

Microemulsions: A Landau-Ginzburg Theory

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We present a Landau-Ginzburg theory for oil-water-surfactant mixtures with a scalar order parameter ψ for the oil-water subsystem and a vector τ for the surfactant part. A physical interpretation of the parameters in terms of single-membrane energetics is given. A detailed density-functional calculation yields three-phase coexistence between oil-rich, water-rich, and microemulsion phases, and modulated phases including lamellar, columnar, and cubic phases. The computed structure factor for water in the microemulsion phase shows a variety of trends in qualitative accord with experiments.

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Oil-water-surfactant mixtures exhibit¹⁻⁵ a variety of phases and phase equilibria. Surfactant molecules reduce the bare oil-water interfacial tension and hence favor the formation of bulk phases with a large density of microscopic oil-water interfaces. Phase equilibria in such systems can be quite complex;³ here we concentrate on some of the experimentally observed phenomena.

Phenomenological⁶⁻¹⁰ theories have been successful in accounting for some of these phases, their equilibria, and the correlation functions found therein. In this paper we present a simple Landau-Ginzburg theory for oil-water-surfactant mixtures with many appealing features. We discuss the results of a detailed, physically motivated density-wave-theory analysis for the free-energy functional obtained within a one-loop expansion. The phase diagram includes three-phase coexistence between oil-rich, water-rich, and microemulsion phases, and a variety of modulated phases including lamellar, hexago-

nal, and cubic phases. The structure factor of the disordered phase of the model is similar to that found in microemulsions, permitting us to identify this regime with the microemulsion phase, in agreement with the prediction of a lattice model we had developed earlier.¹¹ The dependence of various features of the structure factor on different parameters shows trends similar to experimental systems. We provide a single-membrane interpretation of some of the coupling constants in terms of curvature energies and use this to correlate different structure factors with different microgeometries.

Our Landau-Ginzburg theory is based on two order parameters, ψ and τ : ψ is large and positive (negative) in the water-rich (oil-rich) phase and τ characterizes the surfactant part [$|\tau|$ is large in surfactant-rich regions and $\tau(\mathbf{r})$ points in the direction of the heads of surfactant molecules at \mathbf{r}]. We display the free-energy functional that is oil-water symmetric:¹²

$$\mathcal{F} = \int d\mathbf{r} \left\{ \frac{1}{2} c_1 (\nabla\psi)^2 + \frac{1}{2} c_2 (\nabla^2\psi)^2 + \frac{1}{2} c_3 (\nabla^2\psi)^3 + a_1\psi + \frac{1}{2} a_2\psi^2 + a_4\psi^4 + a_6\psi^6 \right. \\ \left. + \frac{1}{2} r_0 |\tau|^2 + \frac{1}{2} K_1 (\nabla \cdot \tau)^2 + r_2 \psi^2 |\tau|^2 - \tau \cdot \nabla (J_1 \psi + J_2 \nabla^2 \psi) \right\}. \quad (1)$$

The parameter c_1 (> 0) is a measure of the bare oil-water interfacial tension. Since the surfactant molecules can change the sign of c_1 , we include higher-order gradients for stability. a_1 is proportional to the difference between the chemical potentials of water and oil. The parameters r_0 and K_1 characterize the surfactant and are chosen positive so that the surfactant subsystem does not order on its own. The last three terms describe interactions between τ and ψ . r_2 is a measure of the miscibility of the surfactant in water and oil. The last two terms account for the amphiphilicity of the surfactant molecules: $J_1 > 0$ favors surfactant molecules residing at oil-water interfaces. The interpretation of the J_2 term is discussed below; a continuum approximation to a microscopic model would naturally contain such higher-derivative terms. Only terms quadratic in τ are considered because we will not address the ordering of surfactant molecules in the absence of oil and/or water in this paper.

An intuitive interpretation of the terms proportional to c_1 , c_2 , J_1 , and J_2 can be obtained in the language appropriate to interfaces,¹³ allowing us to make connections between our bulk theory and the interface approach developed by others.¹³⁻¹⁵ Assume that the interface thickness is of order l , the length of a surfactant molecule, and that the surfactant molecules are aligned exactly along the local interface normal $\hat{\mathbf{n}}$, i.e., $\tau = \tau_0 \hat{\mathbf{n}}$, with τ_0 the surfactant density at the interface. If $+\psi_0$ ($-\psi_0$) is the bulk value of ψ in water (oil), then the terms proportional to J_1 and c_1 clearly represent surface-tension effects. Using elementary differential geometry one can argue that the c_2 term yields $(2c_2\psi_0^2/l) \times \int ds H^2$ and the J_2 term, $J_2\tau_0\psi_0 \int ds (4H^2 - 2K)$, where H is the local mean curvature, and K the local Gaussian curvature. Thus by tuning c_1 , c_2 , J_1 , and J_2 the effective surface tension and the curvatures of the internal micro-

scopic interfaces that constitute the microemulsion phase can be varied. If the effective surface tension is negligible, then these interfaces are like the membranes envisioned by de Gennes and Taupin⁷ and the term proportional to c_2 incorporates the physics pointed out by them for a single interface: When J_1 reduces the effective coefficient of the $(\nabla\psi)^2$ term to zero, the $c_2\int q^2 n_q^2 ds$ term leads to a logarithmic divergence for the appropriate correlation function.⁷ A term which favors spontaneous curvature can be incorporated easily, e.g., by adding the term $\int d^3r (\nabla^2\psi)\tau \cdot \nabla\psi \propto \int H ds$ to Eq. (1). The sign of this term can be chosen to agree with Bancroft's rule: The best solvent of the amphiphile is "outside."

For nonzero r_2 we have calculated the one-loop correction to the free-energy functional by integrating out the surfactant degrees of freedom. Neglecting the q -dependent corrections to the ψ^4 term we obtain

$$\mathcal{F}_{\text{eff}}^{(2)} = \int \frac{d^3q}{(2\pi)^3} \left[\frac{a_2^{\text{eff}}}{2} + \left(c_1 - \frac{(J_1 - J_2 q^2)^2}{r_0 + K_1 q^2} \right) \frac{q^2}{2} + \frac{c_2 q^4}{2} + \frac{c_3 q^6}{2} \right] \psi(\mathbf{q})\psi(-\mathbf{q}) + \int d^3r \{ a_1 \psi(\mathbf{r}) + [a_4 - 3r_2^2 I_2(0)] \psi^4(\mathbf{r}) + a_6 \psi^6(\mathbf{r}) \}, \quad (2)$$

where

$$a_2^{\text{eff}} = a_2 + \frac{1}{2\pi^2} \left\{ \frac{\Lambda}{K_1} - \frac{\sqrt{r_0}}{K_1^{3/2}} \tan^{-1} \left(\frac{\Lambda \sqrt{K_1}}{\sqrt{r_0}} \right) \right\},$$

Λ is the upper cutoff on the momentum, and

$$I_2(0) = \frac{1}{4\pi^2 K_1^2} \left(\frac{K_1}{r_0} \right)^{1/2} \left[\tan^{-1}(x) - \frac{x}{1+x^2} \right],$$

with $x = \Lambda(K_1/r_0)^{1/2}$. The complete expression including odd terms will be reported elsewhere.

The form of the free energy in Eq. (2) has been used for the calculations reported in this paper. We identify the coefficient of the quadratic term as $\frac{1}{2}[S^{-1}(q)]$ and relabel the coefficient of the ψ^4 term u and that of the ψ^6 term v for convenience. We have investigated the stabilities of disordered and uniform oil-rich and water-rich

phases relative to periodically modulated phases—one-dimensional (lamellar), two-dimensional (hexagonal), and three-dimensional (various cubic)—by using a density-wave theory of freezing.¹⁶

The phase diagram that we have obtained using a density-wave theory (see below) is shown in Fig. 1 (for $u = -0.8$, $v = 1.0$, $r_0 = 0.16$, and $J_1 = 0.39$). There are four phases: microemulsion, oil-rich, water-rich, and lamellar. For small negative values of J_2 and at lower temperatures (or effective a_2) the oil-rich and water-rich phases coexist; as J_2 becomes more negative, leading to a finite- q peak in the structure factor, they give way to the lamellar phase. At higher temperatures, a microemulsion phase is obtained. All phase boundaries are first order which become continuous for positive u with a tricritical point in between. Note the line of three-phase coexistence along which oil, water, and microemulsion phases coexist. The interfacial tensions between these coexisting phases is low for small u , i.e., in the vicinity of a tricritical point. This mechanism for low interfacial tensions is common to many lattice models of microemulsions. The dashed line in Fig. 1 is the disorder line (not a phase boundary). To the left of it, $S(q)$ has a

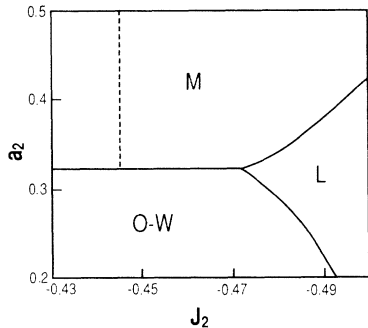


FIG. 1. The phase diagram in the a_2 - J_2 plane. Parameters for this phase diagram are $a_1=0$, $u = -0.8$, $v = 1.0$, $J_1 = 0.39$, $r_0 = K_1 = 0.16$, $c_1 = c_2 = 1$, and $c_3 = \frac{1}{3}$. Microemulsion and lamellar phases are denoted, respectively, by M and L . The region marked $O-W$ shows where the oil-rich and water-rich phases coexist (note $a_1=0$). The solid lines indicate first-order phase boundaries which meet at a triple point. The dashed line denotes the disorder line, to the left of which $S(q)$ has only one peak at $q=0$ and to the right of which there is a peak at nonzero wave vector Q (see Fig. 2). The first-order transitions become continuous via tricritical points if u becomes positive.

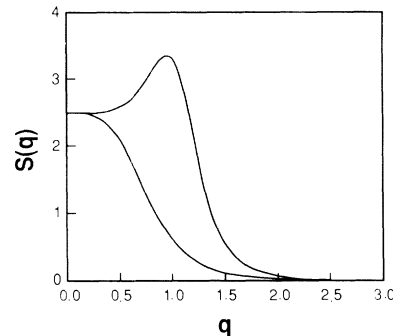


FIG. 2. The structure factor $S(q)$ in the microemulsion phase of Fig. 1. The lower curve ($a_2=0.4$, $J_2 = -0.2$) is obtained in the region to the left of the disorder line of Fig. 1; the upper curve ($a_2=0.4$, $J_2 = -0.492$), to the right of it and close to the microemulsion-lamellar phase boundary whose proximity is signaled by the strong peak.

peak only at zero (see lower curve in Fig. 2); to the right of it, $S(q)$ has a peak at nonzero q with the extremum at $q=0$ either lower or higher than the peak at nonzero q . The upper curve in Fig. 2 shows a structure factor with a prominent peak at nonzero q . While we cannot control the density variables explicitly, it is easy to argue that decreasing r_0 leads to an increase in the surfactant concentration; when r_0 is decreased we find that the lamellar phase is favored, in agreement with experimental trends.⁹

The density-wave-theory calculations were done by retaining the order parameters $\psi_0 = \psi(q=0)$ and $\psi(Q)$,

$$\begin{aligned} \mathcal{F}_{\text{eff}} = & \frac{1}{2} \psi_0 \{S^{-1}(0)\} \psi_0 + \frac{1}{4} N \psi_Q \{S^{-1}(Q)\} \psi_Q + u \psi_0^4 + 3Nu \psi_0^2 \psi_Q^2 + 3u \left[\frac{1}{8} N(2N-1) + n_{\square} \right] \psi_Q^4 + v \psi_0^6 \\ & + \frac{15}{2} N v \psi_0^4 \psi_Q^2 + 45 \left[\frac{1}{8} N(2N-1) + n_{\square} \right] v \psi_0^2 \psi_Q^4 \\ & + \frac{5}{16} v [N + 9N(N-1) + 6N(N-1)(N-2) + 9n_{\Delta} + 144n_{\square} + 72n_{\square}(N-4) + 18n_{\Delta}n_{\square}] \psi_0^6. \end{aligned} \quad (3)$$

In the preceding, N denotes the number of reciprocal-lattice vectors and n_{\square} and n_{Δ} the number of distinct non-coplanar quadrilaterals and triangles that can be formed with the reciprocal-lattice vectors. We have minimized the free energy numerically among the various competing phases. An aside on the calculation: When $S(q)$ has only one maximum at $q=0$, then we use $S(Q) = S(Q^*)$, where Q^* is the value of q at which a maximum appears first as some parameter, say, J_2 , is varied. This simple idea provides a natural way of suppressing modulated phases when there is no peak in $S(q)$ at finite q without introducing any unphysical phase boundaries and without resorting to extensive numerics. We have checked the accessibility of the parameters used by solving numerically the coupled Dyson equations for the self-energy to one-loop order. The details of these calculations will be reported elsewhere.¹²

We have also obtained the phase diagram in the presence of oil-water asymmetric terms.¹² The inclusion of the cubic term, i.e., the $g\psi^3$ term, makes the hexagonal (columnar) and bcc phases stable in different parts of parameter space; thus a variety of phases that occur experimentally are obtained within our density-functional theory.

Experiments on microemulsions yield structure factors with one or two maxima. In our model, neglecting the asymmetry between oil and water, we have $S_{WW} = S_{OO} = -S_{OW}$, where S_{WW} , S_{OO} , and S_{OW} are the water-water, oil-oil, and oil-water partial structure factors, respectively. We now correlate our predictions for S_{WW} from our Landau theory and the microstructures they imply with the experimental data.

Consider first the structure factor $S_{WW}(\mathbf{q})$ in the disordered phase for $J_2=0$ when there is no free-energy cost for configurations with large Gaussian curvature; the structure factor can have only one maximum either at $q=0$ or at $q=Q \neq 0$. The coefficient of the q^2 term in $[S(q)]^{-1}$ can become negative, thus favoring the forma-

tion of a large density of oil-water interfaces. The value of Q , where $S(q)$ has a maximum, depends on c_2 . A peak at $q \neq 0$ in the disordered phase favors the formation of periodically modulated phases as emphasized earlier (see Fig. 2). Thus when the disordered phase coexists with uniform phases (oil and water rich), then $S(q)$ has a peak at $q=0$ and there may or may not be a smaller peak at $q=Q$. The positive definiteness of c_2 implies that the local curvature should be small. Therefore, when the fraction of oil (or water) is small, a mixed droplet phase occurs, whereas for nearly equal amounts of oil and water a bicontinuous phase with low mean curvature is favored.

For $J_2 > 0$, the energetics favor spherical droplets for given values of the mean curvature. In this case, depending on the value of $J_1/\sqrt{r_0}$, one obtains a single peak which can occur away from $q=0$ or two peaks. The width of the peak is approximately half the peak position. This situation is similar to the experiments on sodium di-2-ethylhexylsulfosuccinate (AOT), water, and decane.⁵ We have checked that as r_0 decreases (i.e., as the surfactant concentration increases) the peaks broaden and move outward, reflecting the experimental trend (the increase in a_2^{eff} when r_0 decreases due to one-loop effects is important for this¹⁷).

In the case $J_2 < 0$ we can also arrange to have two peaks in the structure factor in the microemulsion phase, one at $q=0$ and the other at $q=Q \neq 0$. (This is the case for parts of the phase diagram shown in Fig. 1.) The width of the peak at Q is of the same order as Q itself and is relatively insensitive to the parameter values. The peaks in this case are slightly narrower than in the case when $J_2=0$. Our conclusion that two peaks in the structure factor occur when the Gaussian curvature is large and negative is consistent with previous results.¹⁸ Assuming a cutoff Λ of the order of $2\pi/l$, where l is the surfactant length, we find that the peak occurs at length

scales that correspond to 15–20 times longer than l . For moderate values of J_2 , as r_0 is decreased (or as the surfactant concentration is increased), the second peak moves outward and becomes sharper.⁴ Large and negative values of J_2 favor configurations with internal interfaces that have large negative Gaussian curvature and low mean curvature (since $c_2 > 0$) leading to a phase where the interface has many handles. This phase would correspond to the “plumber’s-nightmare” phase,^{15,19} without long-range order. This can undergo a transition into an ordered structure: We have checked by explicit computation in the presence of oil-water asymmetric terms that, as the value of J_2 is tuned from negative to positive, the morphology evolves from a cubic phase (to be associated with a plumber’s-nightmare phase with long-range bcc order), through a first-order transition into a tense bicontinuous structure (or a random, isotropic microemulsion phase depending on the parameters), and eventually into a cubic structure that can be associated with a droplet crystal. Such a scenario is present in a schematic phase diagram of Ref. 15. Note that the inclusion of Gaussian curvature which allows effectively for the formation of passages and fusion of membranes is crucial.

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