# Microemulsion Structure from a Three-Component Lattice Model

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Phase diagrams and all three independent structure functions of oil, water, and amphiphile mixtures have been calculated from a three-component lattice model introduced previously. Both two- and three-dimensional systems were studied, by transfer-matrix methods and mean-field theory, respectively. With increasing amphiphile concentration, the phase diagram shows the commonly observed progression from three-phase coexistence through a microemulsion to two-phase coexistence with a lamellar phase. All three structure functions of the microemulsion are in qualitative agreement with experiment.

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A microemulsion is a phase in which oil and water are uniformly mixed due to the presence of a small concentration of an amphiphile, a molecule with a polar head group, which prefers to be surrounded by water, and an aliphatic carbon chain tail, which prefers oil. One of its characteristic features is the peak at nonzero wave number in small-angle x-ray and neutron scattering intensities[1-4] which implies a characteristic length of order 100 Å. The phase is pictured as consisting of coherent regions of this size of oil and of water separated by sheets of amphiphile, a picture supported by freeze-fracture microscopy.[5]

The microemulsion can coexist with oil-rich and water-rich phases along a triple line. This line is terminated at one end by a critical end point at which the microemulsion merges continuously with the oil-rich phase in the presence of the water-rich phase; a second critical end point, at which the roles of oil and water are reversed, terminates the other end. By varying a parameter, related perhaps to the composition of the oil or of the amphiphile, one can cause the two critical end points to merge at a tricritical point.[6] In addition to the microemulsion, many other phases, which are liquid crystalline, can be brought about by increasing the density of amphiphile. Of these, a lamellar phase is often observed to compete with the existence of a microemulsion.[6]

Most theories of microemulsions have been either phenomenological[7] or microscopic.[8-11] The former have been successful in reproducing aspects of the phase behavior, as well as a structure factor (for scattering contrast between oil and water) which resembles experiment.[12] The latter also have had some success, particularly in obtaining three-phase coexistence[9-11] and a description of the lamellar phases.[8]

We report here that a simple three-component microscopic model that has been introduced previously[9] not only yields the correct phase diagram (three-phase coexistence followed by microemulsion and then a lamellar phase as the surfactant density is increased[11]) but also provides results for all *three* independent density-density correlation functions of the microemulsion which are in qualitative agreement with experiment.

The system which we study consists of a square (or cubic) lattice on each site of which there is one of three components labeled $a$, $b$, and $c$ representing water, oil, and amphiphile. In terms of the projection operator $P_i^\alpha$, which is equal to unity if site $i$ is occupied by component $\alpha$, and is zero otherwise, the Hamiltonian is

$$\mathcal{H} = -\sum_\alpha \sum_\beta \sum_{\langle ij\rangle} E^{ij}_{\alpha\beta} P_i^\alpha P_j^\beta - \sum_\alpha \mu_\alpha \sum_i P_i^\alpha + \mathcal{H}_{\text{amp}} .$$

The first term is simply the sum of all distinct pair interactions, and the second contains the usual chemical potentials. The third term, which mimics the effect of the amphiphile in that energy is gained if $c$ sits between $a$ and $b$ all in a line, and is lost if $c$ sites between two $a$ or two $b$, is

$$\mathcal{H}_{\text{amp}} = -L \sum_{(ijk)} (P_i^a P_j^c P_k^a + P_i^b P_j^c P_k^b - P_i^a P_j^c P_k^b - P_i^b P_j^c P_k^a) ,$$

with $L < 0$. It is convenient to introduce three independent combinations of the nearest-neighbor interactions, $J$, $K$, and $C$, via

$$E_{aa} + E_{bb} - 2E_{ab} = 4J ,$$

$$E_{aa} + E_{cc} - 2E_{ac} = J + K + 2C ,$$

$$E_{bb} + E_{cc} - 2E_{bc} = J + K - 2C ,$$

and $\Delta$, which, to within an additive constant, equals $\mu_c - (\mu_a + \mu_b)/2$. Similar combinations, $J_2$, $K_2$, and $C_2$, of second-neighbor interactions can be introduced.

We have solved the above model exactly in two dimensions on strips of infinite length and circumference $m$ by means of the transfer matrix and obtained the phase diagram by standard methods.[13] The presence of the three-particle amphiphilic interaction requires that either this matrix transfer two rows at a time, or a single zigzag row. We have employed both procedures, the former up to $m = 7$ and the latter to $m = 10$, with consistent results.[14]

When the amphiphilic interaction, $L$, is weak, the phase diagram of our model has a region of two-phase coexistence between oil and water which, for small $\Delta$, ends in a line of critical points. For larger $\Delta$, this line ends at a tricritical point beyond which there is three-phase coexistence between oil-rich, water-rich, and amphiphile-rich phases. All three phases at coexistence are featureless; their structure functions, constructed from the eigenvectors of the transfer matrix,[15] decrease monotonically with wave vector, so that the amphiphile-rich phase is not a microemulsion.

When $L$ is made sufficiently strong, a lamellar phase appears, as in Fig. 1(a) for which $L/J=-3$. The difference in water and oil concentrations, $\delta x$, is zero. The lamellar phase consists of lines of oil, amphiphile, water, amphiphile, oil, etc., along either the (10) or (01) direction of the square lattice. The transition to it appears to be first order.

We have also located the phase transitions from the disordered phase to the oil- and water-rich phases and to the lamellar phase by the Müller-Hartmann–Zittartz approximation.[16] Agreement with the transfer-matrix results is very good, even in the region of the phase diagram where the transition is first order.[17]

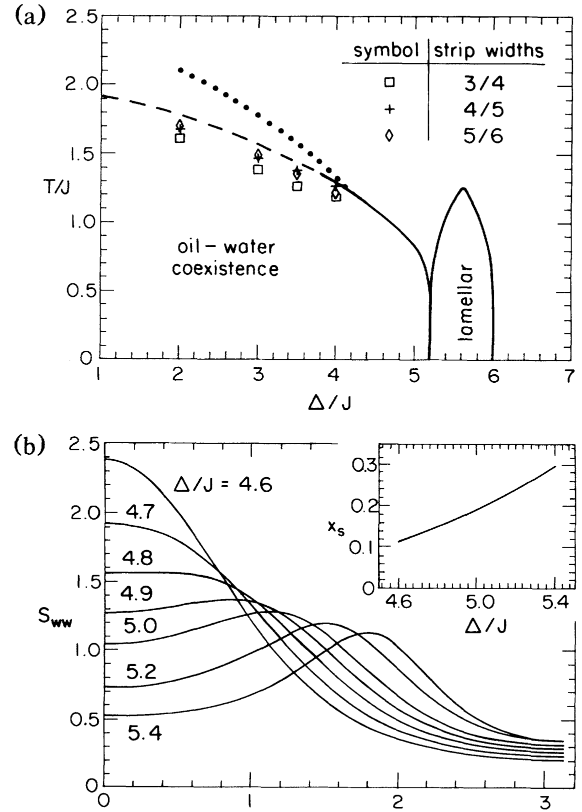

FIG. 1. (a) Phase diagram in two dimensions with $\delta x=0$ and $K/J=2$, $K_2/J=-0.2$, $L/J=-3$, and all others zero. Symbols show results of transfer-matrix calculations in the (10) direction for various strip widths. Full lines and dashed lines, results of the Müller-Hartmann–Zittartz approximation, indicate first order and continuous transitions, respectively. Dotted line is the disorder line. (b) Unnormalized structure function $S_{ww}(q)$ in the (11) direction at $T/J=1.1$ for various values of $\Delta$. Inset: Variation of the surfactant concentration $x_s$ with $\Delta$.

In order to see how the disordered phase in Fig. 1(a), which we identify with the microemulsion, differs from the disordered phase at small amphiphilicity $L$, we show in Fig. 1(b) the structure function $S_{ww}(q)$, the Fourier transform of the water density-density correlation function. The parameters are those of Fig. 1(a), and the temperature is $T/J=1.1$. The seven values of the chemical potential span the region of the microemulsion. It is seen that the peak in $S_{ww}(q)$ moves out and its amplitude decreases with increasing surfactant concentration, $x_s$, as in experiment.[1-4]

The asymptotic form of the correlation function itself for $r\rightarrow\infty$ is $A\exp(-r/\xi)\sin(2\pi r/\lambda+\phi)$, where $A$ and $\phi$ are constants. A convenient theoretical boundary between the microemulsion and the ordinary disordered phase is the line at which $\lambda^{-1}(T_{\mathrm{dis}},\Delta_{\mathrm{dis}})\rightarrow 0$. This is called a "disorder line,"[18] and is shown in Fig. 1(a) as a dotted line. To the left of it is the ordinary disordered phase with simple exponentially decaying correlation functions (i.e., $\lambda^{-1}=0$); to the right is the microemulsion with correlation functions which oscillate with finite wavelength $\lambda$ and amplitude which decays exponentially. This form identifies the microemulsion in a lattice model such as ours as an incommensurate fluid phase.[19] There is no phase transition between the microemulsion and the ordinary disordered phase; i.e., there are no thermodynamic singularities encountered on crossing the disorder line, only the form of the correlation function changes. Of course at the oil-water-microemulsion triple line, the inverse wavelength drops discontinuously to zero.

Results from mean-field theory applied to the model in three dimensions are similar. A phase diagram is shown in Fig. 2(a) for $\delta x=0$, and for parameters $K/J=0.5$, $L/J=-3.5$, and all others being zero.[20] The main difference between this and the two-dimensional diagram of Fig. 1(a) is that the microemulsion no longer extends to zero temperature between oil-water coexistence and the lamellar phase. The latter is characterized by a dimensionless wave vector $\mathbf{q}=\frac{1}{2}\pi(111)$, and transitions to it from the disordered phase are first order.

Structure functions are easily calculated within the Ornstein-Zernike approximation[21]; that is, the free energy is expanded to second order in the Fourier components of the two order-parameter fields, $P_i^a-P_i^b$ and $P_i^c$, and the quadratic form is diagonalized. In general, structure functions are a *linear combination* of $S_-(q)$ and $S_+(q)$, structure functions of the two modes which diagonalize the free energy. Therefore, they are not of the particularly simple form proposed by Teubner and Strey.[4] For sufficiently negative $L$, $S_-(q)$ increases initially with $q$ and has complex-conjugate poles off the imaginary axis, features which are captured by the

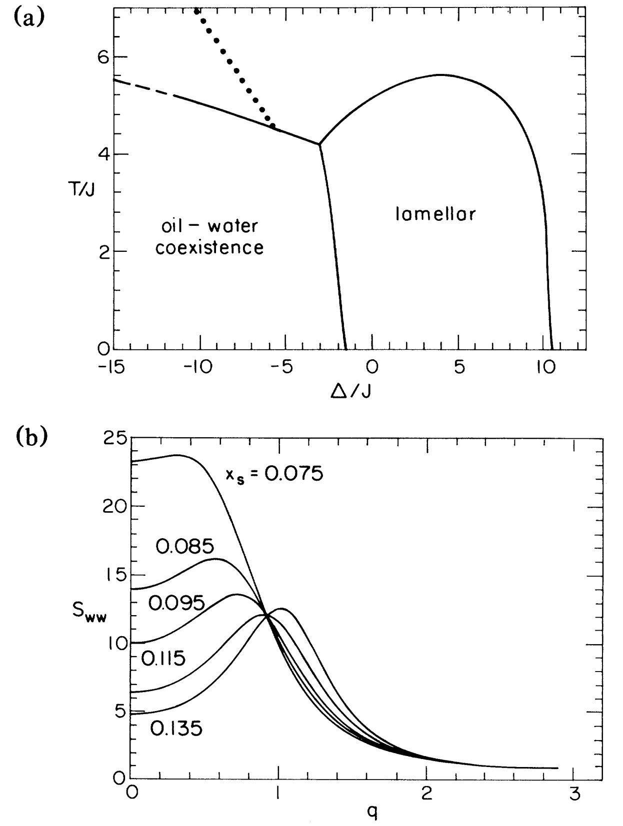

FIG. 2. (a) Phase diagram in three dimensions for $\delta x=0$ and $K/J=0.5$, $L/J=-3.5$, and all others zero, as obtained from mean-field theory. Full and dashed lines indicate first order and continuous transitions. $S_{ww}(q)$ has a peak at $q>0$ for $(T,\Delta)$ to the right of the dotted line. (b) $S_{ww}(q)$ at $T/J=4.45$ for various surfactant concentrations. $\mathbf{q}$ is in the (111) direction.

Teubner-Strey form. The other structure factor, $S_+(q)$, has neither of these features, and would by itself describe a featureless fluid.

Calculated water-water structure factors at $T/J=4.45$ and the parameters of Fig. 2(a) are shown in Fig. 2(b) for surfactant densities between 7.5% and 14%, the span of microemulsion at this temperature.[22] The peak moves out and its amplitude decreases as the surfactant density increases, in agreement with experiment.[1(a),2] With the lattice constant of our model the size of a typical amphiphile, 25 Å, the peaks occur at about 0.02 $\text{Å}^{-1}$, which is a reasonable value. As the lamellar phase is approached, the amplitude increases.

For the same parameters, the surfactant-surfactant structure factor $S_{ss}(q)$ is monotonically decreasing with $q$, again in agreement with experiment.[1(a)] This reflects the fact that the amphiphilic interaction, while inducing correlations between the oil and water, induces no such correlations between amphiphiles. It is the fact that the different experimentally observed structure factors are different linear combinations of the two basic forms $S_+(q)$ and $S_-(q)$ that leads to the striking contrast between the water-water and surfactant-surfactant scattering results.

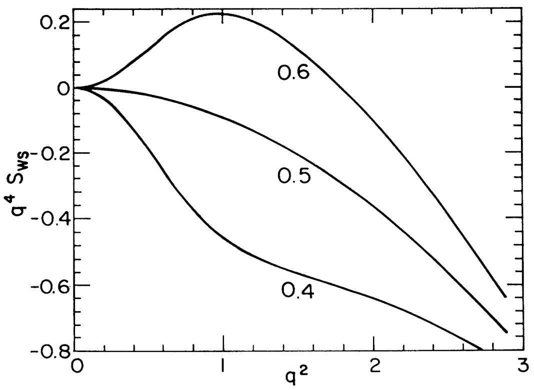

FIG. 3. Scaled water-amphiphile structure factor $q^4 S_{ws}$ vs $q^2$ for three different oil to oil + water ratios. $K/J=0.5$, $L/J=-3.5$, $T/J=4.45$, and $x_s=0.1$.

In Fig. 3 we show the water-amphiphile structure factor, $S_{ws}(q)$, in the microemulsion at the same temperature and $x_s=0.1$. It is presented for three values of the ratio of the volume of oil to the volume of oil and water, and in such a form as to be readily compared with experimentally determined values in Fig. 2 of Ref. 1(b) which it resembles.

The existence of a peak in $S_{ww}(q)$ at a nonzero wave number, $q_{\max}$, is a more experimentally useful (and more restrictive) criterion for the existence of a microemulsion than is a nonzero wave number $\lambda^{-1}$ in the density-density correlation function. The dotted line in the phase diagram of Fig. 2(a) shows the locus $q_{\max}(T,\Delta)\rightarrow 0$ which is given approximately by $x_s(T,\Delta)=-J/4L$. As $x_s \leq 1$, there is no peak at nonzero $q$ unless the amphiphile is sufficiently strong,[23] $|L|/J>1/4$. Note that as the tricritical point is approached along three-phase coexistence, the peak in $S_{ww}(q)$ shifts to zero wave vector. This behavior has, in fact, been observed experimentally.[24] We also find that as the system is driven away from equal fractions of oil and water at a fixed concentration of amphiphile, the peak in $S_{ww}(q)$ grows and occurs at smaller wave number.

Finally, from Monte Carlo simulations of our model in two dimensions we observe in the microemulsion phase that, while almost all amphiphiles are located between an oil and a water molecule, not all oil-water pairs are separated by amphiphiles. Only in the lamellar phase are essentially all oil-water pairs so separated.

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