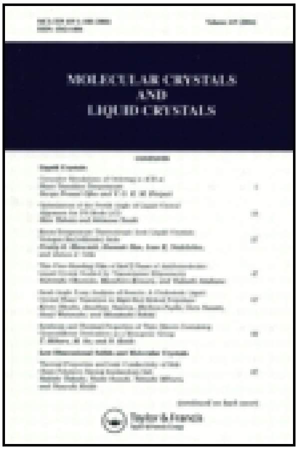

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Lyotropic Liquid Crystals as Structures of Defects

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The most representative lyotropic liquid crystals are those formed by amphiphilic molecules, such as soaps, detergents and lipids, in presence of water. These molecules are able to build structures exhibiting a long range crystalline order, although they are disordered in a liquid-like manner at the local level. This clearly shows that the individual molecules can not be the building blocks of the structures and that the elements of structures are indeed the interfaces built by the molecules or, better, the symmetric films built by two facing interfaces. These structures can therefore be described as crystals of fluid films. In order to bring out a general basis for the understanding of this new class of crystals we develop a model for studying periodic configurations of symmetric films. Its basic hypothesis is the existence of a geometrical frustration resulting from the conflict between forces normal to the interfaces and forces parallel to the interfaces. We determine its possible solutions following a geometrical approach similar to those developed for other cases of frustration in condensed matter physics. The solutions optimizing the frustration appear to be in a satisfying agreement with the observed structures. This leads to consider crystals of films as structures of disclinations.

Keywords: lyotropic liquid crystals, amphiphiles, frustration, disclinations

AMPHIPHILIC MOLECULES

It is a well known fact that polar and organic liquids are not miscible. For instance, a dispersion of oil droplets in water obtained by mechanical agitation is not stable. It has too large an interfacial area. The system evolves, through the coalescence of its droplets, towards a stable state where the two liquids are separated by one flat interface of smallest area. However, if particular molecules, such as soaps, detergents, lipids and their mixtures with others such as alcohols, are added to the system, even at low concentrations, dispersions with quite large interfacial area may be stabilized. A much discussed example of such a stabilization today is that of microemulsions. We shall not deal with them in this lecture, but with lyotropic liquid crystals, which can be considered as the limit situation when the oil content decreases to zero. They are the structures formed by the molecules in presence of water only. The action of these molecules is easy to understand from their chemical structures. From the examples shown in Figure 1 it can be seen that they are built in two parts, one or two paraffinic chains attached to a polar group, which have different affinities for solvents. The paraffinic chains have a good affinity for organic

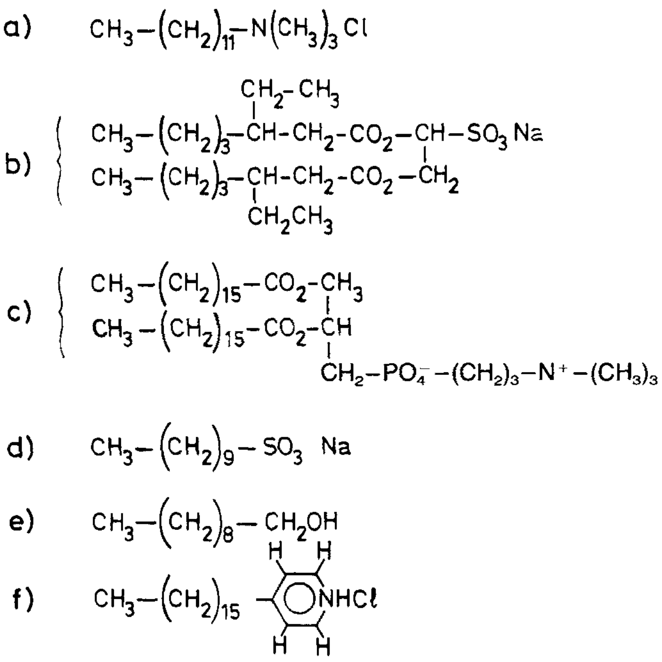

FIGURE 1 Some examples of amphiphilic molecules: a) dodecyl trimethyl ammonium chloride (DTACl), b) aerosol OT, c) dipalmitoyl phosphatidylcholine (DPPC), d) sodium decyl sulfate (SdS), e) decanol, f) cetyl pyridinium chloride (CPCl).

solvents, such as oil, but not for polar solvents, such as water. It is the opposite for the polar group. Such molecules are said to be amphiphilic. When put in presence of the solvents they can therefore build 2-D interfaces of the type of those shown in Figure 2. The shapes and properties of these interfaces depend upon the structure of the molecules, the temperature and the concentrations, as shown by phase diagram studies. (The molecules shown above have a rather low molecular mass, a few hundreds, but copolymers with much larger mass, a few thousands, can exhibit amphiphilic behaviors also with different solvents.)

PHASE DIAGRAMS AND STRUCTURES

Phase diagrams[1] and structures[2,3] have been extensively studied for years, mainly by optical observations of textures and small angle X-ray scattering of polycristalline samples. We present and discuss here a few typical examples only, limiting ourselves to the high temperature region of the phase diagrams where, as we shall demonstrate in the following paragraph, the behavior of the amphiphilic molecules at the interfaces is liquid-like.

The first of these examples is that provided by the binary mixture dodecyl trimethylammonium chloride/water,[4] whose phase diagram is shown in Figure 3. It displays the phases of most general occurrence: lamellar (Lα), "bicontinuous" cubic

(Q′α), hexagonal (Hα), "micellar" cubic (Q″α) and the micellar solution. The classical description of the structures of the phases is given in Figure 4. The lamellar structure is a periodic stacking along one dimension of bilayers of amphiphiles and layers of water. The "bicontinuous" cubic structure is a periodic entanglement along three dimensions of two labyrinths of amphiphiles separated by one film of water. The hexagonal structure is a periodic organization along two dimensions of cylinders of amphiphiles separated by a honeycomb-like film of water. The structure of the "micellar" cubic phase is not firmly established at the moment, it has been proposed to be built of either a labyrinth enclosing spherical micelles[5] or anisotropic micelles,[6] all disposed on cubic lattices. We shall propose a third possibility later on. In the micellar solution finite micelles are dispersed in water without any long range order. In certain cases giant or worm-like micelles are possible. The general trend in such phase diagrams is that, when the water content increases beyond that of the lamellar phase, water becomes the continuous medium and the interfacial curvature becomes more and more concave on the paraffinic side. The second phase diagram is that of the aerosol OT/water mixture.[7] As can be seen in Figure 5, it might be said to be a "mirror" image of the previous one. The lamellar phase

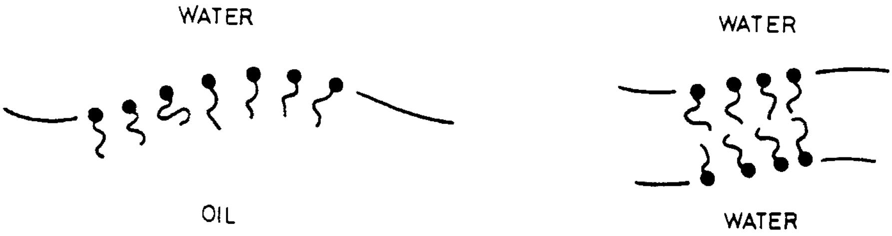

FIGURE 2 Interfacial films built by amphiphilic molecules: a) in presence of oil and water, b) in presence of water only.

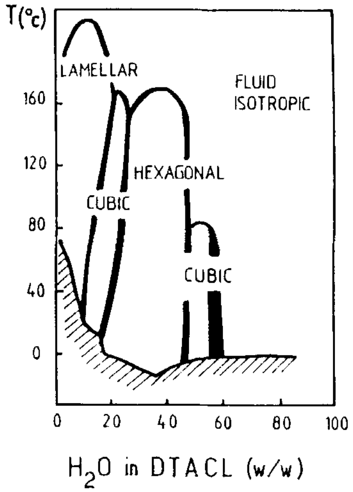

FIGURE 3 Phase diagram of the system DTACl/water.

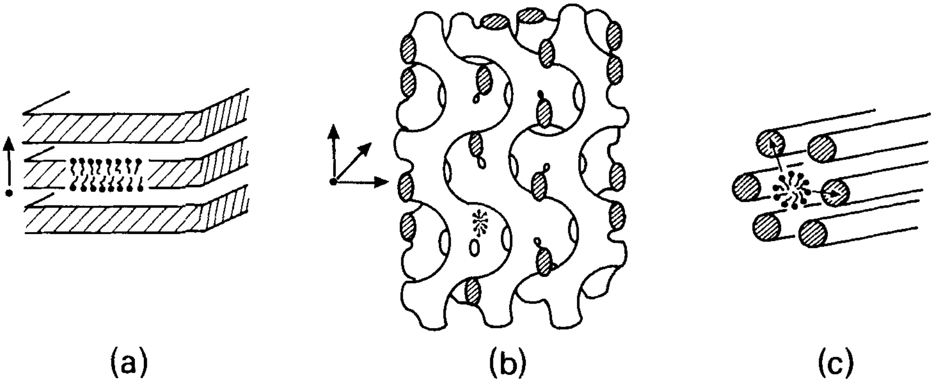

FIGURE 4 Schematic representations of the lamellar a) Ia3d bicontinuous cubic b), and hexagonal c) structures.

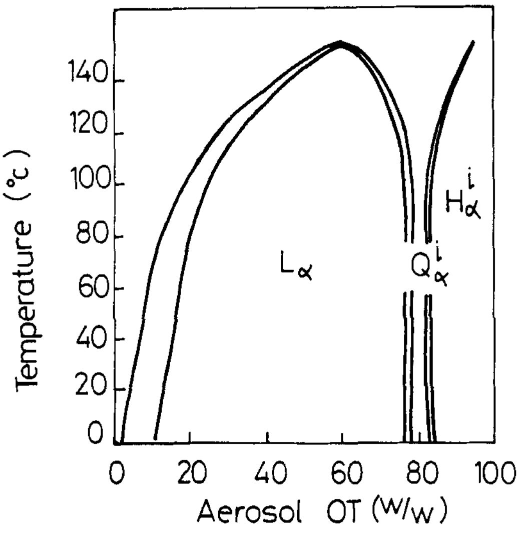

FIGURE 5 Phase diagram of the system aerosol OT/water.

exists for high water content and the other phases appear for decreasing water contents. Moreover, if the structures are similar as far as the symmetries are concerned, their aqueous and paraffinic media are interchanged. For instance, the labyrinths of the "bicontinuous" cubic phase and the cylinders of the hexagonal phase are channels of water separated by a film of amphiphiles. This change is most obviously due to the structure of the molecule which, because of its two chains, forces the concavity of the interfaces in the other sense. Lipids with two chains present similar phase diagrams, with a large biphasic domain between the lamellar phase and pure water from which vesicles can be obtained. The extraordinary polymorphism of the systems described above introduces the question of its relation with the molecular behavior, as it is well known that, in classical molecular crystals, the long range crystalline order is the result of the propagation of the short range order of the molecules. This question was partly answered by X-ray scattering studies at large angles which showed that the paraffinic medium is disordered.[2] However it was necessary to develop other experiments, using techniques sensitive to local fluctuations, to describe this disorder in a more accurate manner. Among them NMR proved to be remarkably simple and efficient.[8] Relaxation studies showed first that the disorder is dynamical, with similar characteristic times in all structures[9,10,11]: the chains are deformed by isomeric rotations around their C—C bonds, with correlation times of about $10^{-9}-10^{-11}$ sec, and diffuse along the interfaces, with translational diffusion coefficient of about $10^{-6}-10^{-7}$ cm^2/sec, as shown in Figure 6. It is quite noticeable that these figures are very close to those known for melted paraffins of similar chain lengths. Then the development of NMR studies of deuterated molecules[12] and of C^{13} NMR[10] permitted to show that the amplitude of the deformations are about the same in all structures, ordered liquid crystals,[12,13] as well as in disordered micellar solutions.[10] Thus there does not appear any definite correlation between one structure and the molecular behavior in it. The chains are about equally disordered in all structures, in spite of important changes of interfacial curvature and mean area per molecule at the interface. It is therefore not possible to analyse liquid crystalline structures in the same terms than those used for classical molecular crystals. These structures are to be described as ordered entanglements of two disordered liquids separated by an interface, and their element of structure is not the individual molecule but the interface built by the molecules or, to respect the basic symmetry, the film formed by two facing interfaces. This point of view is equally supported by the fact that similar structures appear along a similar sequence in phase diagrams, whatever the details of the chemical structures of the molecules. For instance, in the phase diagram of Figure 3, the lamellar phase is followed by a "bicontinuous" cubic phase then by a hexagonal one and, finally, by a micellar phase when the water content

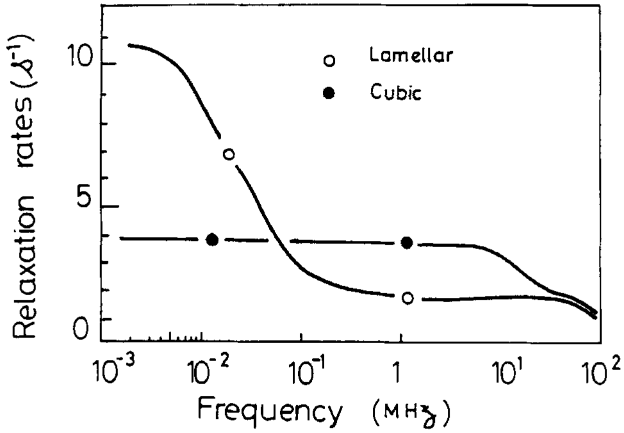

FIGURE 6 NMR relaxation curves, related to the spectral densities, obtained in the lamellar and cubic phases of the system potassium laurate/water, the relaxation due to rapid deformations appears in the 10^2 range, that due to translational diffusion in the 10^1 range and that due to very slow deformations or collective motions in the 10^{-2} range.

increases. Similar sequences, or part of it, can be found in other diagrams too, when their dominant parameter varies. These similitudes can not but hold to the common amphiphilic nature of the molecules and to their ability to build interfaces organized in symmetric films. We therefore analyze lyotropic liquid crystals as crystals of fluid films, the film being defined by its middle surface, as shown in Figure 7.

PERIODIC SYSTEMS OF FRUSTRATED FLUID FILMS

The question we want to address now is that of the understanding of the structural polymorphism of films in interaction. Can it be described on a simple basis common to all systems?

To explain our point of view on this problem let us consider the classical methods which were developed to analyze organizations of atoms and molecules. It is well known that it is not possible to deduce their structures from their interactions potentials directly, in a simple manner. Two directions were taken. The first consists in calculating the free energies of interacting particles assembled on lattices of given symmetries. The comparison of the results with the observed symmetries is a test of the validity of particular potentials. In this case the catalogue of lattices is provided by crystallography, which can be defined as the investigation of possible geometrical configurations to pack together particles of certain symmetries. The second direction is that of the simulation of the system of particles in a computer which build a structure. This is a very heavy method, particularly in the case of complex 3-D structures. We are now facing the same problem in the case of our systems, but at a higher level of complexity because we are dealing with 2-D objects, films, and not O-D objects, atoms or molecules.

Up to now, the direction of simulation on a computer could not be followed, because of the high numbers of molecular degrees of freedom and molecules per unit cells. The first direction could not be strictly followed either, in the absence of any crystallographic information about film organizations. Nevertheless this information could be replaced by considering the structures as they are given by the observations, at least for the simplest of them, lamellar, hexagonal and micellar.

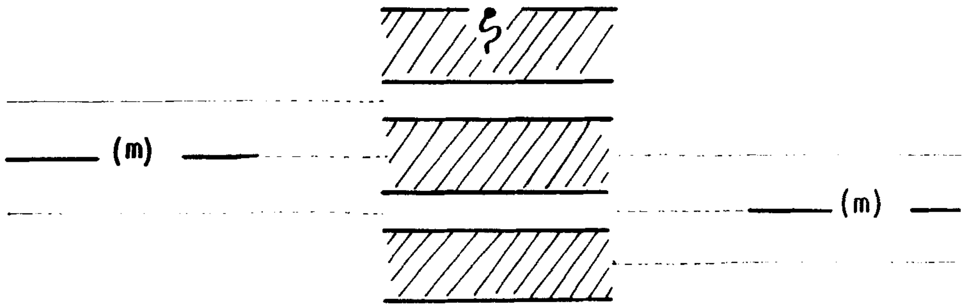

FIGURE 7 Definition of the film and its middle surface in a lamellar structure, it can be either a film of amphiphile or of water.

Free energy calculations were developed on this basis with a precise account of the forces acting in the system, between molecules, ions, interfaces, particularly those of electrostatic origin.[14] A quite reasonable agreement was observed between the calculated locations of lamellar, hexagonal and micellar structures in some phase diagrams and the experimental data, particularly for ternary diagrams. This gave a strong weight to electrostatic forces. However, recent observations of rectangular or nematic phases within domains of certain of these phase diagrams thought before to be hexagonal or micellar, and of intense hexagonal or rectangular fluctuations within their lamellar phases thought before to have infinite lamellae,[15] should temper this first conclusion. In anyway, the general success of this approach pushed us to think of a real crystallographical basis to support it. As for atoms or molecules, the way films can be packed are obviously driven by their "shape", or their interfacial curvatures, and their distances; but, in the case of films, strong topological constraints appear which impose states of frustration.

Interplay of Forces and Frustration

The forces acting in a system of films of amphiphiles are many of different origins.[16,17] They are not all well known at the moment. However their detailed knowledge is not necessary at this stage. We just need to use the fact that the role of their components normal to the interfaces is to maintain constant distances between them, if the interfaces are supposed homogeneous, and that the role of their components parallel to the interfaces is to determine the interfacial curvatures, as they do not vary necessarily in concordance at different levels within the layers limiting the film. Owing to the symmetry of the film with respect to its middle surface it is clear that the fact that two facing interfaces may have symmetric curvatures is not always compatible with constant distances between the interfaces, if a lamellar-type stacking is kept, as shown in Figure 8. The left and right drawings of this figure present situations of conflict between forces normal to the interfaces and forces parallel to them. Such a situation is a typical case of frustration. The

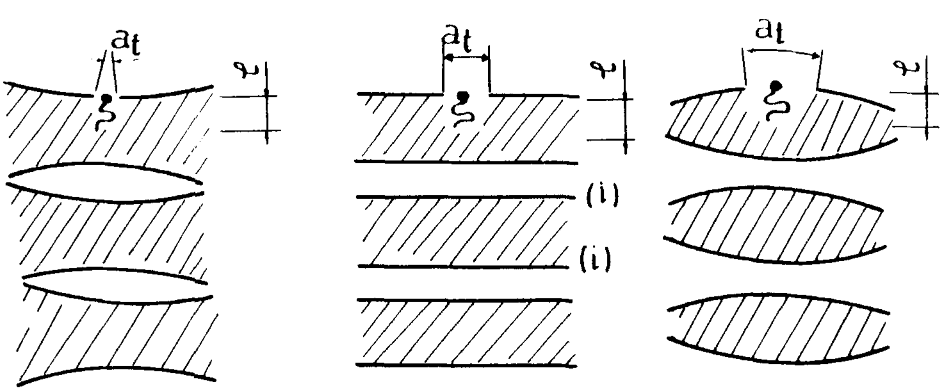

FIGURE 8 Representation of a periodic system of films with flat interfaces (center), constant interfacial distances and zero curvatures are compatible, the same with curved interfaces (right and left), constant interfacial distances and non-zero curvatures are no longer compatible and the system becomes frustrated.

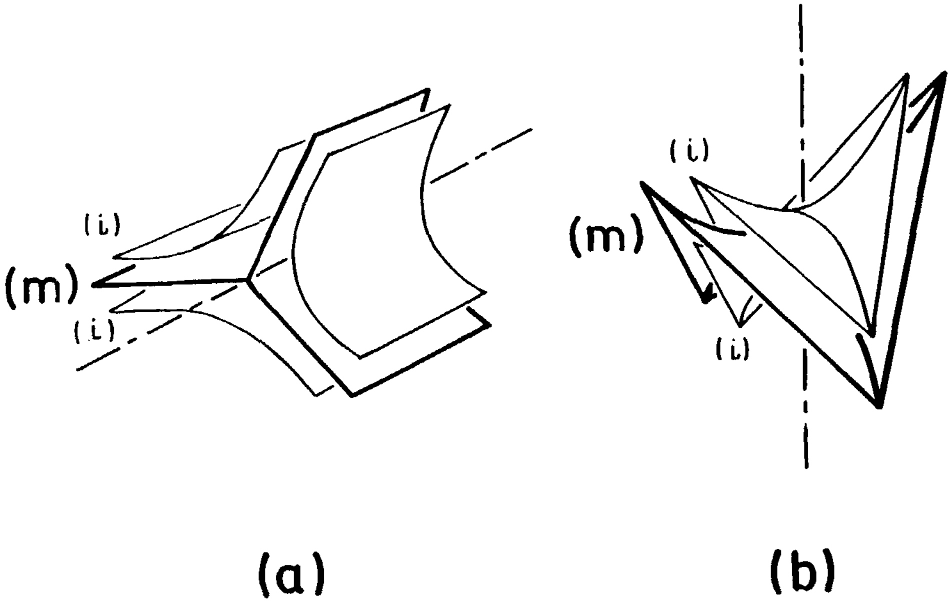

FIGURE 9 Two configurations optimizing the frustration of an isolated film: the junction (a) and the saddle (b).

forces are therefore obliged to compromise and new structures should be built. Is it possible to find configurations optimizing this frustration? A clue is suggested considering the configurations of an isolated film satisfying the area difference between the interface and middle surface, or the interfacial curvature. They are two of them, which are shown in Figure 9. The first one is that of the junction between three films, it is obvious that the interfacial area is smaller than the middle one in this case. The second is that of a saddle shaped film, in this case the principal radii of curvature of the middle surface have opposite signs and, if they have equal length R, any surface parallel to it at a distance 1 has an area smaller by a ratio $(R^2 - 1^2)/R^2$. An important point here is that these configurations can not relax the frustration totally, they can but optimize it. This is obvious in the case of the junction. In Figure 9 we have tried to draw the junction giving its interface a constant curvature but this imposes a modulation of the distance between the interfaces and the middle surface, if we had kept this distance constant the curvature would have been singular along one line. A similar remark holds for the saddle: a parallel surface at constant distance from the middle surface cannot have a constant curvature and, a surface with constant curvature cannot be strictly parallel. This is indeed because these configurations can not be obtained from the flat film without introducing defects in it. If it can be intuitively felt that a junction implies a defect in a film, this is not so easy in the case of a saddle with respect to a flat film. We develop this point below.

Defects

The study of defects in condensed matter physics was much stimulated when it was realized that most of the ordered systems, crystals or liquid crystals, can present defects in their microscopic organization which may control many of their macroscopic properties. The gedanke experiment for creating a defect in a material is known as the Volterra process. It consists first in cutting a volume of unstressed material along a surface bordered by a line, then the two lips of the cut are displaced with respect to each other without changing their form, the empty space being filled in with unstressed material or the unstressed material in excess being removed, and, finally, the system relaxes so that the stresses are localized along the line limiting the cut which becomes a line of defect. Of course these operations must respect the symmetry of the ordered material. As the relative displacements of the two lips can be analyzed in general as the sum of a translation and a rotation, one can define defects of translation, or dislocations, and defects of rotation, or disclinations.[18,19,20] Examples of a dislocation and a disclination in a simple 1-D crystal are given in Figure 10. The introduction of disclinations parallel and normal to a film are given in Figure 11. These disclinations create the local configurations proposed above. It is important to notice here that the statistical number of first neighbours around one molecule in the saddle-shaped film must be higher than what it was in the flat film, because the type of disclination used here adds matter. This can be spontaneously achieved, keeping the density of the film constant, only if the film is fluid, not if it is solid. Inversely, if the disclination had taken away some matter, the film would have become bowl-shaped. These two aspects, shape of a surface and environment of its points, are indeed related by a topological relation.

Structures of Disclinations

The fact that the introduction of disclinations in the frustrated system is the method for determining the configurations optimizing the frustration can be demonstrated rigorously. We do not work out the argument here but just sketch its broadlines, its presentation and developments being exposed in several recent articles.[21-25] The frustration between interfacial curvature, or area difference, and distances exists because the system is embedded in the 3-D flat Euclidean space R_3, it is however possible to find appropriate 3-D curved spaces where ideal lamellar-like structures conciliating the two antagonistic terms exactly can be built. The possible configurations in the flat space are then generated from these perfectly ordered configurations in curved spaces. For this it is necessary to transform the curved spaces into the flat one. This problem is similar to that of the mapping of the spherical surface of the Earth onto the flat surface of the sheet of a geographical map, an operation which can not be done without continuous deformations or the introduction of localized defects. More precisely, in our case, the mapping of the curved spaces onto R_3 can be obtained by introducing disclinations only, as displacements in curved spaces are rotations and, furthermore, the introductions of these disclinations must obey precise rules respecting the symmetry of the relaxed structure in the curved space. In the course of the mapping process the ideal

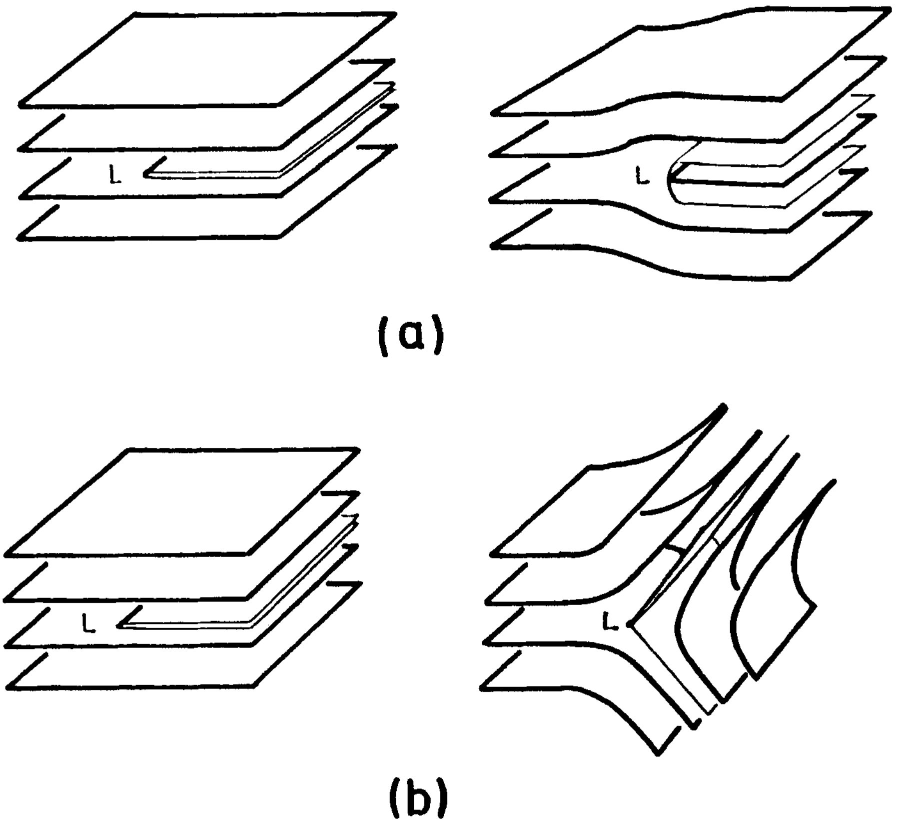

FIGURE 10 Two defects in a layered material: the addition of one layer in between the lips of the cut adds one translation vector on the right of L and creates an edge dislocation (a), the addition of half a crystal makes the normal rotates by $-\pi$ around L and creates a disclination (b).

configurations in the curved spaces are necessarily distorted by the defects and new configurations are generated.[21] This approach gives access to configurations in R_3 having topologies and symmetries similar to those observed in the structural studies of systems of amphiphiles, and organized in the phase diagrams following the same sequence.[24] A particular cubic organization possible for the film is given in Figure 12,[22,25] it is indeed one of the infinite periodic minimal surfaces with zero mean curvature ($1/R_1 + 1/R_2$, where R_1 and R_2 are the radii of principal curvatures), everywhere and distributed negative Gaussian curvature ($1/R_1R_2$) studied by mathematicians and crystallographiers.[26] Such a surface can be seen as an assembly of saddles periodically organized along normal disclination lines, which are themselves ordered in a crystalline manner. It separates two labyrinths of a cubic structure. Figure 12 also shows the honeycomb organization, with zero Gaussian curvature and lines of singularities, corresponding to the hexagonal structure.[21] These lines are the disclination lines running in the film, they are also ordered in a crystalline manner. These lines of disclinations, which are $-\pi$ lines because of the symmetry requirements, are not the only one present in the structures. The axes of the rods

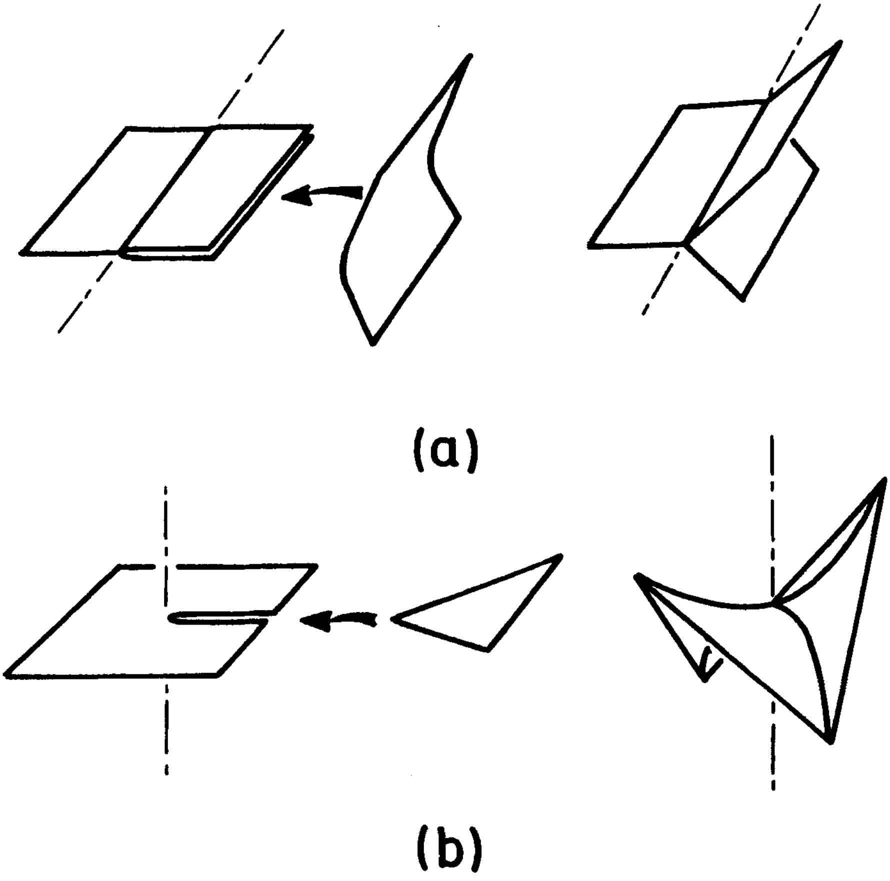

FIGURE 11 A disclination parallel to the film creates a junction (a), a disclination perpendicular to the film creates a saddle (b), the latter can be easily built with a sheet of paper.

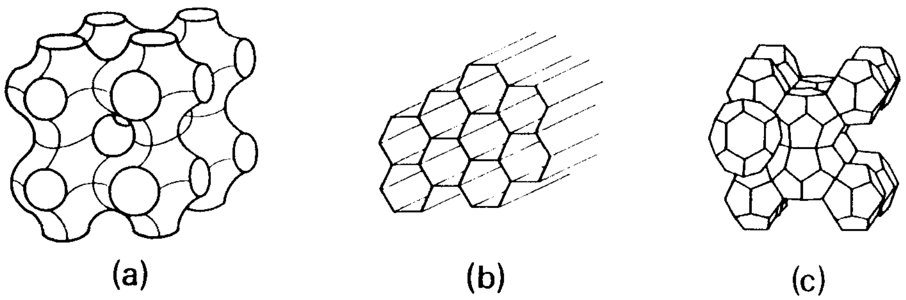

FIGURE 12 Three ordered configurations of the middle surface of the film obtained following the frustration approach: the Schwarz's surface separating the two labyrinths of the bicontinuous Im3m cubic structure (a), the honeycomb configuration containing the cylinders of the hexagonal structure (b), the polyedral configuration of the Pm3n micellar cubic structure (c).

of the labyrinths in the cubic phase or of the cylinders in the hexagonal phase, around which the normal to the interfaces rotate by an angle of 2π, can also be seen as disclination lines. A closer look at the structures shows that $-\pi$ and 2π lines compensate each other, as required in a flat space. Finally, ordered micellar structures can also be obtained.[23] Thus the structures found in the Euclidean space R_3 after the introduction of the disclinations, that of the cubic, hexagonal and micellar phases, are crystals of films which can also be seen as crystals of disclinations. It should not be forgotten that the frustration is not suppressed in these structures but only optimized because of the very nature of the defects. Indeed, it is only when the interfaces are flat that a structure without frustration and defect, that of the lamellar phase, can be built directly in the Euclidean space R_3. Finally, it can be shown that these structures exist for discrete values of the frustration only, not for all the values of its variation range.[24] It is interesting to quote that the steps followed here, analysis of a system in term of frustration, search for perfect structures in curved spaces and then mapping onto R_3 by disclinations, was previously followed for understanding amorphous structures[27] and large cell Frank and Kaspers' structures of alloys,[28] in more classical domains of solid state physics.

CONCLUSION

The structures formed by amphiphilic molecules in presence of water have been considered for a long time as tricky particular cases of solutions and, therefore, have been approached mainly in terms of the thermodynamics of solutions and aggregation. This type of approach proved to be extremely useful to understand diluted micellar solutions when the aggregates of amphiphiles may be assumed to have simple shapes with a simple topology of the spheroid type, and when they are so diluted and disordered that the notion of a film with constant thickness separating them is of no significance. The situation is different in the case of the concentrated liquid crystalline structures of complex topologies, where the notion of aggregate is not very operative as there is no simple argument to propose any particular shape for the aggregates. Fortunately enough, the proximity of the aggregates gives the notion of film a sense and, this new element of structure being defined, a new approach could be tried, following a program very much inspired of that developed in classical solid state physics. The fact that this film is fluid is extremely rich of consequences, concerning the polymorphism particularly. The fluidity is indeed the only state of matter permitting the changes of topologies, because the number of first neighbours around one molecule can be varied at constant density in a fluid film only. This latter point, variation of the number of first neighbours, justifies the use of the notion of defects, particularly disclinations, in this problem. Another consequence of the fluidity is of course the lability of the structures, permitting large dynamical fluctuations as well as ruptures and connections within and between films. This is very important structurally but also for the mechanical properties of these crystals of films. Finally, it might be thought that the use of notions developed within the frame of solid state physics should be inadequate in a domain where fluidity is so important, however it must not be forgotten that we are concerned with ordered structurations of space, i.e. that geometry is preponderant.

References

1. P. Ekwall, in *Adv. Liq. Cryst.*, **1**, 1, edited by G. H. Brown, Academic Press, New York (1975).
2. V. Luzzati, in *Biological Membranes*, **1**, 71, edited by D. Chapman, Academic Press, New York (1968).
3. A. Skoulios, *Ann. Phys.*, **3**, 421 (1978).
4. R. R. Balmbra, J. S. Clunie and J. F. Goodman, *Nature*, **222**, 1159 (1969).
5. P. Mariani, V. Luzzati and H. Delacroix, *J. Mol. Biol.*, **204**, 165 (1988).
6. K. Fontell, K. Fox and E. Hansson, *Mol. Cryst. Liq. Cryst.*, **1**, 9 (1985).
7. J. Rogers and P. A. Winsor, *J. Coll. Interface Sci.*, **30**, 247 (1969).
8. J. Charvolin and Y. Hendrikx, in *Nuclear Magnetic Resonance of Liquid Crystals*, p. 449, edited by J. W. Emsley, Reidel Publishing Company, Dodrecht (1985).
9. J. Charvolin and P. Rigny, *J. Chem. Phys.*, **58**, 3999 (1973).
10. H. Walderhaug, O. Soderman and P. Stilbs, *J. Phys. Chem.*, **88**, 1655 (1984).
11. W. Kühner, E. Rommel, F. Noack and P. Meier, *Z. Naturforsch*, **42a**, 127 (1987).
12. J. Charvolin, P. Manneville and B. Deloche, *Chem. Phys. Lett.*, **23**, 345 (1973).
13. E. Sternin, B. Fine, M. Bloom, C. Tilcock, K. Wong and P. Cullis, *Biophy. J.*, **54**, 689 (1988).
14. B. Jonsson and H. Wennerström, *J. Phys. Chem.*, **91**, 338 (1987) and reference therein.
15. Y. Hendrikx, J. Charvolin, P. Kekicheff and M. Roth, *Liq. Cryst.*, **2**, 677 (1987).
16. J. N. Israelachvili, Intermolecular and surface forces, Academic Press, New York (1985).
17. W. Helfrich, *Z. Naturforsch.*, **33a**, 305 (1978).
18. J. Friedel, Proceedings of the Sixth General Conference of the European Physical Society, Prague (1984).
19. W. F. Harris, *Scientific American*, **237**, 130 (1977).
20. M. Kleman, Points lignes et parois, Edition de Physique (1977).
21. J. F. Sadoc and J. Charvolin, *J. de Physique*, **47**, 683 (1986).
22. J. Charvolin and J. F. Sadoc, *J. de Physique*, **48**, 1559 (1987).
23. J. Charvolin and J. F. Sadoc, *J. de Physique*, **49**, 521 (1988).
24. J. Charvolin and J. F. Sadoc, *J. Phys. Chem.*, **92**, 5787 (1988).
25. J. F. Sadoc and J. Charvolin, *Acta Cryst.*, A**45**, 10 (1989).
26. A. H. Schoen, NASA Tech. Note D-5541 (1970); L. E. Scriven, *Nature*, **263**, 123 (1976); S. T. Hyde and S. Andersson, *Z. Krystall*, **168**, 221 (1984); A. L. Mackay, *Nature*, **314**, 604 (1985); E. L. Thomas, D. M. Anderson, C. S. Henke and D. Hoffman, *Nature*, **334**, 598 (1988); H. G. von Schnering and R. Nesper, *Angew. Chem.*, **26**, 1059 (1987); H. A. Schwarz, Gesammelte Mathematische Abhandlungen 1, Springer Verlag (1890).
27. J. F. Sadoc and R. Mosseri, *Philisophicol Magazine B*, **45**, 467 (1982).
28. J. F. Sadoc and R. Mosseri, Order, frustration and space curvature in Physics of Disordered Materials, edited by D. Adler, H. Fritzsche and S. R. Oshinsky, Plenum Press (1985).