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Classification

Physics Abstracts

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L₃ (sponge) phase in the very dilute regime : spontaneous tearing of the membrane ?

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Abstract. — We use light scattering and conductimetry to investigate the very dilute range of the domain of existence of the sponge (L₃) phase in the quaternary OBS/pentanol/brine system. In this part of the phase diagram we find a line of maximum turbidity where the scattered intensity shows a very sharp maximum and has a pure Ornstein Zernicke q -dependence. These features are not consistent with what is expected close to the symmetric asymmetric transition line. We question the possibility of the spontaneous tearing of the membrane first considered on theoretical grounds by Huse and Leibler (*Phys. Rev. Lett.* **66** (1991) 437).

Introduction.

It is now well established that, in some easy to provide experimental conditions, amphiphilic molecules prefer to self assemble into sheet like structures (rather than small micelles or flexible rods) even in dilute mixtures [1]. As a matter of fact, the so-called swollen lamellar phase L_α and the anomalous isotropic phase L₃ correspond to situations where the 2D aggregation process leads to the formation of very large (presumably infinite) bilayers having different large scale arrangements in space. L_α shows smectic order and consists of a regular stack of parallel infinite bilayers. In contrast, L₃ is not long range ordered and the topology of the bilayers is multiconnected along the three directions of space over macroscopic distances [2, 3] (see Fig. 1).

These phases have received much attention in the recent years and it seems well admitted that their relative stability and physical properties are monitored by the bending elasticity of the fluid membranes [4] :

$$E_{el} = \int_A \left[\frac{1}{2} K (c_1 + c_2)^2 + \bar{K} c_1 c_2 \right] dA \quad (1)$$

(*) (UA 233 CNRS).

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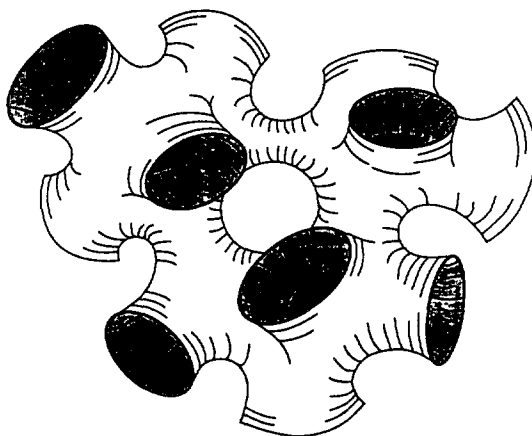


Fig. 1. — Schematic picture of the multiconnected structure of L_3 .

where c_1 and c_2 are two principal curvatures of the area element dA of membrane, K and \bar{K} the mean and Gaussian rigidity moduli and the integration is carried over the total area of membrane A . Note that the bilayer is here intrinsically symmetrical with respect to its mid surface : it is built up of two chemically identical monolayers stuck opposite to each other and being in contact with the same solvent on both sides of the membrane. Therefore the spontaneous curvature of the membrane is identically zero and does not appear in (1). In the moderate dilution range, the domains of stability of L_α and L_3 are roughly parallel to dilution lines and it has been proposed [5] that the phase transformation is mainly controlled by \bar{K} : according to the Gauss-Bonnet theorem, \bar{K} essentially acts as the chemical potential of the topological complexity of the membrane's connectivity. At higher dilution, however, the $L_\alpha \rightarrow L_3$ phase transition actually occurs upon decreasing the concentration. In this range, the transition is thought to be driven by the thermal curvature fluctuations which increase upon dilution [6, 7] : K is then the leading control parameter.

Anyway, both L_α and L_3 consist of presumably infinite membranes. And the question arises of what happens at extreme dilution since we know that certainly the structures should end up into a random dispersion of small vesicles and/or micelles : at some stage, the dispersion entropy of disconnected pieces *must* overcompensate the cohesion energy of the infinite membranes. At the present time, two different scenarii can be sketched to describe the structural transformation from infinite bilayers to disconnected subunits. The first one is naturally derived from the pioneering work of Roux *et al.* [8] on the symmetry of the L_3 phase. The second one has been discussed by Huse and Leibler in a recent article [9].

As stated just above, the bilayers in these systems show an intrinsic local symmetry with respect to changing the sign of their normal. This symmetry is indeed reflected by the invariance of the elastic Hamiltonian (1) upon changing the signs of both c_1 and c_2 . Provided that the bilayer is assumed free of rims and seams, it separates space into two and only two disconnected subvolumes. The intrinsic symmetry of the membrane implies, in general, that the two subvolumes are statistically identical on a global scale. However this global statistical symmetry may break spontaneously upon dilution [8-10]. There is presently experimental evidence that this symmetry breaking is continuous (second order) in some cases [10]. Moreover, the order parameter η associated with the symmetry must be coupled quadratically to the internal variable ρ ($= C - \bar{C}$) related to the local concentration C of the membranes (coupling term of the form $\rho \eta^2$) in the symmetric L_3 structure. The

quadratic coupling $\rho \eta^2$ has a noticeable consequence on the q -dependence of the structure factor $I(q)$. In the Gaussian approximation (valid far from critical conditions), the following expression has been obtained [8] :

$$I(q) = A + B [\tan^{-1}(q\xi_\eta/2)/(q\xi_\eta/2)] \quad (2)$$

where ξ_η is the correlation length of the order parameter η . The A term in (2) corresponds to the fluctuations of ρ at constant η while, on the other hand, the B term corresponds to the fluctuations of ρ that are mediated by those of η . Such a unique scattering behavior has been observed experimentally [10, 11] (light scattering) for several systems and supports this idea of a hidden symmetry of sponge phases.

Within this picture and starting from the symmetric ($\bar{\eta} = 0$) L₃, the spontaneous symmetry breaking should occur upon dilution below some critical concentration C_c . Just below C_c , the asymmetric L₃ structure still consists of an infinite membrane multiconnected isotropically in space. But further increase of the dilution disconnects more and more the structure which becomes increasingly asymmetric. Below some particular value C_p , the infinite cluster (membranes) no longer persists and the structure ends up into disconnected closed vesicles randomly distributed in space. This second transition at C_p is presumably not a thermodynamical transition but a geometrical connectivity transition.

However [8, 9], the very idea of the global symmetry only makes sense for surfaces totally free of « holes ». Actually, the excess free energy involved in forming holes can be characterized by a line tension λ (— i.e. the free energy per unit length of an edge forced on the membrane). At high λ , holes are scarce and small. The idea of the symmetry then persists since one can replace by continuity the real membrane by an ideal surface with no defects : the labelling of the two subvolumes therefore remains unambiguous. At lower λ however, the number density and the average contour length of the edge loops increase. Even more, below some critical value λ_c the configurational entropy of large loops overcompensates the energy price to be paid in increasing their size. The transition at λ_c is similar to the polymerization transition in systems of equilibrium loops which has been predicted and shown to be Ising like [12, 13]. At λ_c , the membrane is still infinite but bears infinite edges : this structure, Huse and Leibler called it the « sponge with free edges » (SFE) [9]. Clearly, the idea of the global symmetry has no relevance for such a structure since the initial subvolumes are now highly connected. At still lower λ , the edges proliferate more and more so that below some particular value λ_p the infinite cluster is killed off and the structure ends up in disconnected pieces of membranes (ultimately micelles). Here again, the connectivity transition at λ_p is geometrical rather than thermodynamical.

So, from these pictures, the structural transformation from the infinite membrane (L₃) to disconnected pieces (either vesicles and/or micelles in L₁) can occur along two distinct processes : either spontaneous breaking of the statistical symmetry of L₃ or spontaneous proliferation of edges on the membrane.

We investigate here the dilute part of the phase diagram of the system Na-octylbenzenesulfonate (OBS)/n-pentanol/brine (0.5 M NaCl). We use two techniques : light scattering which probes the thermal concentration (ρ) fluctuations and conductivity which probes the obstruction opposed by the structure to the mobility of the small free ions. A line of maximum turbidity (LMT) can be defined in the dilute range where the scattered intensity at zero wavevector $I(0)$ exhibits a sharp maximum when plotted *versus* the pentanol/OBS ratio at constant C . This line has very much the same geometry as that reported for a different system [10, 14, 15]. This sharp peak indeed suggests some critical behavior, so we have undertaken a systematic investigation of the static light scattering patterns ($I(0)$ and q -dependence) close to this LMT. Along some part of the LMT at least, the general behavior exhibits features that are

not compatible with those expected close to the S/AS transition line. We argue that these observations indicate that another transition takes place here which might be the transition to the sponge with free edges (SFE).

The experimental facts are reported in section 1. We discuss the nature of the transitions together with the detailed geometry of the phase diagram in section 2.

1. General phase behavior and experimental facts.

Phases of fluid membranes are commonly observed in the dilute range in the phase diagram of systems consisting of ionic surfactant, n-alcohol and brine. At constant temperature and salinity of the brine solvent, the phase behavior can be represented along the two independent composition variables : the volume fraction of the ionic surfactant C_S and that of the n-alcohol C_A . Since most of the surfactant and alcohol are involved in building up the primary structures (micelles or bilayers), C_A/C_S represents essentially their chemical composition while $C = C_A + C_S$ rather represents the volume fraction of the objects. Three phases generally appear successively at moderate dilutions (typically $0.02 < C < 0.2$) upon increasing C_A/C_S : the micellar phase L_1 , the lamellar phase L_α and finally the sponge phase L_3 . At such moderate dilutions, the phase sequence is mainly monitored by C_A/C_S and remains quite insensitive to C [5]. At high dilution however (typically $C < 0.01$) things go differently and one encounters two different cases. For some systems [5, 11], both L_α and L_3 stop swelling at some stage and coexist with excess brine containing presumably a very low concentration of small micelles and/or vesicles : a first order phase transition (with phase separation) thus occurs upon diluting the sponge phase of these systems. For other more interesting systems [10, 14, 15], only L_α stops swelling, the L_3 domain being connected continuously to the lower L_1 domain around the dilute end of L_α . The system investigated here, as well as the system SDS/n-pentanol/brine investigated in [10, 14, 15], actually behaves in this way (Fig. 2). The very dilute isotropic region connecting L_3 to L_1 is where the structural transformation from infinite membranes to small disconnected subunits is expected to take place continuously.

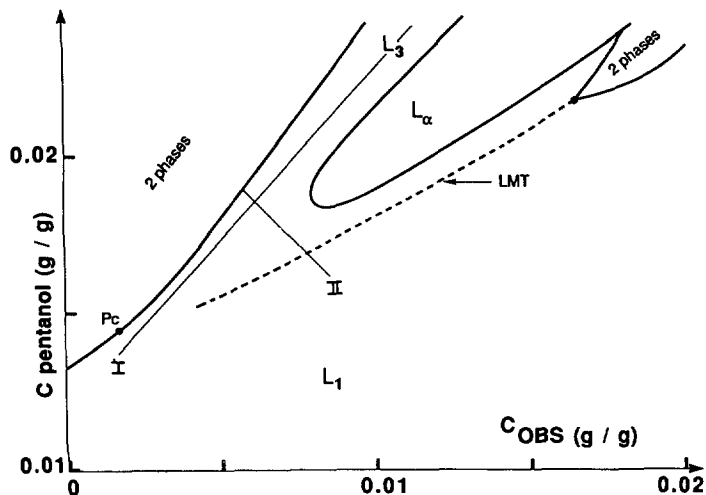


Fig. 2. — Very dilute part of the phase diagram of the system OBS/n-pentanol/brine. Line I (dilution line) and II are represented.

The upper phase boundary is a coexistence curve with a critical point $C_A = 0.014$, $C_S = 0.0017$) denoted P_c . Above that line, the sample phase separates into two isotropic L₃ phases of different concentrations. The position of the critical point P_c is here determined by optical observation of many samples with compositions close to the coexistence curve: we demand that the « critical sample » phase separates upon a small temperature variation (+ 0.2 °C) in two almost identical L₃ phases (almost identical turbidity) of equal volumes. At relatively higher C 's and below the coexistence curve, we find the quite narrow domain of L₃ which, as we shall see, is here symmetrical. This narrow domain, squeezed in between the coexistence line and L_α, actually extends very far towards high C (at least up to $C = 0.25$ where L₃ merges into the large « L₂ » domain) far off the limited part of the diagram represented in figure 3. Upon decreasing C_A/C_S , one first meets the biphasic L_α/L₃ and then enters L_α. L_α stops swelling at $C_S = 0.008$. Below this concentration, the isotropic domain of L₃ merges into the broad L₁ (micellar domain) at lower C_A/C_S . hence there is clearly a continuous path connecting the fully grown L₃ structure (infinite membrane) to the micellar dispersion in L₁ close to the horizontal axis. The full line drawn across this region of interest is the line of maximum turbidity (LMT). In the present article, we investigate its vicinity using light scattering and we compare our observations with those reported in [10, 15] for the system SDS/n-pentanol/brine. In some cases, the light scattering data are complemented with conductivity measurements.

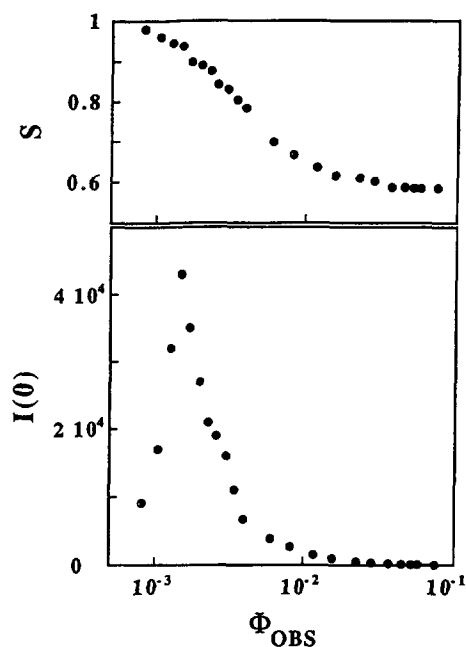


Fig. 3. — Osmotic compressibility $I(0)$ and obstruction factor S as function of $\log C_{OBS}$ along the dilution line I .

For the sake of consistency in the evaluation of the osmotic compressibility ($I(0)$ intensity at zero q) in different parts of the phase diagram, $I(0)$ is obtained by fitting $I(q)$ with the universal asymptotic form :

$$I(q) = \frac{I(0)}{1 + aq^2 + bq^4 + cq^6}. \quad (3)$$

On the other hand, when our purpose was rather to interpret the q -dependence of $I(q)$ in terms of the density-density correlation function, we have used the following more specific expressions :

i) the classical Ornstein Zernicke form :

$$I(q) = I(0)/(1 + q^2 \xi_\rho^2) \quad (4)$$

which holds when the direct ρ fluctuations (correlation length ξ_ρ) dominate the scattering.

ii) the general expression

$$I(q) = \frac{A}{(1 + q^2 \xi_\rho^2)} + \frac{B}{(1 + q^2 \xi_\rho^2)^2} \cdot \frac{\tan^{-1} q \xi_\eta/2}{q \xi_\eta/2} \quad (5)$$

first computed by Coulon *et al.* [10] for the case where both the direct ρ fluctuations (A term) and those mediated by the η fluctuations (B term) bring significant contributions to the scattering. More precisely (5) is obtained in the Gaussian approximation [10] and generalizes (2) to the cases where ξ_ρ is not negligible in the investigated q -range.

We have first investigated the scattering behavior of the sponge phase along a dilution line (line I on the phase diagram of Fig. 2) extending all through the domain of existence of L_3 ($0.001 < C_{OBS} < 0.1$). Note that such a line necessarily comes close to P_c at high dilution. As shown in figure 3, the evolution of the osmotic compressibility $I(0)$ shows a sharp maximum about $C_{OBS} = 0.0017$ when the line comes closest to P_c . Qualitatively, this behavior is quite similar to that reported in [10] for the other system. But an important difference is revealed when investigating the q dependence of the light scattered by samples having compositions close to that of P_c . As an example, figure 4 shows the scattering pattern of a sample standing on the dilution line with a composition ($C_{OBS} = 0.0024$) close to the critical composition ($C_{OBS} = 0.0017$). For such samples, the classical OZ expression actually provides a very good fit of the q -dependence. This suggests that, close to P_c , the direct ρ fluctuations totally dominate the scattering. This feature is just opposite to what was reported [10] in the case of the other system for which the fluctuations of η were shown to diverge when approaching P_c along similar dilution lines.

Our observations therefore suggest (see discussion in next section) that the scattering behavior at low concentration along the dilution line is strongly influenced by the existence of the nearby critical point P_c standing on the coexistence line. On the other hand, close to P_c , the q -dependences are so steep (Fig. 4) that extrapolating $I(q)$ to zero q provides a very inaccurate estimate of $I(0)$. And it is hazardous to study the critical behavior around P_c under such conditions. So, in order to get rid of this influence, we have investigated the scattering behavior close to the LMT but far from P_c along directions normal to dilution lines (i.e. varying C_A/C_S at constant $C = C_A + C_S$).

The variations of $I(0)$ versus C_A/C_S along such a line (line II in Fig. 2) are shown in figures 5 and 6. We observe a sharp maximum at the LMT where the osmotic compressibility seems to diverge. Such steep variations of $I(0)$ well inside the monophasic domain indeed suggest that some critical phenomenon takes place at the LMT. However, the $I(0)$ evolution shows two characteristic features : i) a quite strong asymmetry : the scattered intensity which is maximum at the LMT drops faster on the alcohol poor side than on the alcohol rich side ; ii) $I(0)$ does not truly diverge at the LMT but rather levels off at a quite high but finite value.

These features are also observed at constant C_A and C_{OBS} when one rather uses the salinity of the brine solvent as the monitoring parameter. Figure 7 represents the variations of $I(0)$ versus salinity for samples with constant $C_A = 0.010$ and $C_{OBS} = 0.0184$. Again we observe a quite sharp maximum having nevertheless a finite value ($I(0)_{max} \sim 10^4$ times the

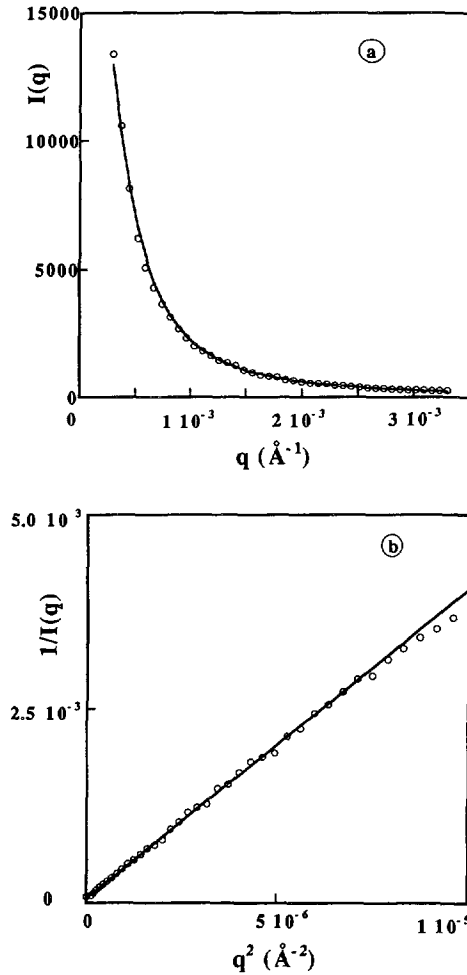


Fig. 4. — a) Scattering pattern $I(q)$ of the sample ($C_{\text{OBS}} = 0.0024$ g/g and $C_A = 0.0147$ g/g) close to the critical point P_c . Full line corresponds to the best fit with the OZ form. b) Same data but using the appropriate coordinates ($1/I(q)$ versus q^2) emphasizing possible deviations beyond OZ. Note that OZ gives an excellent fit of the data.

intensity scattered by the reference benzene sample), and the evolution clearly shows some asymmetry. We otherwise checked (data not represented here) that the existence of the sharp maximum persists on a very large part of the LMT and not only close to one given point of it.

Also the q dependences deserve some careful attention. As expected from previous studies of the symmetric sponge phases [8, 11], the q dependence of the intensity scattered by samples far from critical conditions (i.e. far from both the critical point P_c and from the LMT) is not well fitted by the usual OZ expression. Figure 8 shows an example of such a sample which belongs to line II but far from the LMT on the alcohol rich side : clearly the OZ expression fails to provide an accurate fit of the measured q dependence. On the other hand, a much better fit is obtained in figure 9 for the same data but using expression (5) which means that far from critical conditions both the direct ρ fluctuations and those of η actually bring significant contributions to the scattered light. Upon approaching the LMT on the alcohol rich side, the picture changes progressively : the contribution of the direct ρ fluctuations becomes more and

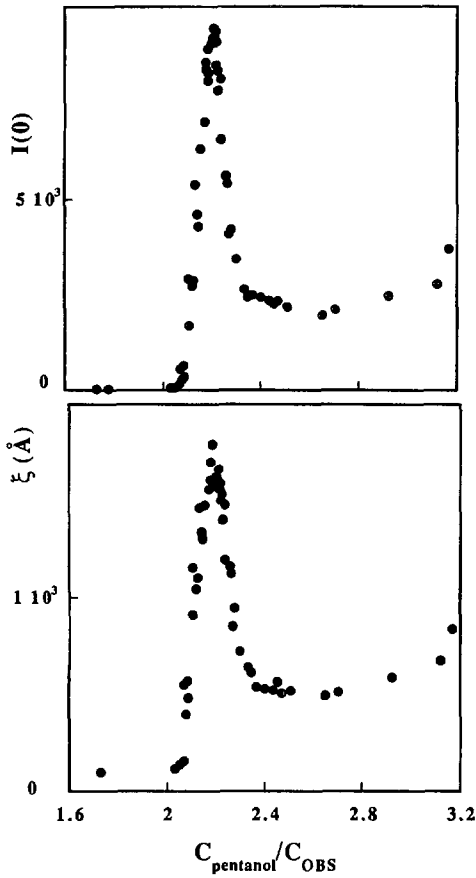


Fig. 5.

Fig. 5. — $I(0)$ versus C_A/C_{OBS} (g/g) along line II. And ξ_p (correlation length as derived from the a coefficient of q^2 in (3)) along the same line.

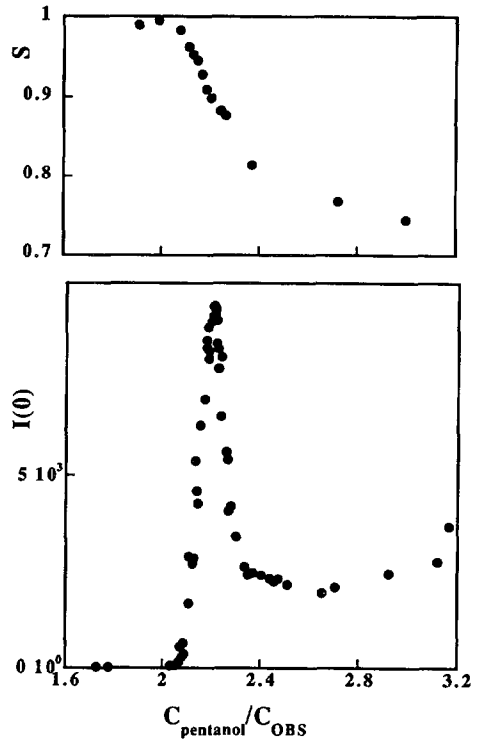


Fig. 6.

Fig. 6. — Obstruction factor S versus C_A/C_{OBS} (g/g) along line II. And $I(0)$ versus C_A/C_{OBS} along line II. Note that S keeps a smooth evolution at the point where $I(0)$ has its sharp maximum.

more dominant. So that, finally, in the critical region, close to the LMT but still on the alcohol rich side, extremely good fits are obtained for the q dependence with the OZ expression. An example of such a pure OZ q -dependence, observed in the critical region in the symmetric sponge side of the LMT, is shown in figure 10.

At lower C_A/C_{OBS} , on the alcohol poor side of the LMT, the q -dependence changes again. As shown in the example of figure 11, we again observe significant deviations from the pure OZ q -dependence. However these deviations are quite different from those observed in the symmetric sponge far from the LMT (see Fig. 8 for a comparison) and we could not obtain a good fit of figure 12 using (5) as we did in the former case of figure 9.

Conductivity data are also reported in figures 3 and 6. They are expressed in terms of the obstruction factor S opposed by the membranes to the mobility of the small ions :

$$S = \frac{\sigma}{\sigma_0} \left(\frac{1}{1 - C} \right)$$

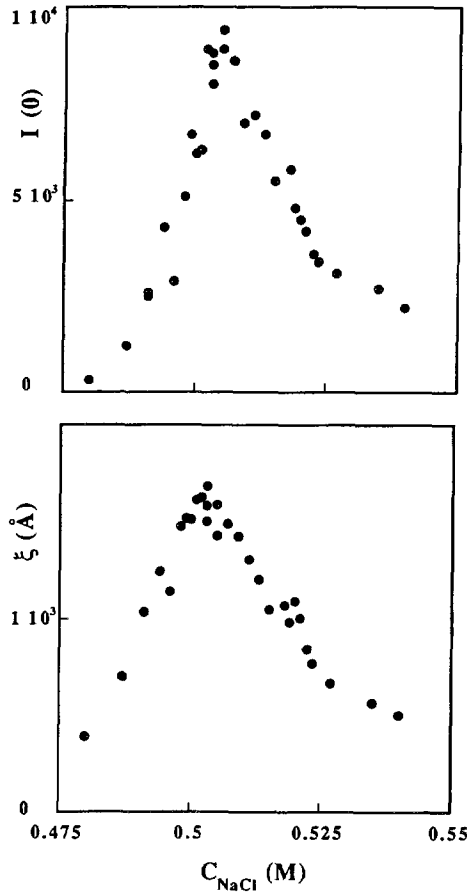


Fig. 7. — $I(0)$ and ξ_p versus salinity for samples having a fixed composition $C_{\text{OBS}} = 0.010$ g/g, $C_A = 0.0184$ g/g.

where σ and σ_0 are the conductivities of the solution and the brine solvent, respectively. $1/(1 - C)$ is here introduced as a correction factor accounting for the fact that the total volume of membrane does not contribute to the conductivity of the mixture. In the symmetrical L₃ phase at moderate concentration, the obstruction factor is generally found to be independent of C and close to 0.6 [2, 3]. This quite universal value is believed to be a characteristic feature of *symmetrical bicontinuous structures*. Within this frame work we interpret any significant increase of S beyond 0.6 as related to some departure from this description. A deviation from exact symmetry corresponds to a decrease of the area of membrane per unit cell of the multiconnected structure and therefore to an increase of the mobility of the free ions. By symmetry we expect this effect to be indeed quadratic in η :

$$S - 0.6 = \Delta S \sim \bar{\eta}^2 \quad (6)$$

On the other hand, the spontaneous proliferation of holes on the membrane makes it more permeable to the free ions and therefore also increases S .

Actually, the value 0.6 is found in the moderate concentration range ($C_{\text{OBS}} > 0.01$) in figure 3. At higher dilution, however, significant increases of S are observed. Interestingly,

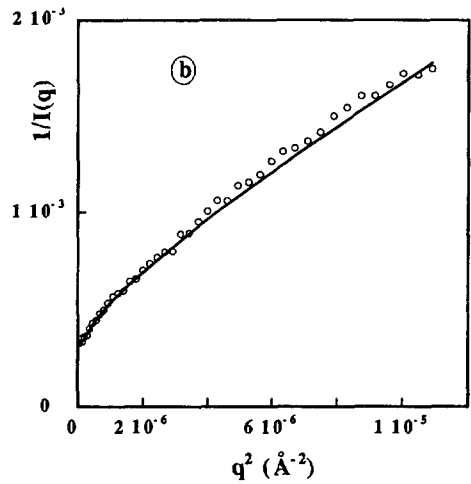
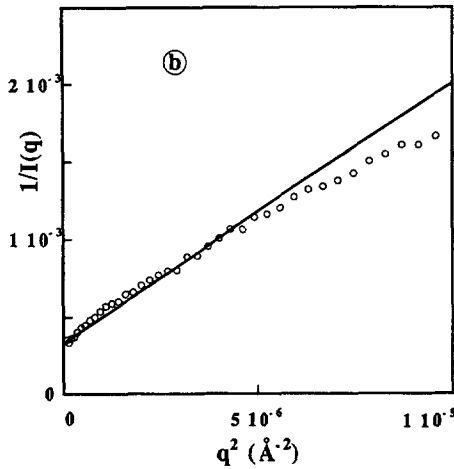
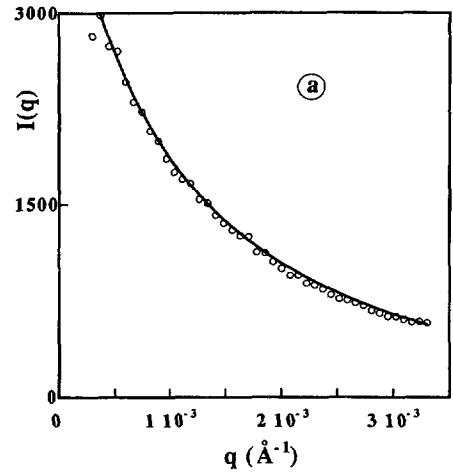
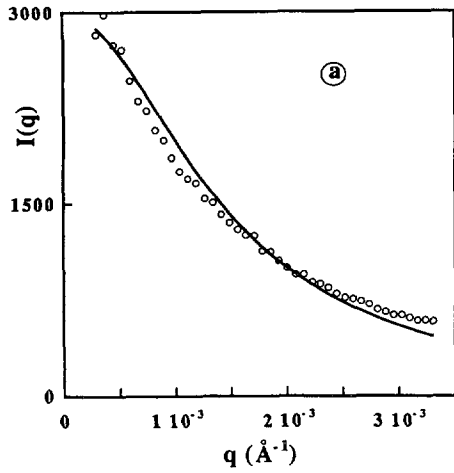


Fig. 8.

Fig. 9.

Fig. 8. — Scattering pattern of a sample on line II but far from the LMT: $C_{\text{OBS}} = 0.0063$ g/g $C_A = 0.019$ g/g. a) $I(q)$ versus q : full line correspond to the best fit with OZ; b) $1/I(q)$ versus q^2 : the straight line emphasizes the strong deviations beyond OZ.

Fig. 9. — Same data as in figure 8 but fitted with the complete expression (5). Note that the fit is much better. We obtain: $A = 986$ and $B = 2670$; $\xi_\rho = 327$ Å and $\xi_\eta = 5636$ Å.

these deviations become appreciable somewhat below $C_{\text{OBS}} = 10^{-2}$ but still quite far above the concentration ($C_{\text{OBS}} = 0.0017$) where $I(0)$ diverges. Since there is no reason to invoke a proliferation of holes at such high C_A/C_{OBS} (see next section), the deviation in S more likely reveals significant increase of $\bar{\eta}^2$. This suggests that, below $C_{\text{OBS}} \cong 10^{-2}$, the dilution line I comes close to the S/AS transition line and ultimately crosses it at a concentration significantly higher than that of P_c . But quite puzzling, in this picture, is the absence of any sharp accident in the C dependence of $I(0)$ (Fig. 3) at this 2nd order transition concentration: the most we can see in figure 3 in the corresponding concentration range ($0.0017 < C_{\text{OBS}} < 10^{-2}$) is a slight shoulder visible on the $I(0)$ decay versus C_{OBS} .

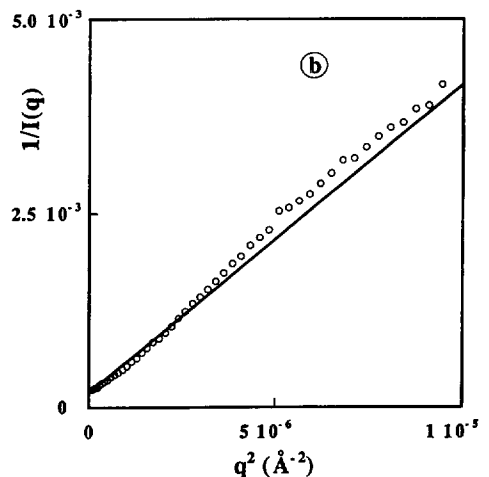
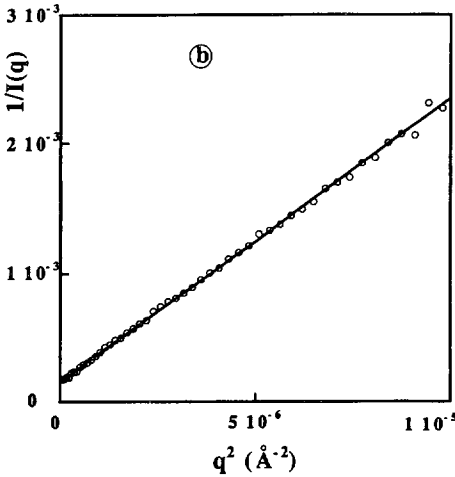
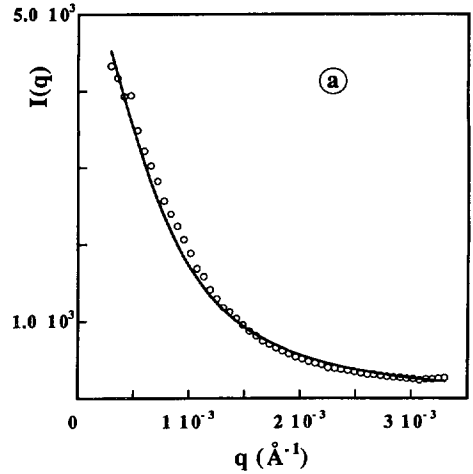
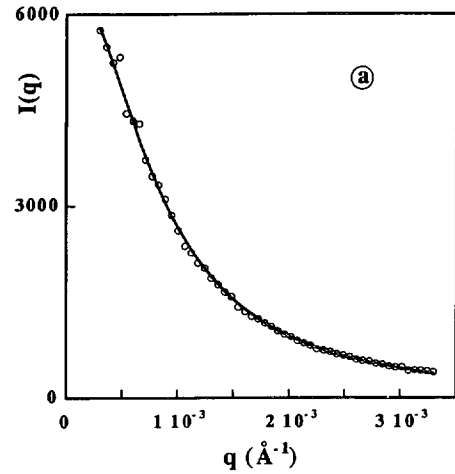


Fig. 10.

Fig. 11.

Fig. 10. — Scattering pattern of a sample on line II close to the LMT on the alcohol rich side. $C_{OBS} = 0.0076$ and $C_A = 0.0173$. a) $I(q)$ versus q and best fit with OZ. b) $1/I(q)$ versus q^2 . Note that OZ provides an excellent fit.

Fig. 11. — Scattering pattern of a sample on line II close to the LMT but on the alcohol poor side. $C_{OBS} = 0.0078$ and $C_A = 0.0169$. a) $I(q)$ versus q and best fit with OZ; b) $1/I(q)$ versus q^2 . Note that some deviation from OZ is appreciable.

Along lines III, S also shows smooth sigmoidal variations (Fig. 6). We discuss these conductivity data together with the light scattering patterns in the next section.

2. Discussion.

The most intriguing findings reported in the experimental section are related to the light scattering behavior close to the LMT but far from P_c . They can be summed up as follows :

- a sharp maximum (but not a true divergence) is seen for $I(0)$ at the LMT *far inside the one phase domain* ;

- the $I(0)$ evolution is asymmetric ;
- $I(q)$ is of the OZ form on the alcohol rich side of the LMT ;
- while it shows significant deviations from the OZ form of the alcohol poor side.

We note that these features are not specific of our system : a very similar behavior has been reported in [14] for another system.

Let us discuss first the experimental observations obtained along the dilution line (line I) which comes close to the critical point P_c . Indeed, the sharp maximum of $I(0)$ suggests that the dilution line crosses through a 2nd order transition line.

Actually, a qualitatively similar behavior, reported in [10, 15] for the system SDS/pentanol/brine, has been interpreted by the authors as the signature of the S/AS transition. This picture was, for this system [10, 15], further supported by the evolution of the q -dependences : accurate fits were in fact obtained using expression (5) and ξ_η was found to diverge as well as $I(0)$. However, there was one puzzling difficulty in this picture where the critical fluctuations of η ultimately drives the divergence of $I(0)$. The η fluctuations have in principle no direct effect on the light scattered which is only sensitive to the ρ (density) fluctuations. Nevertheless, since ρ and η are certainly coupled, fluctuations of η have an effect on those of ρ : in that sense, light scattering is indirectly sensitive to the η fluctuations. However, as discussed at length in [8], the exact symmetry of the membrane elasticity (1) with respect to changing the sign of the curvature implies that the free energy density of sponge must be invariant upon changing the sign of η . The lowest order term in the free energy that couples η and ρ must therefore be of the form $\rho \eta^2$ (quadratic coupling). A particular consequence of such quadratic coupling is that the contribution in $\langle \rho(0) \rho(r) \rangle$ that arises from the η fluctuations is of the form of the « energy-energy » correlation function. Then, at an *ordinary S/AS critical point*, the indirect contribution of the η fluctuations should only induce a *very weak specific heat singularity of $I(0)$* [16, 17] in contrast with what was observed in [10, 15] along the dilution line. In this context, the only way to interpret the existence of a strong divergence is to assume that the investigated dilution line crosses the S/AS transition line at a point which is *close to a tricritical point* : in this case, the quartic term (η^4 term) in the free energy density is zero, the « energy-energy » correlation function is thus computed in the Gaussian approximation leading to a steep divergence (while for an ordinary critical point the existence of a non-zero quartic term makes the singularity very weak). Finally, the data obtained in [10] for the system SDS/pentanol/brine were interpreted in [15] according to this picture of the dilution line crossing the S/AS transition line close to a tricritical point.

In spite of the qualitative similarities between our present observations and those of [10], some quantitative differences exist which make the latter interpretation not appropriate for our case. The main difference here is that the closer the sample to the divergence point, the more accurate the fit of $I(q)$ with the classical OZ expression. This feature is not compatible with a tricritical behavior for which a q^{-1} (rather than q^{-2}) q dependence should be observed. Therefore, if we keep the picture where the maximum of $I(0)$ is related to the S/AS critical line, we cannot explain the steep divergence observed. Another plausible picture can be proposed which seems to fit our observations better : the maximum of $I(0)$ could be not related to a S/AS second order transition but simply to the fact that the dilution line comes close to an *ordinary liquid gas critical point* at P_c . This idea is consistent with the fact that the maximum of $I(0)$ takes place where the dilution line comes closest to P_c . If P_c is an ordinary critical point related to the « liquid gas » phase separation at the coexistence curve, the direct ρ fluctuations are expected to dominate and ultimately diverge in its vicinity : it is therefore natural that the OZ expression effectively fits the scattering pattern close to P_c .

The question arises in this context about where does the S/AS transition expected upon

dilution actually take place. Since P_c behaves as an ordinary critical point, the S/AS transition does not take place in its immediate vicinity (if it did this would imply a tricritical behavior for P_c). Interestingly, the conductivity data in figure 3a indicate that the obstruction factor S starts increasing significantly at concentrations quite large compared to that of P_c ($C \gg 0.0017$). Assuming that strong variations of S actually reveal strong variations of $\bar{\eta}^2$ (see (6)), this behavior suggests that the S/AS second order transition actually occurs upon dilution long before reaching the vicinity of P_c (about $C_{OBS} \sim 10^{-2}$). Then, the absence of any clear signature of this transition in light scattering (Fig. 3b) is probably due to the fact that far from « tricritical conditions » only a very weak singularity is expected for $I(0)$ at this transition : such a very weak singularity might well be totally hidden in the $I(0)$ strong variations when approaching the liquid gas ordinary critical point P_c . So finally the special features of the critical behavior observed in our system along the dilution line can be qualitatively rationalized assuming a different scenario from the one proposed by the authors of [15] for their system. Actually, these differences in behavior are probably not so much a matter of systems but rather of experimental conditions. The phase diagram in figure 2 represents only part of the total phase behavior of the system since it corresponds to a fixed temperature and to a given salinity of the brine solvent. Following Roux *et al.* in [15], we believe that choosing a different section of the total phase behavior (different temperature and/or salinity) might well bring P_c closer to a tricritical point : we would then have observed a behavior similar to that of the other system in [10, 15]. And conversely, other experimental conditions would drive the SDS system to a behavior similar to that reported here for the OBS system.

Let us now consider the behavior close to the LMT but far from P_c (line II). Again we do observe a strong maximum of $I(0)$ with steep decays on both sides, but in a region of the phase diagram that stands *far from any « liquid gas » coexistence line*. This behavior is then much more difficult to understand here than along the dilution line. As mentioned above, S/AS critical fluctuations can drive a strong $I(0)$ singularity only if the critical line comes into close vicinity of a tricritical point. But a tricritical point necessarily stands on the coexistence line (or more precisely on the coexistence surface), and there is very little chance that the tricritical conditions could pertain so deep into the one phase domain. This guess is further supported by the fact that close to the LMT (but on the alcohol rich side) good fits of $S(q)$ are obtained with the OZq^{-2} dependence (while tricritical fluctuations would imply q^{-1}). Clearly, the light scattering behavior observed at the LMT does not correspond to a tricritical situation. Then, for the S/AS transition we would expect a very weak singularity for $I(0)$ with a dissymmetry which is just opposite to what we observe in figures 5 and 7 : it is well-known [18] that the specific heat in the Ising model shows a very asymmetric profil having a higher level below T_c i.e. on the ordered asymmetric side of the transition. Therefore, the LMT here does not correspond to S/AS transition line. But now the interpretation proposed for the singularity observed on the dilution line (i.e. direct ρ fluctuations due to the vicinity of the ordinary critical point P_c) is here no more appropriate because the region of interest is too far from P_c .

Another possibility one could think of is that the LMT corresponds to a *different critical line* the order parameter m of which is linearly (rather than quadratically) coupled to the membrane density ρ . In this picture, the $\langle \rho \rho \rangle$ correlation function (or more precisely that part of it which is mediated by the m fluctuations) would be simply proportional to $\langle mm \rangle$: $I(0)$ would therefore diverge at the transition line with the same exponent as the susceptibility of m and its q dependence would simply be the same as that of $\langle m_q m_{-q} \rangle$ -i.e. of the OZ form.

So assuming a linear coupling between ρ and m would explain both the strong divergence of $I(0)$ and the OZ character of the q dependence of $I(q)$. However, such a coupling implies that the membrane concentration $\langle \rho \rangle$ acts as a « magnetic field » for the transition. This should

mean that to have a true critical point (with a true divergence) not only the quadratic coefficient of m must be zero but the surfactant density must be turned so to make the « field » zero as well [19]. This would imply that in general one should not observe a « line of second order » transition on the phase diagram, but only one isolated critical point where the surfactant concentration happens to be just right for the « field » to vanish. Apart from that particular point, the « field » has a finite value and its main effect would be to make round the singularity of the transition [20]. The fact that the maximum of $I(0)$ at the LMT is rounded, in our experimental observations might well be reminiscent of such a « finite field » arising from a linear coupling between m and ρ . However, the persistence of the maximum along substantial part of the LMT indicates that this coupling remains weak.

Following these lines, we now consider the possibility that the LMT far from ρ_c corresponds to the « spontaneous tearing of the membrane » i.e. to the S/SFE transition line. Hereafter, we first note that this idea is well supported by simple considerations on the spontaneous curvature of the amphiphilic film. We then discuss how the critical proliferation of edges couples to the membrane density fluctuations in order to evaluate whether the « tearing » scenario agrees with the experimental features or not.

It has been stressed many times that a basic role of the alcohol/surfactant ratio is to monitor the spontaneous curvature c_0 of the amphiphilic monolayer [5, 21-23] : the higher C_A/C_{OBS} , the lower c_0 . The local conformation of the amphiphilic molecules in an edge involves a very high local curvature for the monolayer. Therefore, the line tension λ of the edges is lower at higher c_0 — i.e. at lower C_A/C_{OBS} . In that sense, the alcohol/surfactant ratio monitors the line tension λ . Then, if we identify the LMT with the critical line of spontaneous tearing of the membrane, its position in the phase diagram of figure 2 seems natural : starting at high C_A/C_{OBS} in the symmetric sponge, the line tension λ decreases upon decreasing C_A/C_{OBS} and the critical proliferation of edges occurs at the particular C_A/C_{OBS} value where λ reaches its critical value λ_c . Consistently with this picture, there is experimental evidence [24] that at very low C_A/C_{OBS} (close to the horizontal axis of the diagram in Fig. 2) the amphiphile ultimately itself assembles into small globular micelles (small hydrodynamic radius measured by quasi-elastic light scattering) where the local curvature of the surfactant is indeed very strong.

The S/SFE transition from the symmetric sponge to the sponge with free edges is considered by Huse et Leibler as driven by the proliferation of larger and larger closed loops edges. A transition of the same type has been formerly studied in the context of reversible polymerisation [12, 13] and it was shown to belong to the Ising universality class. The order parameter m is related to the concentration of large (infinite) loops present in the ordered phase (more precisely, the product hm is well defined where a small magnetic field h is coupled to the order parameter m). On the other hand, Huse and Leibler [9] have considered the S/SFE transition in the context of the Z_2 lattice gauge model [25] which can describe both the S/AS and the S/SFE transitions. It is built up in the following way.

Consider a simple cubic lattice. Label the elementary cubes with indices i . The plaquette separating cubes i and j is denoted ij . Put Ising gauge field $U_{ij} = \pm 1$ on each plaquette. The plaquette ij is occupied by the surface if $U_{ij} = -1$. The link shared by cubes i, j, k, ℓ has an edge on it if an odd number of the four adjacent plaquettes are occupied by the surface so that $U_{ij} U_{jk} U_{k\ell} U_{\ell i} = -1$. The appropriate action in terms of this field is then :

$$H = -\mu \sum_{ij} U_{ij} - \lambda \sum_{\langle ijkl \rangle} U_{ij} U_{jk} U_{k\ell} U_{\ell i} \quad (7)$$

where the sums run over all plaquettes and links, respectively. This model simply contains both the surface chemical potential μ and the edge chemical potential λ . Two limits of the

model can be mapped directly onto the Ising model : the pure S/AS transition ($\lambda = \infty$, no edges) and a special case of the S/SFE transition ($\mu = 0$).

For other values of the chemical potentials, little is known apart from some Monte Carlo simulations [26]. In the two just above mentioned limits of the model, it can be shown that, for *both transitions*, the low q density density correlation function represented by the surface-surface correlation function should show *weak* specific heat singularities. This means that in the context of this model (and in the $\mu = 0$ pure limit) the S/SFE transition should have a static light scattering signature (weak singularity) essentially similar to that of the S/AS transition. And it seems therefore that identifying the LMT with the critical proliferation of edges does not help us in the interpretation of our scattering data. However the lattice gauge model, in its simplest form, shows some artificialities. It does permit « seam » like defects with the same local energy as a simple edge defect (Fig. 12). Moreover, in the $\mu = 0$ limit, H in (7) is totally invariant upon changing the signs of all U_{ij} . Doing so, one changes all the « edges » of one given configuration into « seams » and conversely. This means that, in this $\mu = 0$ limit, « edges » and « seams » have identical statistical distributions. This is in contrast with the actual physical situation where edges and seams correspond to opposite local curvatures for the surfactant monolayer (Fig. 12) : so when c_0 (or C_A/C_{OBS}) is turned to make the line tension of edges smaller, it symmetrically makes that of the seams larger. Therefore, the respective line tensions of edges and seams have opposite variations *versus* C_A/C_{OBS} and they will not become critical simultaneously. So, in order to make the model more realistic, one should at least introduce in (7) additional local terms allowing edges and seams to have independent energies. One could for instance use a term of the form :

$$\frac{\lambda_A}{4} \sum (1 - U_{ij} U_{jk} U_{kl} U_{li})(U_{ij} + U_{jk} + U_{kl} + U_{li}) \quad (8)$$

where λ_A is the difference in line tensions between edges and seams. Introducing (8) into (7) indeed makes the analysis of the statistical problem much more difficult even in the $\mu = 0$ limit. And, at the present time, we do not know how to compute directly the critical behavior of this refined model. One nevertheless notes that the additional term (8) brings in a contribution having the form of the product of plaquette terms and edge terms — i.e. a linear coupling between the local density of membrane and the local density of edges. However we must keep in mind that the density of edges is *not* the order parameter m of the S/SFE

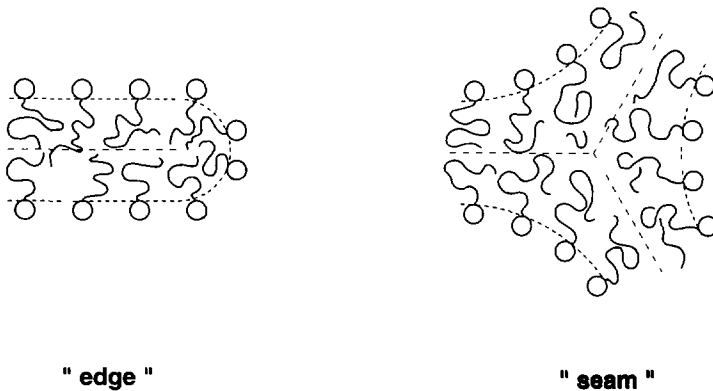


Fig. 12. — Schematic picture of the internal structure. a) Of an « edge ». b) Of a « seam ».

transition. Therefore the linear coupling between edge and membrane densities at the level of the Hamiltonian (7) + (8) does not necessarily imply a linear coupling between m and ρ in the effective Landau free energy $f(\rho, m)$ describing the S/SFE transition. So, it is not clear at the present time whether the additional term (8) will suffice to introduce the $m\rho$ linear coupling which could explain the observed scattering behavior. Although this does not seem unrealistic, it remains to be checked carefully.

In conclusion, our experimental results prove that the LMT far from P_c does not correspond to the S/AS line of second order transition. The alternative possibility is discussed just above that it could rather correspond to the S/SFE transition first considered on theoretical grounds by Huse and Leibler. This scheme is strongly suggested by the general phase behavior of ternary amphiphilic systems which has proved that both the salinity and the alcohol to surfactant ratio have strong effects on the spontaneous curvature c_0 of the surfactant film. Then it seems natural that these externally tunable parameters actually monitor the line tension of the edges, and ultimately trigger the S/SFE transition. However, in its initial simplified version, the gauge field model used by Huse and Leibler is not able to explain the observed scattering behavior close to the LMT. A more realistic version of this model should involve at least one extra term allowing « edges » and « seams » to have different line tensions. Detailed Monte Carlo simulations remain to be performed to check whether the more realistic model agrees with the features of the scattering behavior. On the experimental side, the presence of high densities of edge defects should be evidenced by small angle neutron scattering. An experimental investigation on this point is under current progress.

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