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Middle-Phase Microemulsions and Random Surfaces

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I. Introduction

A characteristic feature of microemulsions, as opposed to simple liquid mixtures, is that the oil and water remain separated by surfactant monolayers with coherent domains, typically tens or hundreds of Angstroms in size [1]. The configuration of these domains varies with composition. For small fractions of oil in water or water in oil, the structure is that of globules [2] whose colloidal properties are well understood [3]. On the other hand, when the volume fractions of oil and water are comparable and the surfactant concentration is low, one expects random, bicontinuous [4] structures to form. The theoretical characterization of these structures and the predicted phase diagrams are a topic of current interest.

A common aspect of the phase diagrams of random microemulsions at low surfactant concentration ($\lesssim 5\%$), is the presence of two- and three-phase regions [1, 5]. In the two-phase region, there is a coexistence between an almost pure phase (small amounts of either surfactant in oil or surfactant in water) and a microemulsion (lower- or upper-phase, respectively). In the three-phase region, a middle-phase microemulsion coexists simultaneously with almost pure water and almost pure oil. At higher surfactant concentrations, there is typically a first-order transition from the isotropic, disordered, microemulsion to an ordered, lamellar phase (or to other ordered phases).

DE GENNES and TAUPIN [6] were the first to suggest that at low surfactant concentration a random microemulsion phase may be favored over the ordered, lamellar phase. This is because (i) the random microemulsion has a greater entropy of mixing - first considered by TALMON and PRAGER [7], and (ii) the bending of the surfactant layer forced by the randomness of the oil and water domains occurs at the persistence length of the surfactant monolayer defined by

$$\xi_K = a\, e^{4\pi K/\alpha T}. \tag{1.1}$$

Here K is the bending constant which parameterizes the "splay energy" of a surfactant monolayer, a is a molecular length, T is the temperature, and α is a numerical constant which depends on the details of the calculation. (De Gennes and Taupin set $\alpha=2$, but below we will find it convenient to use a different value.) However, this model did not predict three-phase equilibria, which is characteristic of these systems [8].

In Refs. [9] and [10] we proposed a simple model which took into account the thermal undulations of the fluctuating surfactant interface [6]. The calculated phase diagrams did show both two-and three- phase equilibria in qualitative agreement with experiment [5]. An alternate model, which also results in two- and three- phase equilibria was previously proposed by WIDOM [11] for compressible surfactant interfaces in microemulsions. In our model, the free energy of the microemulsion consists of the entropy of mixing of water and oil domains, and the bending energy of the surfactant film, which is assumed to be an incompressible

$$E_c = 8 \pi K(\xi) \left(1 - \xi / \rho_0 \right)^2 ,$$

where ρ_0 is twice the spontaneous radius of curvature and is defined to be positive for curvature towards the water and negative for curvature towards the oil. In our model the probability of having a bend is related to the probability of having an edge. However, we take the radius of curvature to be comparable to ξ, rather than presuming the interface to have a sharp edge. Thus, the total energy of curvature per unit volume is given by

$$f_c = \frac{8\pi K(\xi)}{\xi^3} \phi(1-\phi) \left[1 - 2\xi (1-2\phi)/\rho_0 \right] + \ldots . \qquad (2.4)$$

We have explicitly incorporated into our model the renormalization of the bending constant by thermal fluctuations, since $K(\xi)$ is a function of the lattice size, ξ. In our calculation of the phase diagram (see Refs. [9] and [10] for details), we use the expression first derived by HELFRICH [14] and later by perturbation theory [15]

$$K(\xi) \equiv K_0 \left[1 - \tau \log(\xi/a) \right] + \ldots , \qquad (2.5)$$

where $K_0 \equiv K(a)$ is the bare bending constant, a is the molecular size, and $\tau = \alpha T/(4\pi K_0)$. The downward renormalization of K indicates that it becomes relatively easy to bend a sheet of size $\xi \gtrsim \xi_K$, since such a sheet is already spontaneously wrinkled by thermal fluctuations. The result presented in Eq.(2.5) is correct for small values of ξ; the extension to larger values of ξ is discussed in Sec. III.

B. Phase Behavior and Transition to Lamellar Structure

The phase diagram for the case of zero spontaneous curvature ($\rho_0 \to \infty$) is shown in Fig. 1. It exhibits a one-phase region (the random microemulsion) and three polyphasic regions at low surfactant concentration: two two-phase regions where a microemulsion phase is in equilibrium with a very dilute phase of surfactant in either water or oil, and a three-phase region where a middle-phase microemulsion is in equilibrium with both dilute phases. The length scale ξ in the middle phase is proportional to ξ_K. Moreover, along the two-phase coexistence curve, ξ remains on the order of ξ_K even far from the middle phase. The concentration of surfactant in the middle phase scales as $1/\xi_K \sim \exp(-\tau)$; the phase diagram is a strong function of the persistence length and hence of the bare curvature modulus, K_0.

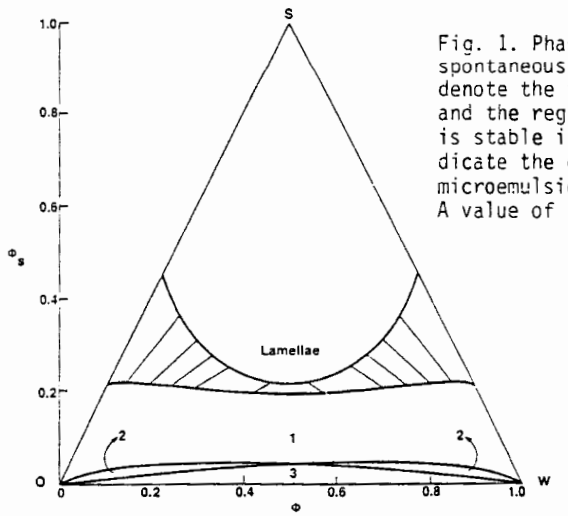

Fig. 1. Phase diagram for the case of no spontaneous curvature ($\rho_0 \to \infty$). The numbers denote the number of coexisting phases and the region where the lamellar phase is stable is indicated. The tie-lines indicate the coexistence of a disordered microemulsion phase with a lamellar phase. A value of $\tau = 0.2$ was chosen.

monolayer [2, 12, 13]. The effects of thermal fluctuations on length scales smaller than the domain size ξ are accounted for by calculating the curvature energy with a size-dependent bending constant, $K(\xi)$ [14, 15]. Our simple model leads to a phase diagram with both two- and three-phase regions; the "middle-phase" microemulsion, which coexists with both nearly pure oil and water, is characterized by a length scale $\xi \sim \xi_K$ and by a surfactant concentration, $\phi_s \sim 1/\xi_K$. At higher values of the surfactant concentration, the bending constant assumes its bare value; the random microemulsion is then unstable to an ordered lamellar phase due to the high energy cost of bending the surfactant monolayer in a random manner.

In this paper, we review our model and its major results, with an emphasis on the role of the renormalized bending constant, $K(\xi)$. We analyze the role of thermal fluctuations in the renormalization of the bending constant for a one-dimensional model at length scales $\xi < \xi_K$ as well as $\xi > \xi_K$. The analysis suggests that at large length scales, $\xi > \xi_K$, the free energy cost of a bend saturates at a value of order T. Finally, we discuss the connection between our microemulsion model and the general problem of the random surface.

II. Microemulsion Model

A. Free Energy of a Random Microemulsion

We consider microemulsions to be ternary mixtures of oil, water and surfactant. Space is divided into cubes of size ξ filled either with water or oil. The surfactant is constrained to stay at the water-oil interface; we divide it equally between the oil and water domains. Using the random mixing approximation, the probability ϕ for a cube to contain water is

$$\phi = \phi_w + \phi_s/2 ,$$

where ϕ_w and ϕ_s are respectively the volume fractions of water and surfactant. The probability for a cube to contain oil is $1-\phi$. The constraint for the surfactant to fill the water-oil interface allows us to relate the volume fractions of the components and the domain size ξ within the random mixing approximation:

$$\phi_s \Sigma_0 = z v_s \frac{\phi(1-\phi)}{\xi} , \tag{2.1}$$

where z=6 is the coordination number of the cubic lattice; v_s is the molecular volume of the surfactant and Σ_0 is the surface area per surfactant molecule, which is fixed in our model. Within this approximation relation (2.1) gives the domain size ξ at each point of the phase diagram (for fixed ϕ, ϕ_s)

$$\frac{\xi}{a} = z \frac{\phi(1-\phi)}{\phi_s} , \tag{2.2}$$

where, for convenience, $a=v_s/\Sigma_0$ is chosen to be equal to the lower cutoff in Eq. (1.1).

Since the area per surfactant is kept fixed, the free energy per unit volume, f, has only two terms: the entropy of mixing of the water and oil domains, f_s, and the energy of curvature of the interface, f_c. The first term is calculated using the random mixing approximation

$$f_s = \frac{T}{\xi^3} [\phi \log(\phi) + (1-\phi)\log(1-\phi)] . \tag{2.3}$$

The second term f_c is calculated as follows. First we associate the bending energy E_c of a cube of water (oil) of size ξ surrounded by oil (water) with that of a sphere of diameter ξ

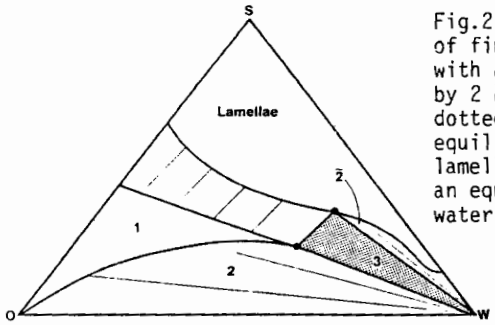

Fig.2 Schematic phase diagram for the case of finite spontaneous curvature ($\rho_0=\xi_K/5$), with a value of $\tau=0.15$. The region denoted by 2 has been calculated in Ref. [10]. The dotted three-phase region consists of an equilibrium between the microemulsion, lamellar and water phases, while $\bar{2}$ indicates an equilibrium between a lamellar phase and water.

For finite spontaneous curvature (e.g. $\rho_0>0$ favoring bending towards the water), there is an asymmetry in the extent of the two two-phase regions. For small enough values of ρ_0/ξ_K, the three-phase region disappears, as shown schematically in Fig. 2 where $\rho_0=\xi_K/5$. In that case, the length scale ξ along the two-phase coexistence curve bounding region 2, scales not with the persistence length ξ_K, but with the spontaneous radius of curvature, ρ_0; for small values of ϕ and ϕ_s, phase separation occurs when $\xi\sim\rho_0$. This is an indication of the emulsification failure instability which precludes the formation of globules with a size larger than ρ_0 [3]. At large values of ϕ and ϕ_s, a single phase of droplets is unstable to coexistence with a lamellar phase.

Returning the case of the symmetric microemulsion ($\rho_0\to\infty$), we note that the renormalization of the bending constant to values on the order of T, allows the energy cost of the random systems to be compensated by the entropy gain from the random mixing of the water and oil regions. However, at large values of ϕ_s, the length scale ξ decreases [see Eq. (2.2)], and $K(\xi)$ approaches its bare value K_0. The energy cost of the curved interfaces in the random microemulsion is no longer compensated by the entropy of mixing. Instead, the lamellar phase dominates, as shown in Fig. 1.

III. Renormalization of Bending Constant and Random Surfaces

Since the size dependence of the bending constant plays a crucial role in our model of microemulsions, it is important to go beyond the first-order perturbation formula for $K(\xi)$ [Eq. (2.5)], which is used to calculate the free energy cost of the bends imposed by the random mixing of the oil and water regions [Eq. (2.4)]. This free-energy cost, ΔF, can be easily calculated for a one-dimensional, semi-flexible (worm-like [16]) rod of length L. Here we sketch a calculation of $\Delta F(L)$ in a model which includes the bending energy and do not make any a priori assumptions about the persistence length. The details of this calculation will be presented elswhere.

The free energy ΔF, is calculated by taking the difference of the free energies of a chain constrained to bend and one which is free. The bending constraint is expressed as

$$< \vec{t}_1 > = \vec{\beta} < | \vec{R}_0 | > / L , \tag{3.1}$$

where $\vec{t}_1$ is the n=1 Fourier mode of the tangent vector $\vec{t}(s)$. The coordinate s is measured along the arclength of the chain.

$$\vec{t}(s) = \vec{R}_0/L + \sum_{m=1}^{N} \vec{t}_m \cos(m\pi s/L) \tag{3.2}$$

with N=L/a. In (3.1) $\vec{\beta}$ is a constant vector which determines the angle and direction of the bend, $\vec{R}_0$ is the end-to-end vector of the chain, and <...> represents a statistical average with the weight function $P[\vec{t}(s)]$, to be determined below. This choice for $\vec{t}_1$ ensures that the spatial displacement of the bend is of the same order as the mean end-to-end distance $< |\vec{R}_0| >$; the bend is visible on scales of order $< |\vec{R}_0| >$.

The free energy F is calculated variationally; F is minimized with respect to the statistical weight, $P[\vec{t}(s)]$ where,

$$F = T < \log P > + < H_b > . \tag{3.3}$$

Here, the first term is the entropy and $H_b = (\kappa_0/2) \int ds \, (d\vec{t}/ds)^2$, is the bending energy, where κ_0 has the units of energy × length. The incompressibility of the chain, which forces $\vec{t}^2(s)=1$, is approximated as a global constraint, which is imposed by a Lagrange multiplier conjugate to $\tau = \int ds \, \vec{t}^2(s)$. With these constraints, we determine $P[\vec{t}(s)]$ from $\delta G/\delta P=0$, where

$$G = F - \mu < \tau > - \bar{\mu} < \vec{t}_1 > . \tag{3.4}$$

The Lagrange multiplier $\bar{\mu}$ is chosen so that (3.1) is satified. The parameterization of the chain by its arclength allows the calculation of ΔF in both the stiff (R_0~L) and floppy ($R_0 \sim L^{1/2}$) limits for chains without self-avoidance. Excluded volume effects can be included at the end of the calculation by a Flory argument.

The variational calculation yields an end-to-end distance, $R_0 = (\lambda/2z)^{1/2} L$. The Lagrange multiplier $z \equiv \mu L\lambda/2T$ with $\lambda = (4LT/\pi^2\kappa_0)$ is determined by the incompressibility constraint

$$\sum_{m=1}^{N} \frac{1}{m^2 + z} = \frac{4}{3\lambda} \left(1 - (1+\beta^2/2) \frac{R_0^2}{L^2} \right) . \tag{3.5}$$

For small values of λ, R_0~L, and the chain is stiff. The free energy per unit length due to bending,

$$\Delta F(L)/L \approx \beta^2 (\pi^2/4) \kappa(L)/L^2 ,$$

where the effective bending constant is

$$\kappa(L) \approx \kappa_0 (1 - \gamma (TL/\kappa_0) + \ldots)$$

for $\beta<<1$, where γ is a numerical constant of order unity. The bending constant is renormalized by L and not log(L), due to the stronger effect of the one-dimensional fluctuations. As the length scale increases, $\kappa(L)$ decreases. In the limit $\lambda \to \infty$, the chain is floppy, leading to $R_0 \sim L^{1/2}$ in the absence of excluded volume, and

$$\Delta F/L \approx T \beta^2 (1 - \bar{\gamma} \beta^2 (\kappa_0/TL))/2L ,$$

where $\bar{\gamma}$ is a numerical constant. The free energy is higher for the bent chain; the change in free energy due to bending is on the order of kT per bend. An examination of the higher order terms in $\Delta F/L$ shows that they are positive and proportional to κ_0^2/L^3.

A similar treatment of the two-dimensional interface (a surface) in a three-dimensional system can be carried out. An estimate of ΔF for the surface can be made by assuming that only the phase space in the Fourier decomposition [Eq. (3.4)] changes in going from the chain to the surface (this also implies that for the surface, where the bending constant K_0 has the units of energy, the parameter λ in (3.5) is proportional to T/K_0, independent of L). One predicts that for small values of L, the free energy per unit area due to the bend,

$$\Delta F/L^2 \approx K(L)/L^2,$$

with

$$K(L) \approx K_0 \, (1 - \tilde{\gamma} \, (T/K_0) \log(L/a) + \ldots) \, ,$$

where $\tilde{\gamma}$ is a numerical constant. This is in agreement with the functional form predicted by the perturbation theories [14, 15]. For large values of $L \gg \xi_K$, the free energy per unit area,

$$\Delta F/L^2 \approx T\beta^2/L^2 + \ldots \, ,$$

again representing the loss of entropy of one degree of freedom per surface.

While the small L limit of the stiff interface relates to recent treatments of membranes, the large L limit of the floppy interface may be relevant to the random surface discussed by Kantor et al. [17]. When L is much larger than the relevant persistence length, a large number of microscopic models may converge in a single universality class. The surface then executés the equivalent of the random walk of a polymer chain. Ref. [17] suggests that excluded volume interactions are extremely crucial in this regime; they change the expected radius of gyration from a weak logarithmic dependence on L to a power law.

The application of the statistics of a random surface to the microemulsion problem requires some care. In our microemulsion model, the length scale of the water/oil domains never grows larger than the persistence length ξ_K, because the entropy of mixing favors small ξ. If ξ is increased beyond $\sim\xi_K$, the system phase separates, since the microemulsion with $\xi \sim \xi_K$ is a local minimum (for fixed ϕ) of the free energy. Thus, for length scales $\xi \lesssim \xi_K$, one may use calculations of the effective free energy of bending such as those discussed above, as inputs to microemulsion thermodynamics. However, for length scales larger than ξ, the random walk of the surfactant interface as well as its excluded volume interaction are taken into account by the lattice construction. The random microemulsion is a random surface that is different from that considered in the previous discussion or by Ref. [17] in that (i) it has a sideness with respect to the oil/water and (ii) it is not one continuous surface; in random mixing, the characteristic surface size is of order ξ (iii) the coordination number is not fixed as in the tethered surface; coordination defects can lead to additional fluctuations which may increase the size of the surface even in the absence of excluded volume effects [18]. The random microemulsion is perhaps more analogous to the problem of equilibrium, branched polymerization. Nonetheless, the physics of the random surface and the analogy to the worm-like chain play an important role in our understanding of the free energy and the renormalization of the bending constant of microemulsions.

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