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Periodic systems of frustrated fluid films and « micellar » cubic structures in liquid crystals

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Résumé. — On étudie les configurations ordonnées possibles permettant de résoudre la frustration d'un système périodique de films fluides frustrés, tels que ceux construits par les molécules amphiphiles en présence d'eau, et présentant une topologie cellulaire de type simplement connecté. On montre qu'elles correspondent à des organisations périodiques des milieux aqueux et amphiphile en cellules polyédriques, semblables aux structures de type I et II des clathrates. Les murs de ces cellules supportent un film d'un milieu séparant des micelles finies de l'autre milieu. Cette description est en bon accord avec les structures des phases liquides cristallines de symétries cubiques rencontrées dans certains diagrammes de phases, entre les phases hexagonale et micellaire.

Abstract. — We examine the possible ordered configurations with cellular topology of the simply-connected type, solving the frustration in a periodic system of frustrated fluid films, such as those built by amphiphilic molecules in presence of water. We show that they are periodical organizations of amphiphilic and aqueous media in polyhedral cells, similar to type I and II structures of water clathrates. The walls of these cells support a self-intersecting film of one medium separating finite micelles of the other. This description applies well to liquid crystalline phases with cubic symmetries found in some phase diagrams, in between the hexagonal and micellar phases.

1. Introduction.

In a small number of cases the phase diagrams of amphiphilic molecules in presence of water exhibit liquid crystalline phases with structures of cubic symetries in two distinct concentration domains [1, 2]. An example of such a phase diagram is shown in figure 1.

Structures of cubic phases observed in the immediate vicinity of lamellar phases are now well described. Their space groups are Ia3d or Pn3m in most cases ; perhaps Im3m in some others. They are presented as structures with « bicontinuous » topology, where two congruent, or oppositely congruent, infinite labyrinths of one medium are separated by one intersection-free film of the other [3].

Structures of cubic phases observed in the vicinity of micellar phases are not so well described. Their most probable space groups might be Pm3n, Fd3m or P4₃32 [3]. Two models have been proposed for the structure with the first space group [2, 3], but Fig. 1. — Phase diagram for the dodecyltrimethylammonium chloride/water system, $L\alpha =$ lamellar, $H\alpha =$ hexagonal, M = micellar, $Q\alpha'$ and $Q\alpha'' =$ cubic, from reference [1].

there is no consensus about them, and no description has been proposed for the two last ones.

Because of their different location in the phase diagrams there is no reason for these second cubic

structures to have the same « bicontinuous » topology as the first ones. We might expect instead a cellular or « micellar » topology where an infinite number of finite cells of one medium are separated by an infinite self-intersecting film of the other. Indeed the two models proposed for the structure with space group Pm3n are partly, or totally, built with micelles. They are represented in figure 2. The first one is an infinite cage-like network of rods with



Fig. 2. — The two structures proposed for cubic phase $Q\alpha''$ of space group Pm3n: a) amphiphilic molecules build rods and micelles, the rods are connected 3 by 3 or 4 by 4 and build an infinite network determining cages containing the micelles, from reference [4], b) amphiphilic molecules build identical prolate micelles, the micelles on the black sites are isotropically disordered, those on the white sites are anisotropically disordered around the axes shown in the figure, from reference [6].

enclosed spherical micelles [4]. It has been shown to be incompatible with NMR experiments which were unable to detect the long range translational diffusion of amphiphilic molecules implied by the infinite network [2, 5]. The second one is a cubic packing of identical prolate micelles in either isotropic or anisotropic fast rotations on their respective sites which is compatible with NMR data [2, 6]. However, in spite of this agreement, we can not adopt this latter model immediatly. It proceeds from a formal analogy with the structures proposed for solid γ -O₂, β -F₂ and N₂ and the physics of these molecular crystals may be suspected to be different from that of films and aggregates built by amphiphilic molecules in presence of water.

For these reasons, and in order to get a guide for the building of structural models, we developed our analysis of liquid crystalline structures as assemblies of frustrated fluid films in this case [7, 8]. We recall that, on the basis of this analysis, we recently proposed an approach consisting in the search for the geometrical configurations optimizing the frustration in the films. This approach, which gave account of the topologies of liquid crystalline structures [7] and of the geometries of the structures of cubic phases with « bicontinuous » topology [8], proves to be valid in the present case too, providing ordered geometrical configurations whose properties may agree with the observed ones.

2. Generation of geometrical configurations.

Our approach was presented in references [7, 8] and is just summarized here. Our point of view is that the polymorphism of amphiphilic systems is associated with the set of geometrical configurations which optimize the frustration between forces perpendicular to the interfaces, maintaining them at constant distances, and forces parallel to the interfaces, controlling their curvature, as shown in figure 3. As soon as the interfaces become curved this frustration



Fig. 3. — Schematic representation of the idea of frustration: a) flat interfaces, or equal interfacial and middle area in the film, are compatible with constant distances between them, this is the situation in lamellar phases, b) curved interfaces, or different interfacial and middle area, are not compatible with constant distances between them if the lamellar symmetry is kept, this frustration can be solved by changes of topology and symmetry.

is imposed by the properties of our Euclidean space R_3 . However it can be homogeneously relaxed if the structure is transfered into the curved space with constant positive curvature S_3 , the hypersphere in R_4 . Then, as the structure exists in R_3 not in S_3 , the necessary mapping of S_3 onto R_3 is obtained by introducing the adequate disclinations along the symmetry axes of the relaxed structure in S_3 . This procedure provides the possible configurations of periodically stacked curved interfaces in presence of the spatial constraints of R_3 . It leads to see liquid crystalline structures as structures of disclinations.

2.1 GENERATION OF THE « MICELLAR » TOPOLOGY [7]. — A symmetric film, made of two facing interfaces, supported by a great sphere S_2 of S_3 is a representation of a frustrated lamellar structure whose frustration has been relaxed by the transfer into the curved space. This results from the fact that S_2 separates S_3 in two identical finite subspaces : the interfaces at equal distances from S_2 have area smaller than that of S_2 , so that the frustration is relaxed, and every displacement along a geodesic great circle S_1 normal to S_2 periodically crosses the film and the two media separated by it, so that the periodicity of the system is preserved. This relaxed structure admits C_2 symmetry axes which are great circles of S_2 . The introduction of a disclination along one of these axes brings in a third finite sub-space, as shown in figure 4. The repetition of this process, up to the point where the curvature



Fig. 4. — A disclination along a C_2 axis of S_2 in S_3 (for the sake of clarity only half a sphere S_2 is shown in this stereographic projection of S_3 onto R_3 , and the symmetric film supported by S_2 is not represented) : a) S_2 separates S_3 in two identical sub-spaces, b) S_2 is partly split in two sheets limited by the C_2 axis, c) a third sub-space, identical to the two first, is introduced between the sheets.

of S_3 has decreased to zero, just multiplies the number of identical finite sub-spaces. We get therefore a space-filling packing of identical finite cells which has the required topology, the cells being separated by walls connected along disclination lines which join at vertices. At this stage it is important to notice that the topological stability of the cells implies 'that the walls limiting them meet three by three along common edges which meet four by four at each vertex [9]. We have now everything in hands to search for ordered organizations of these cells and, because of their identity, the first step is the search for eventual space filling assemblies of regular polyhedra, or polytopes.

2.2 SEARCH FOR REGULAR POLYTOPES. — The law of topological stability imposes the search for polytopes having three faces per edge and four edges per vertex or, having three faces belonging to the same polyhedron around one vertex and three polyhedra around one edge. This means, in Schläfli's $\{p, q, r\}$ notation [10], the polytopes of the $\{p, 3, 3\}$ family. They are four which, unfortunately, exist in curved spaces only [11]:

— in spherical spaces with constant positive Gaussian curvatures $\{3, 3, 3\}$, $\{4, 3, 3\}$ and $\{5, 3, 3\}$ — in a hyperbolic space with constant negative curvature $\{6, 3, 3\}$.

As there is no $\{p, 3, 3\}$ polytope in a flat Euclidean space our problem admits no solution with identical regular polyhedral cells [12]. We are therefore driven to search for eventual non-regular but, nevertheless, periodic solutions. For this it is useful to consider the fact that the regular $\{p, 3, 3\}$ polytopes are found in spaces of decreasing curvatures and are therefore met one after the other

during the progressive introduction of disclinations needed to map S_3 onto R_3 . They are met at well defined steps of the process, when the curvature of the space is such that it can be tiled by a $\{p, 3, 3\}$ polytope. In between two steps, when the curvature of the space is not compatible with a regular polytope, the filling of the space can not be regular. This is the situation we shall be confronted with as our Euclidean space R_3 is not compatible with either $\{5, 3, 3\}$, which exists in the spherical space of lowest positive curvature for a $\{p, 3, 3\}$ polytope, or the following polytope $\{6, 3, 3\}$, which exists in a hyperbolic space of negative curvature. Indeed it can be shown, writting the curvature as a function of pand making it equal to zero, that, in R_3 , p =5.1 and is not an integer [13]. If non regular solutions exist in R₃ they should be assemblies of polyhedral cells with an average number of edges per face close to 5.1.

The polytope of interest for us is obviously $\{5, 3, 3\}$ which exists in the space of lowest positive curvature. We must start from it and find the disclination process realizing the final mapping of S_3 onto R_3 which leads to ordered cellular structures.

2.3 Disclinations in $\{5, 3, 3\}$ and non-reg-ULAR PERIODIC CONFIGURATIONS. — This question was previously adressed in the case of clathrate structures of water and silicon-sodium alloys and, in a related manner, in the case of the dual polytope $\{3, 3, 5\}$ to analyse the Frank and Kasper's structures of Laves phases and A15 alloys [14]. It was shown that disclinations normal to pentagonal faces of a dodecahedron transform it into the tetrakaidecahedron and hexakaidecahedron shown in figure 5. These non-regular polyhedra are particularly interesting here as it is known that, when slightly distorted, they can be packed so that they build periodic space-filling assemblies of cells [15]. These assemblies are indeed the organizations of cages trapping host molecules in clathrates of water molecules, the vertices being occupied by oxygen atoms and the edges by hydrogen bonds [16]. Coming back to our problem, these organizations should be those of the film and micelles permitted by



Fig. 5. — Transformation of a dodecahedron (a) into a tetrakaidecahedron (b) by one $-2 \pi/5$ disclination along an axis normal to pentagonal faces and into a hexakaidecahedron (c) by four half disclinations, hexagons created from pentagons by disclinations are hatched.

the properties of our Euclidean space, the film being supported by the faces of the polyhedra and each cage delimited by it containing a micelle. Several structures can be built along the above principle and, among them, we can distinguish two larges families according to the fact that their dihedral and edge angles stay close to 120° and 109° 28' or show departures from these values [16, 17]. If we limit ourselves to the first family, whose angles are the closest to those of fluid films balancing their tensions, we are left with two relatively simple structures. One, type I structure, has space group Pm3n and its crystallographic unit cell contains 2 dodecahedra and 6 tetrakaidecahedra, the local arrangement of its polyhedra being shown in figure 6. The second, type II structure, has space group Fd3m and its



Fig. 6. — Aggregation of distorted 12-hedra and 14-hedra in type I structure, on the right the positions of the 12-hedra (\bullet) and 14-hedra (O) in the cell of the Pm3n lattice, from reference [15].

crystallographic unit cell contains 16 dodecahedra and 8 hexakaidecahedra, the local arrangement of its polyhedra being shown in figure 7. If larger departures from the classical angles of films are accepted, other structures, involving also pentakaidecahedra, are possible [15], they are reviewed in [16].



Fig. 7. — Tetrahedral aggregation of distorted 12-hedra with one 16-hedron in the centre (hatched faces) in type II structure, on the right the positions of the 12-hedra (\bullet) and 16-hedra (O) in the elementary crystallographic cell of volume 1/4 that of the Fd3m lattice, from reference [15].

3. Comparison with observations.

We recall that the failure of NMR spin echo experiments to detect any long range translational diffusion in cubic phases in the vicinity of micellar phases imposed the idea that the aggregates forming these phases are finite with rather limited sizes [2]. We therefore chose to work with the cellular, or « micellar », topology generated in [7] and searched for possible ordered configurations of films and micelles in this case. This investigation led to nonregular periodic cellular structures whose space groups are indeed among those considered as possible for these cubic phases, see the introduction and [3]. If we now focus our attention on structures with space group Pm3n, about which we have the larger set of data, we can try more quantitative tests about the structures of the micelles contained in the cells of type I structure with the same space group.

The first one concerns the mean size of a micelle in type I structure, can it be reasonably compared with the size of one amphiphile ? We shall make this comparison in the case of the system dodecyltrimethylammonium chloride/water which forms a Pm3m cubic phase with parameter 86 Å for a volume concentration of amphiphile of 43 % [4]. If the structure were type I, its unit cell of volume $636\ 000\ \text{\AA}^3$ would contain 2 dodecahedra and 6 tetrakaidecahedra, as each tetrakaidecahedron has a volume equal to 1.2 times that of a dodecahedron because of the very nature of the disclination process the volume of one dodecahedron would be $69\ 000\ \text{\AA}^3$, that of the micelle contained in it 29 000 $Å^3$ and the mean radius of the micelle would be of about 19 Å. This micellar radius compares well with the length of the amphiphile.

The second test concerns the existence of two sites with different symmetries in type I structure; are they detected experimentally? The dodecahedra, of highest symmetry, can be considered as providing an isotropic environment to the micelles; the tetrakaidecahedra, of lowest symmetry and with an aspect ratio of 1.16, provides an anisotropic environment [16]. The amphiphilic molecules should experience isotropic reorientations in the first case and anisotropic ones in the second. Their NMR spectra should therefore contain a narrow component, with a purely relaxational linewidth, and a broader one, with a linewidth dominated by residual interactions. Experimental spectra indeed show a complex shape with two components [2]. The broad component is about three times more intense than the narrow one, as it should be in our model because of the relative numbers of polyhedra, its linewidth being of about 2 kHz in the case of an NMR experiment with deuterated molecules, as one might expect from the anisotropy of the tetrakaidecahedron [18]. There is therefore no disagreement between what might be observed, if the systems adopted the possible ordered geometrical configurations, and the actual observations.

we point out the absence of any compact f.c.c. packing of spherical micelles among the observed structures, or among our configurations. This suggests that a simple approach in terms of a compact packing of hard spheres is not adequate and justifies an approach in terms of films, optimizing their periodical stacking, which does not impose any constant distance between first neighbour aggregates. The second comment is to recall that we have studied two structures in details ony, Pm3n and Fd3m, although others may be generated following the same procedure, as discussed at the end of the preceding paragraph. Our argument for focussing our attention on these two structures is that they are built with intersecting films having dihedral and edge angles close to those of fluid films balancing their tensions, while the others are not. However this does not means that we consider that the latter are impossible. Indeed the same constraint of optimized periodicity quoted above might impose the distorsions of angles existing in these structures. Finally, we want to stress upon the fact that the « micellar » structure proposed here must not be confused with that proposed in [2]. In the latter identical micelles rotate isotropically or anisotropically according to their sites in the unit cell whereas, here, micelles on different sites are different in volume and shape.

4. Conclusion.

The interplay, or frustration, of forces acting in a periodic system of fluid films built by amphiphilic molecules in presence of water can find ordered geometrical solutions within the frame of a topology of finite cells separated by a self-intersecting film. These solutions can be described as periodic packings of polyhedral cells - slightly distorted dodecahedra, tetrakaidecahedra and hexakaidecahedra --- certain of which are formally similar to type I and II structures of water clathrates. This description is in correct agreement with the results of known structural studies of cubic phases found in between hexagonal and micellar phases of some phase diagrams. This agreement, as the one previously obtained in the case of « bicontinuous » cubic phases [8], exemplifies the fact that liquid crystalline polymorphism proceeds from the action of physical forces, existing in systems of films, within the frame of the geometrical constraints of our Euclidean space. If we suppress one force, for instance the interaction between two films, the order is lost, as in macroscopic soap bubble froths [12]. Also it must not be forgotten that the structures found here are but possible geometrical configurations and that we do not discuss their physical stabilities relative to that of neighbouring hexagonal and disordered micellar phases. For instance there are systems which do not present ordered micellar phases and in which the ordering of the micelles appears as short range fluctuations only [19], and others which might exhibit ordered phases with more complex structures and fluctuations in the same region of the phase diagram [20].

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