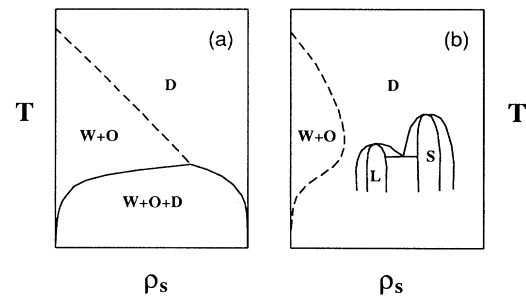


FIG. 2. The phase diagrams from Fig. 1 shown as they would appear in the temperature-vs-density plane ($0 \leq \rho_s \leq 1$). Note in case (b) that the coexistence regions, $D+L$, $L+S$, and $S+D$, have not been labeled, and that the first-order lines have not been extended to zero temperature.

twelve edges, and the eight corners. Similarly, the energy of the faces becomes negligible as the L phase is approached and the energy of the corners does not depend on the size of the defect. The energy due to the edges, however, increases with the size of the defect preventing them from becoming large. Because of this, the $W+O$ region should not become disordered prior to the L phase in three dimensions.

The argument that the $W+O$ to D transition should be second order down to $T=0$ for $J_2/J_1 > \frac{1}{2}$ stems from the fact the phase diagram should evolve continuously as J_2/J_1 increases. The contradiction that arises if one assumes otherwise is only noticeable in the temperature-density phase diagrams, Figs. 2(a) and 2(b). (This may in part be why such a contradiction was not noticed in Refs. [5] and [6] as only temperature-chemical-potential phase diagrams were plotted.) If one assumes the $W+O$ to D transition remains first order at low temperatures for $J_2/J_1 > \frac{1}{2}$, then as J_2/J_1 increased past $\frac{1}{2}$ the line separating the $W+O+D$ and D regions in Fig. 2(a) would have to make a discontinuous jump at $T=0$ from $\rho_s=1$ to some smaller value of ρ_s to the left of the L phase. In three dimensions, the D phase does not extend between the $W+O$ and L phases down to zero temperature, and so the phase diagram can evolve continuously into phase diagrams like those shown in Ref. [1], for which the $W+O+D$ triple line remains.

While the above argument strongly suggests that the $W+O$ to D transitions should not exhibit a tricritical point for $J_2/J_1 > \frac{1}{2}$, it is not a rigorous proof. The weakness in the argument is that the D phase may not extend to zero temperature despite the numerical evidence in Refs. [5] and [6] and the fact it is proven to happen similarly in the ANNNI model [17]. Admittedly, all it takes is a long-range attraction between lamellae to drive the $W+O$ region to the L phase by a first-order transition. In this case, the W/O surface tension does not become ultralow and the above argument breaks down. For this reason, it is important that at $T=0$ the W/O surface tension actually becomes zero as the proposed $W+O+D+L$ multiphase point is approached. This does occur in the present model, but whether this is sufficient can be questioned. Alternatively, it may be better to demonstrate the above claim by actually calculating the position of the tricritical point as a function of J_2 . If one illustrated that the tricritical temperature T_t in the BC model approaches zero as J_2/J_1 increases from 0 to $\frac{1}{2}$, the claim by Matsen and Sullivan would be virtually indisputable. Potentially, this could be done numerically using, for example, the Monte Carlo renormalization-group method [14]. Still, generating a sufficiently accurate plot of T_t versus J_2 by such a method would be numerically demanding.

We instead opt for the less demanding method used in Ref. [8]. This method considers a $4 \times \infty$ strip of the two-dimensional lattice acted upon by fields to which the transfer-matrix method is applied. The fields are determined by self-consistent conditions much like in mean-field theory. Likewise, the tricritical point as well as phase transition are calculated in a manner similar to

that in mean-field theory [18]. Just as in mean-field theory, this method will suppress fluctuations and consequently be somewhat inaccurate. More specifically, this suppression of fluctuations will tend to stabilize three-phase coexistence, and thus produce a triple line that extends higher in temperature than the actual triple line. Hence, for a given value of J_2 , the T_t calculated with this approximation should be an upper bound on the true value of T_t .

Figure 3(a) shows the plot of T_t versus J_2 calculated in the above manner. At $J_2=0$, $k_B T_t/J_1=0.746$, which is, as we expect, larger than the accepted value of 0.61 [14,15]. As J_2 increases, T_t decreases monotonically to zero at $J_2/J_1 \approx 0.9$, beyond which we find no evidence of a tricritical point. Remembering that this curve should be an upper bound on the actual curve, Fig. 3(a) is consistent with the belief that T_t should approach zero at $J_2/J_1 = \frac{1}{2}$. On the other hand, it seriously conflicts with the conclusion by Slotte that $k_B T_t/J_1 = 0.52 \pm 0.03$ at $J_2/J_1 = 3$. Figure 3(b) plots the surfactant density at the tricritical point, $\rho_{s,t}$, as a function of J_2 . This plot suggests that as T_t approaches zero, so does $\rho_{s,t}$, supporting our belief that the $T=0$ end of the second-order line in Fig. 2(b) terminates at $\rho_s=0$. This makes sense, since at low temperatures the $W+O$ region presumably becomes disordered due to a small population of very large defects, which essentially contain surfactant only along their edges, contributing very little to the bulk surfactant density.

The failure of the present model to produce a triple line is linked to a more general problem that would plague all two-dimensional models. Even the much different two-dimensional model studied by Chen *et al.* [19], to which the above argument does not apply, still does not seem to exhibit such a triple line according to their Monte Carlo work, contradicting the mean-field prediction [20]. The problem arises because the surfactant monolayers that tend to form between water and oil regions are only one dimensional. Needless to say, the behavior with regards to fluctuations will differ substantially between the one-dimensional monolayers and more realistic two-dimensional monolayers. Although this fact implies that the present two-dimensional model is somewhat inappropriate for modeling real three-dimensional

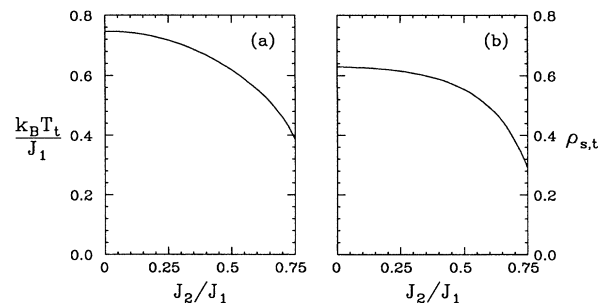


FIG. 3 (a) The temperature and (b) surfactant density of the tricritical point as a function of J_2/J_1 as calculated by the present approximation.

water-oil-surfactant mixtures, this model does exhibit interesting behavior similar to that of the ANNNI model [16]. Just as the ANNNI model was studied primarily because of its interesting behavior rather than its description of a real physical system, we hope the present model attracts such interest. The model certainly presents a challenge due to the strong fluctuations it exhibits. Likewise, we hope its three-dimensional counterpart [1,3], which seems to describe reasonably the above-mentioned ternary mixtures, attracts further interest. Although it has been studied by mean-field-like approximations, the effect of fluctuations has not been studied and we do expect them to be significant when J_2 is large, but not to the same degree as in two dimensions. We note that the

one-dimensional version is already well understood [10].

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