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BLUE PHASES : EXPERIMENTAL SURVEY AND GEOMETRICAL APPROACH

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Résumé - Les phases bleues apparaissent dans les cristaux liquides chiraux entre la phase cholestérique et la phase isotrope. Elles sont chirales et optiquement isotropes, elles présentent des crystallites de symétrie cubique et réfléchissent sélectivement la lumière (diffraction de Bragg). L'existence de ces phases a été interprétée géométriquement en utilisant un paramètre d'ordre uniaxe, le directeur, qui localement tend à s'arranger en configuration de double twist, mais cet ordre local ne peut être étendu à grande distance. Il serait plus ou moins satisfait dans des régions finies de l'espace (cylindres de double twist) qui s'empileraient en donnant des structures cubiques. L'assemblage de tels cylindres engendre l'apparition de défauts linéaires (disclinaisons \( s = -1/2 \)) arrangés périodiquement. L'espace entre les cylindres peut être décrit par une surface triplement périodique et sans intersections, comme par exemple l'une des trois surfaces minimales périodiques infinies P, D ou G. Le champ de directeur serait alors dirigé suivant les directions asymptotiques (courbure nulle) de ces surfaces.

Abstract - Blue phases appear in chiral liquid crystals between the cholesteric phase and the isotropic one. They are chiral, non-birefringent, they grow crystallites with cubic symmetry which scatter light selectively (Bragg scattering). The existence of such phases can be interpreted with use of an uniaxial order parameter, the director, which locally tends to perform a double twist configuration, but this local order cannot be extended at large distance. It would be more or less satisfied inside finite regions of the space (double twist cylinders) which would pile in order to form cubic structures. Such periodic sets of cylinders generate periodic arrays of defect lines (disclinations \( s = -1/2 \)). The space in between the cylinders can be described by a periodic surface with no self intersections, such as one of the three infinite periodic minimal surfaces, P, D or G. The director field would then be parallel to asymptotic directions (with vanishing curvature) of these surfaces.

INTRODUCTION

Although blue phases were first detected hundred years ago, they have only recently begun to be better understood. Intensive blue phase research started about ten years later than the general interest in liquid crystals. The rich polymorphism observed in liquid crystals is due to the shape (rod-like or disc-like) of the molecules which constitute them. These molecules are generally composed of a rigid part made of phenyle rings and of flexible aliphatic chains. The molecules rotate quickly around their mean axis and this induces a global axial symmetry. This local order parameter generates mesophases such as the nematic phase, where the molecular axes tend to be parallel. In such phases, the molecules can diffuse as in a classical liquid and there is no translational order. In the smectic phases, the molecules are organized in parallel layers: there is a positional order but only in one direction. All these mesophases are obtained by slowly decreasing the temperature starting from the liquid phase.
That is why they are called thermotropic liquid crystals whereas in lyotropic liquid crystals, both temperature and water concentration can be changed. They are commonly described and represented using a local order parameter, the director $\mathbf{n}$, which is the mean orientation of the molecules inside some volume. This volume must be larger than the typical size of the molecules in order to obtain a continuous description, but smaller than the physical lengths involved. $\mathbf{n}$ and $-\mathbf{n}$ are equivalent, even when the aliphatic chains apart from the core are different since both orientations are found.

Cubic thermotropic phases which present a great analogy with the lyotropic cubic phases have also been recently exhibited. Some of them are presented in this book. Blue phases are also cubic phases, but are observed when mixing nematic compounds and chiral molecules which have an asymmetric carbon. Some chiral polymers also give rise to blue phases which can be easily frozen (under $T_g$) and studied by electron microscopy. The simplest image to understand what happens with chiral molecules is to assume that these molecules induce a screw symmetry on the director. Let us follow this assumption. Setting two screws in close contact implies that they are tilted one compared to the other as shown in Fig. 1, so that the threads fit together. The tilt angle is just given by the angle $\alpha$ of the helix at the surface of the screw. Piling screws in one direction generates a linear increase of the tilt of the screw axes which is called a twist.

![Twist diagram](image)

Fig. 1 - Twist occurs when piling helical cylinders.

One recovers the orientation of the first screw after a distance $\lambda = d\pi/\alpha$ where $d$ is the screw diameter. $2\lambda$ which is called the pitch can be very large compared to the typical length $d$. Such a description is probably naive but certainly useful to understand the existence of helical phases. In the cholesteric phase, like in the nematic phase, the molecules have no positional order but only an orientational one. Their orientation is the same inside planes perpendicular to one direction but twist occurs when moving in this direction. When the cholesteric pitch lies in the range of visible light, such a phase appears as colored due to selective Bragg scattering. The pitch, and thus the color, usually depends on temperature. When the pitch of the cholesteric is small enough, that is for strong twist, some other phases may appear when cooling down from the isotropic phase before reaching the cholesteric one. These phases are the blue phases. At present three blue phases are known: BPI, BPII, BPIII. The first two are cubic, the structure of the third one is not yet quite understood. A short experimental review on the cubic blue phases is presented in section 1 whereas section 2 is devoted to the crystallographic approach of these cubic systems.

The basic assumption usually done to explain the existence of these phases is that twist occurs not only in one direction like in the cholesteric phase, but in all directions perpendicular to the director: this is called double twist. As shown in section 3, it is impossible to find a director field which fulfills this condition everywhere. Nearly perfect double twisting fields
can be built inside finite domains. Models of cubic structures (section 3) have been proposed which consist in packing such domains. The impossibility to find a perfect double twisting director field is revealed by the presence of disclination lines in between the domains. This would explain why blue phases appear near the isotropic phase where defects do not cost too much of energy. The disclination lines are also organized in cubic arrays and thus blue phases are often described as networks of defect lines. There is at present no experimental evidence for such arrays. Another way to describe these systems is to consider the surface separating the different domains. This surface is triply periodic and non intersecting. Its topology is exactly the same as that of the interface in some cubic lyotropic systems. In order to get some analytical expression of the field near the surface which leads to a minimization of the elastic free energy, and following the analogy with the lyotropic systems, this surface has been approximated by the minimal surface which has the same topology (section 4). Following this assumption, we have shown that the director field lines are parallel to the asymptotic directions (with vanishing curvature) on the surface.

1 - EXPERIMENTAL SURVEY ON CUBIC BLUE PHASES.

During the past ten years, blue phases have attracted the attention of many scientists and thus have been already extensively reviewed /4/, /5/, /6/. In this section, all experimental aspects of research on blue phases will not be covered, but we shall focus on main properties which are useful to understand the basic theoretical concepts introduced to elucidate blue phase structures.

Blue phases were originally encountered in cholesteryl esters where they reflect light weakly at deep violet wavelengths. They are often difficult to detect since they occupy a temperature span less than $1^\circ C$ at a temperature where they are easily confused with transitional effects. At present, three distinct blue phases have been clearly identified in the following sequence:

- cholesteric
- BPI
- BPII
- BPIII
- isotropic phase

Blue phases seem to occur only in cholesteric systems of sufficiently small pitches. In a mixture of nematic compound and of chiral molecules, the pitch can be changed by replacing part of the chiral molecules by chemically identical ones but with the opposite helical sense (racemic). At medium mole fraction, the pitch begins to diverge. When the pitch exceeds some critical value, blue phases and especially BPII disappear. This seems to be a universal feature of blue phases.

The most convincing evidence for the thermodynamical existence of blue phases has come from heat capacity measurement. For cholesteryl nanoate, Thoen /7/ has measured latent heats for the four transitions: chol-BPI, BPI-BPII, BPII-BPIII and BPIII-isotropic. Although the three first ones are significantly smaller than the forth one (one or two order of magnitude), this clearly indicates that the transitions are all first order. From the relative values of the latent heats, it can be seen that order in blue phases is closest to the helical order of the cholesteric phase and that this order is retained up to the isotropic transition.

Optical methods are of great utility to investigate the structures of blue phases since the lattice parameter is of the order of magnitude of a half pitch of the cholesteric phase. The main properties of blue phases BPI and BPII are the following:

- they are chiral and non-birefringent,
they grow crystallites (Fig. 2) which give visible or U.V. light Bragg scattering,
- the Bragg reflections are accompanied by rotatory power anomalies.

Fig. 2 - Observation of a single crystal of BPI showing well-defined facets under an optical microscope (from P. Pieranski). Crystallites up to 0.2mm have been grown.

At this stage, we would like to insist on the liquid nature of these phases despite their crystalline habit. Like in the cholesteric phase or in the nematic one, the molecules diffuse very quickly and there is no positional order. Bragg scattering experiments provide the existence that BPI and BPII are cubic. Let us recall the basic features of Bragg scattering. If q₀ is the incident plane wave vector and q is the scattered one, q - q₀ is the scattering vector. In a periodic medium, q - q₀ is necessarily equal to a reciprocal vector. If D is the distance between two consecutive crystallographic planes (characteristic of the translational periodicity), the Bragg condition can be written as:

\[ 2n_0 D \sin \theta = k \lambda, \]

where k is the order of the Bragg reflection and n₀ is the mean refractive index of the medium. Bragg scattering may be performed either on a single crystal stuck on the surface of the cell or on many small crystallites in the volume. In the first case, the orientation of the crystal is imposed by anchoring conditions and it is always a facet with high symmetry which is parallel to this surface. This symmetry may be easily determined by observing the total shape of the crystallite. The distance D between the planes parallel to this facet corresponds via the Bragg formula to half the wavelength which is selectively reflected. In the second case, crystallites have no prefered orientation in the volume and therefore each set of crystallographic planes is, at least for one crystallite, in Bragg position to scatter one selected wavelength. One observes a set of selected wavelenghts which are the signature of the crystallographic structure. From the ratios of the wavelengths, one can in principal deduce the nature of the lattice. Yet two or three Bragg reflections are not sufficient to decide between a simple cubic and a body centered cubic structure. In the first case, the allowed reflections are:

100, 110, 111, 200, 210, 211, 220, ...

(We use the standard Miller index notations: q - q₀ = h a* + k b* + l c* where (a*, b*, c*) is the reciprocal frame). For the bcc structure, the allowed reflections are given by: h + k + l = even and are thus:

110, 200, 211, 220, 310, 222, 321, 400, ...
The ratios of the wavelengths associated to these reflections are exactly the same except for the seventh reflection. But for the simple cubic structure, the first reflection (110) occurs along a four-fold axis whereas, for the bcc, it occurs along a two-fold axis. The direct observation of the shape of the crystallites is therefore a very useful tool since one can distinguish between these two types of symmetry. Another scattering technique which has been successfully used to determine unambiguously the structure of BPII /8/ is the Kossel diagramm technique. The basic idea is to use an incident cone of monochromatic rays instead of plane waves. For one crystallite, each set of reflecting planes generates a scattered cone which generates a circle (dark) in some focal plane. This method reveals as well the orientation of the crystal as the angles and spacings of the planes. Nevertheless, as we shall see in the next section, a complete determination of the symmetry group requires some care in the analysis of Bragg scattering /9/.

2 - CRYSTALLOGRAPHIC APPROACH OF BLUE PHASES.

Experimental behaviour of BPI and BPII clearly shows that these phases are chiral and cubic. Moreover the shape of the crystallites clearly indicates that the symmetry class contains a four-fold axis. Therefore only eight symmetry groups are compatible with these observations:

\[ P432, P4_132, P4_232, P4_332 \]
\[ F432, F4_132 \]
\[ I432, I4_132. \]

Some of these groups have the same Bravais lattice and only differs by the existence or not of a screw axis. Then the question is: can a screw axis be seen by scattering experiments? The answer which is well known for usual X-ray scattering is not so obvious in the case of blue phases. Indeed interaction between light and liquid crystals is theoretically described by a tensor, the dielectric tensor. Scattering is linked to the anisotropic part \( \tilde{\varepsilon} \) of this tensor and the intensity of any Bragg reflection \( \mathbf{q} = (hkl) \) depends on the Fourier component \( \tilde{\varepsilon}(\mathbf{q}) \). As any symmetric and traceless tensor, \( \tilde{\varepsilon}(\mathbf{q}) \) can be expanded in terms of five basic tensors \( \tilde{\sigma}(\mathbf{q}) \) as:

\[ \tilde{\varepsilon}(\mathbf{q}) = \sum_s \epsilon_s \tilde{\sigma}_s(\mathbf{q}) \]

where \( s = 0, \pm 1, \pm 2 \), and \( \epsilon_s \) is a complex number. In a frame where the \( Oz \) axis is taken along \( \mathbf{q} \), the tensors \( \tilde{\sigma}_s(\mathbf{q}) \) are represented by the following matrices:

\[ \sigma_0 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \sigma_1 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & i \\ 1 & i & 0 \end{pmatrix}, \sigma_2 = \begin{pmatrix} 1 & i & 0 \\ i & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \sigma_{-1} = -\sigma_1, \sigma_{-2} = \sigma_2. \]

The main mathematical property of these matrices is that they are just multiplied by \( e^{i\phi s} \) under a rotation of angle \( \phi \) around the \( z \) axis. This behaviour is the key to understand the action of a symmetry group on \( \tilde{\varepsilon} \) which is the physical order parameter in that case. X-Ray scattering usually deals with a scalar order parameter, the electronic density \( \rho \) (except near an absorption edge). It is well known that a screw axis, \( 4_1 \) for instance, induces extinctions for \( \mathbf{q} \) parallel to this axis. A screw axis \( 4_1 \) is the combination of a rotation of angle \( 2\pi/4 = \pi/2 \)
around the axis and of a translation of $c/4$ where $c$ is the periodicity along the axis. Let us take the screw axis parallel to the $z$ axis. The Fourier component $\rho(q)$ defined by:

$$\rho(q) = \int \int \int_{vol} \rho(r) e^{iq \cdot r} d^3r$$

may be expressed when taking into account the effect of the screw axis. At each point $r = (x, y, z)$ correspond a set of points obtained by applying the screw axis: $r_1 = (x_1, y_1, z + c/4)$, $r_2 = (x_2, y_2, z + 2c/4)$, $r_3 = (x_3, y_3, z + 3c/4)$, $r_4 = (x, y, z + c),...$ When $q$ is parallel to this axis, $q=(00l)$, the Fourier component may be written as:

$$\rho(q = (00l)) = \int \int \int_{vol'} \rho(r) e^{iq \cdot r}(1 + e^{2i\pi l/4} + e^{2i\pi l/2} + e^{2i\pi 3l/4} + ... )d^3r.$$

Integration is then done on a smaller volume $vol'$. Starting from one point $r$, all the points obtained by applying the screw axis are associated with the same scalar order parameter and this can lead to destructive interferences. Another way to express this is to say that the screw axis introduces some new periodicity parallel to its direction equal to $1/4$ of the real one. Therefore $3/4$ of the $(00l)$ Bragg peaks disappear. Only the $(0,0,4n)$ reflections are present.

In the case of a tensorial order parameter, the rotation $R$ of angle $\pi/2$ around the screw axis generates a variation of each component $\sigma_s$ as:

$$\mathcal{R}(\sigma_s) = e^{is\pi/2} \sigma_s.$$

Then, when $q$ is equal to $l c^*$, $(q=(00l)):

$$\overline{\epsilon}(q) = \int \int \int_{vol'} \overline{\epsilon}(r) e^{iq \cdot r}(1 + \mathcal{R}(\overline{\epsilon}) e^{2i\pi l/4} + \mathcal{R}^2(\overline{\epsilon}) e^{2i\pi l/2} + \mathcal{R}^3(\overline{\epsilon}) e^{2i\pi 3l/4} + ... )d^3r.$$

When expanding in the basis of the five independant tensors $\overline{\sigma}_s$, one finds:

$$\epsilon_s(q) = \int \int \int e^{iq \cdot r} \epsilon_s(r) (1 + e^{is\pi/2} e^{2\pi l/4} + e^{is\pi/2} e^{2\pi i l} + e^{is3\pi/2} e^{2\pi 3l/4})d^3r,$$

$\epsilon_s(q)$ vanishes when $(s + l)/4$ is not an integer. When compared to the case of a scalar order parameter, there is no extinction, but the intensity of each Bragg peak is linked to different Fourier components as summarized in Table 1. The five basic tensors also control the polarization of the light in a particular way. Therefore this leads to polarization selection rules. The same analysis can be applied to pure rotation axes. One can easily show that for 4- and 3-fold axes, only the $s=0$ component contributes whereas for a 2-fold axis both $s = \pm 2$ and $s = 0$ contribute. Therefore this should forbid a reflection of circularly polarized light on the 111 planes of all simple cubic space groups.

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Table 1: Contribution of the different tensorial components ($s = \pm 2, s = \pm 1, s = 0$) to the scattered intensity for a scattering vector $(00l)$ in the case of a $4_1$ symmetry axis.
The following step is to estimate the relative importance of each Fourier component. On this purpose, Hornreich and Shtrikmann /10/ have developed a theory of blue phases based on a Landau theory where the order parameter is the anisotropic part of the dielectric tensor. In this theory temperature and chirality are the parameters responsible for the existence of the blue phases. Their conclusion is that the main Fourier amplitude corresponds to \( s = \pm 2 \). This could explain why, for instance, the (111) reflection (associated to the \( s = 0 \) component) is often very low which can lead to a wrong interpretation of the diffraction pattern. This shows that much care is needed in the interpretation of the diffraction patterns. The structure of BPII for instance, has been discussed for a long time. It seems now established that the corresponding space group is \( P4_232 \) whereas the symmetry group of BPI is \( I4_132 \). Nevertheless it now appears that the polarized Bragg scattering mechanism is much more complicated than expected and at present the situation is still not clear.

3 - THE ORIGIN OF BLUE PHASES: THE DOUBLE TWIST

The basic assumption to understand geometrically blue phases is that twist occurs not only in one direction like in the cholesteric phase but in every direction perpendicular to the director \( n \) (see introduction). This geometrical constraint can be expressed with use of the free energy per unit volume usually expanded in terms of \( n \) as:

\[
2F = K_{11}(\text{div}n)^2 + K_{22}(n \cdot \text{curl} + q)^2 + K_{33}(n \wedge \text{curl}n)^2 - (K_{22} + K_{24})\text{div}(n \cdot \text{curl}n + \text{div}n).
\]

where \( q \) is the pitch of the cholesteric. This expression can be simplified in the one elastic constant approximation: \( K_{11} = K_{22} = K_{33} \) and \( K_{24} = 0 \):

\[
2F = K \sum_{k,j} (\partial_k n^j + q\epsilon_{ijk}n^i)^2 - q^2
\]

The cholesteric configuration corresponds to a minimum energy and can thus be stable \( (2F = Kq^2) \). But an absolute minimum of the energy would be obtained if the condition:

\[
\partial_k n^j + q\epsilon_{ijk}n^i = 0
\]

were satisfied everywhere. This is in fact the double twist condition. The problem is that this local condition cannot be extended over long distances: knowing the orientation of the director at point A, its orientation at point B depends on the path AB followed to go from A to B (Fig. 3): there is frustration.

![Fig. 3 - When starting from point A with a given orientation of the director and following step by step the double twist rule, the orientation of the director at point B depends on the path AB.](image)

The mathematical tool first used by Sethna /13/ to describe this frustration is a connection. A connection is a rule for transporting vectors (like the director) from one point...
to another. Let us denote by $\nabla$ this connection. It is defined by: $\nabla_k n^i = \partial_k n^i + q e_{ijk} n^j$.

A vector is said parallel transported when $\nabla_k n^i = 0$, which is exactly the double twist rule. The fact that no parallel vector field can be found reveals the existence of a non vanishing curvature for this connection. At this step of the discussion, it is worth noticing that, like in the case of amorphous state $/11/$ or lyotropic systems $/12/$, a perfect solution can be found in a three-dimensional curved space $/13/$, $/14/$.

In our space, there is no simple solution to this geometrical problem. The models which have been proposed $/15/$, $/16/$ consist in satisfying the double twist condition as best as possible in finite regions like spheres in the model of Saupe or cylinders (Fig. 4) in the model of Meiboom et al. These objects are then packed in cubic arrays. The two conditions for a good packing is on one hand to perform the right symmetry group, and on the second hand to fit the orientation of the director when the objects are in contact. In all these models, the director has some special orientation along the symmetry axes of the structure, for instance the edges of the cubic cell. Around one axis, the Oz axis for instance, one can consider a director field of the form:

$$n = \sin(qr) e_\theta + \cos(qr) e_z$$

where $(r, \theta, z)$ are the usual polar coordinates around the $z$ axis.

Fig. 4 - A double twist cylinder: the director is aligned with the cylinder axis and twists when moving radially.

This configuration gets a zero free energy density in the vicinity of the axis ($r \to 0$). The director field lines are shown on Fig. 4: the director is aligned along the tube axis and twists away from this direction when moving towards increasing $r$. This is called a double twist tube. Crystalline structures can be built by stacking pieces of such tubes filled with the director field previously described. When two such tubes come into contact, the tilt angle at the surface of each tube must be adjusted in order that tubes fit together. This determines the radius of the tubes for a given structure and therefore the size of the cell as a function of the cholesteric pitch. Let us first consider three non-intersecting tubes parallel to the three axes of a cube. As shown in Fig. 5, such an arrangement produces either a $s=+1/2$ or an $s=+1$ disclination line. Only the $s=-1/2$ disclination leads to a discontinuity in the director field and is a real defect. Such arrangements can be ordered in cubic networks with the symmetry groups which are experimentally observed. The interesting point is that a network of disclination lines can be associated to each stacking of cylinders. Along these
lines, it is assumed that there is no orientational order as in the isotropic phase.

Fig. 5 - Three tangent double twist cylinders which are perpendicular (the cut plane is normal to the three-fold axis) either generate a defect line (a) which is a disclination \( s = -1/2 \) either not (b). In the second case, the director can escape in the third dimension.

In the simple cubic structure proposed by Meiboom et al (Fig. 6), double twist cylinders are arranged parallel to the cube axes producing \( s = -1/2 \) disclination lines along half of the three-fold axes of the cube (111 direction). The symmetry group of this structure is \( P4_232 \). When taking away half of the cylinders of this structure, one recovers a \( I4_132 \) space group (Fig. 7). The disclination lines which still lie along the three-fold axes are no longer intersecting.

Another way to obtain cubic structures is to consider intersecting double twist tubes instead of tangent ones as shown in Fig. 6 and 7. The simplest model of Fig. 8 corresponds to the Saupe model and does not lead only to defect points as expected by Saupe but also to defect lines. The disclination lines are still along the three-fold axes, whereas the double twist tubes are parallel to the four-fold axes. The symmetry group of this structure has never been observed experimentally in the blue phases (\( I432 \)) but has often been considered.

The other structures that we propose /17/ are reminiscent from the models of rods /18/ proposed by the Luzzati group for cubic lyotropic phases. As said in the introduction, the space groups of the blue phases are sub-groups of symmetry groups of the cubic lyotropic
Fig. 6 - Cubic network of double twist cylinders with a symmetry group $P4_232$ (a) and the corresponding array of defect lines (b).

Fig. 7 - Cubic network of perpendicular double twist cylinders with a symmetry group $I4_{1}32$ (a) and the corresponding array of disclination lines (b).

Fig. 8 - Cubic network of intersecting cylinders (symmetry group: $I432$)(a) and the corresponding array of defect lines (b).
phases where all the mirror operations incompatible with chirality have been removed. For BPI, the double twist tubes are set along the two-fold axes of the $I4_{1}32$ or $Ia3d$ groups. They form two labyrinths and each labyrinth is not connected to the other one. The network of disclination lines is identical to the one of Fig. 7b.

Fig. 9 - In this model, the double twist cylinders are finite and parallel to the two-fold axes. They are aligned along the black and the white rods which are equivalent. This structure is equivalent to that proposed for cubic $Ia3d$ lyotropic phases.

Let us compare the two geometrical models consisting in packing double twist cylinders and leading to the same space groups $I4_{1}32$. Right through the black helical labyrinth of Fig. 9 which is wrapped around a $4_{1}$ axis, one can insert a double twist tube parallel to the $4_{1}$ axis. This means that the two stackings lead to the same distribution of directors and that the double twist is perfectly fulfilled along the $4_{1}$ axes as well as along the $A_{2}$ axes. The question is what happens through the second labyrinth (in white) of cylinders which is wrapped around a $4_{3}$ axis. To fill this space, we propose the following approximation of the director field:

$$n_{z} = sin(qu), n_{x} = cos(qz) cos(qu), n_{y} = sin(qz) cos(qu)$$

with:

$$u = -x sin(qz) + y cos(qz),$$

where $z$ is the coordinate along the axis of the cylinder. It is easy to verify that such a configuration satisfies the double twist condition when $u \to 0$, i.e. on the $4_{3}$ axis.

For BPII, in the model of Meiboom, half of the three-fold axes are defect lines (disclination $s=-1/2$). The second half are disclinations of order $s=+1$ along which the director can escape to form in fact a double twist tube. Let us consider the network formed by these tubes. They are organized into two disconnected diamond labyrinths, which are the same as in the model
of rods proposed for the $Pn3m$ lyotropic phase.

Fig. 10 - Other geometrical model for BP11 $P4_232$. The double twist cylinders are organized in two intertwined diamond structures

4 - BLUE PHASES AND TRIPLY PERIODIC SURFACES.

The link between cubic lyotropic phases and the blue phases is that double twist tubes in the second case play exactly the same rôle as the rods formed by amphiphilic molecules in the second case. We have used this analogy to try to fill the space in between the tubes in the geometrical models of blue phases /19/. Indeed let us assume that the director configuration is obtained by swelling the tubes, that means filling them as best as possible with a double twisting director. The question is what happens in between the two labyrinths in the case of the two observed structures ($I4_32$ and $P4_232$) or of the hypothetical one ($I432$). Like in the lyotropic cubic phases and in the three cases, the two labyrinths of rods are disconnected and split the whole space into two parts. In between one can draw non self intersecting surfaces. Examples of surfaces which fulfill these conditions are infinite periodic minimal ones. Their main property is that their mean curvature vanishes everywhere. Other surfaces which have exactly the same symmetry and the same topological properties are shown in this book /20/.

In the following we shall only consider minimal surfaces and we shall build a director field on these surfaces which minimizes in some way the double twist energy given in section 3.

In order to get expressions of the Cartesian coordinates $x^i$, $(i=1,2,3)$ of the points lying on one infinite periodic minimal surface, the surface is first mapped onto its spherical image by taking the normal at each point. It is then mapped onto the complex plane via a stereographic projection:

$$P(x^i) \rightarrow N^i(\sum n^i_n^2 = 1) \rightarrow \omega = \sigma + i\tau$$

Taking the pole of the projection at the south pole of the sphere involves the following relations between $n$ and $\omega$:

$$n^1 = (\omega + \bar{\omega})/(1 + \omega \bar{\omega})$$
$$n^2 = i(\omega - \bar{\omega})/(1 + \omega \bar{\omega})$$
$$n^3 = (\omega \bar{\omega} - 1)/(1 + \omega \bar{\omega})$$

The cartesian coordinates of a point $P(x^i)$ on a minimal surface are then related to the complex $\omega$ by:
\[ dx^i = (\gamma/2)(a^i(\omega)R(\omega)d\omega + CC) \]

where CC stands for complex conjugate. \( \gamma \) is linked to the lattice parameter. The three complex functions \( a^i(\omega) \) are given by:

\[
\begin{align*}
a^1(\omega) &= 1 - \omega^2 \\
a^2(\omega) &= i(1 + \omega^2) \\
a^3(\omega) &= 2\omega
\end{align*}
\]

\( R(\omega) \) is a holomorphic function of \( \omega \) and can be written as:

\[ R(\omega) = r(\omega, \bar{\omega}) \exp^{i\theta(\omega, \bar{\omega})} \]

\( r(\omega, \bar{\omega}) \) is the norm of \( R(\omega) \), \( \theta(\omega, \bar{\omega}) \) is its argument and is therefore harmonic.

The periodic minimal surfaces we are concerned with are associate. They can be transformed one into the other by adding a constant phase \( \theta_0 \) to \( \theta(\omega) \). The P surface is obtained by using the following holomorphic function:

\[ R(\omega) = 1/\sqrt{1 + 14\omega^4 + \omega^8} \]

The F-surface and the G-surface can be deduced from the P-surface by adding a constant phase equal respectively to: \( \theta_F = \pi/2 \) and \( \theta_G \approx 35^\circ \). All associate minimal surfaces have the same distribution of Gauss curvature. The argument function which changes by a constant term from one minimal surface to an associate one, defines the orientation of the principal directions in the natural frame \( (\sigma, \tau) \). At each point of the surface, each tangent direction defines with the normal a normal plane and a curve on the surface with a specific curvature \( k \). There exists one pair of orthogonal directions for which the curvature \( k \) is maximum. They are the principal directions. The directions along which \( k \) vanishes are called the asymptotic directions. At each point of a minimal surface, there are two perpendicular asymptotic directions whose orientation is defined in the natural frame \( (\sigma, \tau) \) by the angles:

\[
\begin{align*}
\mu_A &= -\theta/2 + \pi/4, \\
\mu_A' &= -\theta/2 + 3\pi/4
\end{align*}
\]

When straight lines lie on the minimal surface, they are necessarily along some asymptotic directions.

In geometrical models of blue phases, pieces of cylinders are filled with a director field which more or less satisfies the double twist configuration. Let us assume that these cylinders are separated by a triply periodic minimal surface. We would like to build a director field on the surface which locally optimizes the double twist constraint. This field could be later on considered as a boundary condition. From symmetry arguments, this field is either normal or tangent to the surface. But a director field normal to the surface would be defined everywhere and would not generate disclinations. Taking into account that geometrical models predict defect lines along the three-fold axes which are perpendicular to the surface, this suggests to consider only tangent director field. To select one of these fields, we can use an energetical criterion linked to the double twist constraint. The connection evoked in section 3 enables to define a double twist energy as follows:

\[ 2F = \int (\nabla_i n)^j (\nabla_k n)^l g^{ik} g_{jlv} vol \]
This expression includes gradient terms tangent and normal to the surface. In order to build a surface contribution to the energy, we do not take into account the terms coming from the normal component. It is equivalent to neglect the influence of the cylinders on the field near the surface. Following this assumption, the surface energy therefore simply reads:

\[ 2\mathcal{F} = \sum_{k=1,2,3} \int ((\nabla_\sigma X)k)^2 + ((\nabla_\tau X)k)^2 dS \]

where \( dS \) is:

\[ dS = (\gamma r(\omega, \bar{\omega})(1 + \omega \bar{\omega}))^2 d\sigma d\tau \]

A unit vector field on the surface is defined by \( \mu(\omega, \bar{\omega}) \) in the natural frame \((\sigma, \tau)\):

\[ \mathbf{X}(\omega, \bar{\omega}) = \cos\mu(\omega, \bar{\omega})e_\sigma + \sin\mu(\omega, \bar{\omega})e_\tau \]

Its components \( X^i, i = 1, 2, 3 \) in the Euclidean frame of \( \mathbb{R}^3 \) are given by:

\[ X^i = 1/2(1 + \omega \bar{\omega})^{-1}(a^i(\omega)exp^i(\mu(\omega) + \theta(\omega)) + CC) \]

One can then compute the free energy as:

\[ 2\mathcal{F} = \int d\sigma d\tau 4 \left| \frac{\partial \mu}{\partial \omega} + \frac{\partial \theta}{\partial \omega} - i\frac{\bar{\omega}}{1 + \omega \bar{\omega}} \right|^2 \]

\[ - 4q_0\gamma r(\omega, \bar{\omega})\sin(2\mu + \theta) + 4/(1 + \omega \bar{\omega})^2 \]

Minimizing \( \mathcal{F} \) with respect to variations of \( \mu \) leads to the following equation for \( \mu \):

\[ \frac{\partial^2 (\mu + \theta)}{\partial \omega \partial \bar{\omega}} + \frac{\partial^2 (\mu + \theta)}{\partial \omega ^2} = -8q_0\gamma r(\omega, \bar{\omega})cos(2\mu + \theta) \]

Let us recall that \( \theta \) is a harmonic function since it is the argument of a holomorphic function, i.e. it satisfies:

\[ \frac{\partial^2 \theta}{\partial \omega \partial \bar{\omega}} + \frac{\partial^2 \theta}{\partial \omega ^2} = 0. \]

Therefore obvious solutions for the angle \( \mu \) are:

\[ \mu_1 = -\theta/2 + \pi/4 \quad (+k\pi) \]
\[ \mu_2 = -\theta/2 + 3\pi/4 \quad (+k\pi) \]

Depending on the sign of \( q_0 \) which determines right or left twist, one solution is minimum and the other one is maximum. The two solutions \( \mu_1 \) and \( \mu_2 \) are exactly the same as those which correspond to the asymptotic directions on the minimal surface. This result is valid for any minimal surface which can be deduced from a Weierstrass function. For such a minimal surface, we have shown that the director field which minimizes some double twist energy lies along the asymptotic directions of the minimal surface. There are two perpendicular sets of asymptotic directions. One is associated to right twist, the other one to left twist. Fig. 11 shows one of the asymptotic direction fields on the P surface which is the simplest to draw.
Such construction also exists on the D- and G-surface which have the same symmetries as BPII and BPI.

Fig. 11 - The director field on a triply periodic minimal surface: a first step to fill the space in between the cylinders.

This result is quite satisfying since asymptotic directions exhibit a singularity around the three fold axis where the total curvature is zero: all the tangent directions are asymptotic. Those points of the surface which are flat correspond to defects of the director. Moreover this singularities are \( s = -1/2 \) disclination. This is in good well agreement with the model of cylinders. The next step would be to prove whether the minimal surfaces are the only good candidates for the partition surface between the two graphs of cylinders.

REFERENCES