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MICROEMULSIONS AND THE L₃ PHASE

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Abstract - Microemulsions and the L₃ phase provide two different examples of equilibrium random surface structures. In this paper we review recent progress toward understanding these materials on the basis of continuum elastic theory for two-dimensional fluid films.

1 - INTRODUCTION

A microemulsion /1/ is a ternary (or pseudoternary) mixture of oil, water, and surfactant in which the surfactant film forms a monolayer that divides partitions space into two disjoint regions occupied by the two dissimilar solvents. Depending on the volume fractions and other parameters, these regions may consist of droplets of one solvent in the other or they may represent a bicontinuous structure (which may also contain discrete, droplet-like components). An approximately "symmetric" microemulsion can be made by mixing equal volume fractions of water and oil, and tuning parameters such as salt concentration so that there is no strong energetic preference for the surfactant film to bend toward one solvent rather than the other.

The L₃ phase /2/ is formed in binary (or pseudobinary) systems of dilute surfactant in water or oil. Such a phase is formed when there is a strong local stability associated with the two-dimensional packing of the surfactant into a bilayer. Recent models of this phase involve a structure that closely resembles a microemulsion in a formal sense. The bilayer is thought to form a “sponge-like” random surface without edges, which then necessarily divides space into two disjoint regions. This is no longer a consequence of having two solvents, but an intrinsic properties of two dimensional surfaces in three dimensional space. In the limit of a perfect bilayer (no edges or holes) the system is then isomorphic to a perfectly symmetrical microemulsion in which the two “different” solvents are in fact identical. This exact symmetry has some deep consequences experimentally.

In this article we focus mainly on the L₃ phase but emphasize throughout the analogy with symmetric microemulsions. Some ways in which asymmetric microemulsions differ are described in Section 9.
2 – IDEAL RANDOM SURFACES

A surfactant bilayer may be modelled as a continuous film of incompressible, two-dimensional fluid. For simplicity we assume that the film is “ideal”, having neither torn edges nor seams both of which are expensive in packing energy – at least for those surfactants which prefer to make bilayers. Therefore the important configurations of bilayer-forming surfactants in solution consist of self-and mutually avoiding random surfaces. This system of surfaces has a certain number \( n_c \) of disjoint pieces or components and a certain number \( n_h \) of handles. As emphasized above an ideal bilayer, even if it has many components, divides space everywhere into an “inside” (I) and an “outside” (O).

This definition is unique up to an overall exchange; thus, once a given point has been chosen and labelled as I the classification of all other points is determined. If the two sides of the fluid film are equivalent, then the Hamiltonian of the entire system is unaffected by the interchange I ↔ O.

3 – CONTINUUM ELASTIC THEORY

At lowest order in a curvature expansion, the elastic energy of a bilayer film (per unit area) may be written locally as /1–3 /

\[
H = \frac{K}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)^2 + \frac{\tilde{K}}{R_1 R_2}
\]  

(1)

where \( R_1 \) and \( R_2 \) are the local principle curvature radii of the film. Often one is interested, not in the bending energy of a certain film configuration that is specified everywhere, but in the free energy of a state with a certain average curvature on a coarse-grained scale. To calculate this, one must allow for the change in the entropy spectrum of short scale undulation modes which results from imposing a large scale “bend”, with radius of curvature \( \xi \gg a \), say. The calculation of the effective bending constant \( K(\xi) \) is quite complicated, but can be set up as a perturbation expansion (about a flat sheet) in the parameter \( \tau = T/4\pi K_0 \) (where \( K_0 \equiv K(a) \) is the “bare” bending constant). The result to first order is /4 /

\[
K(\xi) = K_0 - \frac{dT}{4\pi} \log(\xi/a)
\]  

(2)

where \( d \) is the dimension of space. Thus the effect of thermal fluctuations is to make the fluid bilayer less rigid at large distances. The perturbative result, Eq.2, makes sense only for \( \xi \leq \xi_K \approx \exp[4\pi K_0/dT] \). The parameter \( \xi_K \) is called the persistence length; for bilayers this may be a few hundred to a thousand Angstroms /5/. For \( \xi \leq \xi_K \) an unconstrained film is roughly flat, whereas at larger distances it is a fully developed random surface so perturbation theory about a flat sheet breaks down.

We have not yet discussed the gaussian curvature term \( \tilde{K}/R_1 R_2 \) in Eq.1. A well-known theorem (Gauss–Bonnet) tells us that

\[
\int \frac{1}{R_1 R_2} \, d^2S = 4\pi (n_c - n_h)
\]  

(3)

So \( \tilde{K} \) is like a chemical potential for topology. Notice that if \( \tilde{K} \) is positive, a fluid film system described by Eq.1 has a ground state instability leading to the formation of a periodic minimal surface
which has many handles, only one component, and zero mean curvature (i.e., with $1/R_1 + 1/R_2 = 0$ everywhere) /6/. The energy of such a state with unit cell size $l$ diverges as $-K/l^3$. This will eventually be cut off by anharmonic terms, but nonetheless the general expectation is for phase separation to a rather concentrated cubic phase whenever $K > 0$. Similarly if $K$ is too negative ($K \leq -2K_0$) there is an instability to the formation of very small spherical vesicles. The Gaussian rigidity $K$ also has a logarithmic renormalization at large length scales which is positive /7/, favouring more handles at large distances.

4 - SCALING LAWS: THE OSMOTIC COMPRESSIBILITY

The statistical mechanics of a two dimensional film without spontaneous curvature admit a very interesting scaling property that has been considered by Huse and Leibler /6/ and Poste et.al. /8/. We assume a random surface structure with some a characteristic length scale $\xi_0$. For any given state of the system, a scale change $\xi_0 \rightarrow \lambda \xi_0$ is associated with a change in the curvature elastic energy density $f \rightarrow f\lambda^{-3}$ (calculated from Eq.1 with fixed $K$ and $\bar{K}$). This is a special property of the elastic hamiltonian for bilayers which has no intrinsic length scale. To dilate the elastic film leaves its energy invariant.

What is the relation between dilation of the surface and dilution of the $L_3$ sponge-like phase? In view of the invariance of the elastic energy, the two seem at first sight to be in one-to-one correspondence /6,8/. Since the volume fraction $\phi$ of the film is proportional to its specific surface area, this yields a simple scaling law for the free energy density:

$$f \sim \phi^3.$$  \hspace{1cm} (4)

However this is not quite correct since the dilation also increases the thickness of the bilayer, which we do not want. The specific entropy (and the excess area) due to the undulations is decreased under the dilation and we must restore the short cutoff to its original value if we are to estimate the free energy density correctly. Within perturbation theory, the result must have the form

$$f \sim \phi^3[a + b \log \phi]$$  \hspace{1cm} (5)

with $a, b$ parameters that depend on $K$ and $\bar{K}$. This description may fail if $\xi_0$ is too large (i.e., beyond the range of any perturbation theory) but it should give the leading behaviour for systems that are not too dilute. The form of Eq.5 is exactly as predicted by semi-empirical lattice models of the sponge phase /9–12/. The resulting osmotic compressibility (measured in light scattering as the intensity $I(q = 0)$ in the limit of small wavevector) may be written as

$$I(0)^{-1} \sim \phi \log[\phi/\phi_0]$$  \hspace{1cm} (6)

with $\phi_0$ a combination of the previous constants. Eq. 6 has been unambiguously confirmed by experiment /12,13/, providing some of the first direct evidence for logarithmically renormalized elastic energies in fluid films. This strongly supports the view that random surface phases of surfactant films can be understood in terms of continuum elastic theory.
It is notable that the sponge-like structure presumed for the L3 phase is not essential to the scaling argument; one requires only a characteristic length and an elastic hamiltonian. Hence Eq.5 should also hold in the Lα (smectic) phase (at least, at the level of perturbation theory) but with different $a$ and $b$. This is consistent with more explicit calculations of the free energy /14/. Notice also that the logarithmic renormalization terms are essential if one is to understand the transition from a smectic (Lα) to isotropic (L3) phase under dilution. Without these terms, both free energies would scale as $\phi^3$ so that there could be no concentration dependence of the transition temperature.

5 - INSIDE/OUTSIDE SYMMETRY BREAKING

Recall that the elastic hamiltonian (and indeed any other hamiltonian for perfect bilayers) has exact I/O symmetry. This can break spontaneously; the symmetry is Ising like so the transition can be either continuous or first order. In the first case, one start from a “symmetric sponge” or random surface labyrinth, and progresses continuously to one in which there is an infinitesimal difference in the statistics of I and O regions (e.g., slightly more O than I). In the second case, the system has a miscibility gap and a transition to a strongly asymmetric phase, for example a set of dilute vesicles.

It is this transition that is signposted by the divergence at $\phi = \phi_0$ in Eq.6 (which of course ceases to be reliable close to any transition). It is natural that entropy favours the formation of small objects (vesicles) when the surfactant concentration is low enough. Note that the “dilution symmetry” of the sponge, leading to Eq.4, is violated in the broken symmetry phase.

The symmetry breaking is exhibited by phenomenological models /9,10/ but to be more general we can construct a Landau theory. This depends on two order parameters even in a binary system of surfactant + solvent. One order parameter is the volume fraction of bilayer $\phi$ (or its departure from a reference value $\rho = \phi - \phi_0$) and the other one is a parameter $\eta$ which we may take as the difference in volume fraction of the “inside” (I) and “outside” (O) regions of solvent. This parameter vanishes in a symmetric state and, since I and O are made of identical material, it can enter only in even powers in the Landau expansion. We expect $\rho$ and $\eta$ to be coupled at the lowest order allowed by symmetry. This argument gives the following Landau expansion of the thermodynamic potential /13,15/:

$$\Delta \Phi = \mu \rho + \lambda \rho^2 + \alpha \rho^4 + \beta \eta^2 + \delta \eta^4 + \nu \rho \eta^2$$

Under variation of the expansion coefficients, several different types of “pseudobinary” phase diagram can be generated /13/. The transition between the sponge and the dilute phase can be either first order or second order; indeed we predict a line of second order transitions on the $\phi, T$ plane at which the I/O symmetry is spontaneously broken. In addition, a regular liquid gas critical point can exist either between two symmetric sponge phases, or two broken symmetry phases, of different volume fraction. Symmetric tricritical behaviour should be unusually easy to obtain in these systems (that is, it arises with finite probability even if the parameters in Eq.7 are chosen “at
random"). It should also be relatively easy to study various other higher order critical points. A
typical example, reparameterised in terms of the natural variables \( \phi \) and \( T \) is shown in Fig.1.

6 - EXPERIMENTS ON \( L_3 \) PHASES: ANOMALOUS LIGHT SCATTERING

There is now clear evidence of a line of second order phase transitions in the pseudobinary phase
diagram of one “sponge” system (the water-rich \( L_3 \) phase of SDS / dodecane / pentanol / water). A
detailed analysis of the light scattering near such a line has been made /12,13,15/, which leaves little
room for any other interpretation of the data. The scattering signal is quite unusual since there is
no scattering contrast between the I and O regions; instead one measures the autocorrelation of the
surfactant density which (within a gaussian treatment of fluctuations) varies as \( q^{-1} \) instead of \( q^{-2} \)
close to the transition. The existing data on this system (though not conclusive) is consistent with
a pseudobinary phase diagram similar to Fig.1, with a line of second order transitions merging via
a tricritical point with the binary fluid type miscibility gap. In other systems (such as the oil-rich
\( L_3 \) phase of the same ternary mixture) the transition is first order at all temperatures, but weakly
enough so that similar scattering anomalies are clearly seen.

Leaving aside the issue of symmetry breaking, there are many other experiments that confirm the
general picture of the \( L_3 \) phase as a multiply-connected random surface that partitions space; these
are reviewed in /12/. It is still a matter of argument whether the proper hamiltonian for the bilayer
is the elastic one (Eq.1) but the experimental confirmation of Eq.5 /13/ strongly suggests that this
is indeed the appropriate description.
A very similar Landau theory can be used to describe the transition from a symmetric sponge phase to a lamellar $L_\alpha$ state. In fact the theory is identical to Eq. 7 if one now takes $\eta$ as the amplitude of smectic order. Of course, the expansion coefficients have different values and indeed the broken symmetry phase arises at high concentrations and low temperatures (the opposite being true of the symmetric asymmetric transition). An interesting question is: what physical quantity corresponds to the order parameter $\eta$? A strong case can be made that the smectic amplitude that arises in the Landau expansion is in fact that of the I/O variable rather than the surfactant density itself /17/. This is clear from consideration of a strongly ordered $L_\alpha$ where there is clear alternation between layers of I and O solvent (just as in the analogous phase of a ternary system). If this is correct, then once again we have an “invisible” order parameter with no scattering contrast. The measured quantity is the surfactant density; since this couples quadratically (Eq.7) we obtain the prediction that (within mean field theory) the observed amplitude of the smectic modulation is linear in the distance from the transition rather than the usual square root.

More generally it is known that the Landau theory is inadequate to describe the transition from an isotropic to a smectic phase, which is always driven first order by fluctuation effects /18/. The fluctuations also suppress the transition to lower temperatures and/or higher volume fractions. Thus in the $L_3 \rightarrow L_\alpha$ transition the second order line (analogous to that of Fig.1 for the symmetric/asymmetric transition) is shifted and becomes a first order line with a finite miscibility gap. A detailed treatment that includes both fluctuations and the coupling to a second order parameter has recently been given /17/. This leads to a miscibility gap that is in general of order the mean concentration at the transition. In this sense, the transition is not “weakly” first order; nonetheless we may hope that a description based on Landau Ginzburg theory should still be qualitatively accurate.

A very interesting aspect of the $L_3 \rightarrow L_\alpha$ transition is its coupling to an imposed flow fields. In the presence of a steady convective shear, the fluctuations are reduced and this “de-suppresses” the transition. Indeed there is increasing evidence that the transition from sponge to lamellar phase may be induced by shear /19/. Such an effect can be seen simply in shaking a sample between crossed polars, though it is of course hard to tell that a true phase transition occurs in this type of “experiment”. Work in progress /20/ on light scattering from flowing samples should, we hope, confirm the picture of a flow induced phase transition.

8 - ROLE OF GAUSSIAN RIGIDITY

The discussions based on scaling and on Landau theory yield no specific information of how the state of the system depends on the elastic constants $K$ and $\bar{K}$. We have seen already that $K$ sets a characteristic length scale for random surface structures: this is the persistence length $\xi_K$. However, the relative stability of symmetric and asymmetric sponge states, and that of the lamellar phase, are influenced also by $\bar{K}$. We can say that more negative $\bar{K}$ favours fewer handles and more
components, thus stabilizing both the lamellar phase and the asymmetric sponge or vesicle phase over the symmetric sponge labyrinth in which there are, presumably, many handles and rather few components.

Conversely it has been argued that the normal (symmetric) $L_3$ phase is stabilized by a value of $K$ that favours handles $^{/8,21/}$; this is the basis of models of the sponge as a “melted cubic phase” with a single infinite surface and many handles having no long-range order. This model differs slightly from the “maximally random” structure proposed in $^{/10/}$, but not in a way that affects the scaling laws or symmetry arguments given above. The dependence on $K$ may explain why the $L_3$ phase is stable to quite high concentrations in a narrow composition range. In the pseudobinary representation the “hidden” composition variables are presumed to alter the elastic parameters of the film; the observed behaviour is several systems $^{/8,22/}$ is consistent with the idea that the gaussian rigidity must be carefully tuned to obtain a stable $L_3$ phase at high volume fractions ($\geq 20\%$). It may even be that a positive value is required, which implies either that anharmonic stabilizing terms are important, or that the positive value arises through renormalization only above a certain distance scale.

If one accepts that the “hidden” composition variables allow tuning of $K$, then it is interesting to ask what happens as this parameter is slowly made more negative. It may be possible in principle to drive a transition from a symmetric (handle-rich) $L_3$ phase to a lamellar phase, and thence (by further adjustment in the same direction) to an asymmetric $L_3$ phase that has a strong vesicle character (rich in components). A phase of “nested” vesicles $^{/6/}$ is certainly a possibility if the inequality $K \leq 2K$ is satisfied by the renormalized bending constants above some length scale. (If it is satisfied by the unrenormalized coefficients, a solution or crystal of tiny vesicles will be favoured instead.) There is some evidence of such behaviour in the water rich part of the SDS / dodecane / pentanol / water system $^{/15/}$.

9 – MICROEMULSIONS

In a microemulsion, the inside component (say) of our ensemble of surfaces is water and the outside component oil. The surfactant film is now a monolayer with a definite direction and there is no inside-outside symmetry. However, this symmetry can be approximately restored by (i) tuning parameters such as the concentration of added salt and alcohol, so as to avoid a strong preferred curvature of the monolayer towards one solvent rather than the other; and then (ii) using equal amounts of oil and water. Under these conditions, the phase diagram for the bilayer model (Fig.1) can be reinterpreted as that of a “balanced” microemulsion system. In this limit, our previous description is valid. The main difference of interpretation is that any broken-symmetry state ($\eta \neq 0$) must be interpreted, not as a single phase, but a coexisting symmetric pair of states related by the interchange of oil and water. Thus the region of coexistence between the symmetric and asymmetric sponge phases in Fig.1 becomes a coexistence between a symmetric, bicontinuous microemulsion and a pair of dilute phases of surfactant in water or surfactant in oil. Since the microemulsion has a density less than that of the oil-rich phase and more than that of water, it floats between the two in a test-tube and is referred to as a “middle phase” microemulsion. At higher temperatures, the second order line now divides one symmetric micromulsion from a symmetric pair of slightly asymmetric ones.
In microemulsions, as indicated already, it is extremely easy to break the oil/water symmetry of the hamiltonian, either by detuning parameters so that the monolayer has a spontaneous curvature toward water or oil, or merely using unequal amounts of water and oil as ingredients. These effects can quite easily be incorporated into models of the kind described above /23/ and of course yield asymmetric pseudoternary phase diagrams /24/. The various phase equilibria (both experimentally and in theory) can become quite complicated and will not be discussed further here. It is interesting that the existence of a finite spontaneous curvature sets a new length scale in the problem. Unless this is infinite, the invariance of elastic energies under dilation is not maintained and the scaling laws given in Section 4 are no longer applicable. Note in contrast that the requirement of a particular oil/water volume fraction is fully compatible with the “dilution invariance” of the elastic energy on changing the specific surface area. Paradoxically, then, if the spontaneous curvature is weak enough, the scaling law, Eq.5 should be maintained in an asymmetric microemulsion whereas it is liable to be violated in an asymmetric sponge. The reason is that the relative volume fractions of I and O are, in the latter case, changing with composition.

The absence of exact I/O symmetry in microemulsions has some interesting consequences for the phase diagram under flow. There is in general a cubic interaction in the Landau Ginzburg description of transitions to ordered phases. If the cubic term is large enough, it should be possible to observe a flow induced transition to a hexagonal phase (with cylindrical domains aligned in an hexagonal array with axes along the streamlines) rather than a lamellar one, even if there is no hexagonal phase on the static phase diagram /25/.

10 – DEFECTS

Random bilayer phases differ from symmetric microemulsions in a deep way: they permit in principle defects such as holes in the surfactant film. These may have rather high energies but should nonetheless be present with some finite probability, which may in fact be experimentally controllable by varying salt concentration /12/. It is not yet clear how to include these systematically in the theoretical description based on Ising-like order parameters. In particular there is a counting problem: if on (say) a lattice model one represents the surface as the interface between up and down spins, then when a part of the surface is absent there is liable to be a local overcounting from changes of spin configuration which only affect the part of the surface that is missing. This is a serious theoretical difficulty that requires treatment of the Ising parameter as a gauge variable /26/. It has been suggested /13/ that by spoiling the unique partitioning of space, defects could lead to the destruction of I/O symmetry at large distances, thus giving a rounding off of the critical behaviour at any symmetric/asymmetric sponge transition. However, this is not the only possibility. An alternative is that the transition survives up to some finite defect density in the film /26/. Despite any ambiguity over the partitioning into I and O, it may still be possible to define an order parameter (and a spontaneously broken symmetry) for example in terms of the mean curvature of the infinite component of the film. (This is well defined, up to a sign, unless the defects are so numerous that the infinite component no longer exists.)
The response of a sponge or microemulsion phase to time dependent perturbations would be of general interest even if it were not manifested in extreme nonlinearities such as flow induced phase transitions (see section 7 above). For example one expects there to be a "topological relaxation time" for local equilibration of the number of handles which is governed by the activated process of fusion between sheets /27/. This enhanced relaxation time may partly be responsible for the fact that flow induced structural change to the $L_3$ phase occurs at rather low shear rates – typically of order 100 Hz /20/. Larger flow rates are usually needed for microemulsions and this could result from a lower activation barrier to fusion, in the case of a monolayer. The topological relaxation time should also in principle be observable as a crossover time scale in dynamic light scattering /27/.

An open issue concerns whether the topological time plays a determining role in the linear stress response as measured in the frequency dependent viscosity /28/. It is as yet not clear whether a sponge can relax rapidly by flow within the two-dimensional liquid film at fixed topology (e.g., by "diffusion of handles" along the surface), or whether local topological relaxation is also needed.

A reasonably clear understanding of microemulsions and $L_3$ phases is now emerging, based on the concepts of symmetry, scaling, and the continuum elasticity of two dimensional fluid films. More detailed statistical mechanical and structural model have played an important role in the evolution of these ideas although our aim here has been to emphasise the universal and model-independent features as much as possible. The special symmetry of the $L_3$ phase makes it suitable for the study of critical and tricritical phenomena in fluids; its large length-scale permits study of flow-induced phase transitions at very modest shear rates ($\sim 100$ Hz) and in future experiments it should be possible to probe in detail the coupling between flow-induced order and composition. The role of defects in determining the critical behaviour of the sponge is a focus of current study: much remains to be understood about this problem. Another area of rapid progress concerns the dynamics of random surface phases, as probed by dynamic light scattering, transient birefringence and frequency dependent viscosity. Here local topological relaxation processes may play a role, although the details of this remain to be clarified.

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