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Classification

Physics Abstracts

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L_α to L_3 : a topology driven transition in phases of infinite fluid membranes

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Résumé. — La structure de la « phase isotrope anormale » L_3 du système cétalpyridinium chlorure/hexanol/eau salée est discutée à partir de données de diffusion de neutrons. A l'échelle locale, l'élément de base est la même bicouche que dans la phase lamellaire gonflée L_α voisine. A plus grande échelle, les données suggèrent une topologie bicontinue où la bicouche infinie sépare deux domaines eau salée équivalents imbriqués l'un dans l'autre. On propose que la transformation de structure de L_α à L_3 est principalement contrôlée par la valeur du module de rigidité de courbure gaussienne \bar{K} , \bar{K} étant déterminé par la courbe spontanée de chaque monocouche constituant la bicouche. Ce mécanisme plausible est confronté au comportement de phase du système ainsi qu'à l'étude en diffusion de lumière de la phase L_3 en fonction de la dilution.

Abstract. — The structure of the anomalous isotropic phase L_3 in the system cetylpyridinium chloride/hexanol/brine is discussed on the basis of neutron scattering data. On a local scale, the basic building unit is the same bilayer as in the neighbouring swollen lamellar phase L_α . On a larger scale, the data suggest a bicontinuous topology where the infinite bilayer separates two interwoven equivalent self connected brine domains. It is argued that the L_α to L_3 structural transformation is mainly triggered by variations of the saddle splay rigidity \bar{K} of the bilayer, \bar{K} being determined by the spontaneous curvature of each constituting monolayer. This plausible mechanism is checked against the general phase behavior of the system and additional light scattering data collected in the L_3 phase at various dilutions.

Introduction.

In the recent years, increasing attention has suddenly been focused on diluted phases consisting of infinite bilayers dispersed in large amounts of brine (or eventually oil) in surfactant systems [1-7]. A particular opportunity of these phases is that the bilayers are fluid bidimensional objects having an internal structure symmetric with respect to their mid-surface. Therefore, they bear no spontaneous curvature and the most general expression for their bending elasticity takes the very simple form [8] :

$$E_{\text{bilayer}} = \frac{1}{2} Kc^2 + \bar{K}g . \quad (1)$$

In (1) E_{bilayer} is the density of elastic energy (per unit area). c and g are respectively the local mean and Gaussian curvatures :

$$c = \frac{1}{R_1} + \frac{1}{R_2} ; \quad g = \frac{1}{R_1 R_2}$$

where R_1 and R_2 are the two principal radii of curvature. K and \bar{K} are the bending rigidity moduli respectively associated to the mean and Gaussian curvatures. K thus expresses the resistance to spherical splays and \bar{K} is associated to the energy cost involved in saddle like deformations.

At the present time, two different diluted phases have been well characterized as consisting of bilayers. The first one is indeed the well known lamellar phase (L_α) which consists of a regular stack of parallel bilayers (smectic order). In some interesting cases [2-4], L_α can be swollen enormously by appropriate addition of solvent (water or brine). The average interlayer distance \bar{d} can so be made very much larger than the thickness d_0 of the bilayers. In the high dilution regime, it has been shown that the properties of the phase are basically determined by the so-called steric interaction between membranes [9]. This interaction arises from the steric hindrance to the spontaneous bending fluctuations of a given membrane induced by the presence of the adjacent bilayers. The corresponding free energy per unit area of membrane has been derived by Helfrich [9] :

$$\left(\frac{\Delta F_{\text{st}}}{A} \right) = a_0 \frac{k_B T}{K \bar{d}^2} \quad (2)$$

where a_0 is a numerical constant of order 1.

Interestingly, K is alone involved in [2] but not \bar{K} . This is directly related to the Gauss Bonnet theorem which states that the integral of the Gaussian curvature over a given structure only depends on its topological type. In a lamellar phase, each fluctuating bilayer keeps the topological type of a flat plane. The contribution of the Gaussian term in (1) for the lamellar stacking remains therefore constant all along the swelling process and \bar{K} has no incidence on the physical properties of the phase.

The later phase has been investigated in some details only recently [5-7]. It is usually called the « anomalous isotropic phase » (L_3). It is commonly encountered in many systems amongst which non ionic surfactant/water binary systems, ionic surfactant/alcohol/brine ternary systems and also brine rich or oil rich microemulsions. It is optically isotropic at rest but exhibits striking streaming birefringence upon gentle shaking. In the most interesting cases, it can be swollen enormously just like the neighbouring L_α phase [4, 5].

In a recent article [6], a modified version of the well known model of de Gennes and Taupin [10] for microemulsions has been developed in order to describe the structure and the physical properties of L_3 . The structure is there pictured as a connected random surface, the basic idea being that, upon dilution, the ordered L_α phase should melt at some stage into a phase with a higher symmetry (more disordered). In this approach K remains the main control parameter, little attention being paid to \bar{K} .

The purpose of the present article is to propose a different description of the L_α to L_3 phase transformation where the triggering quantity is rather the Gaussian curvature rigidity modulus \bar{K} . In order to settle our approach on experimental grounds, we briefly recall in section 1 the phase behavior of the system cetylpyridinium chloride/n-hexanol/brine (0.2 M NaCl) as reported in more details in [5]. The scattering data, collected for the L_3 phase, strongly suggests a topology similar to this of the « molten cubic » model first proposed

by Scriven [11] to describe the structure of bicontinuous microemulsions. The topological genus — i.e. — average density of « handles » per unit volume — of such a structure varies quickly with the dilution. \bar{K} is therefore expected to play a significant role in the physical properties of the phase.

Following reference [12], we relate in section 2 the Gaussian rigidity \bar{K} of the bilayer to the spontaneous curvature c_0 of each constituting surfactant monolayer and thus obtain a simple explanation of the relative positions of L_α and L_3 in the phase diagram of our system.

In section 3, a general scaling law for the free energy of phases consisting of one self connected single bilayer is worked out. Its main implication on the osmotic compressibility of the L_3 phase is then checked against additional light scattering data.

1. Phase behavior and structure

The system CPCl/hexanol/brine (0.2 M NaCl) has been presented in details in previous articles [5, 13-15]. It is a quasi-ternary system — i.e. the brine can be considered as a single component at least in the diluted phases of interest here ($\phi_w > 0.8$ where ϕ_w is the volume fraction of the brine). For such systems, the phase behavior is usually examined within the conventional triangular representation. Here, it is more illustrative to use rather the representation of figure 1 for the diluted part of the phase diagram : the horizontal axis being the volume fraction ϕ of surfactant + alcohol ($\phi = 1 - \phi_w$) and the vertical axis being the alcohol to surfactant ratio in the solution (ϕ_A/ϕ_S). In this representation the phase boundaries approximately correspond to horizontal straight lines over quite a large range of dilution $0.02 < (1 - \phi_w) < 0.2$. This indicates that in the dilute regime, *the phase transformations are mainly triggered by the variations of ϕ_A/ϕ_S and are quite insensitive to the degree of dilution ϕ_w* . The phase sequence taking place while ϕ_A/ϕ_S increases is quite rich.

First, one meets the L_1 micellar phase. Within this phase, a neutron scattering investigation [5] has shown that the micelles undergo a globule to rod shape transformation when ϕ_A/ϕ_S increases.

For intermediate values of ϕ_A/ϕ_S , we find the domain of stability of the swollen lamellar phase L_α . The neutron scattering study performed with well oriented samples has shown that it consists of parallel bilayers bearing no noticeable density of structural defects such as pores,

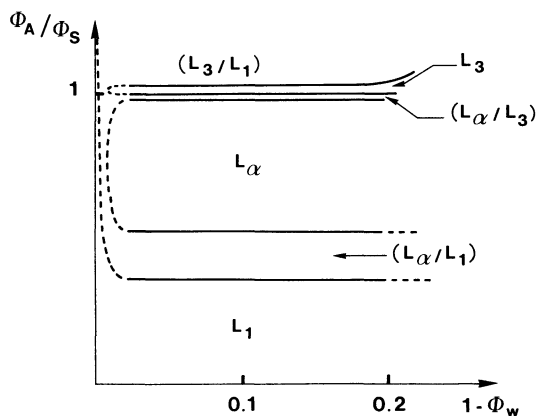


Fig. 1. — Brine rich part of the phase diagram of the system CPCl/hexanol/brine (0.2 M/NaCl). The phase behavior of very diluted samples ($\phi_w > 0.98$) is hardly observable : dotted lines.

fractures or passages. Its swelling behavior upon dilution as revealed by the variation of the Bragg maximum position q_B versus ϕ_w :

$$q_B = \frac{2\pi}{d_0} (1 - \phi_w) \quad (3)$$

is regular indicating an apparent thickness d_0 for the bilayer ($d_0 = 26.5 \text{ \AA}$) independent of the dilution ϕ_w .

The L_3 phase (denoted L_2^* in [5]) of interest here, takes place beyond the L_α phase within a very thin range for the ϕ_A/ϕ_S ratio. On the other hand, it extends over a very large range of dilution in the ϕ direction. Below its lower phase boundary L_3 coexists with L_α , the biphasic region being extremely thin. Beyond the upper phase boundary, L_3 collapses and shrinks spontaneously expelling excess brine (L_3/L_1 biphasic domain). L_3 being stable against dilution for the appropriate ϕ_A/ϕ_S ratio, its swelling behavior can be readily investigated just like that of the L_α phase. Neutron scattering data have been collected over a very large q -range so that the different characteristic lengths of the structure can be evidenced.

The typical scattering profiles obtained (Fig. 2) exhibit a low q broad maximum at q_c followed by a long decreasing tail at higher q . The quantitative analysis (in absolute units) of the high q decay showed that *on a local scale* the structure consists of bilayers of thickness $d_0 \approx 25 \text{ \AA}$ (very similar to d_0 in the L_α phase) with random orientations. On the other hand, the position q_c of the broad maximum at lower q , is of the same order of magnitude as this of the Bragg wave vector in L_α at the same dilution. q_c can therefore be interpreted as the signature of the average distance \bar{d} between the bilayers in the L_3 structure : $q_c = 2\pi/\bar{d}$.

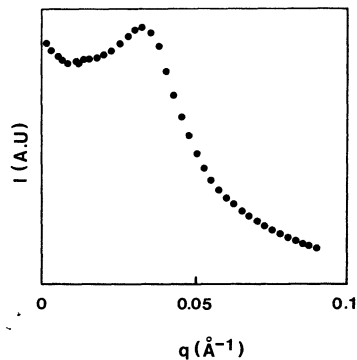


Fig. 2. — Typical neutron scattering pattern of a L_3 sample : $\phi = 0.156$.

The variation of q_c versus ϕ (Fig. 3) is linear over a full order of magnitude for the dilution :

$$q_c = \frac{2\pi}{\alpha d_0} (1 - \phi_w) \quad \text{with} \quad \alpha = 1.4 \pm 0.1. \quad (4)$$

But, in contrast with L_α , the numerical constant α involved is close to 1.5 (α is indeed 1 in L_α). As discussed in details in [5], the swelling relation is closely related to the average *topology* of the investigated phase (α being a measure of the average degree of connection between small brine domains of side \bar{d} in the mixture). In contrast with other topologies, bicontinuous structures where one single infinite bilayer, self connected throughout the

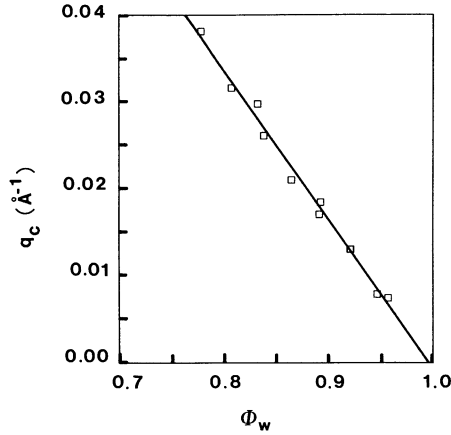


Fig. 3. — Swelling behavior of L_3 : q_c versus ϕ_w .

sample, separates two equivalent self connected interwoven brine domains were found consistent with the actual value of α (1.5). As an illustrative example of such a topology, the classical Schwartz periodic minimal surface is very often presented [11] (Fig. 4). Indeed we do not mean that L_3 presents such a well ordered cubic structure. Actually, the scattering pattern (Fig. 2) rather indicates a strongly fluctuating structure with no long range order. However, the schematic drawing of figure 4 helps to visualize two essential features of bicontinuous structures.

i) Everywhere the two principal radii of curvature have similar magnitudes but opposite signs. The mean curvature of the bilayer is therefore *everywhere*, and not only on the average, weak ($c \ll \bar{d}^{-1}$). It is even exactly zero for periodic minimal surfaces.

ii) On the other hand, the Gaussian curvature has almost everywhere a high magnitude and a negative sign ($g \approx -\bar{d}^{-2}$).

As a direct consequence, the *mean* curvature contributions to the elastic energies involved on one side in the lamellar structure and on the other side in the bicontinuous structures are basically comparable. And the main difference between L_α and L_3 then arises from the Gaussian term in (1). A considerable opportunity is brought in by the Gauss Bonnet relation :

$$\int_A g \, dA = 4 \pi (1 - N) \tag{5}$$

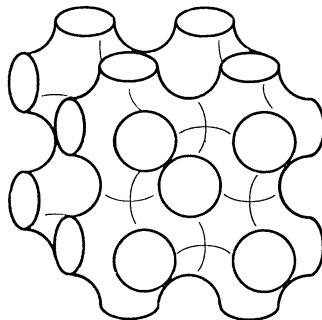


Fig. 4. — Schwartz's primitive periodic minimal surface, with simple cubic symmetry.

for any self connected closed surface of area A and genus N (N is the number of handles or the « holeyness » of the surface). So finally, the difference in elastic energy per unit area between L_α and L_3 is basically of order $-4 \pi \bar{K} n$ where n is the number of handles per unit area of bilayer. We therefore expect that negative values of \bar{K} stabilize L_α while positive \bar{K} 's favor L_3 .

2. Mechanical interpretation of \bar{K} [12].

We here consider separately the two monolayers constituting the complete bilayer. These substructures are asymmetric with respect to their mid surface and are hence expected to bear some spontaneous curvature c_0 . Accordingly, we write their density of elastic energy as :

$$E_{\text{mono}} = \frac{1}{2} K_{\text{mono}} (c - c_0)^2 \quad (6)$$

where we drop out the Gaussian term for the sake of simplicity (but with no loss of generality). As pointed out in a former section, increasing ϕ_A/ϕ_S results into a morphological sequence — i.e. globule \rightarrow rod \rightarrow bilayer — corresponding to decreasing effective curvatures for the monolayer. Accordingly, we assume that ϕ_A/ϕ_S actually controls c_0 . This assumption corresponds to a very general trend in ternary system as revealed from a detailed survey of the current literature [16, 17]. When stuck opposite to each other in the complete bilayer, each monolayer « feels frustrated » [17, 18] for any finite value of c_0 . Using [6] and counting the radii of curvature of each monolayer at a distance ε (of order $1/2 d_0$) from the mid surface Σ of the bilayer (Fig. 5) one obtains :

$$E_{\text{bilayer}} = \frac{1}{2} (2 K_{\text{mono}}) c^2 + (-4 \varepsilon c_0 K_{\text{mono}}) g \quad (7)$$

where c and g for the bilayer are counted at the mid surface Σ .

As a consequence of the frustration of the monolayers, \bar{K}_{bilayer} is found in general finite even when $\bar{K}_{\text{monolayer}}$ is neglected in the starting expression (6) :

$$\bar{K}_{\text{bilayer}} = -4 \varepsilon c_0 K_{\text{mono}} \cdot \quad (8)$$

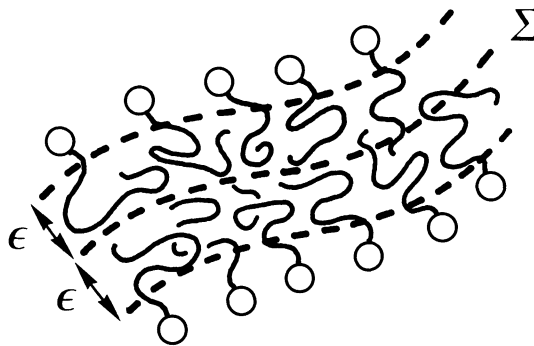


Fig. 5. — Schematic structure of a bilayer. The surfaces of inextention of each monolayer stand at a distance ε ($\approx d_0/2$) of the mid surface Σ of the bilayer.

According to our basic assumption, when ϕ_A/ϕ_S is moderate c_0 is positive : \bar{K}_{bilayer} is negative and stabilizes rather L_α . Increasing ϕ_A/ϕ_S results in a monotonic decrease of c_0 which becomes at some stage negative : \bar{K}_{bilayer} is positive and rather favors L_3 with a high density of handles.

A basically similar interpretation but expressed in more geometrical terms has been proposed by Anderson *et al.* in a very recent article [7].

3. ϕ dependance of the free energy in L_α and L_3 .

To proceed beyond a purely mechanical description and to check the consistency of our approach with the phase behavior exhibited by the real system (Fig. 1), we need reliable scaling laws for the free energies of both L_α and L_3 as a function of the dilution. For L_α , using the expression of Helfrich (2), we immediately obtain :

$$(\Delta F/A)_{L_\alpha} = c_{L_\alpha}(K, T) \cdot \phi^2 \tag{9}$$

where

$$c_{L_\alpha}(K, T) = a_0 \frac{(k_B T)^2}{Kd_0} \tag{10}$$

For the L_3 phase, our argument roughly parallels the derivation proposed by Huse and Leibler [19] for cubic bicontinuous structures with long range order but it is applicable to any self connected surface of given genus with no respect to its eventual order (« presumably » liquid like structure of L_3). We consider a large enough bilayer (thermodynamic limit) of area A , first in a reference state where it is flat on the average and fluctuates freely in the 3D space and then in a final state where its topological genus N is ascribed (Fig. 6). For the sake of concision we denote this system as the 1-system and the free energy variation between its reference and final state as $\Delta F_1(K, \bar{K}, T, N)$. We also consider the λ -system of total area

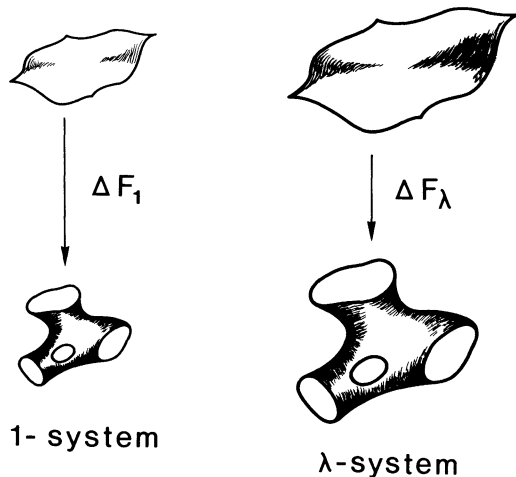


Fig. 6. — The 1-system and the λ -system.

$A_\lambda = \lambda^2 A_1$ in the same reference and final states (same N). Our purpose is to compare ΔF_1 and ΔF_λ . From the Gauss Bonnet theorem we can write :

$$\begin{aligned}\Delta F_1(K, \bar{K}, T, N) &= \Delta F'_1(K, T, N) - 4 \pi \bar{K} N \\ \Delta F_\lambda(K, \bar{K}, T, N) &= \Delta F'_\lambda(K, T, N) - 4 \pi \bar{K} N .\end{aligned}\quad (11)$$

In the final states, N defines the average distances $\bar{d}_1 \cong \sqrt{\frac{A}{N}}$ and $\bar{d}_\lambda \cong \lambda \sqrt{\frac{A}{N}} = \lambda \bar{d}_1$. Following Huse and Leibler [19], we realize that small ripples of wavelength smaller than \bar{d} are basically not affected by the topological change from the reference to the final state : they do not contribute to $\Delta F'$. For larger spatial length scales deformations, we associate to any configuration of the 1-system a « dual » configuration in the λ -system by simple spatial homothety of ratio λ . The mean curvature elastic energy of the given $c_1(\mathbf{r})$ configuration of the 1-system is :

$$E_1(c_1(\mathbf{r})) = \int_{A_1} \frac{1}{2} K c_1^2(\mathbf{r}) dA_1 \quad (12)$$

and for the dual configuration in the λ -system :

$$E_\lambda(c_1(\lambda \mathbf{r})) = \int_{A_\lambda} \frac{1}{2} K c_\lambda^2(\lambda \mathbf{r}) dA_\lambda . \quad (13)$$

Since :

$$c_\lambda(\lambda \mathbf{r}) = c_1(\mathbf{r})/\lambda ; \quad dA_\lambda = \lambda^2 dA_1$$

we have :

$$E_1(c_1(\mathbf{r})) = E_\lambda(c_\lambda(\lambda \mathbf{r})) .$$

Dual configurations have the same elastic energy and hence the same probability of occurrence :

$$\Delta F'_1(K, T, N) = \Delta F'_\lambda(K, T, N) = \Delta F'(K, T, N) \quad (14)$$

where $\Delta F'$ does not depend on λ . Noting, on the other hand, that ΔF is an extensive quantity we get immediately :

$$\Delta F'(K, T, N) \equiv NB(K, T) \quad (15)$$

and finally :

$$\Delta F(K, \bar{K}, T, N) \equiv (B(K, T) - 4 \pi \bar{K}) N . \quad (16)$$

Now, since each handle corresponds to an average area of order d^2 and using relation (4), one derives easily the free energy of L_3 per unit area of bilayer :

$$(\Delta F/A)_{L_3} = \chi (B(K, T) - 4 \pi \bar{K}) \phi^2 \quad (17)$$

where χ depends on the exact structure of L_3 (e.g. for the periodic minimal structure of figure 4 we get $\chi \approx 1/27 d_0$).

Note that the scaling law (17) is only based on the invariance of the elastic energy with respect to simple homothety. (We neglect here the renormalization of K and \bar{K} with the length scale and the approach is valid only for rigid bilayers : $K \gg kT$). As a counterpart of the wide generality of this approach, we cannot obtain the dependance of $B(K, T)$ on K and T . (Actually, we can proceed a little further when noting that K and T appear in the form of their ratio K/T in the partition functions associated to $\Delta F'$. Hence, $B(K, T)$ has the form $TB'(K/T)$. But still, the K/T dependance of B' remains unknown at the present time).

Nevertheless (17) can be checked against experimental facts. From (17), one obtains the scaling law of the osmotic compressibility *versus* the dilution :

$$\left(\frac{\partial \pi}{\partial \phi} \right)^{-1} \sim \phi^{-2} \quad \text{at constant } K, \bar{K} \text{ and } T. \tag{18}$$

The light scattered at very low q ($I(q \rightarrow 0)$) by L_3 should therefore increase dramatically when ϕ decreases :

$$I(q \rightarrow 0) \sim \phi \cdot \left(\frac{\partial \pi}{\partial \phi} \right)^{-1} \sim \phi^{-1}. \tag{19}$$

Figures 7 and 8 represent the light scattering profiles of two L_3 samples ($\phi = 0.183$ and $\phi = 0.0237$). For the more concentrated samples ($\phi > 0.07$, Fig. 7) no appreciable q dependance is observed. On the other hand, for the more diluted samples (Fig. 8), $I(q)$ is peaked towards the low q 's. We here do not try to interpret this feature. But in order to derive consistently the $I(q \rightarrow 0)$ all profiles are fitted to the very general expression :

$$I(q) = \frac{I(q \rightarrow 0)}{1 + aq^2 + bq^4 + \dots} \tag{20}$$

and the obtained $I(q \rightarrow 0)$ are then plotted *versus* ϕ in figure 9. As expected from the model, $I(q \rightarrow 0)$ indeed diverges at high dilution but the exponent is somewhat different from the expected value :

$$I(q \rightarrow 0) \sim \phi^{-\nu}, \quad \nu = 1.3 \pm 0.05. \tag{21}$$

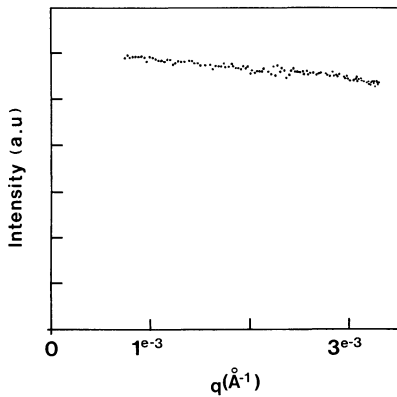


Fig. 7. — Light scattering pattern of a L_3 sample with $\phi = 0.183$.

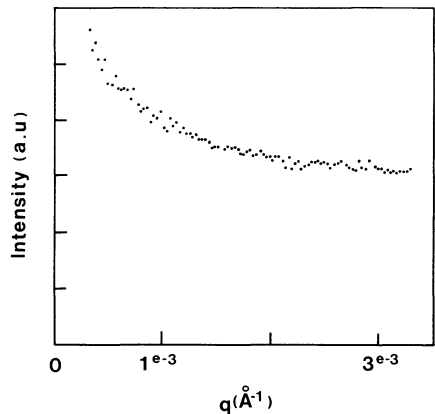


Fig. 8. — Light scattering pattern of a L_3 sample with $\phi = 0.0237$.

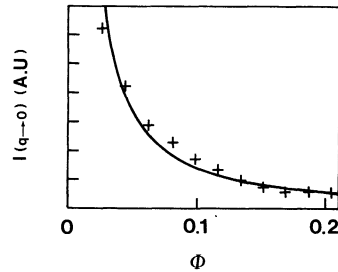


Fig. 9. — $I(q \rightarrow 0)$ versus ϕ in the L_3 phase. The continuous line corresponds to the best fit with a power law : $I \sim \phi^{-\nu}$, $\nu = 1.3$.

However we guess that this deviation is simply related to the divergence of the osmotic compressibility at high dilution. Just like in the vicinity of a critical point, the mean field approach then becomes inappropriate and an Ising like exponent ($\nu = 1.28$) is rather expected.

Comparison of (9) and (17) allows to derive the geometry of the phase boundaries of L_3 in the coordinate system where the horizontal axis corresponds to ϕ variations and the vertical axis to $\bar{K}(\phi_A/\phi_S)$ variations (Fig. 10). Since both expressions scale like ϕ^2 , the phase boundary between L_α and L_3 at constant T and K is a horizontal straight line. On the other hand, when \bar{K} becomes larger than $B(K, T)/4\pi$ the osmotic compressibility of L_3 becomes negative and the structure shrinks spontaneously expelling excess brine solvent. Here again this upper phase boundary of L_3 is a horizontal straight line (as long as we neglect anharmonic terms of higher order in ϕ which are expected to be significant at higher ϕ). So finally, the general geometry of the experimental phase diagram (Fig. 1) around the domain of existence of the L_3 phase finds a quite natural explanation within our approach.

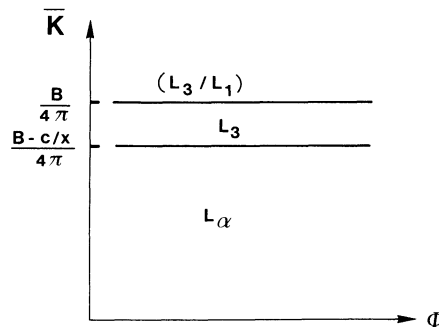


Fig. 10. — Phase behavior of L_3 and L_α as function of ϕ and \bar{K} .

Discussion.

The basic scientific interest of the swollen L_α and L_3 phases is that the characteristic lengths of the structure — i.e. \bar{d} and local radii of curvature — are very large compared to the lengths that are relevant at the molecular level : i.e. the thickness of the bilayer d_0 and the range of the molecular forces. All molecular specificities can thus be included into the phenomenologi-

cally defined curvature elasticity of an equivalent ideally thin surface : (K and \bar{K}). This provides a very safe ground for any attempt of a statistical description of fluctuating surfaces. The model of reference [6] for the L_3 phase is such an attempt.

It is built up according to the following procedure. A simple cubic lattice is drawn with unit cell of size \bar{d} . The cells are then randomly filled up with two fictitious different components A and B with adjustable proportions, and the bilayer is forced to lie at the interface between A and B. Forgetting afterwards the fictitious difference between A and B, one so obtains a « random bidimensional walk » with *no rims*. The next step is then to relate the structural length \bar{d} of the model to the elastic persistence length ξ_K of the flexible bilayer [10]. The driving idea of the model is thus to generalize the classical picture of flexible rods with a given persistence length ξ_R to the case of flexible surfaces. However important differences exist between the unidimensional and the bidimensional cases.

For a flexible thread the rigidity constant K has the dimension the product of an energy by a length. The persistence length ξ_R is therefore very naturally introduced by the ratio :

$$\xi_R = \frac{K}{k_B T}.$$

For flexible surfaces, K and \bar{K} have the dimension an energy. Their ratio with $k_B T$ are pure numbers, and no typical length can be derived readily from the analytical form of the curvature energy. The persistence length ξ_K first introduced intuitively by de Gennes and Taupin must be understood as a consequence of the renormalization of the modulus $K(\ell)$ by the small wavelength bending fluctuations :

$$K(\ell) = K_0 \left(1 - \eta \frac{k_B T}{4 \pi K_0} \ln \left(\frac{\ell}{a} \right) \right) \quad (22)$$

where K_0 is the bare rigidity constant, ℓ is the scale length of observation, η is a numerical constant of order one and a is a length of order a molecular size. This effect is noticeable over reasonable distances ($\ell \approx 10^2 \text{ \AA}$) only for very flexible membranes ($K_0 \approx k_B T$ or less). In the case of our system, this possibility is ruled out by the exceptional stability of the lamellar phase L_α with respect to high dilution [5]. The de Gennes-Taupin persistence length ξ_K

$$\xi_K \approx a \exp \left(4 \pi \frac{K_0}{\eta k_B T} \right) \quad (23)$$

is therefore expected to be very large ($\xi_K \gg 10^3 \text{ \AA}$) while values of order 10^2 \AA are typically measured for \bar{d} in the L_3 phase.

The second difference is related to the definition of the local curvature. In case of a thread, it is defined by one quantity which is the radius of curvature R . The ground state of minimum elastic energy is single and corresponds to the all straight configuration. For a surface, the local curvature is defined by the two quantities R_1 and R_2 . Then, in the particular case where \bar{K} is zero, all configurations with $1/R_1 + 1/R_2 \equiv 0$ correspond to a ground state — i.e. — the plane configuration but also at least all known periodic minimal surfaces (whatever the size of the unit cell). So bicontinuous sponge like structures can occur even with very rigid membranes ($K/k_B T \gg 1$). Closely related to this high level of degeneracy, we expect (at finite temperature) the bilayer to explore randomly all these ground states and to exhibit a liquid like structure with no long range order. But still its local conformation is far from

random since local curvature with R_1 and R_2 having similar magnitude but opposite signs will be strongly favored.

As a consequence of the Gauss Bonnet theorem, \bar{K} acts as a topological chemical potential. Finite values of \bar{K} in fact remove the degeneracy between the plane and the saddle like conformations. Within this frame, the basic difference between the L_α phase and the L_3 phase is not so much the number of accessible configurations gained when melting the smectic order of L_α but rather the respective topological types (« holeyness ») of the two competing structures. In the case of the system investigated here, this point of view is strongly supported by the phase diagram geometry. The L_α to L_3 phase transformation is triggered by ϕ_A/ϕ_S variations and is insensitive to dilution. A natural explanation is here readily provided by considering in a first step the general effect of ϕ_A/ϕ_S on the spontaneous curvature c_0 of the monolayers and by expliciting, in a second step, the relation between c_0 and the Gaussian rigidity \bar{K} of the bilayer.

However, different phase behaviors are sometimes observed with other systems [7, 20]. In particular, the L_α to L_3 phase separation is obtained by increasing the dilution at constant temperature (presumably constant K and \bar{K}) in the case of the $C_{16}EO_3$ /water binary system [20]. For such situations our description indeed does not apply. We therefore guess that a comprehensive approach of L_3 accounting for all known particular situations should involve at least both the renormalization of the rigidities as emphasized in [6] and the topological analysis of the structure as underlined herein. Several regimes are then expected :

i) $-2K < \bar{K} \ll -K$; locally bent conformations with R_1 and R_2 having the same sign are rather favored. At very high dilution, L_α should disrupt directly into a dispersion of vesicles, and a bicontinuous structure should be unstable at all dilutions ;

ii) $\bar{K} = -K$; the elasticity of the bilayer becomes simply :

$$E_{\text{bilayer}} = \frac{1}{2} K \left[\left(\frac{1}{R_1} \right)^2 + \left(\frac{1}{R_2} \right)^2 \right]. \quad (24)$$

The probability of a given local conformation only depends on the magnitude of R_1 and R_2 but not on their relative signs. The modelization of L_3 as a « random bidimensional walk » is then consistent and the prediction of [6] that L_3 replaces L_α at very high dilutions should be valid in this particular case ;

iii) $\bar{K} \gg -K$; beyond some particular (presumably positive) value of \bar{K} , L_3 takes place at all dilutions rather than L_α . But saddle like local conformations are strongly favored and the structure of L_3 is now far from totally random. This is the situation investigated here.

In conclusion, the most distinctive property of infinite non intersecting fluid films is their ability to accommodate various conformations having *different topologies but similar low (everywhere) mean curvatures*. The basic implications of this property were actually well understood and clearly presented in the pioneering articles of Scriven [11]. In the present article, we simply apply them to the structure and properties of L_3 where the bilayers are known to bear no spontaneous curvature. Thus we obtain a simple explanation of the phase behavior of this model bicontinuous structure.

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