

Spin-1 model of a microemulsion

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We formulate a spin-1 model of a microemulsion in which the spin values $+1$, 0 , and -1 correspond to water, surfactant, and oil, respectively. Physical considerations dictate our choice of interactions. In addition to the usual attractive interactions at short range between molecules of the same kind, the surfactant induces a competing attractive interaction between molecules of different kinds at a distance equal to the size of the surfactant. For sufficient surfactant concentrations, this induces a phase in which numerous walls of surfactant separate distinct regions of oil and water. In a continuum model, these walls would be rough, producing a critical phase without either the long-range order of a solid or the exponential decay of correlations of a disordered liquid. We identify this phase with the "bicontinuous" phase of Scriven. The phase diagram of the system within mean-field theory is calculated, as is the surface tension between oil and water as a function of surfactant concentration. Depending upon temperature, the value of the latter at the triple point can be reduced by a factor of a thousand or more from that in the absence of surfactant.

Liquid mixtures of hydrocarbon, water, and a surfactant exist in a rich variety of phases of which some display properties of great commercial importance.¹ Of particular interest to the problem of tertiary oil recovery is the extraordinarily low surface tension between oil-rich and water-rich phases which is exhibited in some systems for sufficient surfactant concentration. The physical configuration of such systems depends strongly on the relative amounts of the components. When the fraction of water dominates, the state of the system is almost certainly a solution of micelles, which consist of a nucleus of hydrocarbon (oil) surrounded by surfactant; if the oil fraction dominates, the roles of water and oil are reversed and the micelles are said to be inverted. Less clear is the configuration of the system when the fractions of oil and water are comparable. If there is little surfactant, then a simple interface between the oil-rich and water-rich phases exists. However, as the fraction of surfactant increases, this phase may break up into one with many interfaces which separate distinct, identifiable regions of oil and water which interpenetrate and fill space. One particularly interesting model of this phase has been provided by Scriven,² who denoted it a "bicontinuous" microemulsion.

The mechanism by which the unusual phase with large surface area can be brought about has been known in broad outline for some time.³ The surfactant is preferentially adsorbed at an oil-water interface due to its amphiphilic nature. Interactions between these molecules produce a spreading pressure which, in favoring a greater interfacial area, decreases the surface tension of the system. If the tension can be reduced to zero, a new phase with an extensive amount of surface is to be expected.

Several models, phenomenological and otherwise, have been studied,^{1,4-9} and they illustrate some of the features of microemulsions. However, they miss essential features of the bicontinuous phase: that is a phase distinct from the ordinary disordered fluid phase and that a phase

boundary separates them; that there are macroscopic identifiable regions of oil and water in the bicontinuous phase whereas these components are mixed down to microscopic scales in the disordered phase; that the roughness of the interfaces between the regions of oil and of water in the bicontinuous phase can cause the density-density correlation function to decay with distance differently from the exponential decrease characteristic of the disordered phase.¹⁰ In this paper we investigate a simple spin-1 model of a three-component system, and by choosing interaction parameters to mimic the behavior of the amphiphile we are able to bring about such a phase. It is of the class of so-called "massless" or "critical" phases which have arisen in many contexts within the last several years in which the tension of walls separating different domains can be made to vanish.¹¹ Microemulsions are thereby placed in a context of systems which have received considerable attention and are also seen to present realizations of known models. Widom has recently made this important observation independently.¹²

We consider a spin-1 model which for simplicity we place upon a three-dimensional cubic lattice. At each site there is a statistical variable S_i , which can take the values $+1$, 0 , -1 , representing water, surfactant, or oil, respectively, at that site. The general pair-interaction Hamiltonian defines the Blume-Emery-Griffiths (BEG) model¹³ and can be written

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} [J_{i,j} S_i S_j + K_{i,j} S_i^2 S_j^2] + C_{i,j} (S_i S_j^2 + S_i^2 S_j) - \sum_i (H S_i - \Delta S_i^2).$$

The interactions which are essential to a description of the microemulsion are not difficult to discern. Nearest-neighbor values of J and K are positive, reflecting the stability of pure oil and water in the absence of surfactant. The crucial nature of the surfactant is that, by its construction, it is energetically favorable for it to be found

between an oil and a water molecule. It thereby generates an effective attraction between unlike molecules at a distance equal to the size of the surfactant. This property is incorporated by making negative the value of J between two spins on opposite sides of any lattice site (i.e., between fourth neighbors in the cubic lattice). It is the competition between the nearest-neighbor attractive interactions of like molecules and the effective attraction between unlike molecules at a further distance brought about by the amphiphile that gives rise to the phases with extensive surface area. In particular, as the chemical potential of surfactant, Δ , is changed so that the concentration of surfactant increases, this component will make a single wall, separating the oil and water regions, whose free energy decreases. Beyond a critical surfactant chemical potential $\Delta_c(T)$, it becomes free-energetically favorable to make many such walls which separate many distinct regions of oil and water. For concentrations of oil and water which are not too dissimilar, this phase will have the properties described by Scriven.² The walls have an average spacing which is governed by the amount of surfactant. In the lattice model, this spacing is not in general commensurate with the underlying lattice. In a continuum, and in the lattice model at sufficiently high temperatures, the walls are rough and preclude conventional long-range order. However, the phase is distinct from a high-temperature disordered liquid which also lacks long-range order in that its correlation function will reflect the variation in composition with a wave vector inversely proportional to the distance between walls and can have an amplitude which does not decrease exponentially with distance. Whether the walls form a laminar array or curl into long tubes depends on the details of the interactions. In the former case, the correlation functions would resemble those of a smectic liquid crystal.¹⁴ Lastly, the low surface tension between the oil-rich and water-rich phases reflects the low free energy of the walls. The surface tension between these phases is not expected to vanish in general, however, because the transition to the microemulsion is expected to be first order.

Many of the above properties are well known in the three-dimensional axial next-nearest-neighbor Ising (ANNNI) model,^{11,15} and the similarities between this model and the one we employ should be clear. We emphasize, then, the differences. The BEG model which we employ is isotropic and can therefore describe phases which do not exist in the ANNNI model such as ones containing close-packed tubes or cubes. The parameter space of the ANNNI model consists of the ratio of coupling constants and the temperature so that the phase diagram is generated in this space. The BEG model contains additional chemical potentials and the phase diagrams in which we are interested are generated in the surfactant chemical potential-temperature plane with all interactions fixed. This results in additional differences. Whereas in the ANNNI model the phase transition between the disordered phase and all other phases, including the critical phase, is continuous, in our model only the transition between the disordered phase and the uniform ordered (oil-rich or water-rich) phases is continuous. In particular, the transition to the microemulsion is first order. Further,

the ANNNI model in three dimensions displays a Lifshitz point¹¹ at which meet the lines of continuous transitions separating the disordered from uniform ordered, and critical phases. As a consequence, the uniform ordered phases of the ANNNI model can be made to undergo, by changing the ratio of coupling strengths, a transition to a critical phase in which the walls are arbitrarily far apart. In our model, lines of first-order transitions separating these phases meet at a single point. As a consequence, the uniform phases can be made to undergo, by changing the chemical potential of the surfactant, a first-order transition to a critical phase with a definite average wall separation which depends upon the temperature. This is in accord with experiment^{2,16} in that the structures of the microemulsion typically are found with dimensions less than 100 nm.

We turn now to our specific choice of interaction parameters. We wish to employ the smallest set that will suffice to describe the phenomena. We choose the interactions $J_{i,j}$ and $K_{i,j}$ to be positive when i and j are nearest neighbors and denote these interactions J and K , respectively. As noted earlier, we must take $J_{i,j}$ to be nonzero when i and j are fourth-nearest neighbors. This interaction, denoted J_4 is negative. Lastly, in order to distinguish laminar, tube, and cube phases, we make $K_{i,j}$ nonzero for i and j second-neighbor interactions and denote it K_2 . For simplicity, we set the symmetry-breaking terms $C_{i,j}$ and H equal to zero so that the concentrations of oil and water are equal. Restrictions on the magnitudes of these interactions follow from examination of several possible states at zero temperature. These states include

(1) The state with all spins up or all down representing pure water or oil, respectively [Fig. 1(a)]. The energy per unit volume is

$$E_F = -3(J + K + J_4) - 6K_2 + \Delta.$$

(2) The laminar state with n layers of oil separated from n layers of water by a layer of surfactant [Fig. 1(b)]. The energy per unit volume is, for $n > 1$,

$$E_L^{(n)} = E_F + E_W / (n + 1),$$

where E_W is the energy per unit area to make a wall and is given by

$$E_W = \Delta_c - \Delta$$

with

$$\Delta_c = 4(J + K) + 6J_4 + 10K_2.$$

For $n = 1$,

$$E_L^{(1)} = -(J + K + \frac{1}{2}J_4 + K_2 - \frac{1}{2}\Delta).$$

(3) The tube state which is shown in Fig. 1(c). The state is uniform in the direction perpendicular to the paper. Its energy can be written

$$E_T^{(n)} = E_F + 2E_W / (n + 1) + E_X / (n + 1)^2, \quad n > 1,$$

where E_X is an energy per unit length and has the interpretation of an energy of curvature. It is given by

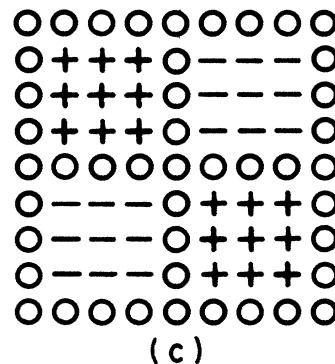
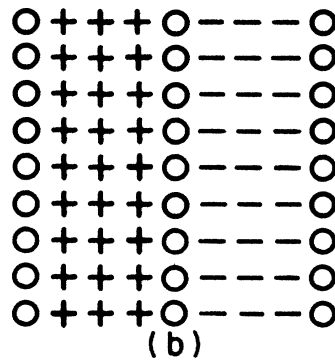
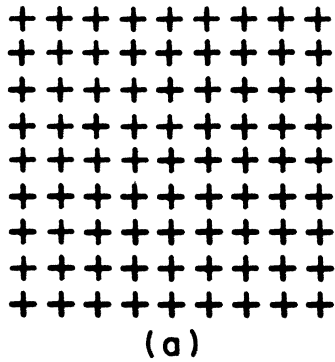


FIG. 1. Representation within the model of (a) the uniformly ordered phase of water, (b) the laminar phase ($n=3$ is shown), (c) the tube phase ($n=3$ is shown).

$$E_X = -[5(J+K) + 9J_4 + 16K_2 - \Delta].$$

The natural curvature is $|E_W/E_X|$. With the symmetry-breaking terms set to zero, this curvature term is independent of the direction of curvature so that the Bancroft parameter⁷ is set to zero. If $n=1$, then the energy is

$$E_T^{(1)} = -\frac{1}{4}(J+K - J_4 - \Delta).$$

(4) The cube state which has the same cross-section as in Fig. 1(c), but in each of the three principal directions. Its energy is given by

$$E_C^{(n)} = E_F + 3E_W/(n+1) + 3E_X/(n+1)^2 + E_Y/(n+1)^3,$$

$$n > 1,$$

where the E_Y is an energy associated with the corners or curvature in all directions. It is equal to

$$E_Y = 6(J+K + 2J_4 + 4K_2) - \Delta.$$

If $n=1$, then

$$E_C^{(1)} = (3J_4 + \Delta)/8.$$

For ease of calculation, we choose the parameters such that the microemulsion phase is laminar only. Thus we need calculate composition profiles in only one direction. In order that the zero-temperature phase diagram exhibit with increasing surfactant chemical potential the progression from uniform ordered phase (representing pure oil and pure water phases in coexistence) to the laminar phase, to the pure surfactant phase, the following inequalities must be satisfied:

$$-J_4 > (J+K)/3 + 4K_2/3,$$

$$-J_4 < (J+K)/3 + K_2,$$

$$-J_4 < (J+K) + 4K_2.$$

Note that these inequalities immediately dictate a choice of negative K_2 . An additional constraint can be obtained from the Landau expansion of the mean-field theory free energy.^{13,17} When there are no symmetry-breaking fields, this quantity is given by

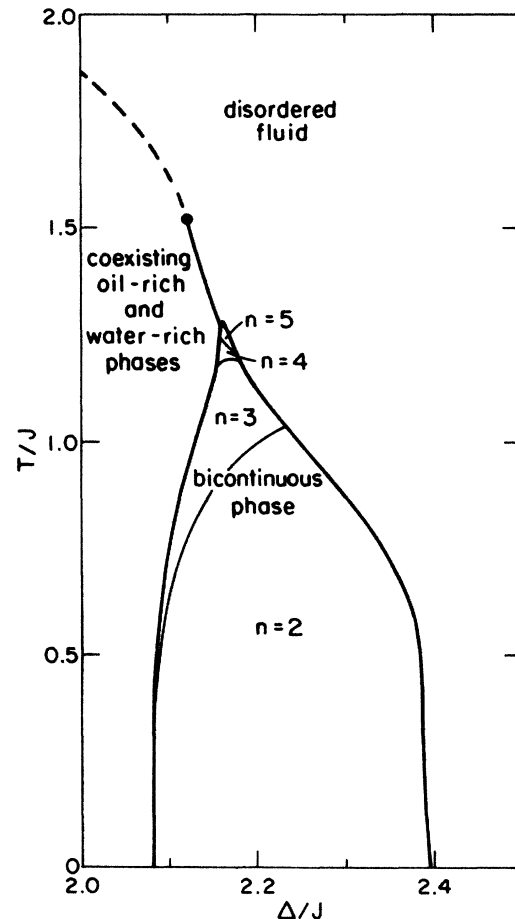


FIG. 2. Phase diagram of the model in the temperature-surfactant chemical potential plane with the specific choice of parameters given in the text. Solid lines denote first-order transitions, dashed line a continuous transition. The dot denotes a tricritical point.

$$\begin{aligned} \phi(T, \Delta) &= \frac{1}{2} \sum_{i,j} (J_{i,j} M_i M_j + K_{i,j} Q_i Q_j) \\ &\quad - T \sum_i \ln[2 \cosh(a_i) \exp(b_i) + 1], \\ a_i &= \beta \sum_j J_{i,j} M_j, \\ b_i &= \beta \left[\sum_j K_{i,j} Q_j - \Delta \right], \end{aligned} \quad (1)$$

where $\beta = 1/T$ and M_i and Q_i are the average values of S_i and S_i^2 , respectively. They are obtained by minimization of the free energy which leads to the set of self-consistent equations

$$M_i = \frac{2 \sinh(a_i)}{2 \cosh(a_i) + \exp(-b_i)}, \quad (2)$$

$$Q_i = \frac{2 \cosh(a_i)}{2 \cosh(a_i) + \exp(-b_i)}. \quad (3)$$

The free energy has the Landau expansion

$$\begin{aligned} \phi(T, \Delta) &= \sum_{\mathbf{q}} A(T, \Delta, \mathbf{q}) M_{\mathbf{q}} M_{-\mathbf{q}} + \sum_{\mathbf{q}' \neq 0} B(T, \Delta, \mathbf{q}') Q_{\mathbf{q}'} Q_{-\mathbf{q}'} \\ &\quad + \sum_{\mathbf{q}} \sum_{\mathbf{q}' \neq 0} C(T, \Delta, \mathbf{q}, \mathbf{q}') M_{-\mathbf{q}} M_{\mathbf{q}+\mathbf{q}'} Q_{-\mathbf{q}'} + \dots, \end{aligned} \quad (4)$$

where $M_{\mathbf{q}}$ and $Q_{\mathbf{q}}$ are the Fourier transforms of M_i and Q_i and

$$A(T, \Delta, \mathbf{q}) = \frac{1}{2} N J_{-\mathbf{q}} [1 - T^{-1} Q_0(T, \Delta) N J_{\mathbf{q}}], \quad (5)$$

with $J_{\mathbf{q}}$ the Fourier transform of the interaction $J_{i,j}$, N the number of lattice sites, and Q_0 the uniform component of Q_i . This component is not small as it is coupled to the chemical potential Δ . In the above expansion Q_0 is given by the solution of

$$Q_0 = \frac{2}{2 + \exp \left[\beta \left(\Delta - Q_0 \sum_j K_{ij} \right) \right]}. \quad (6)$$

A continuous transition from the disordered state to an ordered state characterized by a wave vector \mathbf{q} can occur at the maximum of all temperatures $T_c(\Delta, \mathbf{q})$ defined by

$$A[T_c(\Delta, \mathbf{q}), \Delta, \mathbf{q}] = 0. \quad (7)$$

This temperature is determined by that \mathbf{q} which maximizes $J_{\mathbf{q}}$. For the form of the interaction we have chosen, this \mathbf{q} is equal to zero provided that

$$-J_4/J < \frac{1}{4}, \quad (8)$$

and is nonzero otherwise. Thus with the interaction fixed, we can choose it so that the continuous transition occurs between the disordered fluid and the uniform ordered phase or between the disordered fluid and the critical phase but *not both*. We choose the former, which gives the desired constraint, Eq. (8). The continuous portion of the phase boundary between the disordered and uniformly ordered fluid (the consolute line) is given by the solution of Eqs. (5)–(7). The continuous portion ends in a tricritical point which is also easily obtained from the Landau expansion.¹³ In accord with the above inequalities we

have chosen the following set of interaction parameters: $K/J = \frac{1}{2}$, $K_2/J = -\frac{1}{4}$, $J_4/J = -\frac{17}{72} \approx -0.236$.

We have solved numerically the set of equations (2) and (3) and have found the solution which makes the free energy of Eq. (1) an absolute minimum. The resultant phase diagram is shown in Fig. 2. In the region of the diagram in which the laminar phase appears, we have investigated solutions with various n to determine that which corresponds to the lowest free energy. We have delineated the boundaries between different n simply to indicate the general dependence on temperature of n , the characteristic size of oil or water regions. Phase transitions between states of different n are solely a consequence of the discreteness of the lattice and would be absent in a continuum model due to the roughness of the walls. For this same reason we have not sought to determine the presence or absence of other laminar phases,¹¹ characterized by more than one value of n , which would also exist only by virtue of the lattice. All lines of transitions except part of that between the disordered and the uniform ordered phase (the consolute line) are first order. The tricritical point on this line is shown with a dot.

As the surfactant chemical potential Δ is increased at zero temperature and the triple line at $\Delta = \Delta_c$ is approached, the surface tension between the coexisting uniform phases (oil and water) vanishes. This is due to the fact that, for a finite range of $\Delta < \Delta_c$, it is energetically favorable for a single wall of surfactant to intrude between the oil and water phases. As Δ_c is approached, the energy of this wall, which at zero temperature is the surface tension, vanishes. The concentration of surfactant is infinitesimal as it is all concentrated at a single wall. At finite temperatures, the surface tension falls to a nonzero, but small, value at the triple line and the surfactant concentration is also nonzero but small. We have calculated the surface tension at nonzero temperatures by solving the mean-field equations (2) and (3) subject to the boundary conditions that the M_i and Q_i take the same values as

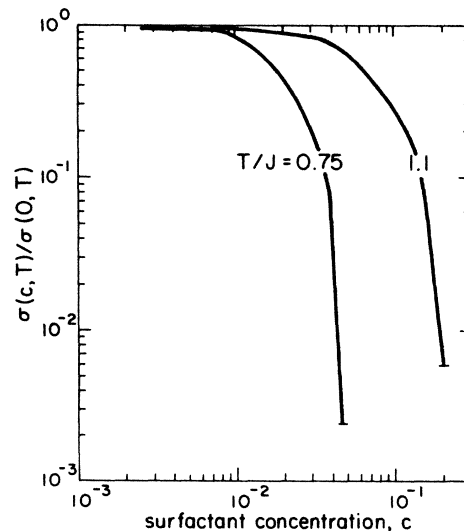


FIG. 3. Surface tension between oil-rich and water-rich phases at temperatures T/J of 0.75 and 1.1 as a function of surfactant concentration. The curves end at the concentration at which the triple line is encountered.

they assume in the uniform water-rich phase at the right-hand edge of a slab N layers thick, and in the uniform oil-rich phase at the left-hand edge. The difference between the free energy of Eq. (1) evaluated with this inhomogeneous solution and evaluated with either the uniform oil-rich or water-rich solution converges to the mean-field surface tension $\sigma(\Delta, T)$ with increasing N . For clarity, we have eliminated the chemical potential Δ in terms of the concentration and temperature. The resultant surface tension, $\sigma(c, T)$ for $T/J=0.75$ is shown, normalized by the zero-concentration value at the same temperature, in Fig. 3. At the triple line, this normalized surface tension has fallen to 2.4×10^{-3} while the concentration of surfactant is only 4.6×10^{-2} . These are reasonable values. At the higher temperature of $T/J=1.1$, the normalized surface tension and the concentration at the triple line are 6.1×10^{-3} and 20×10^{-2} , respectively. Results at this temperature are also shown in Fig. 3.

In summary, we have presented a spin-1 model which, with simple interactions which mimic the properties of the amphiphile, produces a unique phase with properties similar to that of a microemulsion. It is a phase characterized by walls of surfactant which separate regions of oil and water. In a continuum, these walls, being rough, destroy long-range order. Nonetheless, the phase differs from the disordered fluid phase in the behavior of its

correlation functions. There are clearly many aspects of microemulsions which can be studied with this model. For example, the model can encompass transitions from one conformation of the microemulsion to another such as laminar to tubular. This transition with increasing surfactant concentration reflects the greater surface area of the tubular phase. Transitions such as these are well known.^{18,19} In addition, it is clearly of interest to consider the breaking of symmetry introduced by varying the relative fraction of oil and water in order to study the evolution of micelle phases from bicontinuous ones as well as introducing symmetry-breaking effects of curvature. Lastly it is clear that the model can also encompass the phenomenon of critical micelle concentration.²⁰

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