

Random Surface Model for the L_3 -Phase of Dilute Surfactant Solutions.

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Abstract. – We present a simple model for the anomalous (flow-birefringent) isotropic phase, known as L_3 , that is seen in certain surfactant solutions at volume fractions of a few percent. The proposed structure consists of locally sheetlike sections of semi-flexible surfactant bilayer, connected up at larger distances into a multiply connected random surface, having a preferred structural length scale of order the persistence length of the bilayer. A first-order transition between this isotropic sheetlike phase and the nearby swollen lamellar phase is described.

In certain dilute surfactant systems, such as the nonionic surfactant $C_{12}E_5$ in aqueous solution, an unusual isotropic phase (L_3) is found in a small region of the phase diagram at surfactant volume fractions of a few percent [1-6]. Similar phases of surfactants in oil are also seen [7-11]; in what follows, for definiteness, we suppose oil to be the solvent. The L_3 -phase is strongly flow-birefringent, and has a large structural length scale, of order hundreds of Angstroms [3-5, 7-11]. These data rule out a phase of small spherical micelles, which is what one might normally expect for an isotropic phase at such compositions. The

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presence of the L_3 -phase is associated with strong stability of the nearby lamellar phase under dilution; there is usually a weak first-order transition between these two phases [6, 7, 10]. The lamellar phase consists of widely spaced surfactant bilayers in an ordered array; these undulate thermally, providing a swelling pressure that favors uptake of oil. In these «unbound» lamellar systems, the coexistence that is finally reached, when more oil is added, is not usually with a phase of excess oil [12], but with an L_3 -phase [10].

A possible explanation is that the L_3 -phase occurs in systems that vigorously oppose any strong local bending of the surfactant monolayer (as would be needed to make a compact micelle). In this work, we propose that the observed L_3 -phase can be tentatively identified with a certain *sheetlike phase* that we will call the S-phase. We picture this phase as consisting locally of relatively flat pieces of surfactant bilayer, joined together randomly in such a way as to avoid all regions of strong curvature. Thus a low bending energy (and relatively high entropy) can be achieved at very low volume fractions of surfactant. The properties of the surfactant monolayer that favor such a state are i) a relatively high bending constant, and ii) no spontaneous curvature [13]. Clearly, the same properties tend to stabilize swollen lamellae, with respect to a phase of micelles.

It remains to be decided whether the dominant configurations of the bilayer consist of large isolated vesicles, or some more highly connected random surface (possibly bilayer-continuous). We will present a simplified model which allows for both possibilities, and indicates that the latter is more stable in a large part of the phase diagram. We find that the sheetlike phase S is preferred to the lamellar phase (L) once the system is dilute enough that the interlamellar spacing would exceed roughly ξ_K , the de Gennes-Taupin persistence length [14] of the semi-flexible bilayer. We also study equilibria between these two phases and an extremely dilute phase of surfactant micelles (or isolated surfactant molecules), stabilized by entropy of mixing at low enough volume fraction.

The proposed S-phase should be contrasted with the isotropic phase of giant wormlike micelles which is also seen at low volume fractions in certain surfactant solutions [15]. This phase is expected for surfactants whose monolayer has strong spontaneous curvature [16], unlike the S-phase which can occur only when a locally flat surfactant film is favored. (Correspondingly, we expect the wormlike phase to be found close to an ordered (hexagonal) phase of cylinders, as opposed to lamellae.)

To formulate a model for the S-phase, we construct an ensemble of surfaces (consisting locally of surfactant bilayer) characterized by a structural length scale ξ . We exploit a strong analogy with a model previously studied in the context of middle-phase microemulsions [17]. As in that work, we assume the surfactant film to be incompressible, so that the surfactant volume fraction, and the specific area of bilayer in the system, are proportional. We start with a discretized representation (on a cubic lattice of side ξ) by building up an arbitrary collection of connected surfaces from elementary plaquettes (faces of the unit cube). In such a surface, the curvature is concentrated along the joins between plaquettes. Under certain conditions, however, the surface can be «smoothed out» so as to have nowhere a radius of curvature smaller than $\xi/2$. To achieve this on a cubic lattice, the following configurations must be avoided: *a*) a plaquette edge that is not joined to any other edge; *b*) a plaquette edge that is joined to two others. The first case corresponds to an edge or «tear» in the bilayer, with a local radius of curvature of order its thickness $a \ll \xi$. The second gives an angled «seam» between sections of bilayer; this also has a radius of curvature of order a along the seam. In contrast, a junction involving two (or four) plaquette edges may be interpolated with a surface (or pair of surfaces) having radius of curvature of order ξ or less, as shown in fig. 1.

As regions of high curvature are to be avoided, we insist on the elimination of configurations of types *a*) and *b*) above. This rule can be enforced by dividing the cells of the

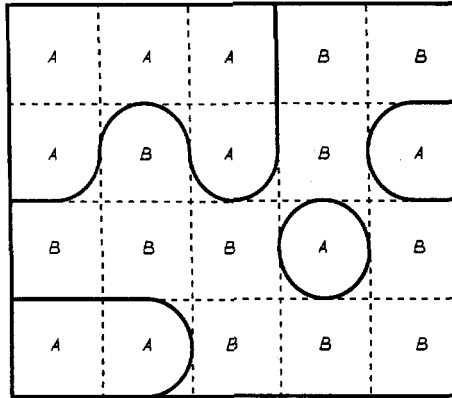


Fig. 1. – Construction of a randomly connected bilayer surface as an interface between two fictitious, different types of oil, A and B , drawn for simplicity in two dimensions.

lattice into two types (A and B), and allowing plaquettes to lie only at the A - B interface (which must be completely covered). Consequently, the random-surface configurations of the bilayer that we wish to allow correspond to those that represent the interface in a mixture between two, fictitious, *different types of oil*. The relative fractions ψ and $1 - \psi$ of oils A and B are not determined *a priori*, since in the real system these two «species» are, of course, identical. We will, therefore, use ψ as a variational parameter. It is easy to see that, in conjunction with the random mixing approximation for A and B , this allows a continuous interpolation between a phase of *dilute spherical vesicles* ($\psi \ll 1/2$) and one that consists of a bilayer-continuous, «maximally random» interface ($\psi = 1/2$).

Adopting this construction for the S-phase, we now estimate its free-energy density F_S . We denote the volume fraction of surfactant and oil by ϕ , and $1 - \phi$, respectively, and presume $\phi \ll 1$. We write $1 - \phi \equiv \phi_A + \phi_B$, where ϕ_A and ϕ_B denote the two different fictitious oil species, described above. Defining also $\psi \equiv \phi_A + \phi/2 \approx \phi_A$, we obtain the following estimate for the entropy density:

$$S = - (1/\xi^3) k_B [\psi \ln(\psi) + (1 - \psi) \ln(1 - \psi)] . \quad (1)$$

This is the usual random mixing expression for an A - B mixture. That species A and B must finally be set identical, does not affect this result for the entropy of the interface.

The other contribution to the free-energy density is from the bending energy of the bilayer. Following ref. [17], we estimate this heuristically as

$$F_{\text{bend}} = (1/\xi^3) 8\pi \psi (1 - \psi) K(\xi) . \quad (2)$$

Here we have assumed no spontaneous curvature of the bilayer, as expected on symmetry grounds; the factor $\psi(1 - \psi)$ counts (in random mixing) the total area of the surface, whose radius of curvature is taken to be everywhere of order ξ . The (somewhat arbitrary) factor 8π relates the bending energy of an isolated unit cube to a sphere of diameter ξ .

As explained below, the effective bending constant $K(\xi)$ in eq. (2) is taken to be explicitly length scale dependent [18]:

$$K(\xi) = K_0 [1 - \alpha \tau \ln(\xi/a)] . \quad (3)$$

Here α is a numerical coefficient that we will take to be unity⁽¹⁾, and the reduced temperature is $\tau \equiv T/(4\pi K_0)$; a denotes the bilayer thickness, a molecular parameter. The cell size ξ in eqs. (1)-(3) obeys

$$\xi = 6a\psi(1 - \psi)/\phi. \quad (4)$$

This result is found by equating (in random mixing) the specific surface area and volume fraction of the interfacial bilayer to ϕ/a and ϕ , respectively.

The form (3) for the effective bending constant describes, in perturbation theory [18], the softening of the sheet by thermal undulation modes. The result should be adequate for $\xi \leq \xi_K = a \exp[1/\tau]$, which is the persistence length [14] of the bilayer. The physical content of eq. (3) is that bends in the bilayer on a length scale larger than ξ_K are possible at low free-energy cost, since an unbent sheet will anyway be thermally crumpled in this scale. As a result, ξ_K is the favored structural length scale for an isotropic phase of random bilayer surface.

The analogy here with balanced oil/water microemulsions is very close. Indeed, in our formulation, the description of the sheetlike phase is exactly the same as that of ref. [17] for a balanced A/B microemulsion. (A balanced system is one in which the chemical potentials of A and B are equal, and there is no spontaneous curvature at the interface.) The only difference is that species A and B are now finally taken to be identical. This has no effect on the mathematics, but does alter its interpretation to give a phase diagram, as will be explained below.

Combining eqs. (1)-(4), we write a free-energy density $F_{\text{tot}}(\phi, \psi, a, \tau) = F_{\text{bend}} - TS$. Since ψ is not determined by the constraints, we compute the free-energy density as

$$F_S(\phi, a, \tau) = \min_{\psi} F_{\text{tot}}(\phi, \psi, a, \tau). \quad (5)$$

On minimizing over ψ (taken $\leq 1/2$, without loss of generality), we find two regimes:

i) $\phi > \phi_1 \equiv 12 \exp[-(1/\tau + 1)]$: for these moderate ϕ , the minimum of F_{tot} over ψ occurs at $\psi = 1/2$, which corresponds to a «maximally random» interface. The structural length scale ξ is given by eq. (4): $\xi = 3a/(2\phi)$. For ϕ close to ϕ_1 , ξ varies as $\xi \approx \xi_K$.

ii) $\phi < \phi_1$: at these lower volume fractions, the minimization over ψ yields values of $\psi < 1/2$. There is a smooth evolution, as ϕ is decreased, from the maximally random structure, through a state of large vesicles (of radius $r \gg a$) to small vesicles ($r \approx a$). The latter arise for $\phi = \phi_2 \equiv 18 \exp[-2/\tau] \approx \phi_1^2$; for $\phi < \phi_2$, the variational parameter saturates its lower bound $\psi = \phi/2$. While the estimate (2) for F_{bend} is not quantitatively accurate for these very small ξ ⁽¹⁾, our variational approach does reflect the possibility of a local minimum in the free energy $F_S(\phi)$, corresponding to a phase of extremely dilute small objects, stabilized by entropy of mixing. We refer to these objects as «micelles», although they could equally well be isolated surfactant molecules.

⁽¹⁾ Values of $\alpha = 1$ and $\alpha = 3$ have each been proposed. (See ref. [18].) Given our lattice expression (1) for the entropy of mixing, the resulting phase equilibria do depend on the precise value of α ; in particular, the coexistence between the sheetlike phase S and the dilute phase D, found below, may disappear if α is too large [17]. However, the critical α , at which this coexistence disappears, is itself strongly dependent on detailed assumptions of the model, some of which clearly break down in this limit of extreme dilution (*e.g.*, the harmonic expression for the bending energy, eq. (2)). Thus there remains several open theoretical questions concerning the stability of the D-phase; we hope to return to some of these in a future publication.

To calculate phase equilibria, it is necessary to estimate also the free-energy density F_L of an oil-swollen lamellar phase. We adopt the following expression for F_L [19, 9]:

$$F_L(\phi, a, \tau) = \frac{3\pi^2}{128} \frac{\phi}{a} \frac{(k_B T)^2}{K_0 d^2}. \tag{6}$$

Here $d = a(1 - \phi)/\phi$ denotes the interlamellar spacing. Equation (6) represents the entropic Helfrich repulsion between undulating lamellar sheets [19]⁽²⁾. Using eqs. (5) and (6) for F_S and F_L , the phase diagram was computed numerically, with the result shown in fig. 2. (In considering the dependence on the reduced temperature $\tau \equiv k_B T/4\pi K_0$, note that the bare bending constant, K_0 , depends on the details of molecular interactions, and may itself be strongly temperature dependent.) The following features are notable:

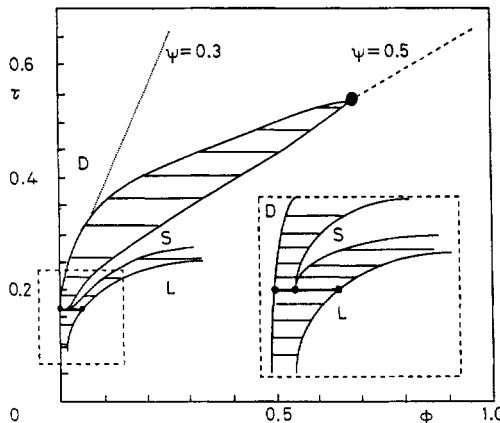


Fig. 2. - Phase diagram computed from eqs. (5), (6). The vertical axis is the reduced temperature, $\tau = T/(4\pi K_0)$; the horizontal axis is ϕ , the surfactant volume fraction. Regions marked D, S, and L, correspond, respectively, to a dilute (micellar) phase, the sheetlike isotropic phase, and lamellae. The dashed line indicates the boundary between $\psi = 1/2$ and $\psi < 1/2$. As one moves to the left of this line, the isotropic phase becomes gradually more vesiclelike in character; the percolation threshold of the bilayer is estimated as $\psi = 0.3$ (dotted line). Moving further to the left one enters the dilute (D) phase in which ψ saturates its lower bound, $\phi/2$.

i) At low temperature ($\tau \leq 0.16$) the lamellar phase L extends down to very small ϕ , finally phase separating to an extremely dilute phase, D, consisting of small micelles. This D-phase corresponds to volume fractions of order $\phi \approx \phi_2 \approx \exp[-2/\tau]$.

ii) At intermediate temperatures, the sheetlike phase (S) is present between the lamellar and dilute phases; as lamellae are diluted with oil, separation takes place first to the S-phase. Further dilution of this phase leads to a first-order separation to the extremely dilute phase, D. At the coexistence of L and S, the interlamellar spacing d is of order ξ_K , as is the structural length scale ξ in the isotropic S-phase. Note that the volume fraction $\phi \approx \exp[-1/\tau]$ in the L-phase at coexistence with S actually *increases* with τ . This contrasts with an earlier theory of lamellar unbinding [12], in which raising T increases the Helfrich

⁽²⁾ The zero of free energy in eq. (6) is taken at infinite separation d . With this choice of zero, it is arguable that there should be a Helfrich-like term in the free energy of the S-phase. We expect this term to be small however [17], and omit it from our treatment.

repulsion, allowing the lamellae to swell further before separation occurs (to excess oil). Here since separation is to the entropic S-phase, the temperature trend is reversed.

iii) At higher temperature ($\tau \geq 0.3$) the lamellar phase is destabilized and the isotropic phase S is the only stable one at moderate ϕ ; there remains a first-order coexistence between S and the very dilute phase, D. Finally at a reduced temperature τ of about 0.5, there is a critical point, above which the two-phase region disappears⁽³⁾.

Also shown in this figure is the dividing line between the region where the variational parameter ψ takes on the value $1/2$, and that where $\psi < 1/2$. The «maximally random» configuration ($\psi = 1/2$) is preferred over a large region of the phase diagram, which includes all S states that are in coexistence with lamellae. Above the critical point⁽³⁾, however, the continuous pathway from S to D is by way of states containing large vesicles ($\psi \ll 1/2$) whose average size decreases smoothly with ϕ . The line $\psi = 0.3$ is also indicated in fig. 2. This denotes a rough estimate, based on our lattice construction, of the percolation threshold of the bilayer. To the right of this line, one expects the isotropic phase to be bilayer-continuous, although ϕ remains only a few percent.

To understand the connection with balanced A/B microemulsions mentioned earlier, one should remember that, were A and B to be distinguishable species, all single phases with $\psi < 1/2$ would in fact correspond to a *symmetric pair* for coexisting phases (one with A and B interchanged). Thus the S/D coexistence region in fig. 2 would correspond to the well-known three-phase equilibrium between a (middle-phase) microemulsion (S) and a symmetric pair of dilute phases (D). Similarly the dashed line, $\psi = 1/2$, would divide a region of single-phase microemulsion from a region in which two microemulsions coexist. In the present system, since A and B are the same, the three phases are reduced to two, and there is no true phase transition across the $\psi = 1/2$ line.

The various phase equilibria shown in fig. 2 are in good qualitative agreement with the available experimental data [1-11]. In general, the L_3 -phase is indeed found experimentally to lie between an extremely dilute phase (D) and a swollen lamellar phase (L), separated from each by a first-order coexistence. Moreover, for nonionics in water, the diffusivity of the surfactant is measured to be higher, and that of the solvent somewhat lower, than would be expected for a phase of finite aggregates [6]. These facts are consistent with a bilayer-continuous phase, in which the diffusion of the solvent is reduced by a geometrical factor related to the tortuosity of the solvent-filled regions. In the case of oil-based solutions, it is often possible to make a stable L_3 -phase even in the presence of small amounts of added water [7-11]; this third component should reside in the middle of the bilayer, as it does in the nearby lamellar phase⁽⁴⁾. For this oil-based (pseudo-) ternary system, there are conductivity measurements [11] which suggest the presence of water-continuous pathways, although the volume fraction of water is only a few percent. This is again consistent with the idea of a random sheetlike phase S exhibiting continuity of the (water-swollen) surfactant bilayer.

⁽³⁾ The precise location of this critical point is strongly dependent on model parameters, such as the choice numerical prefactor in eq. (2). With the present choice, the critical point occurs at rather large ϕ , for which our model free energy is not realistic. Qualitatively, however, the existence of such a critical point is reasonable; moreover, for slightly different choices for the numerical factor, it can occur at much smaller ϕ .

⁽⁴⁾ To account for the presence of a small amount of water, we simply increase the bilayer thickness a by a geometrical factor: $a \rightarrow a(1 + \phi_{\text{water}}/\phi)$. So long as one also allows for any explicit dependence (on water content) of the bare bending constant K_0 of the bilayer, the calculation already presented may be carried over unchanged.

Although these results are encouraging, refinements to our model will be needed before the picture is complete. For example, a unified treatment of the S-L coexistence requires some smooth interpolation between eqs. (5) and (6) for F_S and F_L . Also to be considered are corrections to random mixing; a realistic treatment of the dilute phase (D); incorporation of Gaussian curvature terms; and a study of polydispersivity effects. Despite these issues, we expect many of our qualitative predictions concerning the sheetlike isotropic phase to remain valid. A more complete description, in any case, must await a fuller understanding than now available of the statistical mechanics of semi-flexible random surfaces with liquid-like internal degrees of freedom [20].

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Erratum

Random Surface Model for the L_3 -Phase of Dilute Surfactant Solutions.

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The authors wish to correct a numerical error in the location of the critical point at $\phi \approx 0.7$ on the phase diagram shown in fig. 2, and described in the text following the figure. For the model with parameters as chosen in eq. (1)-(4), this critical point in fact lies exactly at $\phi = 1$. Thus the dashed line ($\psi = 1/2$) in the figure should be covered by a very narrow finger in continuation of the two phase (shaded) region. As discussed already in footnote⁽³⁾, however, the precise location of the critical point is highly model-dependent and with slightly different assumptions can occur at $\phi < 1$, as shown. In this case, the dashed line represents the spontaneous breaking of an exact ($\psi \rightarrow 1 - \psi$) symmetry and is therefore associated with a second-order phase transition. The transition is Ising-like, as has been discussed by HUSE D. A. and LEIBLER S., *J. Phys. (Paris)*, 49 (1988) 605; see also MILNER S. T., SAFRAN S. A., ANDELMAN D., CATES M. E. and ROUX D., *J. Phys. (Paris)*, 49 (1988) 1065.

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