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Lattice model of microemulsions

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A simple model of oil, water, and amphiphile, in which the third is favored energetically to sit between the other two, is studied in three dimensions via mean-field theory. Oil-rich, water-rich, disordered fluid, and lamellar phases exist. Phase diagrams show the progression from two-phase to three-phase to two-phase coexistence commonly observed in such systems. Three independent structure functions characterizing the disordered fluid are calculated to determine whether it can be identified with a microemulsion. It is found that the region in which this fluid phase exists can be divided into a part in which correlation functions decay monotonically at large distances, and another in which their decay is nonmonotonic. We identify the latter with the microemulsion. There is no phase transition between the two regions. In the microemulsion, the water-water structure function *at low wave number* has the form proposed by Teubner and Strey, with coefficients that we determine. The behavior of the structure functions along different thermodynamic paths, and for systems both balanced and not, is presented. Agreement with experiment is qualitatively good.

I. INTRODUCTION

Systems of oil, water, and amphiphile exhibit many interesting properties which have made them the object of a great deal of study.[1] In the absence of the amphiphile, it is commonplace that oil and water do not mix. What is remarkable is that the addition of only a small amount of amphiphile, typically a few percent by weight, causes oil and water to form one isotropic phase. The smaller the amount needed to solublize the oil and water, the better the amphiphile is said to be.

Although isotropic, the disordered mixture of oil, water, and amphiphile does not appear to be homogeneous. Rather, the fluid is thought to be structured, consisting of coherent regions of oil and of water which are separated by the amphiphile. This picture is reasonable because the construction of the amphiphile is such that its polar head prefers to be surrounded by water, whereas its aliphatic tail prefers the oil. Thus, the molecule tends to create an oil-water interface. The conception is bolstered by scattering experiments[2-6] which often show the fluid to be characterized by a structure function peaked at a nonzero value of a wave vector. The inverse of this wave vector provides a characteristic length in the system which is identified with the size of the coherent oil or water regions. This length is typically of the order of 150 Å or greater, larger than the size of the amphiphile which may be about 25 Å. The idea that the amphiphiles are found predominantly at internal oil-water interfaces combined with the large characteristic distance between interfaces then explains the relatively small amount of amphiphile in the system. What brings about the characteristic length, or to what it can be naturally related, is not clear.

The phase behavior of these systems is also interesting.[7,8] In general, the disordered fluid can coexist simultaneously with oil-rich and water-rich phases. By varying an external parameter, typically the temperature when the amphiphile is nonionic and the concentration of a fourth component, salt, when the amphiphiles are ionic, one can vary the relative proportions of the three phases in coexistence along a triple line until a critical endpoint is reached. There the disordered fluid and water-rich phase become identical at a continuous transition in the presence of the oil-rich phase; the triple line terminates at its other end at another critical endpoint where the roles of oil and water are interchanged. Upon variation of a second external parameter, perhaps the length of the oil molecule or of the amphiphile, the two critical endpoints can be made to coalesce at a tricritical point.[8-10] An increase in the concentration of amphiphile often results in the creation of more ordered arrangements of the amphiphile such as in sheets in the lamellar phase, or rods in the hexagonal phase. When either the oil or water component is predominant, the others are usually found in the form of micelles; small, usually spherical, aggregates of amphiphile surrounding the minority component and thereby separating it from the majority component without.

We shall be most concerned in this paper with the disordered fluid phase. When it can coexist with both oil- and water-rich phases, and when it is characterized by nonmonotonically decaying correlation functions, we shall refer to this phase as a microemulsion. If we have been careful to define a microemulsion by measurable properties, it is because there is not a generally agreed upon definition of the phase. We shall have a few words to say later as to why this should be so.

A third very interesting property of the three-component system is that, at the triple line, the interfacial tension between oil and water can, at times, be decreased by several orders of magnitude below the corresponding value without amphiphile.[11] Just what conditions are required to bring this unusual, and commercially important, property about are not completely clear.[12] Whether this property is characteristic of a microemulsion, or is independent of the defining properties of a microemulstion is an interesting question, one which we shall only touch upon briefly here. It is precisely the relationship between the various interesting properties of three-component systems which poses the most intriguing questions about these systems.

Theoretical approaches to the study of microemulsions have been either phenomenological or microscopic. In the former, it is assumed that the free energy can be written either in the form of a Landau expansion[13] or as a sum of factors thought to be of importance such as an entropy of mixing, a bending energy, etc. This second approach has been very well reviewed recently by Andelman *et al.*[14] In more microscopic approaches, a Hamiltonian describing the system is the starting point, and the free energy follows from standard statistical mechanics manipulations. Several such Hamiltonians have been proposed[15–22] all of which incorporate to some extent the interactions between the amphiphile and the other components. All produce oil-rich and water-rich phases, a uniform fluid phase, and other phases with more structure. The order of the phase transitions between these phases are not the same in all models nor is the identification of the microemulsion the same.[19]

We discuss in this series of two papers a model, introduced[17,18] earlier, which we show to have several satisfying features. It produces a phase diagram in which there exists a triple line ending in critical endpoints. By raising the temperature, the critical endpoints coalesce into a tricritical point. The disordered fluid phase which coexists with oil- and water-rich phases can be brought about by the addition of a few percent of amphiphile. As the amphiphile concentration is increased, a first-order transition to a lamellar phase occurs. This progression, which is in agreement with experiment, also results from the model of Stockfish and Wheeler.[16(c)] We calculate the three independent structure functions of the disordered fluid phase and their dependence on the oil-water ratio and the concentration of surfactant. We find that they are all in qualitative agreement with experiment. On the basis of these scattering functions, we identify the microemulsion with a disordered, isotropic fluid phase, an identification also made by others,[16(b)] but we also show that all such fluid phases in these systems are not microemulsions.[18] We propose either of two possible boundaries to distinguish the microemulsion from the ordinary disordered fluid; either the Lifshitz line[23] at which the peak of the water-water structure function moves off of zero wave vector,[24] or the disorder line[25] at which the asymptotic decay of the water-water correlation function becomes nonmonotonic. There are no singularities in the bulk free energy of the fluid on crossing either of these lines. Thus, the microemulsion is not truly a distinct phase in the thermodynamic sense. It is presumably this reason which accounts for the lack of a uniform definition of a microemulsion. We investigate the properties of our model in three dimensions in this, the first of two papers. In the second,[26] its properties are calculated in one and two dimensions. Many of the conclusions of these papers were first presented in a short work.[18]

The Hamiltonian we employ describes a simple lattice model of a three-component system. On each site of the lattice is a statistical variable P_i^α which is equal to 1 if the ith site of the lattice is occupied by a molecule of species α, and is zero otherwise. The index α takes the values a, b, and c representing water, oil, and amphiphile, respectively. There is always one molecule of some kind on each site of the lattice. The Hamiltonian is

$$\mathcal{H} = -\sum_{\alpha}\sum_{\beta}\sum_{\langle ij\rangle} E^{ij}_{\alpha\beta} P_i^\alpha P_j^\beta - \sum_{\alpha}\mu_\alpha \sum_{i} P_i^\alpha + \mathcal{H}_{\mathrm{AMP}} \cdot \tag{1.1}$$

The first term is simply the sum of all distinct pair interactions between particles, and the second contains the usual chemical potentials. The third term distinguishes molecule c as an amphiphile and mimics its effect in that energy is gained if c sits between a and b all in a line, and is lost if c sits between two a or two b. A simple form of such a term which contains only one new parameter, the strength of the amphiphilic interaction $L<0$, is

$$\mathcal{H}_{\mathrm{AMP}} = -\sum_{(ijk)} L_{ijk}(P_i^a P_j^c P_k^a + P_i^b P_j^c P_k^b - P_i^a P_j^c P_k^b - P_i^b P_j^c P_k^a) \, , \tag{1.2}$$

where

$$L_{ijk} = \begin{cases} L, & i,j,k \text{ three adjacent sites in a line} \, , \\ 0, & \text{otherwise} \, . \end{cases}$$

Such an interaction can be thought of arising from a more fundamental direction-dependent one by averaging over all possible orientations between the amphiphile and oil and water. Because it captures the essential physics of the interactions of isolated amphiphiles, it should be adequate for the discussion of the microemulsion in which their density is very low.

It is convenient to reformulate the three-component mixture in the language of a spin-one magnetic system. To do so, we define the spin variable S_i at the ith site via

$$P_i^a = S_i(1+S_i)/2 \, ,$$
$$P_i^b = -S_i(1-S_i)/2 \, ,$$
$$P_i^c = 1 - S_i^2 \, ,$$

so that $S_i = 1, -1, 0$ corresponds to the presence at site i of a molecule of type a, b, or c, respectively. In terms of the spins, the Hamiltonian of Eq. (1.1) takes the form

$$\mathcal{H} = -\sum_{\langle ij\rangle} [J_{ij}S_iS_j + K_{ij}S_iS_j + C_{ij}(S_iS_j^2 + S_i^2S_j)] - \sum_{i}(HS_i - \Delta S_i^2) - L\sum_{\langle ijk\rangle} S_i(1-S_j^2)S_k \tag{1.3}$$

to within a constant. The first sum is over all pairs, the second over all sites, and the third over all groups of three neighboring sites which are in a line. The interactions in the magnetic model can be related to those of the mixture. In particular, if the pair interactions of the mixture are between nearest neighbors only, then the pair interactions in the magnetic system, J,K,C are given by

$$E_{aa}+E_{bb}-2E_{ab}=4J\ , \tag{1.4a}$$

$$E_{aa}+E_{cc}-2E_{ac}=J+K+2C\ , \tag{1.4b}$$

$$E_{bb}+E_{cc}-2E_{bc}=J+K-2C\ . \tag{1.4c}$$

Furthermore, the magnetic field H is related to the chemical potential difference between oil and water

$$H=\tfrac{1}{2}(\mu_a-\mu_b)+d(E_{ac}-E_{bc})\ ,$$

where d is the dimension of the hypercubic lattice, and Δ is related to the chemical potential of surfactant

$$\Delta=\mu_c-\tfrac{1}{2}(\mu_a+\mu_b)-d(E_{ac}+E_{bc}-2E_{cc})\ .$$

The parameter C will be of particular interest to us later. We note here, that from Eqs. (1.4)

$$4C=2(E_{bc}-E_{ac})-(E_{bb}-E_{aa})\ .$$

From this expression, we see that this parameter expresses the difference between the interaction of the amphiphile with water and with oil. When the surfactant is ionic, adding salt to the water affects just this difference. A positive value of C implies that the amphiphile prefers oil to water.

Without the last term, the Hamiltonians of Eqs. (1.1) and (1.3) are of the form of the Blume-Emery-Griffiths model[27] which describes a simple three-component mixture. For the case of nearest-neighbor interactions, the model has been well studied in two[28] and three dimensions.[29] The last term, representing the interaction of the amphiphile introduces into the system new phases and new behaviors of old phases. We discuss the mean-field theory of our model and the phase diagrams which result in Sec. II, the relevant structure factors in Sec. III, and conclude with a brief summary in Sec. IV.

II. MEAN-FIELD THEORY AND RESULTING PHASE DIAGRAMS

In order to calculate the properties of our model system in three dimensions, we employ the mean-field theory.[30] To do so, we approximate the density matrix w in the exact expression

$$F=\mathrm{Tr}w\mathcal{H}+T\mathrm{Tr}w\ln w$$

by $w_{\rm ss}$, a product of single-site density matrices,

$$w_{\rm ss}=\prod_i w_i\ ,$$

where, in the basis $S_i=1,0,-1$,

$$w_i=\begin{bmatrix}\dfrac{Q_i+M_i}{2} & 0 & 0\\ 0 & 1-Q_i & 0\\ 0 & 0 & \dfrac{Q_i-M_i}{2}\end{bmatrix}\ ,$$

so that

$$\mathrm{Tr}w_{\rm ss}=1\ ,$$

$$\mathrm{Tr}w_{\rm ss}S_i=M_i\ ,$$

$$\mathrm{Tr}w_{\rm ss}S_i^2=Q_i\ .$$

Thus, the exact free energy is approximated by

$$F_{\rm ss}=\mathrm{Tr}w_{\rm ss}\mathcal{H}+T\mathrm{Tr}w_{\rm ss}\ln w_{\rm ss}\ .$$

Using the Hamiltonian of Eqs. (1.1) and (1.2), we obtain

$$\begin{aligned}F_{\rm ss}(\{M\},\{Q\})=&-\sum_{\langle ij\rangle}J_{ij}M_iM_j-\sum_{\langle ij\rangle}K_{ij}Q_iQ_j-\sum_{\langle ij\rangle}C_{ij}(M_iQ_j+Q_iM_j)\\&-\sum_{(ijk)}L_{ijk}M_i(1-Q_j)M_k-H\sum_i M_i+\Delta\sum_i Q_i\\&+T\sum_i\left[\frac{(Q_i+M_i)}{2}\ln\frac{(Q_i+M_i)}{2}+\frac{(Q_i-M_i)}{2}\ln\frac{(Q_i-M_i)}{2}+(1-Q_i)\ln(1-Q_i)\right]\ .\end{aligned} \tag{2.1}$$

This free energy is then minimized with respect to the M_i and Q_i. The values which minimize the free energy, denoted $\overline{M}_i$, and $\overline{Q}_i$, satisfy the self-consistent equations

$$\overline{Q}_i(\{\overline{M}\},\{\overline{Q}\})=\overline{Q}_i\ ,$$

$$\overline{M}_i(\{\overline{M}\},\{\overline{Q}\})=\overline{M}_i\ ,$$

where

$$\overline{Q}_i(\{M\},\{Q\})=\frac{2\cosh(a_i)}{2\cosh(a_i)+\exp(-b_i)}\ , \tag{2.2}$$

$$\overline{M}_i(\{M\},\{Q\})=\frac{2\sinh(a_i)}{2\cosh(a_i)+\exp(-b_i)}\ , \tag{2.3}$$

and

$$\begin{aligned}a_i=T^{-1}\Bigg[&\sum_j J_{ij}M_j+\sum_j C_{ij}Q_j\\&+\sum_{jk}L_{ijk}(1-Q_j)M_k+H\Bigg]\ ,\end{aligned}$$

$$b_i=T^{-1}\left[\sum_j K_{ij}Q_j+\sum_j C_{ij}M_j-\tfrac{1}{2}\sum_{hj}L_{hij}M_hM_j-\Delta\right]\ .$$

The mean-field free energy is

$$F_{\rm MFT}=F_{\rm ss}(\{\overline{M}\},\{\overline{Q}\})\ . \tag{2.4}$$

In what follows, we confine ourselves to nearest-neighbor interactions only,

$$J_{ij}=\begin{cases} J, & i,j \text{ nearest neighbors },\\ 0, & \text{otherwise },\end{cases}$$

and similarly for the other nonzero pair interactions denoted K and C. Also, as noted earlier we take

$$L_{ijk}=\begin{cases} L, & i,j,k \text{ three adjacent sites in a line },\\ 0, & \text{otherwise }.\end{cases}$$

Phase diagrams follow from the mean-field free energy via standard manipulations.[29] At high temperatures, the system exists in a uniform, disordered phase characterized by $\bar{M}_i=M_0(T,\Delta,H)$ and $\bar{Q}_i=Q_0(T,\Delta,H)$ where these values are obtained from the uniform self-consistent solutions of Eqs. (2.2) and (2.3). At lower temperatures, the system separates into uniform water-rich and oil-rich phases. Depending upon the value of Δ, the nature of this transition is either continuous or first order. When it is the former, its temperature can be found by expanding $F_{\text{ss}}(\{M\},\{\bar{Q}\{M\}\})$ in a power series in the set of M_i which are assumed to be equal. Note that the single-site free energy has been minimized with respect to the Q_i, but not with respect to the M_i. For the particularly simple case $C=0$, the transition takes place at $H=0$ and the Landau expansion of the free energy has the form

$$\begin{aligned} N^{-1}F_{\text{ss}}(\{M\},\{\bar{Q}\{M\}\})=3KQ_0^2+T\ln(1-Q_0)&\\ +A_2(T,\Delta)M^2&\\ +A_4(T,\Delta)M^4+\cdots\ ,& \qquad (2.5)\end{aligned}$$

where N is the number of molecules in the system, and $Q_0(T,\Delta)$ satisfies Eq. (2.2) from which

$$\frac{Q_0}{2(1-Q_0)}=\exp(6KQ_0-\Delta)\ . \qquad (2.6)$$

The factor of 6 arises from the number of nearest neighbors in the three-dimensional cubic lattice which we are employing. The coefficient $A_2(T,\Delta)$ is given by

$$A_2=\frac{T-6Q_0[J+(1-Q_0)L]}{2Q_0}\ .$$

Minimization of the free energy is completed by minimizing Eq. (2.5) with respect to M. The result shows that there is a continuous transition from the disordered phase to one characterized by a nonzero value of $\bar{M}$ which occurs at temperature $T_c(\Delta)$ obtained via $A_2(T_c,\Delta)=0$, yielding

$$T_c/J=6(1-\phi_s)(1+\phi_s L/J)\ . \qquad (2.7)$$

The relation $\phi_s=(1-Q_0)$ between the surfactant concentration and Q_0 has been used. The line of continuous transitions terminates at a tricritical point whose location is given by the solution of $A_4(T_c(\Delta_t),\Delta_t)=0$. This condition gives

$$\begin{aligned}12L^2\phi_{s,t}^3+2\phi_{s,t}^2(6J+K-7L)L&\\ +\phi_{s,t}(3J^2-10JL+2KJ+3L^2)-2J^2=0\ ,&\end{aligned}$$

which determines $\phi_{s,t}$, the surfactant concentration at the tricritical point. The tricritical point temperature then follows from Eq. (2.7)

$$T_t/J=6(1-\phi_{s,t})(1+\phi_{s,t}L/J)\ ,$$

and Δ_t from Eq. (2.6)

$$\Delta_t=6K(1-\phi_{s,t})-T_t\ln[(1-\phi_{s,t})/2\phi_{s,t}]\ .$$

For larger values of Δ, the transition between the disordered phase and oil-rich and water-rich phases is first order. Thus, there is three-phase coexistence. The coexistence line can be found by determining that temperature, as a function of Δ, at which the mean-field free energies of the disordered phase (characterized by $\{\bar{M}\}=0$) and water-rich phase (all $\{\bar{M}\}$ equal but nonzero) are equal. (The free energy of the oil-rich phase is identical to that of the water-rich phase at $H=0$ by symmetry.) Similar procedures obtain for the lamellar phase for which the set of $\{\bar{M}\}$ are spatially dependent. Among nonuniform phases, only lamellar ones were sought as they are the most favorable energetically.

The form of the phase diagram is as follows. In general, there are water-rich and oil-rich phases which either disorder continuously, at low surfactant chemical potentials, or via a first-order transition. A tricritical point separates these two behaviors. When the transition is first order, the disordered fluid coexists with the other two phases, of course. Lamellar phases appear at higher surfactant chemical potentials. These features are illustrated in Fig. 1 which shows the phase diagram of the system with $K/J=0.5$, $L/J=-3.5$, and $C/J=0$. The diagram is shown in the temperature, surfactant chemical potential plane at equal concentrations of oil and water. First-order transitions are shown by solid lines, and the

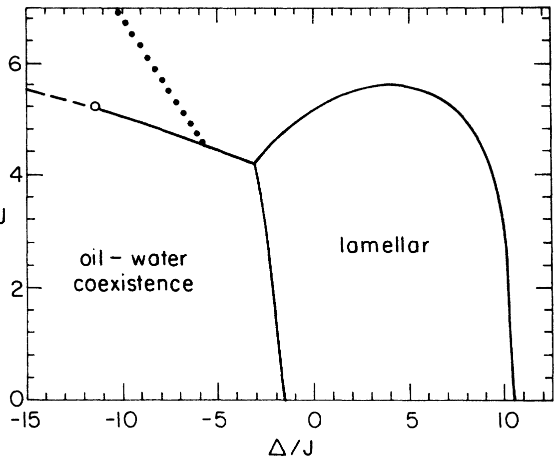

FIG. 1. Phase diagram in the T,Δ plane for a system with $K/J=0.5$, $L/J=-3.5$, $C/J=0$, and equal oil and water concentrations. Solid lines denote first-order transitions and the dashed line denotes a continuous transition. The tricritical point between them is shown with an open circle. The dotted line is not a phase boundary, but is the Lifshitz line, the locus of points at which the peak in the water-water structure function begins to move from zero wave vector. It takes nonzero values to the right of this line.

continuous transition by a dashed line. The dotted line shown can be ignored for the moment.

Because we have used a lattice rather than a continuum model, there is not simply one lamellar phase, but several, with lamella in the (111) or equivalent direction. There are first-order transitions between the phases. For example, as the amount of water is increased relative to that of oil, there is a transition from a $+0-0$ lamellar phase to a $++0-0$ phase. Depending on the parameters in the system, the periods of these phases can be long.[31] In a continuum model such transitions would be absent and there would be only one phase transition in which the relative widths of the water and oil lamella would vary continuously. Transitions from the lamellar phase to the disordered phase can be continuous or first order, depending on the interaction strengths. The simple form of the amphiphilic interaction we have taken in Eq. (1.2) does not lead to the formation of bilayers of amphiphile, hence there are no lamellar phases formed in the two-component limit, water amphiphile, or oil amphiphile. This defect is easily remedied as has been shown elsewhere.[21]

In the next two figures, we show constant temperature sections through the phase diagram of Fig. 1. These figures show the entire range of possible concentrations unlike Fig. 1 in which the oil and water concentrations are constrained to be equal. The temperature of the system is $T/J=4.9$ in Fig. 2. This is sufficiently close to the tricritical temperature, $T_t/J=5.2$, that there exists a continuous path from the water-rich side through the disordered fluid to the oil-rich side at the constant value of the parameter $C/J=0$. A lower temperature, $T/J=4.45$, is shown in Fig. 3. The lamellar phases stretch from a coexistence with the water-rich phase to a coexistence with the oil-rich phase. The disordered fluid which coexists with both of them is now isolated, i.e., there is no longer a continuous path between oil-rich and water-rich phases *at fixed parameter C.*

Interesting behavior is obtained at fixed temperature by varying the parameter C, which expresses the difference between the interaction of the amphiphile with water and with oil. Figure 4 shows the phase diagram of the same system at the same temperature as in Fig. 3 with the one exception that now $C/J=0.3$, so that the amphiphile prefers oil to water. The disordered region adjacent to the triple line has become somewhat smaller, and has moved toward the oil-rich side. On further increasing C/J to 0.5, Fig. 4, we see that the disordered region is now accessible from the oil-rich side. There is no longer three-phase coexistence; the triple line has terminated at a critical end point. Making the changes in C/J of the same magnitude but opposite sign produces the same phase diagrams as those of Figs. 4 and 5, except that the roles of oil and water are interchanged. We see, therefore, that the model produces the sequence of two- to three- to two-phase coexistence as a parameter is varied, like the chemical potential of salt, which is appropriate for ionic amphiphiles. (In order to obtain the behavior appropriate for nonionic amphiphiles, one must extend the model to include the effect of hydrogen bonding between water and amphiphile.[32]) We can also see from Figs. 3–5 that, closely related to this behavior, is the existence of a continuous path from the water-rich region, through the disordered region, to the oil-rich region. In order to traverse this path, the parameter C/J must be varied. This is just the behavior found in systems with ionic amphiphiles in which a continuous path from the oil-rich to water-rich phase exists which can only be traversed if the concentration of salt is varied. (In systems with nonionic surfactants, such a path exists which can be traversed if the temperature is varied.) As the temperature is increased, the length of the triple line from one critical end point to the other decreases and vanishes altogether at the tricritical point. As the temperature is decreased, the region of disordered phase between the triple line and lamellar phase is reduced and disappears; the lamellar phase then coexists with oil- and water-rich phases. This can be seen from Fig. 1.

If a microemulsion exists in our model, it is clear that it must lie within the disordered fluid phase which coexists with water- and oil-rich phases at low concentrations of amphiphile, and with the lamellar phase at higher concentrations. In order to determine whether the identification of this phase with a microemulsion can be made, we turn to the calculation of the structure functions.

III. STRUCTURE FUNCTIONS

In this section we calculate various structure functions in the disordered fluid phase in order to compare them with experiment. To do so, we must calculate the fluctuations of the order-parameter fields M_i and Q_i about their mean-field values $M_0(T,\Delta,H)$, and $Q_0(T,\Delta,H)$. As

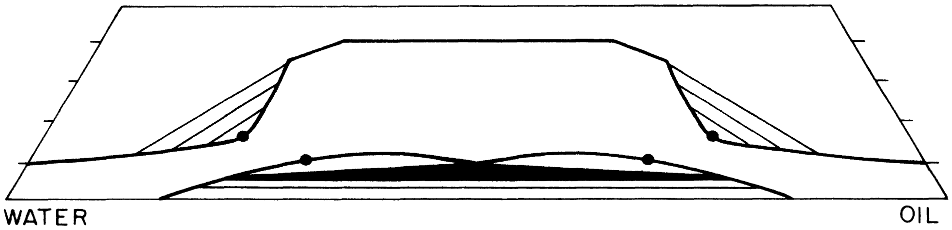

FIG. 2. Portion of the phase diagram at $T/J=4.9$ of the same system as in Fig. 1 showing the limits of stability of the one-phase region. (The tricritical temperature is 5.2.) The three-phase coexistence triangle is shown shaded, and critical points are shown by circles. Some tie lines are indicated for clarity.

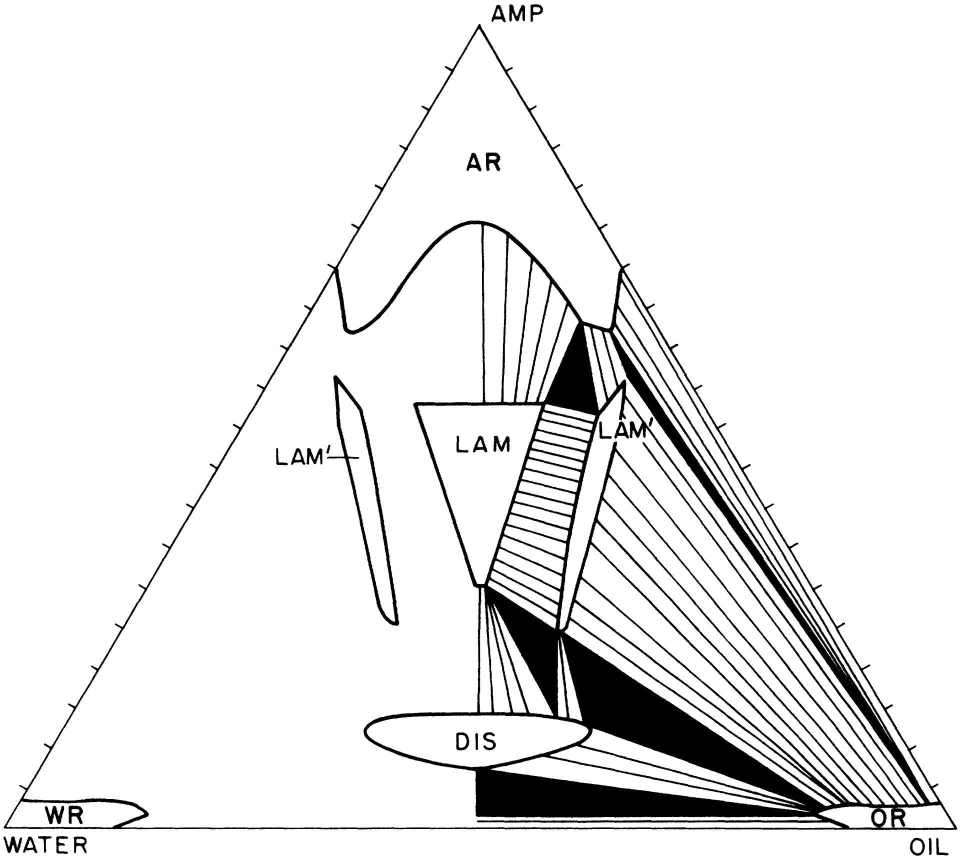

FIG. 3. Full phase diagram at $T/J=4.45$ of the same system shown in Fig. 1. There are seven phases: an oil-rich (OR), a water-rich (WR), and disordered fluid phase (DIS), all at low amphiphile concentration, a symmetric lamellar phase (LAM), two asymmetric lamellar phases (LAM′) which are related to one another by interchange of oil and water, and an amphiphile-rich phase (AR). Three-phase coexistence triangles and tie lines (schematic) are shown on one half of the diagram.

we do not restrict ourselves to equal oil and water composition, M_0 is not generally zero. The deviations from the mean values are Fourier expanded

$$M_i=M_0+\sum_{\mathbf{q}} M_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} ,$$

$$Q_i=Q_0+\sum_{\mathbf{q}} Q_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} ,$$

where it is understood that the $\mathbf{q}=0$ term is not included in the sums. These expansions are substituted into Eq. (2.1) for F_{ss} and the resulting expression is expanded to second order in the small quantities $M_{\mathbf{q}}$ and $Q_{\mathbf{q}}$. Expressed in terms of the difference between the water and oil concentrations $\delta\phi=M_0$ and the sufactant concentration $\phi_s=1-Q_0$, the result is

$$N^{-1}F_{ss}(\{M\},\{Q\})=N^{-1}F_{\mathrm{MFT}}(\{\bar{M}\},\{\bar{Q}\}) + \sum_{\mathbf{q}} [\alpha_{\mathbf{q}} M_{\mathbf{q}} M_{-\mathbf{q}} + \beta_{\mathbf{q}} Q_{\mathbf{q}} Q_{-\mathbf{q}} + \gamma_{\mathbf{q}} (M_{\mathbf{q}} Q_{-\mathbf{q}} + M_{-\mathbf{q}} Q_{\mathbf{q}})] , \tag{3.1}$$

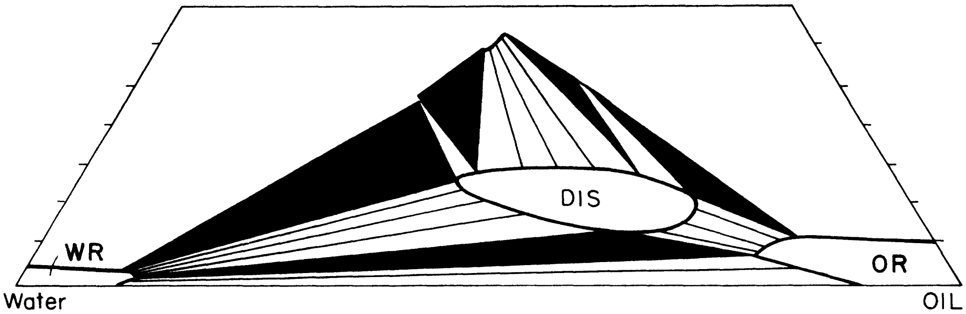

FIG. 4. Portion of the phase diagram at $T/J=4.45$ of the same system as in Fig. 3 except that $C/J=0.3$ instead of zero.

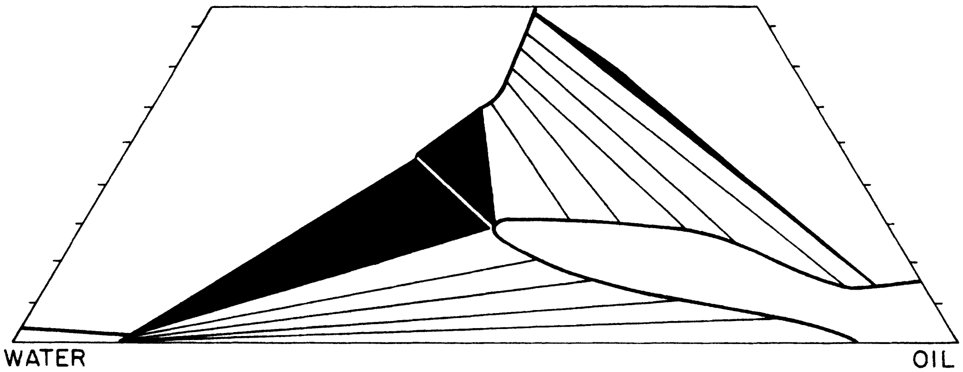

FIG. 5. Portion of the phase diagram at $T/J=4.45$ of the same system as in Fig. 3 except that $C/J=0.5$ instead of zero. The oil-rich (OR) and disordered fluid (DIS) phases of Figs. 3 and 4 have become one.

where

$$\alpha_{\mathbf{q}}=\tfrac{1}{2}T(1-\phi_s)[(1-\phi_s)^2-\delta\phi^2]^{-1} -JD_1(\mathbf{q})-L\phi_s D_2(\mathbf{q})\ , \tag{3.2a}$$

$$\beta_{\mathbf{q}}=\tfrac{1}{2}T\{(1-\phi_s)[(1-\phi_s)^2-\delta\phi^2]^{-1}+\phi_s^{-1}\} -KD_1(\mathbf{q})\ , \tag{3.2b}$$

$$\gamma_{\mathbf{q}}=-\tfrac{1}{2}T\delta\phi[(1-\phi_s)^2-\delta\phi^2]^{-1} -(C-L\delta\phi)D_1(\mathbf{q})\ , \tag{3.2c}$$

and

$$D_n(\mathbf{q})=\cos(nq_x a)+\cos(nq_y a)+\cos(nq_z a)\ . \tag{3.2d}$$

Here a is the lattice constant of our model, a molecular length. The bilinear form of the free energy is diagonalized by the rotation

$$\begin{aligned} M_{\mathbf{q}}&=\cos\theta_{\mathbf{q}}X_{\mathbf{q}}+\sin\theta_{\mathbf{q}}Y_{\mathbf{q}}\ ,\\ Q_{\mathbf{q}}&=-\sin\theta_{\mathbf{q}}X_{\mathbf{q}}+\cos\theta_{\mathbf{q}}Y_{\mathbf{q}}\ ,\\ \sin 2\theta_{\mathbf{q}}&=2\gamma_{\mathbf{q}}/R_{\mathbf{q}}\ ,\\ \cos 2\theta_{\mathbf{q}}&=(\beta_{\mathbf{q}}-\alpha_{\mathbf{q}})/R_{\mathbf{q}}\ ,\\ R_{\mathbf{q}}&=[(\alpha_{\mathbf{q}}-\beta_{\mathbf{q}})^2+4\gamma_{\mathbf{q}}^2]^{1/2}\ . \end{aligned} \tag{3.3}$$

The free energy then takes the form

$$N^{-1}F_{\mathrm{ss}}=N^{-1}F_{\mathrm{MFT}}+\sum_{\mathbf{q}}(A_{\mathbf{q}}^{-}X_{\mathbf{q}}X_{-\mathbf{q}}+A_{\mathbf{q}}^{+}Y_{\mathbf{q}}Y_{-\mathbf{q}})\ ,$$

with

$$A_{\mathbf{q}}^{\pm}=\frac{\alpha_{\mathbf{q}}+\beta_{\mathbf{q}}\pm R_{\mathbf{q}}}{2}\ .$$

From this form, the ensemble average of $X_{\mathbf{q}}X_{-\mathbf{q}}$ and $Y_{\mathbf{q}}Y_{-\mathbf{q}}$ are immediately obtained as

$$\begin{aligned} S^{-}(\mathbf{q})&=\langle X_{\mathbf{q}}X_{-\mathbf{q}}\rangle\\ &=T/2A_{\mathbf{q}}^{-}\ ,\\ S^{+}(\mathbf{q})&=\langle Y_{\mathbf{q}}Y_{-\mathbf{q}}\rangle\\ &=T/2A_{\mathbf{q}}^{+}\ . \end{aligned}$$

These averages are closely related to the experimentally measured structure factors

$$\begin{aligned} S_{\mathrm{WW}}(\mathbf{q})&=\langle n_{\mathbf{q}}^{\mathrm{W}}n_{-\mathbf{q}}^{\mathrm{W}}\rangle\ ,\\ S_{\mathrm{SS}}(\mathbf{q})&=\langle n_{\mathbf{q}}^{\mathrm{S}}n_{-\mathbf{q}}^{\mathrm{S}}\rangle\ ,\\ S_{\mathrm{SW}}(\mathbf{q})&=\langle n_{\mathbf{q}}^{\mathrm{S}}n_{-\mathbf{q}}^{\mathrm{W}}\rangle\ , \end{aligned}$$

where $n_{\mathbf{q}}^{\mathrm{W}}$ is the $\mathbf{q}$th Fourier amplitude of the deviation of the water concentration from its average value, and similarly for the surfactant deviation, $n_{\mathbf{q}}^{\mathrm{S}}$. Because

$$\begin{aligned} n_i^{\mathrm{W}}&=(M_i+Q_i)/2\ ,\\ n_i^{\mathrm{S}}&=(1-Q_i)\ , \end{aligned}$$

ensemble averages of pairs of these quantities can be related to $\langle M_{\mathbf{q}}M_{-\mathbf{q}}\rangle$, $\langle M_{\mathbf{q}}Q_{-\mathbf{q}}\rangle$, and $\langle Q_{\mathbf{q}}Q_{-\mathbf{q}}\rangle$. By the rotation of Eq. (3.3), these are, in turn, related to $\langle X_{\mathbf{q}}X_{-\mathbf{q}}\rangle=S^{-}$, $\langle Y_{\mathbf{q}}Y_{-\mathbf{q}}\rangle=S^{+}$, and $\langle X_{\mathbf{q}}Y_{-\mathbf{q}}\rangle=0$, from which we obtain

$$S_{\mathrm{WW}}(\mathbf{q})=\tfrac{1}{4}[(1-\sin 2\theta_{\mathbf{q}})S^{-}(\mathbf{q}) +(1+\sin 2\theta_{\mathbf{q}})S^{+}(\mathbf{q})]\ , \tag{3.4a}$$

$$S_{\mathrm{SS}}(\mathbf{q})=\tfrac{1}{2}[(1-\cos 2\theta_{\mathbf{q}})S^{-}(\mathbf{q}) +(1+\cos 2\theta_{\mathbf{q}})S^{+}(\mathbf{q})]\ , \tag{3.4b}$$

$$S_{\mathrm{SW}}(\mathbf{q})=-\tfrac{1}{4}[(1-\sin 2\theta_{\mathbf{q}}-\cos 2\theta_{\mathbf{q}})S^{-}(\mathbf{q}) +(1+\sin 2\theta_{\mathbf{q}}+\cos 2\theta_{\mathbf{q}})S^{+}(\mathbf{q})]\ . \tag{3.4c}$$

For the symmetric system $C=0$, prepared at equal oil-water concentrations $\delta\phi=0$, these forms simplify to

$$S_{\mathrm{WW}}(\mathbf{q})=\tfrac{1}{4}[S^{-}(\mathbf{q})+S^{+}(\mathbf{q})],\quad C=\delta\phi=0\ , \tag{3.5a}$$

$$S_{\mathrm{SS}}(\mathbf{q})=S^{+}(\mathbf{q}),\quad C=\delta\phi=0\ . \tag{3.5b}$$

Because of the symmetry between oil and water in this case, the number of independent structure functions is reduced by one with the result that

$$S_{\rm SW}(\mathbf{q})=-\tfrac{1}{2}S_{\rm SS}(\mathbf{q}),\quad C=\delta\phi=0\ . \tag{3.5c}$$

Note that different experimental structure functions are different linear combinations of the two independent functions $S^-(\mathbf{q})$ and $S^+(\mathbf{q})$. That there are two independent functions stems from the two independent density differences in a three-component system. As we now show, the two functions $S^-(\mathbf{q})$ and $S^+(\mathbf{q})$ behave very differently with wave vector. Because the experimental structure functions are different linear combinations of these two functions, their behavior will differ accordingly.

Consider first $S^-(\mathbf{q})=T/2A^-_{\mathbf{q}}$. For simplicity, examine the symmetric system $C=0$. At three-phase coexistence, the disordered fluid has equal concentrations of oil and water, $\delta\phi=0$ (see Figs. 2 and 3). For this reason, it is often denoted "balanced." For this fluid, the functions $\gamma_{\mathbf{q}}$ and $\theta_{\mathbf{q}}$ vanish, so that S^- simplifies to

$$S^-(\mathbf{q})=T/2\alpha_{\mathbf{q}},\quad C=\delta\phi=0\ . \tag{3.6}$$

From the explicit expression for $\alpha_{\mathbf{q}}$, Eq. (3.2a) , we find that $S^-(\mathbf{q})$, in the (111) direction, is given by

$$S^-(1,1,1)=\frac{(T/J)}{(T/J)(1-\phi_s)^{-1}-6\cos(qa/\sqrt{3})+6(|L|/J)\phi_s\cos(2qa/\sqrt{3})}\ . \tag{3.7}$$

For small wave vector, this can be expanded as

$$S^-(1,1,1)=\frac{(T/J)}{a_2+c_1q^2+c_2q^4+O(q^6)}\ , \tag{3.8}$$

with

$$a_2=(T/J)(1-\phi_s)^{-1}-6[1-(\phi_s/4\phi_s^c)]\ ,$$
$$c_1=[1-(\phi_s/\phi_s^c)]\ , \tag{3.9}$$

$$c_2=[4(\phi_s/\phi_s^c)-1]/36\ ,$$
$$\phi_s^c\equiv J/(4|L|)\ . \tag{3.10}$$

This structure function has an extremum when

$$[(\phi_s^c/\phi_s)-\cos(qa/\sqrt{3})]\sin(qa/\sqrt{3})=0\ .$$

There are two possibilities. For weak amphiphilic interactions, $|L|<J/4$, $S^-(q)$ has a maximum at $q=0$ for all ϕ_s. For a strong amphiphile, $|L|>J/4$, the structure function has its maximum at a zero wave vector only for amphiphile concentrations which are less than the value ϕ_s^c. As ϕ_s increases beyond this value, the position of the maximum moves off of the zero wave vector increasing as

$$q^m\propto(\phi_s-\phi_s^c)^{1/2}\ ,$$

more generally,

$$q^ma/\sqrt{3}=\cos^{-1}(\phi_s^c/\phi_s)\ . \tag{3.11}$$

The position of this maximum increases with amphiphile concentration, as is observed for the structure function $S_{\rm WW}(\mathbf{q})$ in experiment.[4,6] [Note from Eq. (3.5a) that the experimental structure function $S_{\rm WW}(\mathbf{q})$ is not equal to S^-, but rather to the sum of S^- and S^+. However, we shall show below that the contribution of this second structure factor is much smaller than the first, so that the behavior of $S_{\rm WW}$ is essentially that of S^-.] The possibility that the structure function could have a peak at a nonzero wave vector was discussed by Stephenson.[24] More recently Teubner and Strey[6] suggested that the water-water structure function should have, for *all q*, just the form of Eq. (3.8) which emerges from our model for *small q*. [Two differences should be noted; terms of $O(q^6)$ and higher were identically set to zero in Ref. 6, and the coefficients a_2, c_1, and c_2 were treated as fitting parameters, rather than derived.] They observed that the peak would move off of the zero wave vector when the coefficient c_1 changed sign. The way in which this happens with increasing surfactant concentration, given in Eq. (3.11), is shown in Fig. 6. Note that the plot of the wave vector of the peak versus amphiphile concentration shows a negative curvature. We also remark that the range of amphiphile concentration shown in the figure may not be accessible; that is, the lowest value of this concentration in the disordered phase may be larger than ϕ_s^c so that the wave vector of the peak is always nonzero.

The condition that $S_{\rm WW}(\mathbf{q})$ have a peak at a nonzero

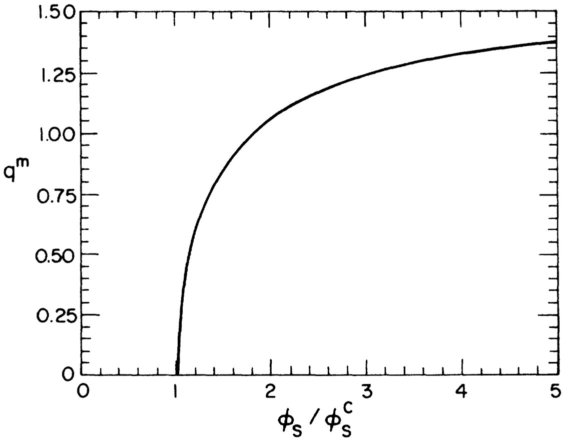

FIG. 6. The wave vector of the peak in the water-water structure function is shown vs the amphiphile concentration. The critical amphiphile concentration, ϕ_s^c is given in Eq. (3.10) of the text. The wave vector is in units of $\sqrt{3}/a$. The curve approaches $\pi/2$ asymptotically.

value of $\mathbf{q}$ provides a convenient defining property of a microemulsion.[18] The line where this first occurs is denoted the Lifshitz line.[23] The peak in S^- first occurs at nonzero values at surfactant densities $\phi_s^c(T,\Delta)$ given by Eq. (3.10); it first occurs in $S_{\rm WW}$ at approximately the same value. In the T,Δ phase diagram of a system with equal oil-water concentrations, the locus of $\phi_s(T,\Delta)=\phi_s^c$ is given by the straight line

$$T=[6K(1-J/4|L|)-\Delta]/\ln[(1-J/4|L|)2|L|/J] ,$$

and is shown dotted in Fig. 1. This is approximately the Lifshitz line. We emphasize that the free energy per unit volume is analytic on this line so that there is no phase transition when this line is crossed. Thus, there is no clear *thermodynamic* distinction between the microemulsion to the right of this line and the ordinary fluid to the left of it. All correlation functions are also analytic on the Lifshitz line. The experimental distinction is in the dependence of the scattering function on the wave number.

An alternate, and perhaps preferable, definition of the microemulsion is by means of the behavior at large distances of the correlation functions, the Fourier transform of the structure functions. This behavior is determined by the limiting form for the small wave vector of $S^-(\mathbf{q})$, which is quite generally the same as in Eq. (3.8). [However, the particular values of the coefficients given by Eq. (3.9) apply only under the condition $C=\delta\phi=0$.] Because of this form, and because $S^-(\mathbf{q})$ contributes to all three measured structure functions in general, it follows that the asymptotic form of all correlation functions at large distances is

$$g(r)\sim r^{-1}\exp(-r/\xi)\sin(2\pi r/d) ,$$

where

$$\begin{aligned} 2\xi^{-2}&=(a_2/c_2)^{1/2}+(c_1/2c_2) ,\\ 2(2\pi/d)^2&=(a_2/c_2)^{1/2}-(c_1/2c_2) . \end{aligned} \tag{3.12}$$

The locus of points at which $d^{-1}(T_{\rm DIS},\Delta_{\rm DIS},H_{\rm DIS})\rightarrow 0$ defines the disorder line.[25] The microemulsion is then defined as that region of the fluid phase in which d^{-1} is nonzero, while the ordinary fluid phase is that region in which d^{-1} is identically zero. This definition has the theoretical advantage that on the disorder line, the correlation functions are generally nonanalytic in their thermodynamic arguments T, Δ, and H.[33] Even so, there are no nonanalyticities in the free energy per unit volume of the fluid on this line. Hence, there is no phase transition between the microemulsion and the ordinary disordered fluid in the classical sense of Ehrenfest.[34] The disadvantage of the criterion is that the correlation function is not measured directly in experiment. A good approximation to the disorder line in the symmetric system $C=0$ at equal oil-water concentrations $\delta\phi=0$ is, from Eq. (3.12), $c_1^2=4a_2c_2$, where these coefficients are given in Eqs. (3.9) (c.f. the approximation to the Lifshitz line, $c_1^2=0$). The disorder line is not shown in Fig. 1, but would appear to the left of the Lifshitz line and would also intersect the triple line of water-rich, oil-rich, and disordered fluid phases.

We now consider the other structure function $S^+(\mathbf{q})$ which, for the symmetric case at equal oil-water concentrations, simplifies to $S^+(\mathbf{q})=T/2\beta_{\mathbf{q}}$. From the explicit expression for $\beta_{\mathbf{q}}$, Eq. (3.2b), we obtain in the (111) direction the expression

$$S^+(1,1,1)=\frac{(T/J)}{(T/J)(1-\phi_s)^{-1}\phi_s^{-1}-6(K/J)\cos(qa/\sqrt{3})} , \tag{3.13}$$

which, for a small wave vector, can be expanded as

$$S^+(1,1,1)=\frac{(T/J)}{\tilde{a}_2+\tilde{c}_1q^2+O(q^4)} , \tag{3.14}$$

with

$$\begin{aligned} \tilde{a}_2&=\frac{(T/J)}{(1-\phi_s)\phi_s}-6(K/J) ,\\ \tilde{c}_1&=(K/J)a^2 . \end{aligned} \tag{3.15}$$

As $\tilde{c}_1$ is positive, S^+ has a maximum at $\mathbf{q}=0$ and decays monotonically with q. From Eqs. (3.5b) and (3.5c), both $S_{\rm SS}$ and $S_{\rm SW}$ should have just this simple behavior. As one moves off of equal oil-water concentrations, the two structure functions are no longer equal. We note at this point that the magnitude of S^+ is much smaller than that of S^- due to the presence of the large term $T/2\phi_s$ in the denominator of the former. Thus, as stated earlier, the behavior of S^- dominates that of the experimentally observable $S_{\rm WW}$.

In the next several figures, we show the three independent structure functions for the system characterized by parameters $T/J=4.45$, $K/J=0.5$, and $L/J=-3.5$. We first consider the balanced system, $C/J=0$, of which the phase diagram was shown in Fig. 3. Figure 7 shows the structure functions at equal concentrations of oil and water, $\delta\phi=0$, for five values of the amphiphile concentration, values which span the region of existence of the disordered phase at this temperature, from the triple line to coexistence with the lamellar phase.[35] The wave vector $\underline{\mathbf{q}}$ is in the (111) direction and its magnitude is in units of $\sqrt{3}/a$, where a is the cell size. The edge of the Brillouin zone is $q=\pi$. As the amphiphile concentrations are all to the right of the dotted line in Fig. 1, the structure factors $S_{\rm WW}$, shown in Fig. 7(a), all exhibit a peak at a nonzero wave number. The magnitude of this peak decreases with increasing amphiphile concentration, while the position of the peak increases. Because our lattice constant must be of a molecular size, it is possible to estimate the absolute values of the peak positions. In particular, if we take the cell size to be $a=30$ Å, then the peak for $\phi_s=0.085$ would occur at a physical $q=3.5\times10^{-2}$ Å^{-1} This is a reasonable value as can be seen by comparison with the experimental results of Ref. 2. The corresponding wavelength, $2\pi/q$ is 181 Å. Thus, we see that our model, while only containing a single length scale of molecular size, produces a water-water structure function which has its peak at a wave vector corresponding to a length much greater than that molecular size.

The surfactant-surfactant and water-surfactant structure functions, shown in Figs. 7(b) and 7(c) are monotonically decreasing in magnitude. As noted earlier, when $C/J=0$ and $\delta\phi=0$, these two functions are related by $S_{SW}=-S_{SS}/2$.

Figure 8 shows the structure functions of the same system, but taken along a different thermodynamic path, one for which all parameters of the system are fixed except for the ratio of oil to oil plus water. (We shall refer to this ratio as the "oil fraction.") The concentration of amphiphile is fixed at 0.12. It can be seen from Fig. 8(a) that the position of the peak in S_{WW} moves toward a *smaller*

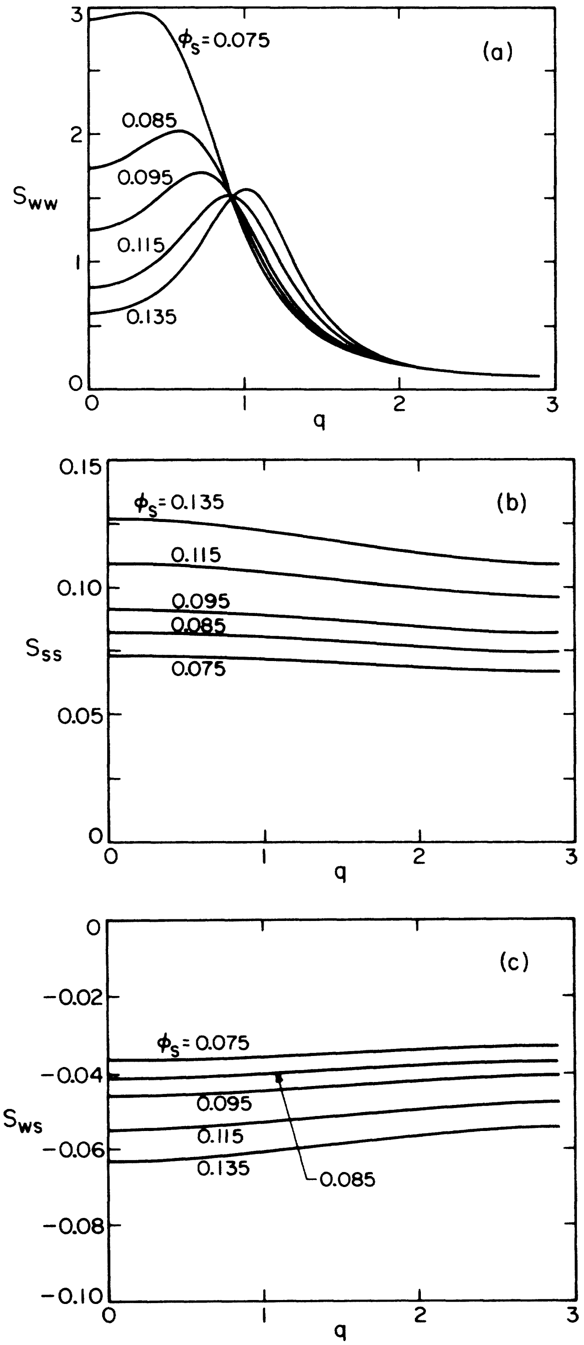

FIG. 7. The water-water, surfactant-surfactant, and water-surfactant structure functions are shown in (a), (b), and (c), respectively, for the system shown in Fig. 3. The wave vector is in units of $\sqrt{3}/a$. The different curves correspond to a thermodynamic path in which the oil fraction is held fixed at 0.5 and the surfactant concentration is varied. Curves are labeled by the surfactant concentration.

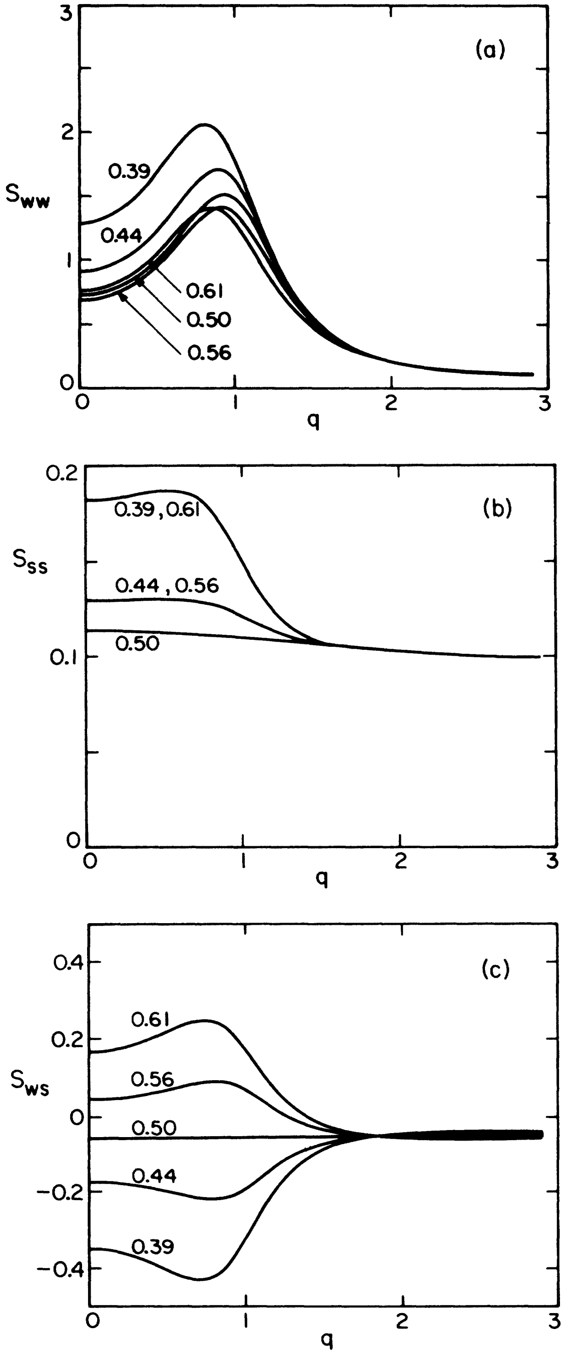

FIG. 8. The water-water, surfactant-surfactant, and water-surfactant structure functions are shown in (a), (b), and (c), respectively, for the system shown in Fig. 3. The wave vector is in units of $\sqrt{3}/a$. The different curves correspond to a thermodynamic path in which the oil fraction is varied, and the surfactant concentration is fixed at 0.12. Curves are labeled by the oil fraction.

wave vector as the oil fraction deviates from 0.5 in either direction. Figures 8(b) and 8(c) show that the other structure functions also show peaks whose positions move toward a smaller wave vector as the oil fraction moves from 0.5. This is not surprising as we have seen that all structure functions are different combinations of the same two basic functions, $S^-(\mathbf{q})$ and $S^+(\mathbf{q})$. It is the former which has a peak at a nonzero wave vector, and the behavior of this peak with varying oil fraction is reflected in all structure functions. We note from Fig. 8(b) that $S_{SS}(\mathbf{q})$ develops a substantial shoulder as the oil ratio deviates from 0.5. This is due to the increasing contribution of $S^-(\mathbf{q})$ to Eq. (3.4b) as the mixing angle θ_q increases with increasing $\delta\phi$, the difference in water and oil concentrations. [See Eqs. (3.2) and (3.3).] Figure 8(c) shows the interesting behavior of $S_{WS}(\mathbf{q})$. It has been argued that $S_{WS}(0)$ is proportional to the average mean curvature of the oil-water internal interfaces.[2] A better indicator would be $S_{WS}(0)-S_{OS}(0)$ which is manifestly zero when the system is symmetric with respect to interchange of oil and water. It follows from the incompressibility of the system as a whole that this difference is equal to $2S_{WS}(0)+S_{SS}(0)$. As the surfactant-surfactant structure function is positive, the water-surfactant structure function must be negative when the average curvature vanishes, taking the value $-0.5S_{SS}(0)$. This *caveat* aside, the general behavior of S_{WS} and the average curvature should be similar, and, as it has been extracted from experimental data,[2,36] it is the quantity we have chosen to present. Huang and Kotlarchyk[36] measured, indirectly, the ratio $S_{WS}(0)/S_{WW}(0)$ in a water-decane-AOT system and obtained a value of approximately 0.2 at the oil fraction of 0.5. From Figs. 8(a) and 8(c) one sees that this ratio of structure functions obtained from our model varies from -0.27 to 0.21 as the oil fraction varies from 0.39 to 0.61. From this, we conclude that the ratios of our structure functions are quite reasonable. Were the results we have obtained for the largest and smallest oil fraction actually experimental data, they would suggest that the system consisted of water-in-oil droplets and oil-in-water droplets, respectively.

The next two figures show the effect of causing the system to be out of balance, in particular by making the amphiphile prefer oil. The system is the same as that of Figs. 7 and 8 except that the value of C/J is no longer zero, but is 0.3. The phase diagram of this system was shown in Fig. 4. The structure functions are shown in Fig. 9 taken along the thermodynamic path characterized by a constant oil fraction equal to 0.645. This path passes through the triple point. A comparison of Figs. 9(a) and 7(a) shows that the differences in S_{WW} are not dramatic. For the same concentration of surfactant, the peaks are higher and closer to the zero wave vector in the unbalanced system. Figure 9(b) shows that the S_{SS} has developed a significant shoulder, the amplitude and location of which both increase with increasing surfactant concentration. The most dramatic difference occurs in S_{WS} which now resembles S_{WW}, although with a considerably smaller amplitude. Along this path, the ratio $S_{WS}(0)/S_{WW}(0)$ varies from 0.15 to 0.24 as the amphiphile density varies from the lowest to highest values. Again this would suggest the interpretation of water-in-oil droplets which become smaller with increasing amphiphile concentration as expected. Figure 10 displays the structure functions along a path in which everything is fixed except for the oil fraction. The surfactant concen-

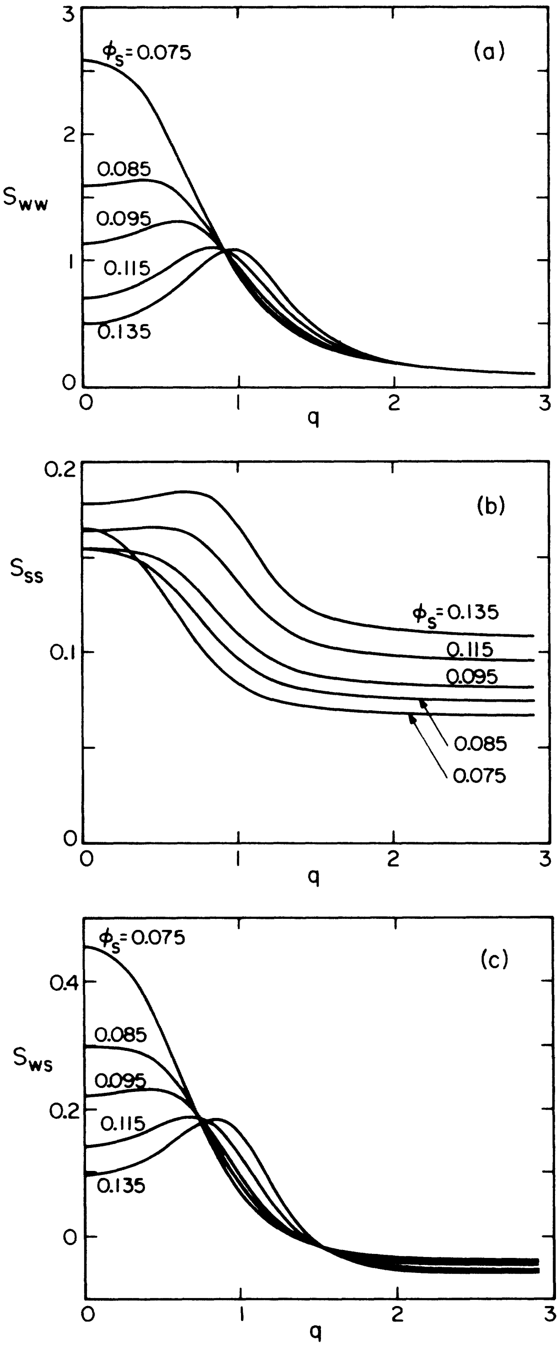

FIG. 9. The water-water, surfactant-surfactant, and water-surfactant structure functions are shown in (a), (b), and (c), respectively, for the system shown in Fig. 4. The wave vector is in units of $\sqrt{3}/a$. The different curves correspond to a thermodynamic path in which the oil fraction is held fixed at 0.645 and the surfactant concentration is varied. Such a path leads to the triple point. Curves are labeled by the surfactant concentration.

tration is again 0.12. All functions show a peak whose position moves toward the zero wave vector as the oil fraction increases. Perhaps the only surprise is that the wave vector of the peak is not the greatest for that oil fraction which corresponds to the triple point 0.645.

Finally, in Fig. 11, we show S_{WW} along a path in which everything is constant except for the value of C/J, i.e., the balance of the system is changing. The surfactant concentration is 0.12 and the oil fraction is 0.61. In such an oil-rich system, one expects and does find that the peak is furthest out in that system in which the amphiphile most favors oil, $C/J=0.3$.

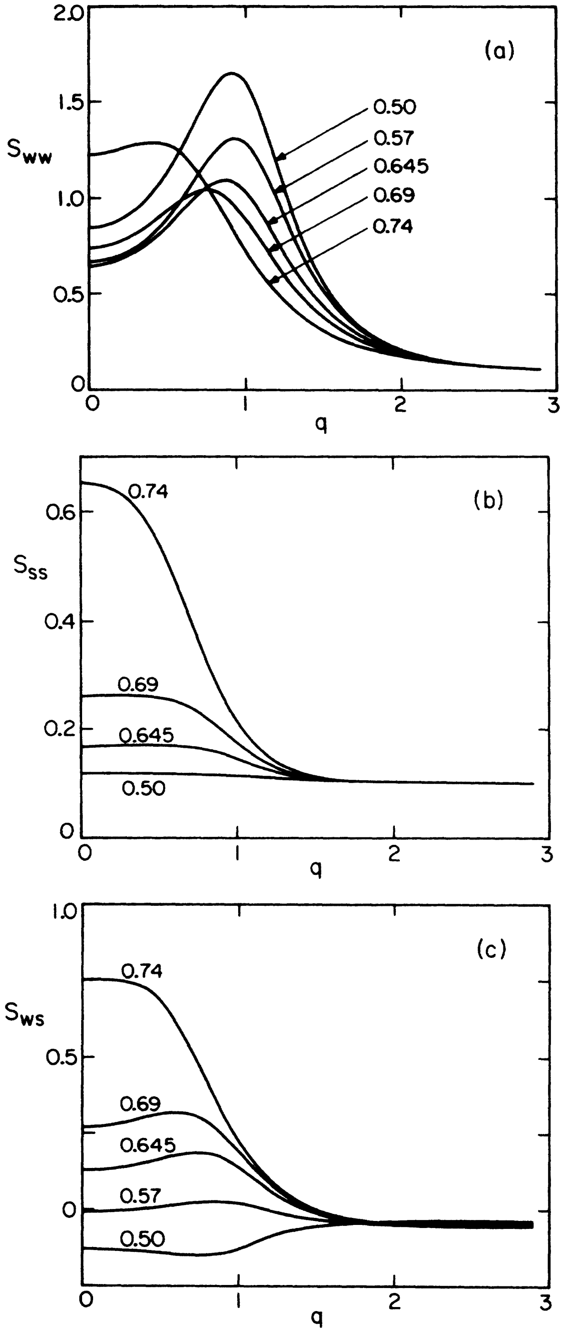

FIG. 10. The water-water, surfactant-surfactant, and water-surfactant structure functions are shown in (a), (b), and (c), respectively, for the system shown in Fig. 4. The wave vector is in units of $\sqrt{3}/a$. The different curves correspond to a thermodynamic path in which the oil fraction is varied, and the surfactant concentration is held fixed at 0.12. Curves are labeled by the oil fraction. In (b), the result for oil fraction 0.57 is not shown as it is almost indistinguishable from that for 0.5.

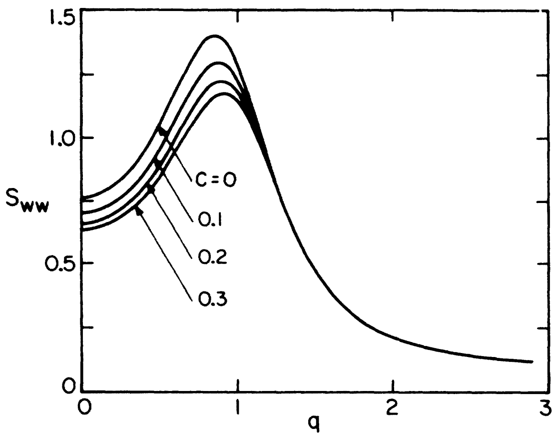

FIG. 11. The water-water structure function for four different systems. The wave vector is in units of $\sqrt{3}/a$. Each is characterized by $T/J=4.45$ and $K/J=0.5$. In each, the oil fraction is 0.61, and the surfactant concentration is 0.12. The systems differ by C/J which label the different curves.

IV. SUMMARY

In this paper we have asked how much of the behavior of a microemulsion can be understood in terms of an extremely simple model; that of a ternary mixture in which one component is favored energetically to sit between the other two. We have studied a model Hamiltonian which differs from the simplest one[27] describing a ternary mixture only by the addition of a term which captures this single property of an amphiphile. We first considered the phase behavior. As regular solution theory of a ternary mixture already exhibits the 2-3-2 sequence of coexisting phases, it is not unexpected that our model does also. Along the triple line, oil-rich and water-rich phases coexist with an isotropic fluid which is a disordered mixture of all three components. To traverse the triple line from one critical end point to the order, C/J, one of the four interactions in the model free energy is varied. If $C/J=0$, a tricritical point can be reached by varying a second interaction, T/J. This phase behavior is the same as that exhibited by microemulsions, and suggests that C/J is a function of the temperature and/or the activity of salt in a physical system. As the strength of the amphiphilic interaction, $|L/J|$, is increased, the amount of amphiphile needed to solubilize oil and water decreases,[37] and lamellar phases appear. Transitions to them can be either first or second order. They are first order in much of the parameter space. The fourth interaction in the model, K/J, is a measure of the interaction between amphiphiles.

In general, the disordered fluid exists as a single phase for surfactant densities between those values which characterize it at three-phase coexistence with oil and water phases and at two-phase coexistence with the lamellar phase. We found, for systems not too near the tricritical point, that there is no continuous path from the oil-rich region, passing through the disordered fluid, to the water-rich region at a fixed value of C/J. However, such a path exists in the larger phase space and can be traversed if C/J is varied. A similar statement can be made for systems with nonionic amphiphiles if "C/J" is replaced by "temperature." Thus, it appears that the model captures not only the broad features of the phase behavior, but also some of the details as well.

To determine whether the disordered fluid could be identified with a microemulsion, we calculated the three independent structure functions which characterize it. In an incompressible ternary mixture, there are two independent order parameters, and therefore, two independent structure functions. We denoted them S^- and S^+. The measured structure functions are different linear combinations of these basis functions, combinations given in Eqs. (3.4). The function S^- dominates the water-water structure function when the system is balanced and when it is measured at an oil fraction of 0.5. The explicit form which we obtained for S^- in this case is given in Eq. (3.7) for a particular direction of the wave vector. (Because of the underlying lattice, calculated structure functions are not rotationally invariant. However, their behavior is qualitatively the same in all directions, as is readily verified.) This function exhibits a peak which can either be at the zero wave vector or nonzero wave vector. A recent study of the water, *n*-decane, AOT system exhibits both of these behaviors.[38] We suggested that the existence of a peak at the nonzero wave vector in the structure function of the disordered fluid could be used to define the microemulsion, although there were theoretical reasons to prefer the existence of a nonmonotonic decay in the water-water correlation function as a defining property. No thermodynamic singularities occur when the line so demarking the microemulsion phase is crossed. The peak position of the water-water structure function moves with amphiphile concentration according to

$$\frac{q^m a}{\sqrt{3}}=\cos^{-1}\left[\frac{J}{4|L|\phi_s}\right]. \tag{4.1}$$

As seen from Fig. 1, the Lifshitz line, at which the peak in $S_{\mathrm{WW}}(\mathbf{q})$ first moves off of the zero wave vector, is crossed as the tricritical point is approached along the triple line. This suggests that if a sequence of systems were prepared which systematically approached the tricritical point (something which could be ascertained from measuring the distance between critical end points), then one would find that the peak position in the disordered fluid at the triple line would decrease systematically. This has, in fact, been observed.[5,39]

The parameters which occur in our model can be extracted from experiment, in principle, as follows. A fit of experimental values of q^m versus ϕ_s to the form of Eq. (4.1) (recalling that only a portion of this curve may be observable), would permit the extraction of the amphiphilic interaction $|L|/J$ for the system, as well as the length a which should be of molecular size.

A fit of experimentally determined values of S_{WW} for a balanced system permits the extraction of T/J as follows. Recall that for a balanced system,

$$\frac{S_{\mathrm{WW}}(q)}{S_{\mathrm{WW}}(0)}\approx\frac{S^-(q)}{S^-(0)}. \tag{4.2}$$

If the right-hand side is expanded for small q, it takes the Teubner-Strey[6] form

$$\frac{S^-(q)}{S^-(0)}\to\frac{1}{1+(c_1/a_2)q^2+(c_2/a_2)q^4} \quad \text{as } q\to 0\,, \tag{4.3}$$

where the coefficients are given in Eq. (3.9). Similarly, the experimental structure function can be parametrized in terms of the location of the peak q^m and the ratio r of the structure function at $q=0$ and $q=q^m$, $r\equiv S_{\mathrm{WW}}(0)/S_{\mathrm{WW}}(q^m)$, as

$$\frac{S_{\mathrm{WW}}(q)}{S_{\mathrm{WW}}(0)}\to\frac{1}{[1-2(1-r)(q/q^m)^2+(1-r)(q/q^m)^4]} \quad \text{as } q\to 0\,. \tag{4.4}$$

Comparing the theoretical and experimental forms for the structure function, Eqs. (4.2) and (4.3) to Eq. (4.4), and using Eq. (3.9), we obtain, *inter alia*,

$$\frac{T}{J}=(1-\phi_s)\left[\frac{9[1-f(q^m a)]}{2}+\frac{60f^2(q^m a)}{[1+4f(q^m a)](1-r)}\right],$$

where

$$f(q^m a)\equiv\frac{(q^m a)^2}{18-4(q^m a)^2}\approx(q^m a)^2/18\,.$$

Because $f(q^m a)$ will be small, the above simplifies to

$$T/J\approx 4.5(1-\phi_s)\,.$$

We do not expect our structure function to provide a good fit to data at large values of q which probes short distances because the lattice nature of the model must be manifest there.

The other independent structure function, $S^+(\mathbf{q})$, dominates the surfactant-surfactant structure function when the system is balanced and when it is measured at an oil fraction of 0.5. The explicit form which we obtained for S^+ in this case is given in Eq. (3.13) for a particular direction of the wave vector. This function exhibits a peak only at the zero wave vector. For a small wave vector, it can be expanded as

$$\frac{S^+(q)}{S^+(0)}\to\frac{1}{1+(\tilde{c}_1/\tilde{a}_2)q^2} \quad \text{as } q\to 0\,,$$

with the coefficients given in Eq. (3.15). If the experimental structure function were fit to this form for small q, then the parameter K/J can be extracted from

$$K/J=\frac{(\tilde{c}_1/\tilde{a}_2)(T/J)(1-\phi_s)^{-1}\phi_s^{-1}}{a^2+6(\tilde{c}_1/\tilde{a}_2)},$$

values of a and (T/J) having been obtained previously.

We found that the structure functions S_{WW}, S_{SS}, and S_{WS} which we calculated show the same qualitative behavior which is observed in experiment, particularly along paths of equal water and oil volume fractions. In addition to the behavior of the peak in S_{WW}, we could also account for the existence of the shoulder which is observed[2] in S_{SS}. There is also qualitative agreement[3,18] in S_{WS}. One interesting result of this simple model is that the wave vector characterizing the peak in S_{WW} in the one-phase region decreases as the oil fraction varies from 0.5 in a balanced system, all other parameters being fixed. We know of little data with which to compare this result. The recent study[38] of water n-decane AOT mixtures does show just this behavior, but there are data for only two different oil fractions. More experimental information on this point would be very interesting.[40]

It seems, then, that much of the phase and scattering behavior of microemulsions can be understood in terms of a very simple microscopic basis. We have not touched upon the low surface tensions that these systems can exhibit. It seems, however, that the basis for this phenomena exists in our model. Consider the oil-water surface tension as the triple line in Fig. 1 is traversed from the tricritical point to the four-phase coexistence with the lamellar phase. At the tricritical point, the surface tension vanishes. Thus as we decrease (T/J), the tension must increase. However, as (T/J) decreases, the stiffness of the order parameter (the coefficient of the square gradient term in a Landau expansion) decreases. In fact, this stiffness is just the coefficient c_1 of Eq. (3.9) and passes through zero just when the peak in the structure function moves from zero. We therefore expect that the surface tension, after an initial increase from zero, will begin to decrease again with decreasing (T/J) reaching a small nonzero value at the four-phase coexistence. This scenario can be investigated within mean-field theory as well as other interesting related phenomena, such as the failure of the microemulsion to wet the oil-water interface.[11,41] We shall report on these issues separately. We have not addressed the question of the topology, or configuration, of the microemulsion. This can be investigated by, *inter alia*, simulation of our model. We report on a few such simulations in two dimensions in the second of these two papers.[26] Lastly, the role of bending rigidity, which plays such a crucial role in phenomenological models,[14] remains to be addressed within our approach. Utilizing the framework we have established here, we intend to address this issue within a microscopic framework.

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