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

J. Charvolin and J. F. Sadoc
Laboratoire de Physique des Solides, associé au CNRS, Université Paris-Sud, 91405 Orsay, France
GRECO microémulsions, CNRS

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Résumé. — On considère les organisations périodiques de deux milieux fluides séparés par des interfaces. Les interactions entre les deux milieux, normales aux interfaces, maintiennent des distances constantes entre interfaces et les contraintes dans chaque milieu, parallèles aux interfaces, contrôlent les courbures interfaciales. Les structures doivent donc concilier les distances et courbures constantes imposées par les paramètres thermodynamiques. Il s’agit là d’un problème purement géométrique dont les solutions constituent les bases des structures de films fluides périodiques. Quand les courbures interfaciales sont nulles, la solution évidente est l’empilement périodique de couches parallèles des structures lamellaires. Quand les courbures ne sont pas nulles, des interfaces adjacents doivent avoir des courbures symétriques incompatibles avec des distances constantes si la symétrie d’une structure lamellaire est conservée. C’est un cas typique de frustration qui implique un changement de structure. Nous avons récemment proposé de rechercher les solutions à cette frustration en suivant une approche géométrique qui fournit des solutions dont les topologies sont semblables à celles des phases liquides cristallines et qui conduit à les considérer comme des structures de disclinations. Nous développons maintenant cette approche pour étudier le cas particulier des solutions de topologie bicontinue, où un film construit par un milieu sépare deux labyrinthes construits par le second milieu. Nous démontrons que ces solutions correspondent à des configurations dans lesquelles le film est supporté par des surfaces hyperboliques ordonnées ayant des topologies et symétries semblables à celles de trois surfaces minimales infinies périodiques calculées par les mathématiciens. Nous discutons la relation entre ces solutions et les structures déterminées pour les phases liquides cristallines cubiques, soit dans les systèmes d’amphiphiles (Qα), soit dans ceux de molécules mésogènes (SmD).

Abstract. — We consider periodic organizations of two fluid media separated by interfaces in which interactions between the two media, normal to the interfaces, maintain constant distances between interfaces and constraints within each medium, parallel to the interfaces, control interfacial curvatures. The structures must therefore conciliate the constant interfacial distances and curvatures imposed by the thermodynamical parameters of the systems. This is a purely geometrical problem whose solutions constitute the foundation of the structures of periodic systems of fluid films. When the interfacial curvature is null, the obvious solution is a periodical stacking of parallel layers. When the curvatures are not null, adjacent interfaces must have curvatures with the same concavities relative to the two media because of the symmetry of the layers and the constant distances between them can no longer be maintained if the lamellar geometry is kept. This is a typical case of frustration which implies a change of structure. We have recently proposed to look for the solutions to this frustration following a geometrical approach which provides solutions whose topologies are similar to those of liquid crystalline phases and which leads to consider the latter as structures of disclinations. We now develop this approach to study the particular case of solutions with bicontinuous topology, i.e. where a film without self-intersection built by one medium separates two labyrinthine nets built by the second medium. We demonstrate that they correspond to configurations in which the film is supported by ordered hyperbolic surfaces having topologies and symmetries similar to those of three infinite periodic minimal surfaces calculated by mathematicians. We discuss the relation between these ordered bicontinuous solutions and the structures determined for cubic liquid crystalline phases, either in amphiphilic systems (Qα) where the two media are paraffinic and polar, or in mesogenic ones (SmD) where the two media are aliphatic and aromatic.
1. Introduction.

Periodical organizations of two fluid media separated by interfaces are very common in liquid crystals where they most often occur under the forms of periodical stackings along one dimension of fluid layers of molecules. In lamellar phases of lyotropic liquid crystals, built by amphiphilic molecules in presence of water [1], paraffinic bilayers of amphiphiles and polar layers of water are alternatively stacked with flat interfaces defined by the polar heads of the amphiphiles, as shown in figure 1a. In smectic phases of thermotropic liquid crystals, built by pure amphiphilic molecules [1] or mesogenic molecules [2], paraffinic or aliphatic layers and polar or aromatic layers are alternatively stacked with flat interfaces defined by the points where the molecular groups with different chemical affinities are connected in the molecules. Besides these phases with periodicity along one dimension the phase diagrams of liquid crystalline systems may present other ordered phases with periodicities along two or three dimensions, curved interfaces and various topologies [1-3]. We want to consider here the particular case of phases with cubic symmetry and bicontinuous topology, named Qα when built by amphiphilic molecules [1] and SmD when built by the so-called mesogenic molecules [3]. They are of the type shown in figure 1b where a film of water without self-intersection separates two identical labyrinths of amphiphilic molecules. We wonder if the complex geometry of such structures could not rely upon the same principle than that which is easily discernable in the much simpler lamellar and smectic phases. The latter are periodic organizations of flat interfaces at constant distances. Could bicontinuous cubic phases be periodic organizations of curved interfaces at optimized distances, adjacent interfaces having the same concavity relative to the media they separate?

We therefore formulate the problem of the description of these cubic structures in purely geometrical terms and reduced it to the search for geometrical elements, points, lines or surfaces, around which, or along which, the films may be organized in order to conciliate optimal distances and symmetric interfacial curvatures. This is reminiscent in a certain way of the analysis of focal conics observed in smectic textures as degenerated evolutes of a family of surfaces, Dupin’s cyclides, along which parallel layers can be bent [4]. The two problems are of the same family in the sense that they are concerned with the possible geometrical configurations of films which are fluid, with low bending modulus, and periodically stacked, with high normal compressibility modulus. However they differ in the sense that the curvatures of two adjacent interfaces are symmetrical and result from an internal constraint within each bilayer in our case while they are similar and result from an external constraint imposed to the whole lamellar crystal in the focal conics case, as shown in figure 2. In our case we are obviously facing a frustration, between curvatures and distances, which does not exist in the case of bent parallel interfaces.

Fig. 1. — a) Schematic representation of the lamellar phase of a lyotropic liquid crystal, hatched layers are the amphiphilic layers, they are separated by water layers ; b) schematic representation of a cubic phase with symmetry Ia3d, two interwoven but not connected labyrinths of amphiphilic molecules are separated by a film of water whose middle surface is at mid-way between the two interfaces, see also figure 19 which is a more rigorous representation of the two labyrinths.

Fig. 2. — a) Symmetric interfacial curvatures in the case of the structural problem studied here, the interfaces have the same concavities relative to the two media ; b) parallel interfacial curvatures in the case of the textural problem of the focal conics.
layers. This difference implies that the search for solutions in our case cannot be done directly in the Euclidean space, as it is done in the latter case, but must go first through the search for solutions in a curved space. Once such solutions are found defects of rotation, or disclinations, are introduced in order to decrease the curvature of the curved space and come back to the Euclidean space. The structures obtained that way can therefore be considered as structures of disclinations. This procedure is currently used in condensed matter physics for solving cases of frustration, as for instance bi-dimensional tilings of regular polygons or tri-dimensional packings of regular polyhedra [5]. Its recent application for solving the curvature-thickness frustration in a liquid crystalline bilayer has provided solutions whose topologies are similar to those observed in liquid crystalline phases [6]. One of these solutions presents the bicontinuous topology of the cubic liquid crystalline phases, i.e. space is divided in two sub-spaces by one infinite film. We apply here the process leading to this solution, studying the effect of ordered disclinations in a periodical stacking of films. We show that the surfaces which are possible solutions to our problem are related to infinite periodic minimal surfaces calculated by mathematicians [7].

2. Physical basis of the frustration.

We focus our attention on the well documented case of films built by amphiphilic molecules and water. In that case the simplest system of periodic films is the lamellar structure represented in figure 1a. The distances between interfaces, measured along the normals to the interfaces, are constant. The interfaces are flat, or the lateral area per polar head and per paraffinic chains are equal, revealing equal equilibrium distances between heads and between chains in planes parallel to the interfaces. Finally the layers have isotropic properties in these planes.

There are several forces which fix the inter and intra layer distances in such a system: Van der Walls forces, electrostatic interactions between polar groups at the interfaces, forces created by water polarization and charge distribution in aqueous layers, hydrophobic interaction which prevent the presence of water in amphiphilic layers and steric forces associated with undulations of the layers [8]. They are not totally known at the moment, as well as their interplay. However it is reasonable to think that the role of the components normal to the interfaces is to define the relative positions of the interfaces, and therefore the thickness of the aqueous and amphiphilic layers, and that the role of the components parallel to the interfaces is to determine the interfacial curvature. Their variations are controlled by the thermodynamical variables which are the degree of hydration and the temperature. The normal components make the distances between interfaces vary but, as we consider homogeneous interfaces, these distances should remain constant when moving along the interfaces. The parallel components make the lateral distances between molecules vary, but not necessarily in concordance at different levels along the normals to the interfaces, so that variations of the parameters away from their values in the lamellar phase may induce differences in the lateral area at different levels of the bilayer and therefore interfacial curvatures. A coarse way to systematize the non concordant actions of these second components might be to say that the interactions between polar heads are mainly dominated by the degree of hydration whereas the lateral gyration radius of paraffinic chains is dominated by the temperature.

Owing to the symmetry of the amphiphilic bilayer with respect to its middle surface it is clear that the fact that two adjacent interfaces have different area than the middle surface between them, or have symmetric curvatures, is not compatible with constant distances between these interfaces if the lamellar structure is kept, as shown in figure 3. This is a situation where two physical forces oppose, i.e. a frustration.

3. The frustration and its relaxation.

3.1 FRUSTRATION IN R3. — This frustration holds to the fact that the structure is embedded in Euclidean space R3 but it might be relaxed if the structure is transferred into a space with different properties. We have shown in a previous paper that the frustration appearing in an isolated bilayer may be relaxed when the bilayer is transferred into the curved space S3 with homogeneous positive curvature [6]. This relaxation was obtained by applying the middle surface of the bilayer on one of the two possible surfaces separating S3 in two equivalent subspaces, the great sphere S2 or the spherical torus T2, so that the two interfaces were applied on surfaces parallel to either S2 or T2 and with smaller area. When T2 was used a structure with bicontinuous topology was obtained. We now extend the use of the process to the case of a periodic system.
3.2 Relaxation of the frustration on the spherical torus \( T_2 \) in \( S_3 \). — The curved space \( S_3 \) can be described as the hypersphere in \( R_4 \), it is a finite space with positive Gaussian curvature. In this space the spherical torus \( T_2 \) can be built by identification of opposite sides of a square sheet, as shown in figure 4 [9]. \( T_2 \) has two \( C_\infty \) axes, which are great circles of \( S_3 \), and an infinity of \( C_2 \) axes normal to its surface. Analytically \( S_3 \) can be characterized by the hyperspherical coordinates \( \theta, \omega, \varphi \), the radius \( R \) of the sphere being fixed, and one of its points has coordinates in \( R_4 \):

\[
X_1 = R \cos \theta \sin \varphi, \quad X_2 = R \sin \theta \sin \varphi, \\
X_3 = R \cos \omega \cos \varphi, \quad X_4 = R \sin \omega \cos \varphi.
\]

\( X_1 = R \cos \theta \sin \varphi, \quad X_2 = R \sin \theta \sin \varphi, \quad X_3 = R \cos \omega \cos \varphi, \quad X_4 = R \sin \omega \cos \varphi. \)

The surfaces at constant \( \varphi \) constitute the family of parallel tori represented in figure 5. \( \theta \) and \( \omega \) are the parameters running along the surfaces and \( \varphi \) is the parameter running along great circles which are the geodesic of \( S_3 \) normal to the surfaces of the tori. Among these tori, those at \( \varphi = 0 \) and \( \varphi = \pi / 2 \) are great circles and the torus at \( \varphi = \pi / 4 \) is equidistant from them. The latter is the spherical torus and the two first its \( C_\infty \) axes. An infinitesimal displacement \( d\ell \) on any torus of the family is given by

\[
d\ell^2 = \sum dX_i^2 = R^2 (\sin^2 \varphi \ d\theta^2 + \cos^2 \varphi \ d\omega^2)
\]

with constant \( \varphi \) and the tori have Euclidean metrics, in general, particularly for \( T_2 \) where

\[
d\ell^2 = R^2 (d\theta^2 + d\omega^2)/2.
\]

\( T_2 \) has therefore zero Gaussian curvature and admits the same tilings by regular polygons than the Euclidean plane which are \( \{4, 4\}, \{6, 3\} \) and \( \{3, 6\} \) [10]. An infinitesimal area on any torus of the family is given by \( R^2 \sin \varphi \cos \varphi \ d\theta \ d\omega \), so that the area of \( T_2 \) is maximal and that two tori parallel to \( T_2 \), at equal distances \( R \Delta \varphi \) on either sides of it, have equal area smaller than that of \( T_2 \).

From the above properties of \( S_3 \) and its family of parallel tori it appears that the set of a spherical torus \( T_2 \) surrounded by two parallel tori at equal distances can be considered as a representation without frustration of the periodic system of frustrated fluid films, as illustrated in figure 6. The periodicity in \( R_3 \), which is the repetition of the films when moving along geodesics normal to the films, is reproduced in \( S_3 \) by the periodical crossings of the spherical torus every \( \varphi = \pi / 4 + n \pi / 2 \) when moving along geodesics of \( S_3 \) normal to \( T_2 \) at \( \theta, \omega \) constant and variable \( \varphi \). The \( \theta, \omega \) periodicity on...
T2 represents the infinite lateral extension of the layers. Also the two sub-spaces separated by T2 are identical as are the two media separated by the film in the cell of the structure. Finally the frustration is obviously relaxed as the two interfaces of the film, which are supported by two tori parallel to T2, have smaller area than the middle surface of the film supported by T2. Once the system has been transferred into S3 possible structures are found by mapping S3 onto R3. We shall limit ourselves to the process which maintains the bicontinuous topology of T2. In the course of this process the positive curvature of S3 will be decreased to zero and the support of the film, the spherical torus with zero Gaussian curvature, will become an hyperbolic surface with negative Gaussian curvature.

4. Disclinations and generation of hyperbolic surfaces.

4.1 The disclination process. — In a space with positive curvature the integration of the Gaussian curvature over the whole space is a multiple of π revealing an angular defect [11]. To decrease the curvature of the space it is therefore necessary to fill in the defect and this is obtained by introducing defects of rotation, or disclinations. The disclinations are introduced following a Volterra process which respects the symmetries of the structure present in that space [12] and their density is related to the curvature to be suppressed [13]. In our case the structure is the spherical torus T2 and we introduce disclinations around its C2 axes. A pictorial representation of the first step of the process is given in figure 7. The torus is cut along half a plane limited by a C2 axis, a rotation separates the two lips, half a torus is inserted and the system relaxes. It is necessary to introduce half a torus in order not to disrupt the continuity of the torus and to respect its C2 symmetry, this is a \(- \pi\) disclination [12]. Such an introduction of disclinations around axes normal to the surface preserves the bicontinuous topology of the torus, i.e. the surface still separates two identical sub-spaces, but its genus has been changed. Finally, as a disclination is a defect of rotation and concerns angles only, distances and area/volume ratio of the cell are preserved.

Each disclination axis pierces the surface at four points. At each of these points the effect of a \(- \pi\) disclination on the element of surface surrounding the point is to introduce a supplementary amount of surface of area one half that of the element. As the disclinations have to be homogeneously introduced to flatten out S3 this element must be one of the tiles of a regular tesselation of the torus, moreover it must respect the symmetry operations which are related to the disclinations around C2 axes and therefore be a square of the \(\{4, 4\}\) tiling. The \(- \pi\) disclination transforms the square into an hexagon without changing the coordination of the vertices, as represented in figure 8. The effect of the complete decurving of S3 on the torus is to transform its \(\{4, 4\}\) tiling into a non planar \(\{6, 4\}\) tiling, as suggested in figure 9. A hyperbolic surface with constant negative Gaussian curvature is generated and we shall work with Poincaré’s model of a hyperbolic plane to determine how this surface, or a portion of it, can be imbedded in R3.

4.2 Hyperbolic surfaces in Poincaré’s representation. — This is a model built in the Euclidean plane: the hyperbolic surface is represented within a circle, its points at infinity are on the limiting circle, the angle between lines are
preserved, the metrics is chosen in order to represent that of the surface, i.e. the distance between two points representing a constant segment on the surface decreases when the two points approach the limiting circle [14]. A {6, 4} tiling of the hyperbolic plane is represented in figure 10, together with its orthoscheme triangles which are the smallest cells, or asymmetric units, from which the whole surface can be constructed by reflexions along the faces. It is clear on this representation that the hexagons and the triangles are not Euclidean. The hexagons have angles of $\pi/2$, the angles of the squares before the introduction of the disclinations, so that the orthoscheme triangles have angles of $\pi/2$, $\pi/4$, $\pi/6$. An examination of the possible structures of these triangles readily shows that the possible surfaces in $\mathbb{R}^3$ fall into three categories according to the natures and organizations of some of their characteristic lines.

![Fig. 10. — The {6, 4} tiling of a hyperbolic surface in Poincaré's model and its orthoscheme triangles with angles $\pi/2$, $\pi/4$, and $\pi/6$, polygons (a, b, c, d), (e, f, g), (h, i, j, k) and (l, m, n, p), are discussed in the text.](image)

We consider the three sides of the orthoscheme triangle, if some of them are straight they determine infinite straight lines on the surface without singularity. The knowledge of these straight lines and their angular relations will help us to build surfaces:

- all three cannot be straight as the triangle is not Euclidean;
- the two sides of the right angle can be straight if the hypotenuse is curved as the quadrangle (a, b, c, d), with straight sides, three angles of $\pi/2$ and one of $\pi/3$, can be built as a saddle shaped polygon,

moreover it is one of the nine Schoenflies' quadrangles which can be organized periodically in $\mathbb{R}^3$, it is shown in figure 11a [15].

- the hypotenuse and either side of the right angle cannot be straight simultaneously as, for instance, triangle (e, f, g) with straight sides and of angles of $\pi/2$, $\pi/6$, $\pi/6$ is impossible;
- the hypotenuse can be straight alone as the quadrangle (h, i, j, k), with equal straight sides, two angles of $\pi/2$ and two angles of $\pi/3$, can be built as a saddle shaped polygon and is also one of Schoenflies' quadrangles, it is shown in figure 11b;
- when either sides of the right angle are straight, either a third Schoenflies' quadrangle (l, m, n, p), shown in figure 11c, or the hexagon of the tiling with straight sides and angles of $\pi/2$, Petrie's polygon of the cube shown in figure 11d which can also be organized in $\mathbb{R}^3$, can be built. But these two cases are associated together and can be built with the quadrangle of the second case as shown in figure 12 [15].

- the last possible case, when all three sides are curved, will be precised later.

![Fig. 11. — Three Schoenflies' quadrangles (a, b, c, d), (h, i, j, k) and (l, m, n, p), and Petri's hexagon.](image)

![Fig. 12. — Polygon (l, m, n, p) and Petrie's hexagon can be built with Schoenflies' quadrangle (a, b, c, d).](image)
In principle we can therefore build three classes of surfaces: surfaces with orthoscheme triangles having the two sides of their right angle straight and a curved hypothenuse which are supported by one of Schenflies' periodic skeleton of straight lines, surfaces with triangles having a straight hypothenuse only which are supported by another Schenflies' skeleton and surfaces with triangles having all sides curved.

5. Relation with infinite periodic minimal surfaces.

We have shown above that the two first classes of surfaces which are solutions to our problem are supported by skeletons of straight lines which can be organized periodically in \( \mathbb{R}^3 \). Surfaces of this type have been studied by mathematicians under the condition that they are minimal or have zero mean curvature, i.e. \( \frac{1}{R_1} - \frac{1}{R_2} = 0 \) where \( -R_1, R_2 \) are the radii of curvature, a condition which we have not introduced yet and whose necessity in our problem will be discussed now. The minimal property of the middle surface stems out from the symmetry of the cell, or the identity of the two sub-spaces separated by the film. It implies that the Gaussian curvatures of the two interfaces, at equal distances \( l \) on either sides of the middle surface, are identical. If the middle surface has curvature radii \( -R_1, R_2 \) those of the two parallel surfaces are respectively \( -(R_1 - l), (R_2 + l) \) and \( -(R_1 + l), (R_2 - l) \). The equality of their Gaussian curvatures \( -(R_1 - l)(R_2 + l) = -(R_1 + l)(R_2 - l) \) imposes \( R_1 = R_2 \) and the middle surface is minimal. Following this the examination of the surfaces of the mathematicians will provide us with the solutions to our problem. Mathematicians first calculated finite minimal surfaces bounded by quadrangles of straight lines, such as those of Schenflies, and showed that they could be used as fundamental regions for building infinite periodic minimal surfaces, or IPMS [16]. Their approach is summarized in [17], including further developments. In this paragraph we describe the two IPMS which are supported by the quadrangles of our two first classes and a third IMPS without straight lines, obtained from the two others by a geometrical transformation, which provides information about our third class.

5.1 SCHENFLIE'S QUADRANGLE OF STRAIGHT LINES \((a, b, c, d)\) AND SCHWARZ' \(F\) SURFACE. — The translation cell for the skeleton built with this quadrangle, and the element of IPMS supported by it, are shown in figure 13. One may notice that the sides of the hexagons of the \( \{6, 4\} \) tiling are straight lines. This cell is the usual representation of the \( F \) surface calculated by Schwarz. However this is not a translation cell for the IPMs itself as it is too small to allow periodic reorientations of the normals to the surface, as can be seen in figure 13 where the normals at the intersections of two straight lines of the skeleton can be easily drawn. A cell respecting the periodicity of the orientations of the normals is drawn in figure 14. The straight lines of the skeleton are the asymptotic lines of the surface, they are orthogonal at hyperbolic points and the points where they intersect \( 6 \) by \( 6 \) are parabolic points, the hypothenuses of the orthoscheme triangles are the principal lines of curvatures. The two labyrinths separated by this surface are congruent and are made of channels whose axes are rods connected four by four at angles of 109°28'.

5.2 SCHENFLIE'S QUADRANGLE OF STRAIGHT LINES \((h, i, j, k)\) AND SCHWARZ' \(P\) SURFACE. — The translation cell, here convenient for the skeleton and
The usual representation of the cell of surface $P$ with the Schoenflies' quadrangles supporting it is drawn in figure 15. One may notice that the sides of the hexagons of the $\{6,4\}$ tiling are here, at a very good approximation, arcs of circles. This is the usual representation of the cell of the $P$ surface calculated by Schwarz. The two labyrinths separated by this surface are congruent and are made of channels whose axes are rods connected six by six at right angles. In figure 16 we show another cell which was obtained from the preceding one by a translation along the diagonal of the cube, its interest is to suggest that there exist a close relationship between $F$ and $P$ surfaces. Besides their similar appearances the elements of surface in the cells also have the same area, as they contain the same number of orthoscheme triangles, and have the same Gaussian curvature, as they have been extracted from the same hyperbolic plane. Indeed the two surfaces are associate surfaces, more precisely in their case adjoint, in Bonnet's transformation, i.e. they can be transformed into one another by a transformation of bending without stretching [17, 18]. For instance, the straight sides of the hexagons of the tiling in the $F$ surface are transformed in the circles limiting those of the $P$ surface.

5.3 SKELETON OF CURVED LINES AND SCHENF'S $G$ SURFACE. — It has been shown recently that an IPMS without any straight line occurs in the course of Bonnet’s transformation of surface $F$ into surface $P$ and is unique [17]. This associate surface to $F$ and $P$ surfaces is called the gyroid, or $G$ surface, as the sides of the hexagons of its $\{6,4\}$ tiling are portions of helices of alternatively opposite chiralities. These helices are the intermediate state between the straight lines and circles of the $F$ and $P$ surfaces. The fact that surfaces $F$, $G$ and $P$ are associate in Bonnet’s transformation means that they have the same Gaussian curvature and are obtained from the same hyperbolic plane. As surfaces $F$ and $P$ have the same orthoscheme triangles than our surfaces this hyperbolic plane is the same than ours and $G$ is also obtained from it. $G$ being unique this indicates that there is only one periodic skeleton of curved lines possible in our third class. We have not represented the cell of the $G$ surface here because of the difficulty of the drawing but photographs of plastic models can be found in the literature [17, 19]. The two labyrinths separated by this surface are oppositely congruent, or of opposite chiralities, and are made of channels whose axes are rods connected three at angles of 120°.

5.4 GENERAL REMARK. — It is important to notice that all these surfaces do not have a constant Gaussian curvature although the hyperbolic plane has. Metric distortions are needed in order to embed a hyperbolic plane in $\mathbb{R}_3$. This is similar to what happens to a torus embedded in $\mathbb{R}_3$, it keeps an average zero Gaussian curvature but regions of positive and negative curvatures appear on it.


Cubic structures with bicontinuous topologies are currently found in systems of amphiphilic molecules [1, 20, 21], they might be formed by some systems of mesogenic molecules also [3] and, quite recently, one was observed to be built by a large copolymer with amphiphilic properties [22]. They are located in the immediate vicinity of lamellar and smectic phases with periodicities along one dimension [23]. In the well documented case of cubic phases built by amphiphiles they are described as assemblies of two interwoven 3D labyrinthine nets which are separated by a film and therefore not connected together. The distribution of water and amphiphilic molecules depends on the location of the cubic phase relative to
the nearby lamellar phase. On the low hydration side the labyrinths are made of water channels and the film separating them is made of amphiphiles, on the high hydration side the situation is inverted as represented in figure 1b. Up to now three structures have been reported, most of them being determined by X-ray scattering. The data we dispose about SmD phases of mesogenic molecules are more fragmentary at the moment but they strongly suggest that this description, including topology and symmetry, is valid in their case too [3].

6.1 Structure with space group Pn3. — It was proposed first for a phosphatidyl ethanolamine/water system, the lipid having been extracted from insects [20]. More recently it was identified in the glycerol monooleate/water system [24]. This is also the structure proposed for the phase formed by the polymeric material quoted above which was studied by electron microscopy [22]. The structure is represented in figure 17. The two congruent labyrinths, each with rods connected four by four at angles of 109° 28', are the labyrinths of surface \( F \).

![Fig. 17. — The two labyrinths of rods in a structure with space group Pn3.](image)

6.2 Structure with space group Im3m. — It was proposed first to interpret electron micrographs of prolamellar bodies of the membrane system of a plant [25] and might have been observed more recently in ternary and binary system by X-ray scattering [21]. The structure is represented in figure 18. The two congruent labyrinths, each with rods connected six by six at right angles, are those of surface \( P \).

![Fig. 18. — The two labyrinths of rods in a structure with space group Im3m.](image)

6.3 Structure with space group Ia3d. — It was the first structure to be characterized with certainty [26]. It is quite widespread and can be found in soap, phospholipid, detergent systems, hydrated or not [1, 20]. The structure is represented in figure 19. The two oppositely congruent labyrinths, each with rods connected three by three at angles of 120°, are those of surface \( G \) and of our third class.

![Fig. 19. — The two labyrinths of rods in a structure with space group Ia3d.](image)

7. Discussion.

The facts that the configurations imposed by geometry are IPMS and that they agree with the structures observed in liquid crystals are quite satisfying but deserves some comments.

First one may ask if it is necessary to follow such an intricate path to arrive at this result. Indeed the analogy between IPMS and cubic liquid crystalline structures had been emphasized before [27, 28]. One might think to invoke a very simple argument to justify this analogy. As these structures are built by one film separating two identical sub-spaces the pressures on either sides of it are equal and, following Laplace-Young law, the film must have a zero mean curvature as IPMS have. However there are reasons to worry about this argument. First, Laplace-Young law assumes a surface tension mechanism which is certainly not a dominant term here as no reservoir is present to feed any increase of the area of the film. Second, calling for IPMS directly in such a context is doubtful. IPMS were built as periodic organizations of fundamental frames supporting finite surfaces with minimal area. They
contain therefore implicit boundary conditions which are the skeletons of lines drawn by the supporting frames. These skeletons do not exist in the physical problem so that the question of the stability of IPMS in the absence of any skeleton and under the action of superficial tension alone must be addressed. Although this point has not been investigated yet it is thought that IPMS should not be stable unless another term intervenes [29]. This is why we have explored the possible role of an intrinsic property of the film, leading to a frustration between curvature and distances, which was suggested to us by previous structural studies. From our geometrical development it appears that IPMS intervene as possible geometrical configurations respecting the constraints of space. Indeed the frustration is optimized for hyperbolic surfaces having the topologies and symmetries of IPMS, taking account of interactions between molecules inside the surface and of the surface with other parts of it, but the exact geometries might be slightly different, owing to the exact properties of these interactions. Another geometrical argument was recently invoked to support the similitude between the organization of the film in the Pn3 structure and the F surface [30]. It was argued that if the number of first neighbours of one molecule in a film became larger than the six possible in the plane the flat film of a lamellar phase should transform into a hyperbolic surface, and the F surface was proposed. This point of view is indeed similar to ours in the sense that the curvature of a surface and the number of first neighbours on it are topologically related [31]. Finally the role of the fact that minimal surfaces are locally equivalent to electrostatic equipotentials was also explored, but not conclusively in the case of the systems under study [32].

The second point concerns the fact that our approach introduces three IPMS only when seventeen IPMS free of self intersection have been calculated [17]. Seven of them, which have non congruent labyrinths, could not be obtained as we considered situations where one film separates two identical sub-spaces only. This is supported by the fact that layers of water, or amphiphiles, are always identical in these systems, a different situation would imply non equilibrium states with gradients of chemical potential. Among the ten left, which have congruent or oppositely congruent labyrinths, five only have the cubic symmetry compatible with the isotropic properties of a fluid film along its surface. Finally among these five two have high genuses, $g = 9, 19$. Indeed a thorough examination of translation sub-groups in the hyperbolic plane shows that solutions with higher genuses are also possible [33]. However one may think that they imply rather high energies of curvatures because of the complexities of their cells. The three cubic IPMS left, with $g = 3$, appear therefore as the most probable solutions. They are the F, P and G surfaces. It should not be forgotten however that the relaxation of one of the above constraints by some physico-chemical mean might induce the occurrence of one of the other surfaces.

The last point to be discussed concerns the fact that the frequencies of occurrence of the three natural structures are very different : structure Ia3d, with surface G, is the most common while structure Im3m, with surface P, was met only twice. This can not be understood from geometry alone but might be related to the stabilities of labyrinths of different connectivities. Most likely knots of 3 rods connected at angles of $2 \pi /3$ are more stable than knots of 6 rods connected at angles of $\pi /2$, as in the well known case of liquid films.

8. Conclusion.

We have considered « bi-dimensional » objects which are fluid films organized by interfaces. Their structures result from the actions of forces normal to the interfaces, which control the periodicity of their stackings, and forces parallel to the interfaces, which control the interfacial curvatures. These physical forces must exert their actions in Euclidean space $R_3$ which has geometrical properties of its own. The structures are therefore to be seen as adaptations of physical forces to geometrical constraints. This is indeed the point of view of classical crystallography which has been mainly developed for « zero-dimen-sional » objects such as atoms and molecules. A typical example of the rigor of geometrical constraints in this case is provided by metallic atoms which tend to pack in a compact tetrahedral structure with tetrahedral interstices. As it is impossible to obtain a dense packing of regular tetrahedra in Euclidean space $R_3$ different solutions are found : the classical f.c.c. or h.c.p. structures in which tetrahedral interstices are mixed with octahedral ones and a large number of structures which correspond to packings of distorted tetrahedra such as Frank and Kasper structures, amorphous metallic structures and quasi-crystals [5]. This point of view should not be limited to point objects. It was recently applied to the understanding of the formation of twisted fibers by non-chiral polymers which are « uni-dimensional » objects [34] and films of molecules appear as good examples to investigate the crystallography of « bi-dimensional » objects.

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References

SADOC, J. F. and MOSSERI, R., Pour la Science (jan. 1985) ;
MOSSERI, R., in Du cristal à l'amorphe, proceedings of the Beg Rohu Summer school 1986 (Editions de Physique), to be published.
[10] The Schlafli notation {p, q} means that the tiling is made of polygons having p edges that meet q at each vertex.

As emphasized by one referee the {6, 4} tiling of the hyperbolic plane represented in figure 10 reminds of some of Escher's drawings, although of much lesser artistic value, the kinship is indeed not fortuitous, see :

[18] BONNET, O., C. R. 37 (1853) 529.
[23] Bicontinuous cubic phases are observed in the vicinity of lamellar ones, cubic phases with different topology may exist far from lamellar phases, in the vicinity of micellar phases, see for instance :
[34] KLEMAN, M., J. Physique Lett. 46 (1985) L-723.