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Transitions between mesophases involving cubic phases in the surfactant-water systems. Epitaxial relations and their consequences in a geometrical framework

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Résumé. — Les phases cubiques dans les systèmes eau/savon sont un exemple tout à fait remarquable d'organisation moléculaire entre liquides. Nous présentons ici une étude de transitions de phases entre elles et d'autres phases de structure beaucoup moins complexe, en montrant comment la structure cubique peut se déduire de celle des autres. Dans la première partie, nous présentons les résultats obtenus pour le système modèle C_{12}EO_{6}/eau, qui offre le cas le plus fréquent de phase cubique bicontinue, de groupe d'espace Ia3d, ainsi que deux transitions vers les phases hexagonale et lamellaire. Des clichés de diffraction des rayons X aux petits angles ont été obtenus pour des échantillons orientés de ces phases, mettant en particulier en évidence les fluctuations des structures observées, par la présence de «diffusions diffuses» entre les réflexions de Bragg. Dans la seconde partie, nous exposons une analyse détaillée des changements de topologie intervenant lors de ces deux transitions, puis discutons des fluctuations pouvant leur être associées, à la lumière des observations précédentes.

Abstract. — In order to approach the fascinating structure of the cubic mesophases, we study phase transitions involving them and another mesophases with simpler structures. In the first part, we give some results obtained in the C_{12}EO_{6}/water binary system, that exhibits the most frequent case of bicontinuous cubic mesophase, with space group Ia3d, and two transitions toward the hexagonal and lamellar mesophases. X-ray scattering experiments and some optical observations in polarized light are presented for oriented single-domains of the mesophases. In the second part, we propose some topological arguments to explain the transformations involved at these two transitions and propose some possible fluctuations associated with them.

Introduction.

The cubic phases found in lyotropic systems (or more generally in liquid crystals) constitute an unusual type of mesophases. They are one of the few examples of 3D periodic arrangements among the great variety of mesophases formed by mesogenic molecules.

The different possible cubic space groups and related structures are, in most cases, established [1]. An important feature of the structures is the connectivity of the two media (water and surfactant). Cubic mesophases are observed at very well defined positions in phase diagrams and are characterized by a narrow range of composition. They appear as
intermediate phases between other phases which have a wider range of stability [2]. Our purpose is to underline how the connectivity of a cubic mesophase depends on that of the neighbouring mesophases.

We restrict ourselves to the most frequent and well known structure: the bicontinuous normal (inverse) cubic mesophase with space group Ia3d, which is located between the lamellar and normal (inverse) hexagonal mesophases in the phase diagrams of binary surfactant-water systems.

Firstly, we report the results of the experimental study of the non-ionic surfactant C_{12}EO_{6}/water system. After that, we discuss the consequences of these results (concentrating on the existence of epitaxial relations between adjacent mesophases) within the framework of the geometry of these structures.

**Experimental.**

The normal cubic mesophase appears between the normal hexagonal and lamellar mesophases in the C_{12}EO_{6}/water binary phase diagram (Fig. 1) [3]. We propose that the phase behaviour of this surfactant system can be generally applied to other similar systems, as the phase behaviour is independent of the actual chemical structure of the surfactant molecule. A non-ionic surfactant is of important practical interest for these studies. It allows us to obtain phase transitions as a function of temperature rather than as a function of composition, as would be the case for ionic surfactants. Narrow biphasic regions separate stability domains of two neighbouring phases, showing that the transitions are first order.

We recall that a hexagonal mesophase consists of parallel cylinders of surfactant molecules, separated by water, arranged with respect to a hexagonal 2D lattice perpendicular to their axis. A lamellar mesophase is a periodic stacking of bilayers of surfactant molecules separated by water layers.

![Phase diagram](image-url)
EPITAXIAL RELATIONS AT MESOPHASE TRANSITIONS. — We take advantage of the existence of epitaxial relations occurring at the two transitions which are studied: the hexagonal/cubic and lamellar/cubic. These relations were first established by Rançon and Charvolin [4] using the small angle X-ray scattering technique and can be summarized as follows:

\[
\begin{align*}
\text{Hexagonal} & & \text{Cubic} & & \text{Lamellar} \\
\{ \text{N director} & \rightarrow \rightarrow \{111\} \text{ direction} \\
\{ \text{Cylinder axis} & \\
\{ \text{dense planes} & \rightarrow \rightarrow \{(211)\} \text{ planes} \rightarrow \rightarrow \text{lamellar planes} \\
\{ \{(10)\} \text{ planes} & \\
\end{align*}
\]

This shows that two adjacent mesophases are always strongly related: a cubic mesophase grows with a fixed orientation with respect to a hexagonal one; a lamellar mesophase develops with the lamellar planes perpendicular to a [211] direction of the cubic mesophase.

We will now illustrate some of these relations in the case of the hexagonal/cubic transition.

PRODUCTION OF ORIENTED SAMPLES OF THE HEXAGONAL MESOPHASE. — In order to obtain an oriented domain of the hexagonal mesophase, we use rectangular glass capillary tubes with a thickness not exceeding 0.2 mm. Rançon and Charvolin [4] have used a slightly different configuration made up of two coaxial cylindrical capillary tubes. The flat faces of the rectangular tube induce an alignment of the cylinders of surfactant molecules: the dense planes of the hexagonal packing of the cylinders are oriented parallel to the faces. The director \( N \) of the mesophase (along the cylinders) is also parallel to the faces and is often (but not always) along the axis of the tube. This can be deduced from observation of the sample under the optical microscope using polarized light: textures due to small undulations of the director \( N \) (see [5] for the observations of these undulations in other systems) reveal the mean orientation of \( N \). One observes thin parallel striations perpendicular to \( N \). X-ray scattering also confirms this alignment effect. One obtains single-domain diffraction patterns and verifies the orientation of a family of dense planes along the flat faces of the tube which is in agreement with the optical texture coincidentally observed (Fig. 2).

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**Fig. 2.** — a) The striated texture in a single-domain. The director is perpendicular to the striations; b) The alignment effect in the flat tube configuration.
HEXAGONAL/CUBIC TRANSITION. — The hexagonal to cubic transition appears on slowly heating the sample. Epitaxial relations are tested using X-ray scattering. Superposition of (211) cubic reflections on (10) hexagonal reflections and of a [111] cubic direction on the N direction are confirmed (Fig. 3).

Fig. 3. — a) The reciprocal space of the hexagonal mesophase. (Compare with Fig. 2b); b) X-ray pattern of the hexagonal mesophase showing the plane $P_0$. Note the extensions of the Bragg spots along N; c) Pattern of the same domain during slow heating: one observes the apparition of the cubic reflections; d) Same domain while only the cubic mesophase is present. Note the diffuse lines between the Bragg spots. The pattern show the reflections of the plane $P_0$ (see the indexation of the reflections below); e) Part of the cubic reciprocal space revealing the epitaxial relations. Only the reflections in the plane perpendicular to N are drawn.
Optical observations also give some interesting results on a more macroscopic scale. As only the hexagonal mesophase is birefringent (the cubic mesophase is optically isotropic), it is possible to visualize the shape of the cubic domains growing in an oriented area of the hexagonal mesophase. The birefringence color is directly related to the thickness of the hexagonal phase. So, by noting variations of this color, we are able to observe the decrease of the hexagonal mesophase at the profit of the cubic mesophase. One very striking fact is that the growth of the cubic mesophase is highly favoured along the director N of the hexagonal mesophase (this corresponds to a [111] direction of the cubic structure). On heating, the cubic mesophase develops in strips along this direction across the whole hexagonal domain (Fig. 4).

The cubic regions have crystalline shapes and a precise study shows that the interface between the hexagonal and cubic regions is preferentially a (211) plane of the cubic mesophase or a (10) plane of the hexagonal mesophase.

On cooling, in a cubic single-domain, a hexagonal mesophase grows along the same direction leading to the same crystallographic interface (Fig. 4). But four equivalent [111] directions exist in the cubic symmetry and so four orientations of the hexagonal mesophase are possible. In our flat tube geometry only three are actually observed.

Fig. 4. — a) The growth of the cubic mesophase in a single-domain of the hexagonal. The direction N is an easy growth direction. The interfaces between the two mesophases are (211) planes of the cubic, parallel to the flat faces; b) The growth of small needles of the hexagonal phase in a cubic single-domain. The orientation corresponding to the former alignment effect of the hexagonal mesophase is reinforced and only three different [111] orientations are observed (the last one seems to be prevent by the flat sample geometry).

So we summarize the following properties of the epitaxial structural elements:

<table>
<thead>
<tr>
<th>Hexagonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>N director</td>
<td>[111] direction</td>
</tr>
<tr>
<td>(10) planes</td>
<td>(211) planes</td>
</tr>
<tr>
<td>Anchoring planes</td>
<td></td>
</tr>
<tr>
<td>Interfaces between two mesophases</td>
<td></td>
</tr>
</tbody>
</table>
**Fluctuations in Mesophases.** — We analyze the diffuse scattering present within the X-ray patterns; this is related to defects or fluctuations. Until now, we have emphasized the possibility of observing the transition between single-domains of both mesophases. For this purpose, fluctuations can be neglected as the Bragg spots always remain clearly visible.

Nevertheless, characteristic diffuse scattering sometimes reveals strong fluctuation effects. This is especially true in the case of the cubic mesophase where the diffuse scattering concentrates in lines between the Bragg spots (Fig. 3). In fact, these lines are at the intersections of the film with planes of the reciprocal space. These planes are periodically stacked within four families, defined by their normals along the four [111] directions. This scattering has been interpreted (4 Rançon, thesis) as linear disorder along the [111] directions: along one of these directions, the structure consists of an assembly of parallel identical periodic linear objects with weak correlations of their positions normal to their direction. In terms of dynamic displacements, the movements of the linear objects decompose in transverse waves, with a displacement vector \( \mathbf{u} \) always along the objects and a wave vector \( \mathbf{k} \) perpendicular to them. The periodicity \( d \) of the linear objects equals the inverse of the periodicity of the diffuse planes along the [111] directions that is \( d = 51 \, \text{Å} = a \times \sqrt{3}/4 \) where \( a = 118 \, \text{Å} \) is the cubic lattice parameter. We will come back later to the nature of these linear objects in the cubic structure.

For the hexagonal mesophase, we observe two principal directions of diffuse scattering: extension of the Bragg spots along \( \mathbf{N} \) (Fig. 3), the mesophase director, and, within the reciprocal plane containing the 2D lattice of Bragg spots, another set of diffuse scattering visible between the six first order reflections (Fig. 5). Density fluctuations are absent because

![Fig. 5. — Pattern of the hexagonal mesophase. One observes the diffuse scattering between the six first order reflections.](attachment:image.png)

the diffuse segments are not oriented toward the origin of the reciprocal space. So the elementary fluctuations consist only of transverse waves (and not longitudinal ones). From a dynamic point of view, diffuse scattering along \( \mathbf{N} \) is related to undulations of the cylinders, with wavelengths \( \approx 100 \, \text{Å} \). Over distances smaller than 100 Å (the inverse of the length of the Bragg « spots » along \( \mathbf{N} \)), the cylinders could be considered as perfectly ordered. The scattering in the other direction is due to deformations of the two-dimensional hexagonal packing. These deformations are a superposition of transverse waves in the two-dimensional
array. As X-ray scattering experiments can not differentiate dynamic from static disorder, another interpretation, other than thermal vibrations for this scattering is the existence of distorted regions near defects such as dislocations of the hexagonal 2D array (Fig. 6).

Transitions toward the cubic mesophase: A geometrical approach

THE CUBIC BICONTINUOUS STRUCTURE. — One of the purposes of this study is a better understanding of the fascinating cubic structure. We now give a brief overview of its main features. Maybe the most striking one is the bicontinuity, that is the existence of only two equivalent surfactant media, separated by a water film. Associated with a 3D-periodic property of the structure, the bicontinuity imposes the shape of the water film [6]. It takes the shape of an I.P.M.S. (Infinite Periodic Minimal Surface), that has the properties to divide the space into two equivalent subspaces and to be at the same time periodic and infinite. The space group Ia3d imposes the choice of Schoen’s Gyroid surface. The two subspaces are filled with two 3D-networks of connected surfactant « rods » ([7] see Luzzati’s description). In the Ia3d case, these two 3D-networks are two enantiomers (one D and the other L) and deduce from each other by a symmetry over the origin. They are the two homogeneousst examples of 3-connected periodic 3D-networks: all the rods have equal length and meet three by three at the angle of 120° at planar nodes. One 3D-network also contain closed polygons of rods that are all congruent twisted decagons.

In figure 7, we represent the Gyroid and the two 3D-networks between the corresponding structures of the hexagonal and lamellar mesophases. For instance, the corresponding « water surfaces » are the stacking of parallel planes in the lamellar case and a « honeycomb surface »
in the hexagonal case. So the honeycomb surface is defined by the set of points at equal distances from cylinder axes. Scales and relative orientations are deduced from the epitaxial relations at the transitions.

**Cubic/Hexagonal Transition.** — The aim is to understand how the infinite parallel cylinders of the hexagonal mesophase establish connections between them to create the two 3D-networks of the cubic structure. We have shown that the cubic mesophase develops preferentially along N, the cylinders direction, that transforms into a [111] cubic direction. So we propose a local fluctuation within the hexagonal mesophase that transforms a cylinder as a whole. At the transition, the cylinders transform following two different ways (Fig. 7):

- two thirds of the cylinders become infinite threefold helices, each helix being entirely contained in one of the 3D-networks (all righthanded helices in one of them and the lefthanded in the other one);
- the last third change into a succession of nodes, in turn contained in both 3D-networks. Theses nodes connect three coplanar rods of the 3D-networks. They are normal to the [111] direction and periodically stacked along this direction.

**Fig. 7.** — Projection along a [111] direction of the three structures. H1: The honeycomb water surface. H2: The hexagonal packing of the infinite surfactant cylinders. Each cell of the honeycomb surface contains one cylinder. C1: The Gyroid I.P.M.S. C2: The two 3D-networks of surfactant rods. Inside the dotted lines, the projection of a superposition of 3-connected nodes of both 3D-networks. A triangle is the projection of a threefold infinite helix. L1: The water planes. L2: The surfactant planes. These planes are the dense planes that are continuously preserved at the two transitions.
We will show that the second transformation (Fig. 8) of one third of the cylinders is sufficient to entirely build the cubic structure. Looking at the correlative transformation for the honeycomb surface (Fig. 7) as a cylinder changes into the succession of nodes, one finds that a hexagonal channel becomes a «tower» surface, drawn in figure 8. This «tower» connects in turn three by three the six neighbouring rods at the successive nodes. The topology of this «tower» surface is taken from the Monkey Saddle Tower with \( k = 3 \) introduced by Karcher [8]. By simply «cutting» the Gyroid along a [111] direction around a circuit shown in figure 9, one obtains also the same topology and the result that the whole Gyroid is a juxtaposition of «towers» (Fig. 9), with an adequate shift along the [111] direction between them. For example, a helix is the final state of a cylinder being in turn connected through three «towers». Such cylinders still have the same topology and are as a whole included at the transition in one of the 3D-networks.

![Fig. 8. — The tower fluctuation; a) The «tower» surface; b) The corresponding successive planar nodes of both 3D-networks.](image)

So the succession of nodes (equivalent to the «tower» surface (Fig. 8)) appears to be the relevant topological change. A «tower» surface alone, asymptotically prolonged by six half-planes, separates the space in two equivalent sub-spaces as the Gyroid does. The bicontinuity of the cubic mesophase is already contained in this fluctuation along one cylinder. It also seems in good agreement with the fact that the cylinders direction is an easy growth direction for the cubic mesophase.

Coming back to the interpretation of the disorder observed in the single-domains of the cubic mesophase (see experimental), we find another aspect of the structural importance of these «towers». The linear objects associated with the observed linear disorder we introduced before are indeed these «towers». They are the only linear objects to have the required periodicity along the [111] directions, as the helices have a periodicity two times greater. So we recover that the cubic structure consists of a juxtaposition of «towers» along the four [111] directions. The «towers» are still well defined periodic objects as their juxtaposition is weakly correlated between parallel «towers».
hexagonal  cubic

\[ \text{Fig. 9.} \quad \text{The juxtaposition of the tower surfaces. One hachured region corresponds to one « tower ».} \]
\[ \text{The dotted lines show the limits of the towers for the same projection as in figure 7.} \]

CUBIC/LAMELLAR TRANSITION. — It corresponds to the transformation of the two 3D-networks into a periodic stacking of lamellae, oriented normal to a [211] direction. This orientation of the lamellae is related to the conservation of the dense planes at the mesophase transitions.

In order to understand the involved topological change, we first describe it locally, independently of the detailed symmetry of the cubic structure. So we consider the water I.P.M.S. simply made of water channels related together. Each channel contains one rod belonging to one surfactant 3D-network and is surrounded by a close circuit of rods belonging to the other 3D-network. In the Ia3d case, the channels meet three by three and a close circuit is a decagon of rods (Fig. 10C). If we now introduce the same water channel between two water planes within the lamellar mesophase (Fig. 10), three surfactant planes are involved in this transformation: the water channel creates a connection (= a rod) between the top and bottom lamellae and goes through the lamella in the middle. Then this last lamella contains a closed circuit around the channel and one recovers the same local configuration as in the cubic mesophase.

It is possible to reconstruct the whole cubic structure by introducing water channels in the lamellar structure. Every second lamella is chosen to build one of the two 3D-networks. Each of these lamellae is connected to the two neighbouring ones and contains holes around the water channels that go through it. So a lamella is changed into a 2D-network of rods and the
TRANSITIONS INVOLVING CUBIC MESOPHASES

Fig. 10. — Lamellar/cubic transition; a) Effect of a water channel in the lamellar structure: two surfactant lamellae are connected by a rod through a surfactant lamella in between; b) A water channel; c) Parts of the two cubic 3D-networks around the same water channel. One white rod at the centre is surrounded by a black decagonal closed circuit.

Fig. 11. — The connected hexagonal 2D-networks. Only two planes are represented. The dark links are oriented upwards, starting from the top 2D-network, the medium links join the two 2D-networks together and the light ones are oriented downwards, starting from the bottom 2D-network.

3D-network consists of the superposition of these 2D-networks linked together by transverse rods (Fig. 11).

Wells [9] used the same approach to build 3D-networks starting from 2D-ones. He even did it for the 3D-networks we are interested in (the left and righthanded nets he called (10, 3)-a). They consist of hexagonal 2D-networks linked plane to plane with two connections upwards and two downwards in each hexagon. Each hexagon then transforms into a twisted decagon. As the 2D-networks correspond to (110) planes of the structure, we will briefly show that the same type of construction is also possible with (211) planes, the orientation actually observed
Fig. 12. — The deformation from a planar hexagon with four links (three upwards and one downwards) to a twisted decagon (the same as in Fig. 10c), with all the edges of the same length and all the angles equal 120°.

Fig. 13. — The decagonal 2D-networks along (211) planes; a) The planes of the 2D-networks; b) The shape of these planes as the hexagons become twisted decagons. In this projection, we symbolize a decagon by only two segments; c) The links between the «planes» are drawn in dotted lines. One half of the «planes» are drawn in black, corresponding to one of the two 3D-networks. The two 3D-networks appear and one recovers the projection of the whole cubic structure (see Fig. 7).

at the transition. Along a (211) direction, the 3D-networks also consist of an ABC stacking of 2D hexagonal networks. But each hexagon is connected three times upwards and one time downwards, or on the contrary, and the transverse links between the planes are never normal to them. Figures 11, 12 and 13 show tentative drawings of this.

However, the water channel mechanism for this transition appears as a natural way to create a bicontinuous structure starting from the lamellar one.

To conclude, we mention the R and T mesophases found by Luzzati and coworkers [10] in the anhydrous cationic soaps. These mesophases are indeed examples of superpositions of unconnected 2D-networks, following Well’s procedure. It is interesting to note that such an intermediate case has been observed in such anhydrous lyotropic systems, that also exhibit lamellar, cubic and hexagonal mesophases.
Conclusion.

In this paper, we have described two sorts of effects associated with the phase transitions:
— the fluctuations of structural units in a mesophase like, for example, the linear disorder in the cubic;
— the topological changes involved and their reduction to local connections between objects like rods or lamellae.

The first effects are deduced from the diffuse scattering interpretation and seem to correspond to dynamical fluctuations (see the decomposition in transverse waves). No critical divergences of these fluctuations are observed, as it is expected for first order transitions.

The second ones derive from the structural models of the mesophases and the epitaxial relations. We have shown that the transformation of the whole topology can be decomposed in some elementary and local topological changes — like it occurs for water channels at the lamellar/cubic transition described in figure 10 —, that could be basic microscopic mechanisms for the transitions.

Up to now, we never observed an intermediate state at a transition, that corresponds to the beginning of the topological changes. These changes happen fast and the intensity scattered by the concerned part of the sample is not measurable. An interesting solution could be provided by the millisecond time-resolved X-ray scattering technique developed by Laggner and coworkers [11], in order to obtain information about the kinetics of the transitions.

However, one can imagine that the topological changes result from the increase of specific transverse waves already present in the fluctuation modes and that become correlated together. For example, the formation of the « towers » at the hexagonal/cubic transition could be explained by the helicoidal oscillations of two third of the cylinders, that lead to the formation of the successive planar nodes. And these oscillations are the result of the superposition of three transverse waves with appropriate phase shifts and wavelengths.

Acknowledgments.

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The X-ray experiments were performed in the first stage with a 2D-counter as detector devised by M. Lemonnier, S. Megert and D. Petermann [12].

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