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Geometry of (non smectic) hexagonal mesophases

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Résumé. — On observe fréquemment un ordre hexagonal dans les cristaux liquides, notamment dans les phases smectiques. Nous considérons ici les phases non smectiques, formées de baguettes indéfinies, flexibles et ordonnées de manière hexagonale. La méthode de Volterra permet de définir les trois composantes principales des défauts de translation : les dislocations transversales de types coin et vis et les dislocations coin longitudinales. On définit également les disclinaisons. Celles formées autour d'axes normaux aux baguettes doivent être fréquentes. Les autres disclinaisons formées autour d'axes parallèles aux baguettes ont peu de chance d'exister à l'état isolé, mais peuvent entrer dans l'architecture du cœur de certains défauts de translation. En l'absence de toute dislocation, les couches réticulaires du système hexagonal forment des surfaces développables, quand la mésophase est déformée continûment. De tels domaines sont limités par une caustique développable, qui dégénère généralement en un axe ; les baguettes forment alors des cercles coaxiaux ou des arcs parallèles autour de ces axes. Certaines comparaisons peuvent être faites avec les smectiques. L'existence d'un ordre hexagonal dans certaines phases cholestériques lyotropes explique l'absence en général de lignes focales dans ces cristaux liquides.

Abstract. — An hexagonal order is frequent in liquid crystals, namely in many smectic phases. We consider here the non smectic phases formed by hexagonally packed, indefinite and flexible rods. The Volterra method enables three main components of the translation defects to be defined : transverse edge and screw dislocations and longitudinal edge dislocations. One also defines disclinations. Those formed about axes normal to rods must be frequent. The other disclinations about axes parallel to rods have little chance of existing. However, they can be involved in the architecture of the core of certain translation defects. In the absence of dislocations, the layers of rods of the hexagonal system form developable surfaces in the continuously distorted mesophases. Such domains must be limited by developable caustics, which often degenerate into axes. The rods then form coaxial circles or parallel arcs about these axes. Certain comparisons can be made with smectics. The presence of an hexagonal order in certain lyotropic cholesterics explains the general absence of focal lines in such phases.

1. Introduction : a brief review of hexagonal structures in liquid crystals. — The examination of X-ray diffraction patterns of several types of liquid crystals reveals the frequent existence of hexagonal packing. In nematic and cholesteric liquids formed by solutions of synthetic polypeptides, the α -helices are arranged hexagonally, the intermolecular distance depending on the concentration [1].

Hexagonal arrays are observed within layers in smectics B. The molecules are either normal to the layers or tilted [2-4].

Hexagonal phases are well known in water-lipid systems and, more generally, in amphiphilic molecules and polymers (review in [5] and [6]).

Another example of hexagonal liquids is provided by the first synthesized discotic components [7-11]. The disc-like molecules form cylindrical piles, which lie parallel in hexagonal order. The distance of two successive molecules in one pile strongly fluctuates.

The disc-like molecules of two adjacent stacks are not in register. The piles can glide with respect to the others and they can bend in parallel [9].

The discotic liquid crystals are thermotropic, but might have lyotropic analogues, as previously suggested [12]. The defects and textures of hexagonal mesophases have been briefly described [9, 13-15]. We study here the geometry of the hexagonal packing of indefinite and flexible rodlike micelles.

2. Symmetries of non smectic hexagonal mesophases. — The two main examples : discotic liquid crystals and hexagonal phases of water-lipid systems show a uniaxial negative birefringence [9, 14]. The director can be represented by a unit vector \mathbf{n} parallel to the optical isotropy axis. The arrow direction is chosen arbitrarily. The symmetries of the perfect crystal are described in figure 1. One can consider the group of displacements which superimpose the

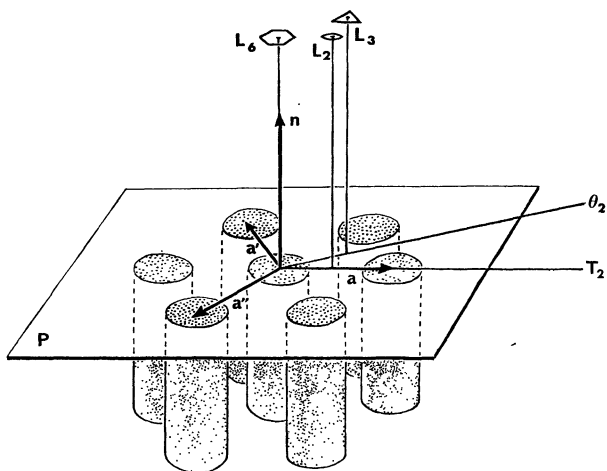


Fig. 1. — Hexagonal array of cylindrical elements of equal diameter. The director is a unit vector \mathbf{n} , lying along the longitudinal axis of an indefinite rod of the hexagonal system. The vector \mathbf{a} lies normally to \mathbf{n} and represents one of the six translations relating one element to one of the six first neighbours. The senses of \mathbf{n} and \mathbf{a} are arbitrary. There are several axes of symmetry. Two-fold axes : longitudinal axes L_2 , transverse axes T_2 (lying along vectors \mathbf{a}), transverse axes θ_2 (bisecting the angles between the axes T_2). Three-fold axes : longitudinal axes L_3 . Six-fold axes : longitudinal axes L_6 . Each point of L_2 or L_6 is a centre of symmetry. Each plane normal to \mathbf{n} is a symmetry plane. The planes (L_6, T_2) and (L_6, θ_2) are planes of symmetry.

crystal onto itself. This group is formed by the following operations :

- All the translations parallel to \mathbf{n} .
- All translations which are a multiple of \mathbf{a} and of the homologous vectors \mathbf{a}' and \mathbf{a}'' (of length $|\mathbf{a}|$ and separating from \mathbf{a} by an angle of $\pm 120^\circ$ in the plane normal to \mathbf{n} ; these translations allow one to pass from one pile to its first neighbours).
- All the rotations by a multiple of π about the L_2 , T_2 or θ_2 axes,
all the rotations by a multiple of $2\pi/3$ about the L_3 axes,
all the rotations by a multiple of $\pi/3$ about the L_6 axes.
- All the products of these displacements.

The microscopic observations and the X-ray diffraction patterns of discotics have not yet confirmed the existence or non existence of a six-fold axis of symmetry. Its presence is quite obvious in hexagonal water-lipid systems. The discotic molecules that have been synthesized so far present six lateral paraffinic chains. Suppose for instance that these external chains tend to be out of the disc plane, three of them on one side, alternating with the three other chains on the opposite side. In figure 2, the chains pointing towards the

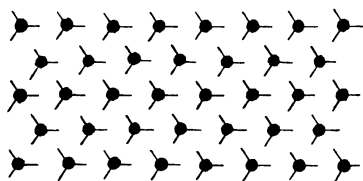


Fig. 2. — An example illustrating the absence of the axes L_6, L_2, θ_2 .

reader are represented and not the chains with the opposite orientation. Such a system present two different L_3 axes, but there is no L_6 axes. This situation is purely hypothetical and simply shows that the presence of a L_6 axis is not obvious. One must also note that the absence of the L_6 involves the absence of the axes L_2 and θ_2 represented in figure 1.

The set of symmetries indicated in figure 1, or the restricted set of symmetries (in the absence of L_6, L_2 and θ_2 axes) allows the definition, by the Volterra process, of translation dislocations (dislocations) and rotation dislocations (disclinations).

3. Dislocations. — Any Burgers vector can be expressed by a linear combination such as :

$$\mathbf{b} = l\mathbf{a} + m\mathbf{a}'$$

l and m being positive or negative integers or zero. As \mathbf{b} lies normally to \mathbf{n} , lines of pure screw dislocation

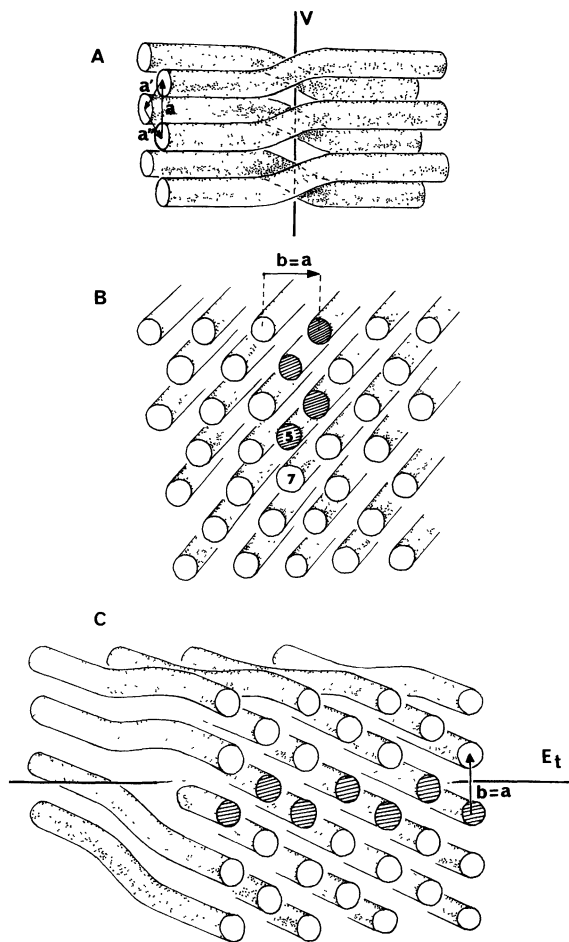


Fig. 3. — Translation dislocations of Burgers vector \mathbf{a} . Three main cases are considered, according to the relative positions of the line L and the vectors \mathbf{n} and $\mathbf{b} = \mathbf{a}$. A : $L \parallel \mathbf{b}$ and $L \perp \mathbf{n}$; screw dislocation; plausible structure of the core. B : $L \perp \mathbf{b}$ and $L \parallel \mathbf{n}$; longitudinal edge dislocation; the core splits into two disclinations indicated 5 and 7 (see Fig. 6). The vector \mathbf{d} joining 5 and 7 is normal to \mathbf{b} . Rods with hatched sections correspond to the supplementary layer of the edge dislocation. C : $L \perp \mathbf{b}$ and $L \perp \mathbf{n}$; transversal edge dislocation; supplementary layer underlined by hatched sections.

are transverse (normal to \mathbf{n}). The pure screw dislocations of vector \mathbf{a} , \mathbf{a}' or \mathbf{a}'' follow one of the three main crystallographic axes. Such a dislocation is represented in figure 3A. There are *longitudinal and transverse edge dislocations*; the vector \mathbf{L} parallel to the dislocation line is normal to \mathbf{b} , which is normal to \mathbf{n} . The directions of \mathbf{L} and \mathbf{n} are thus independent. A longitudinal edge dislocation is represented in figure 3B and a transverse edge dislocation in figure 3C. All translation dislocation lines \mathbf{L} can be replaced by a succession of segments parallel either to \mathbf{b} or to \mathbf{n} or to $\mathbf{b} \wedge \mathbf{n}$. These three kinds of segments are drawn in figures 3A, B, C, in the case $\mathbf{b} = \mathbf{a}$. An important hybrid dislocation (screw and edge) is shown in figure 4. Another interesting Burgers vector is

$$\mathbf{b} = \mathbf{a} - \mathbf{a}'.$$

The three main situations corresponding to this vector are described in figure 5.

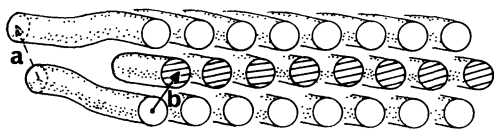
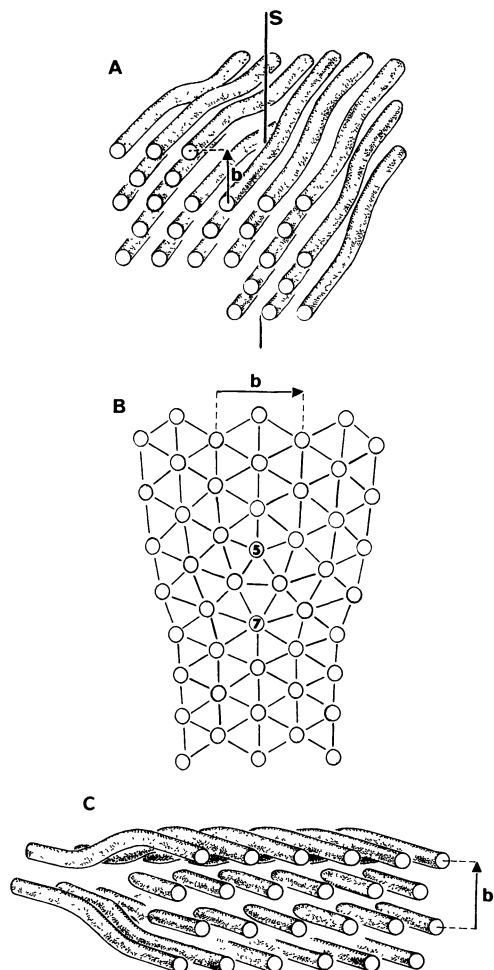


Fig. 4. — Example of hybrid dislocation (screw and edge) of Burgers vector $\mathbf{b} = \mathbf{a}$, which is oblique with respect to \mathbf{L} . Hatched sections of rods indicate the presence of a supplementary layer.



4. **Disclinations.** — The existence of numerous axes of symmetry indicates that a large variety of types of disclinations can be conceived. However, most of them must have prohibitive energies.

4.1 **LONGITUDINAL DISCLINATIONS.** — The rotation vector Ω lies along the longitudinal axes L_6 , L_3 and L_2 . Such disclinations affect the hexagonal order. The smallest rotation angle is $\pm \pi/3$ and occurs around an axis L_6 . The corresponding disclinations are drawn in figures 6A, B. The $\pm 2\pi/3$ rotations occur

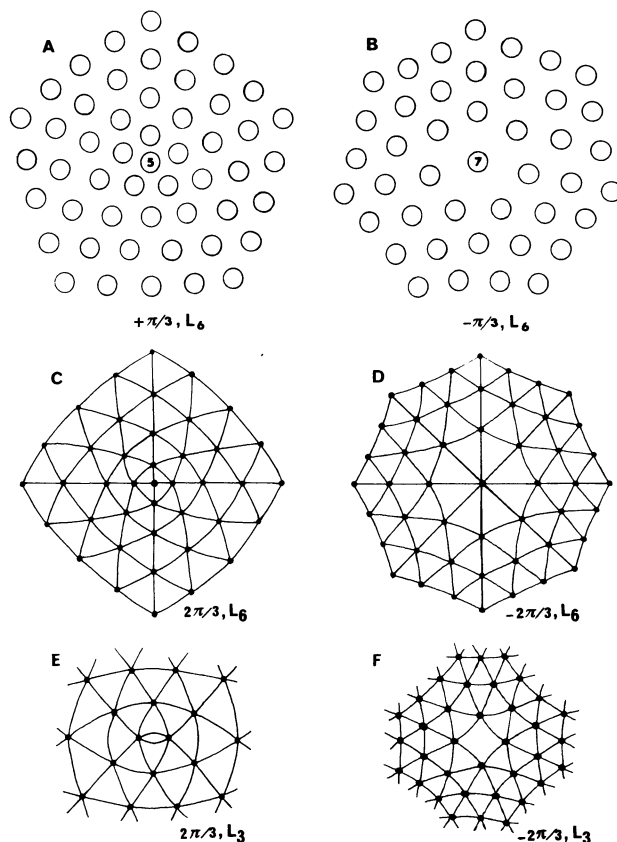


Fig. 6. — A, B : $+\pi/3$ and $-\pi/3$ disclinations of the hexagonal array : The vector \mathbf{a} rotates by $+\pi/3$ or $-\pi/3$ along a circuit closed around the disclination. These defects are classical in many natural hexagonal arrangements such as systems of bubbles at the surface of a liquid [15]. The disclination $+\pi/3$, which leads to a central element enclosed by a ring of five neighbours is found in polyhedral viruses such as adenoviruses and certain bacteriophages. They also exist in the compound eye of insects, which involves an hexagonal array distributed on a convex surface. The $-\pi/3$ disclination forms a decorative pattern in the test of certain diatoms [15]. The disclination $-\pi/3$ has a central element enclosed by a ring of seven neighbours. C, D : disclinations $+2\pi/3$ and $-2\pi/3$ formed around a L_6 axis. Such systems are not observed in natural hexagonal systems and have little chance of existing in really hexagonal mesophases. They may have been used in certain ancient architectures. E, F : disclinations $+$ or $-2\pi/3$ about the L_3 axes.

Fig. 5. — Translation dislocation of Burgers vector $\mathbf{b} = \mathbf{a} - \mathbf{a}'$. Three main cases are considered, according to the relative position of the line \mathbf{L} and the vectors \mathbf{n} and \mathbf{b} . A : $\mathbf{L} \parallel \mathbf{b}$ and $\mathbf{L} \perp \mathbf{n}$; screw dislocation. B : $\mathbf{L} \perp \mathbf{b}$ and $\mathbf{L} \parallel \mathbf{n}$; longitudinal edge dislocation; the core splits into two disclinations indicated 5 and 7 (see Fig. 6). The vector \mathbf{d} joining 5 and 7 is normal to \mathbf{b} and has the length of \mathbf{b} , as in figure 2B. C : $\mathbf{L} \perp \mathbf{b}$ and $\mathbf{L} \perp \mathbf{n}$, transverse edge dislocation.

around the axes L_6 and L_3 and correspond to disclinations represented in figures 6C-F.

The distortions created by these disclination lines are easily studied in a plane normal to the disclination line (Fig. 7). O is the core of the defect. The orientation of \mathbf{a} , one of the crystallographic axes at point $M(x, y)$ makes with Ox an angle φ , which is a function of ω , the azimuthal angle of M. The distance $OM = \rho$. The angle φ is supposed to be a linear function of ω .

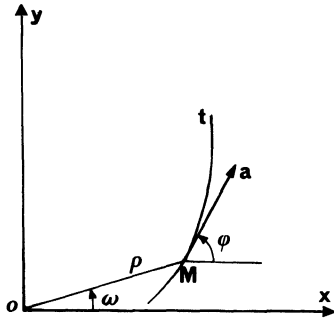


Fig. 7. — Consider a disclination with L parallel to \mathbf{n} ; L cuts the drawing plane in O. The Volterra process involves a rotation Ω around O. The vector \mathbf{a} has an orientation φ , which depends only on ω . One has :

$$d\varphi/d\omega = \Omega/2\pi$$

and along t which is an integral curve of \mathbf{a} , one has :

$$d\rho = \rho d\omega / \tan(\varphi - \omega).$$

This gives a general formula for these curves in polar coordinates :

$$\rho = \rho_0 \sin^{\frac{2\pi}{\Omega - 2\pi}} \left[\varphi_0 + \left(\frac{\Omega}{2\pi} - 1 \right) \omega \right] = \rho_0 f(\omega).$$

As shown in figure 7, at a point $M(\rho, \omega)$, one has :

$$\frac{d\varphi}{d\omega} = \frac{\Omega}{2\pi} \quad \text{and} \quad \frac{d\rho}{d\omega} = \rho / \tan(\varphi - \omega).$$

For $\Omega = \pm \pi/3$, these equations give solutions such as :

$$\rho = \rho_0 / \cos^{6/5} [(5/6)(\omega - \omega_0)]$$

and

$$\rho = \rho_0 / \cos^{6/7} [(7/6)(\omega - \omega_0)].$$

ρ_0 and ω_0 being constants. In such disclinations, one can calculate the varying distance of the reticular rows of the hexagonal system (Fig. 8). One easily observes that the interdistance $a \cdot \frac{\sqrt{3}}{2}$ separating the reticular rows of the hexagonal array increases with the distance ρ to the disclination line, if $\Omega > 0$ and decreases if $\Omega < 0$ (Fig. 6). For $\Omega = +\pi/3$, $|\mathbf{a}|$ varies as $\rho^{1/6}$ and for $\Omega = -\pi/3$, $|\mathbf{a}|$ varies as $\rho^{-1/6}$. In strictly hexagonal media, where the parameter $|\mathbf{a}|$ is rigorously defined, such disclinations cannot have a large extension. The disclinations $+\pi/3$ and $-\pi/3$ should be paired to form translation dislocations as shown in figures 3B and 5B. The vector \mathbf{d} which allows one to pass from one disclination to the opposite is normal

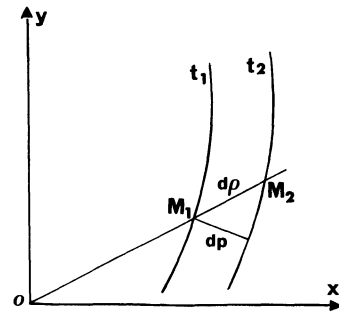


Fig. 8. — One considers two homothetical integral curves of vector \mathbf{a} (t_1 and t_2 with an equal φ_0). The two curves correspond to

$$\rho = \rho_0 \cdot f(\omega) \quad \text{and} \quad \rho = (\rho_0 + d\rho_0) f(\omega).$$

The interdistance of the two curves at the point $M(\rho, \omega)$ is dp . One has :

$$dp/d\rho = \cos \alpha = \sin(\varphi - \omega).$$

One finds that

$$dp = d\rho_0 \cdot (\rho/\rho_0)^{\Omega/2\pi}.$$

This interdistance varies as a power of ρ and does not depend on ω . In the case of $\Omega = \pm \pi/3$, this power is $\pm 1/6$.

to the Burgers vector and has an equal length. The disclinations $\pm \pi/3$ are well developed in media which allow certain variations either of the parameter $|\mathbf{a}|$ or of the angles of the hexagonal array. Such distortions are well known in systems of bubbles floating on water or in the morphology of certain living beings (review in [15]).

4.2 TRANSVERSE DISCLINATIONS. — The rotation vector Ω lies along the axes T_2 or θ_2 . The angles Ω are equal to $+\pi$ and sometime to $+2\pi$. The $+\pi$ disclinations are drawn in figure 9. The existence of these

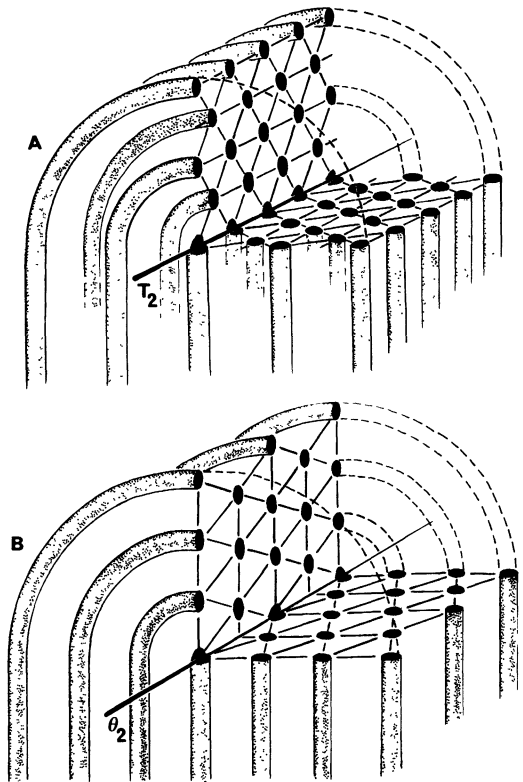


Fig. 9. — Two $+\pi$ disclinations, formed about the binary axes T_2 (A) and θ_2 (B).

disclinations shows that the elements of the hexagonal array can glide one with respect to the other and bend. The disc-like molecules of two adjacent piles in a discotic mesophase are not in register and these mutual motions and deformations are possible. Disclinations corresponding to $-\pi$ and -2π rotations lead to the formation of walls and present probably very high energies. Closed circuits around such systems of defects however correspond to the definition of $-\pi$ disclinations. A theoretical example is shown in figure 10.

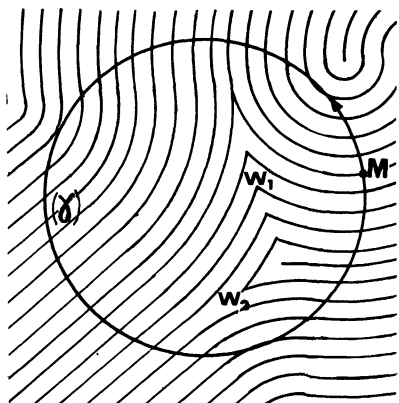


Fig. 10. — A : $-\pi$ disclination ; the director n rotates by an angle $-\pi$ when a point M makes one turn along (γ) in the positive sense. Such disclinations lead necessarily to the formation of walls $w_1, w_2 \dots$ in the vicinity of the core.

As indicated above, the X-ray diffraction patterns do not allow one to establish the presence or absence of a six-fold axis. The symmetry axes L_2 and θ_2 , the symmetry plane (L_6, θ_2) and the symmetry centre are also abolished in the absence of L_6 . Certain associations of disclinations could serve as a proof of the existence of L_6 . Consider for instance a system of two $+\pi$ disclinations forming an angle of 90° and associated as shown in figure 11. The angle of the two

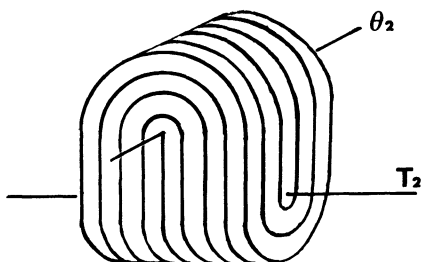


Fig. 11. — System of two $+\pi$ disclinations lying at right angle. Such a situation implies the presence of a L_6 axis. If one disclination is built about a T_2 axis, the other one is formed around a θ_2 axis.

disclination lines is such that one of them is necessarily built about a θ_2 axis, which involves a six-fold symmetry. A similar situation can be considered with an angle of 30° .

The disclinations considered so far are *wedge disclinations*. This means that the rotation vector Ω lies parallel to the disclination line L . One can also consider disclination lines with a rotation vector Ω lying normally to L called *twist disclinations*. This nomenclature is that adopted at a general conference on defects [16]. An example of a twist disclination in an hexagonal mesophase is represented in figure 12.

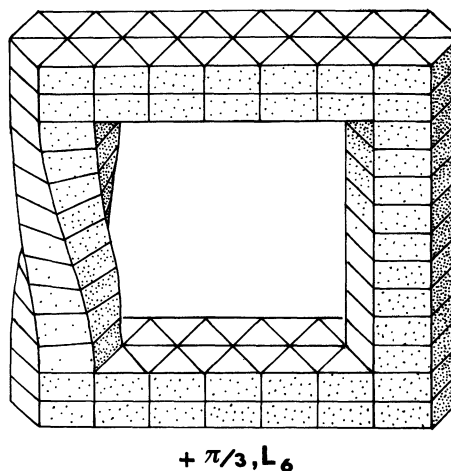


Fig. 12. — Pathological disclination $+\pi/3$ around a L_6 axis. For clarity, the rotation is confined to a unique edge of the frame. This figure finds its inspiration in [25].

The vector of the $+\pi/3$ rotation is normal to the disclination line. Such defects seem to be pathological and have little chance of existing. However, they show how one passes continuously from a longitudinal disclination $+\pi/3$ to the opposite longitudinal disclination $-\pi/3$. The line ceases to be parallel to the rotation vector Ω and becomes a twist disclination and then turns to an opposite disclination $-\pi/3$. The closed circuit of figure 13 shows the possible relation between wedge and twist disclinations.

Opposite wedge disclinations are associated in figures 3B and 5B to form edge dislocations. In screw dislocations such as that represented in figure 3A, one can define two opposite circuits corresponding to the pathological twist disclinations of figure 12. We have built in figure 14 an hybrid disclination with two rotation vectors parallel and normal to the line. This defect also has little chance to be encountered.

5. Pure distortions. — We have defined defects by topological operations. These defects show a core where the hexagonal structure is abolished. At a distance from the core, the structure is deformed but is locally tangent to an ideal perfect crystal. We have now to examine what are the most general deformations, which are compatible with the hexagonal structure and in the absence of defects. We already indicated that the piles may glide and curve. The problem is therefore to know how a system of equidistant curves can form an hexagonal array in cross section. We shall first give a definition of parallel curves in space, like

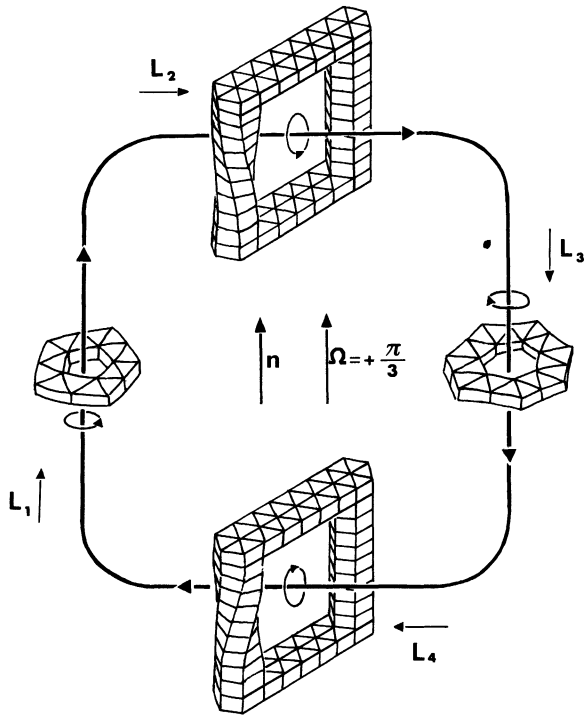
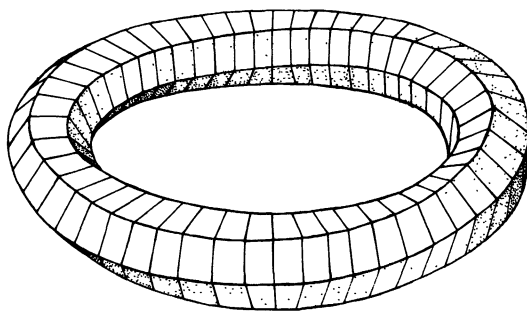


Fig. 13. — Continuous passage from a $+\pi/3$ disclination (on the left) to a $-\pi/3$ disclination (on the right). The $-\pi/3$ disclination is transformed into a $+\pi/3$ disclination by inversion of the sense of L . All the represented defects belong to the same homotopy class.



$-\pi/3, L_6; 2\pi, T_2$

Fig. 14. — Another pathological disclination which involves a $-\pi/3$ rotation about the L_6 axis of the torus and a 2π disclination about any axes normal to L_6 .

that which exists for parallel surfaces. Let us consider a very general curve C with a defined tangent at each point M (Fig. 15). Let there be a plane $P(M)$, normal to C at each point M . In some region of the space, namely in the vicinity of C , the unit vectors n , normal to planes P are defined and present integral curves which will be called the set (C) of parallel curves to C . It is clear that one can consider in a set (C) a subset (H) forming an hexagonal array in transverse section P (Fig. 16). Let us call h this hexagonal array.

The planes P envelop a developable surface D and are tangent to D along generators g . D presents a cuspidal edge E , which is the envelope of g (Fig. 15). The curves C are normal to D and any hexagonal subset (H) of (C) cuts D along an hexagonal lattice h_d .

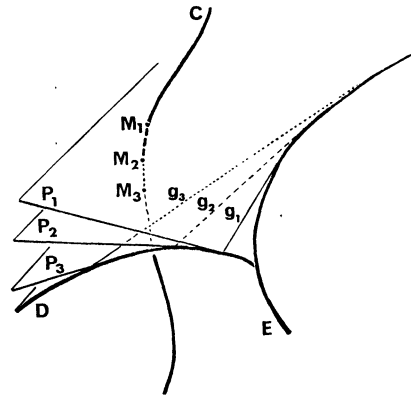


Fig. 15. — A curve C and the set of its orthogonal planes (P_1 in M_1 , P_2 in M_2 etc...) which envelop the developable surface D and the corresponding generators g_1, g_2, \dots which are tangent to the cuspidal edge E .

Consider a given point M in a plane P and a , one of the principal vectors of the hexagonal array. One can define in P the straight line t , set of the points T such as $MT = \lambda a$, λ being any real number (Fig. 16). The line t generates a surface τ when M describes C (Fig. 17). This surface is the envelope of the planes normal to P along t . The surfaces τ are therefore developable. This means that, for a discotic liquid, the set of piles belonging to a row-line of the hexagonal

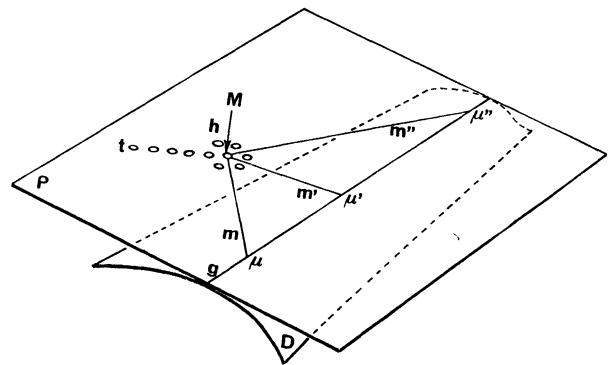


Fig. 16. — Representation of the hexagonal array h in a plane P normal to the indefinite rods forming the hexagonal mesophase; t is a row-line of h . The normals m, m', m'' to the three principal directions in M cut the generator g in three points μ, μ', μ'' . D is the developable surface.

array forms a layer of constant thickness, which has the shape of a developable surface (Fig. 17). These layers of piles are separated by parallel equidistant surfaces σ whose normals m are in planes P (Fig. 17). These normals are tangent to the surface D , which is one of two caustics, the other one being at infinity. There are three sets of layers of columns and their normals at a point M touch D in three different points μ, μ', μ'' , which are aligned along the generator g of D , along which P is tangent. One easily verifies that the cuspidal edges t_d of surfaces σ are curves on D , which are parallel to principal lines of h_d (Fig. 17). The lines t_d are geodesics of the surface D .

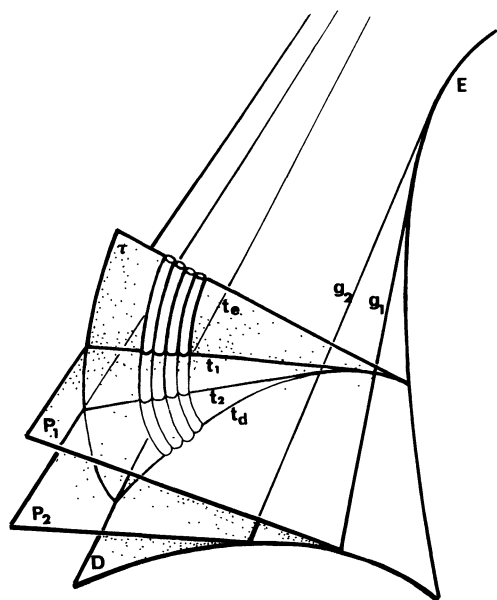


Fig. 17. — Representation of a layer τ of flexible and parallel rods of the hexagonal mesophase. τ is cut by planes P along straight lines t_1, t_2, \dots , associated with the corresponding generators g_1, g_2, \dots of the surface D . The line t_e cuts a generator at its contact with E ; t_d is the envelope of t and belongs to D ; the lines t_d form the hexagonal array h_d of D .

To summarize, any curve E allows the definition of a developable surface D , generated by the set of its tangents g . Planes P tangent to D have normal vectors whose integral lines are the parallel C curves. Conversely, from a given curve C one deduces E . Any hexagonal system extracted from (C) forms layers which follow a set of parallel developable surfaces τ , whose cuspidal edges are geodesics t_d in D . The curves t_d form a regular hexagonal array h_d .

According to the shape or to the topology of D , many cases can be considered D may have the topology of a Riemann surface, if E is an helix. It can be a cone if E reduces to a point, and a cylinder, if the point E is at infinity. In these two latter cases, the hexagonal array h_d can present translation and rotation defects. The total rotation of generators g of D must be an integer multiple of $\pi/3$. Burgers vectors must be integer linear combinations of vectors a, a' or a'' . An example of such a surface D is developed onto a plane, after having been cut along a generator g_0 (Fig. 18); the angle is $+\pi/3$. The position of the hexagonal array must be such that one can join the two generators g_0 in register, to reform the developable cone. The position of h_d presents discrete constraints.

6. Degeneracy of the developable caustics D . —

The parallel stacking of layers of equal thickness leads inevitably to the formation of defects in the regions corresponding to the caustic surfaces. One must note that the bend curvature is infinite all along the surface D . Severe defects are introduced when one tries to extend the hexagonal structure across D , in the concavity of the surface. A very high energy is distri-

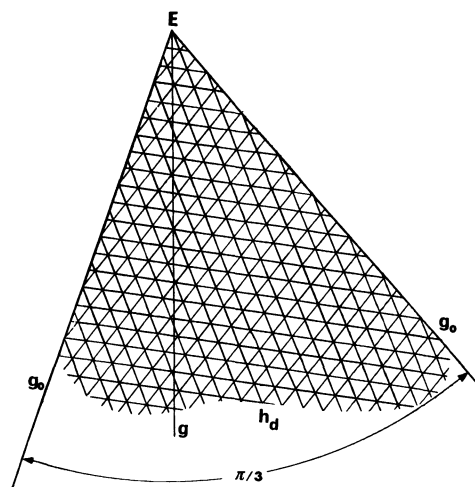


Fig. 18. — The hexagonal array h_d of a conical surface D has been applied onto the horizontal plane, after having been cut along the generator g_0 . The cuspidal edge is reduced to a point. The total rotation of g in D is $\pi/3$.

butted all along D and one expects the degeneracy of such surfaces in all possible cases. One solution can be the reduction of D to one generator δ . The parallel surfaces of the hexagonal structure are coaxial revolution cones or cylinders. In a discotic liquid, the piles of molecules form a set of coaxial circles around the axis δ (Fig. 19). This geometry corresponds partially to that of $+\pi$ disclinations. However, it is not necessary in general that the axis δ coincides with a T_2 or θ_2 axis.

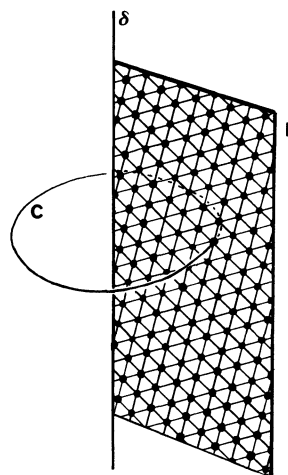


Fig. 19. — Degeneracy of the surface D to a straight line δ common to the planes P . The curves C are coaxial circles; δ has been chosen in the hexagonal array different from θ_2 or T_2 .

7. Comparisons with smectics. — There are obvious analogies between mesophases formed by the stacking of layers of equal thickness and mesophases formed by the hexagonal packing of indefinite rods of equal diameter. There is only one series of layers in the first system and three series in the second one. Certain simple comparisons deserve to be illustrated.

Let us consider a glass cylinder and a mesophase

which surrounds it, with definite anchoring conditions. Let us suppose for instance that smectic A molecules align parallel to the glass surface and normally to the cylinder axis as indicated in figure 20A. The stacked parallel surfaces can form cylinders, whose cross sections are the evolute of the circular section of the glass cylinder. It is not proven that such a texture is energetically stable. This situation is only geometrically conceivable. Let us now consider a discotic mesophase around the glass cylinder, with molecules aligned parallel to the glass surface. The hexagonal array h_d lying on the cylinder can be devoid of defects. There is a discrete series of orientations of h_d which satisfy these conditions. There are also diameters of the glass cylinder which allow one of the vectors \mathbf{a} , \mathbf{a}' or \mathbf{a}'' to be normal to the cylinder axis. One finds again the figure 20A. In general, \mathbf{a} , \mathbf{a}' , \mathbf{a}'' are oblique and h_d is formed by a triple set of parallel helices.

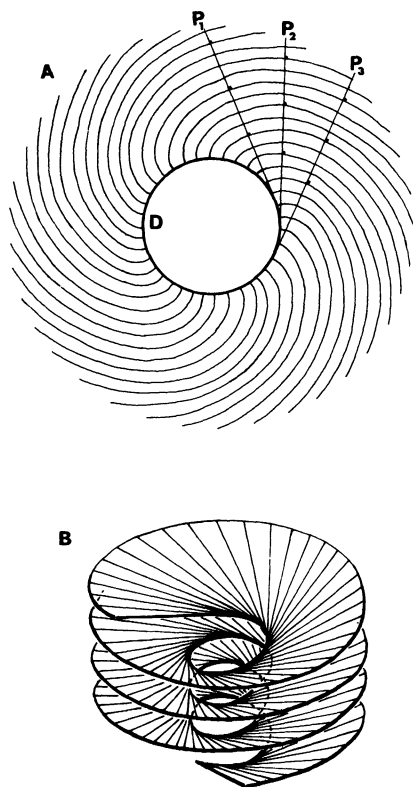


Fig. 20. — A : Set of parallel and equidistant involutes of a circle. This can represent either smectic layers or parallel elongated rods of an hexagonal mesophase around a glass cylinder, with definite anchoring conditions. B : A Riemann surface generated by half tangents to an helix. Parallel curves C are the normal lines to these half tangents in this surface. The helix is thus the evolute of curves C.

The layers of the hexagonal mesophase are the surfaces formed by the sets of half-tangents t to the helices t_d . The flexible rods in these surfaces follow the curves C which are the parallel curves lying normally to the tangents t (Fig. 20B). The existence of a Burgers vector and a rotation vector is obvious in such distortions. This corresponds to the concept of dispiration defined by Harris [15].

It has been indicated above that the developable caustic D very probably degenerates. Similar considerations have been discussed for smectics. In that case, the problem is to know the surfaces whose normals pass through two curves, corresponding to the degeneracy of the two caustics. The general solution corresponds to parallel Dupin's cyclides, the two curves forming a pair of focal conics [16]. For hexagonal mesophases such as discotics and water-lipid systems, one of the two conics is at infinity, the other one being a straight line δ . The parallel surfaces are thus equidistant coaxial revolution cones or cylinders, a situation which is found in the vicinity of focal lines in smectics A. Domains are limited in smectics A by conical surfaces defined by a point of one conic and an arc of the second one. In hexagonal mesophases, if the second conic corresponds to the straight line δ , the limiting surface of a domain is a plane P. Domains of smectics A are tangent along common generators of the two limiting conical surfaces. In hexagonal phases, the domains must have planes P in common.

The director \mathbf{n} is parallel to molecules in smectics A and one has generally : $\text{curl } \mathbf{n} = 0$ and $\text{div } \mathbf{n} \neq 0$. In the presence of dislocations, $\text{curl } \mathbf{n}$ is slightly different from zero. The component of $\text{curl } \mathbf{n}$ parallel to \mathbf{n} corresponds to the density of screw dislocations and the normal component to that of edge dislocations [17]. In non smectic hexagonal mesophases, $\mathbf{n} \cdot \text{curl } \mathbf{n} = 0$ and $\text{div } \mathbf{n} = 0$; the presence of a bend corresponds to $\mathbf{n} \wedge \text{curl } \mathbf{n} \neq 0$. The transverse edge and screw dislocations make $\text{div } \mathbf{n}$ and $\mathbf{n} \cdot \text{curl } \mathbf{n}$ slightly different from zero; the presence of longitudinal dislocations or disclinations do not change the value of $\text{div } \mathbf{n}$ or $\text{curl } \mathbf{n}$ and more simply do not affect the field \mathbf{n} . In hexagonal phases devoid of dislocations one has $\text{curl } \mathbf{a} = \text{curl } \mathbf{a}' = \text{curl } \mathbf{a}'' = 0$; if \mathbf{q} represents any linear combination of \mathbf{a} , \mathbf{a}' or \mathbf{a}'' , one has also $\text{curl } \mathbf{q} = 0$. The density of longitudinal edge dislocations is proportional to $\mathbf{n} \cdot \text{curl } \mathbf{q}$, \mathbf{q} being a vector normal to layers and of constant length.

8. Discussion. — A parallel research on hexagonal mesophases is due to Kléman [18]. It is shown in this work that we admitted intuitively the existence of planes P, which actually deserves a demonstration. Kléman presents a more complete treatment of the problem. The defects of the hexagonal mesophase have been studied by Kléman and Michel [19, 20] in the framework of the theory of homotopy groups [21]. This study covers the main symmetry groups known in liquid crystals. We find useful to pursue the comparison between smectics A and hexagonal (non smectic) phases in this context. In smectics A, at each point M, the director is defined by two parameters, say the longitude and the latitude in an hemisphere representing P_2 , the projective plane. A third parameter is necessary to indicate the position of M within the layer thickness. The hemisphere is easily transformed into a disc and the manifold of the

internal states can be represented by a solid cylinder ; two diametrically opposite points of the lateral surface have to be identified, as points occupying equivalent positions in the two limiting discs (Fig. 21). One distinguishes three types of elementary circuits called (1), (2) and (3). The circuit (1) corresponds to the absence of topologically stable defects. The circuit (2) represents dislocations and the circuit (3) disclinations. All defects correspond to the composition of such circuits. The two subgroups of homotopy are thus $\pi_1(S_1) = \mathbb{Z}$ and $\pi_1(P_2) = \mathbb{Z}_2$; \mathbb{Z} being the additive group of integers and \mathbb{Z}_2 the two-element group of integers (modulo 2).

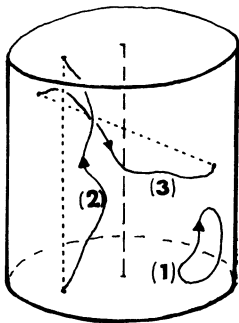


Fig. 21. — Representation of the manifold of internal states of a smectic A and of the submanifold corresponding to rotations in a hexagonal liquid. The elementary circuit (1) represents the absence of any topologically stable defect ; (2) corresponds to the presence of a translation defect in a smectic A or to a rotation defect by an angle $\pi/3$ (or $2\pi/3$), about an axis parallel to \mathbf{n} . The circuit (3) represents a π -disclination about an axis normal to \mathbf{n} in both phases. In the absence of polarity ($\mathbf{n} = -\mathbf{n}$; $\mathbf{a} = -\mathbf{a}$) one has to identify points symmetrical with respect to the horizontal middle plane.

In smectics A, the manifold of internal states is of dimension 3. In hexagonal (non smectic) mesophases, the dimension is 5. The director is represented by the hemisphere P_2 , transformable into a disc. One must also define the orientation of \mathbf{a} ; the corresponding parameter varies from 0 to $\pi/3$ (or to $2\pi/3$ in the absence of a L_6 axis). This allows the building of a submanifold of dimension 3, in the form of a solid cylinder with identifications of points similar to those described in figure 21 for smectics A. Now, the position of a point M in the hexagonal array can be represented by a torus or, by a rectangle, with

identified opposite edges. The manifold corresponding to hexagonal liquids is thus very complicated, the products of certain operations not being commutative. Each discrete change of Burgers vector corresponds to the passage to another class. One also verifies that pathological defects, such as those described in figure 6AB, figure 12 and figure 13, belong to a unique class. The presence of any defect from this class would be a proof of the existence of a L_6 axis. The theory of homotopy groups ignores the existence of focal lines in smectics A. The layers have the shape of revolution domes in the vicinity of focal lines [22, 23] and are not recognized as topologically stable defects. In contrast, focal lines in hexagonal (non smectic) mesophases are represented by δ axes, corresponding to the coaxial alignment of perfect revolution cones. These textures are topologically stable. The indefinite rods of the hexagonal array form coaxial circles about δ . Such a configuration would not be stable for a nematic liquid. There is an *escape in the third dimension* [21] as shown in figures 22A-C. Such a process is impossible for hexagonal phases, since it introduces translation defects, as shown in figures 22D-F. The *escape in the third dimension* is possible for a smectic A. The only point is that one has to start from a radial distribution of molecules instead of a concentric one as in figure 22. This *escape* is physically realized in smectics A along the focal conics.

There is thus a profound difference between focal lines in smectics and δ lines in hexagonal phases, which concerns the topological stability, despite certain geometrical analogies. Another point must be underlined. Thermotropic cholesterics present focal lines in general. However, these defects have never been observed in lyotropic cholesterics such as certain concentrated solutions of synthetic polypeptides [1]. We suggest that the hexagonal order prevents the formation of such defects. At short distance, the reticular layers are developable and the formation of revolution domes (as in smectics A and in thermotropic cholesterics) is forbidden. At longer distance, the high density of dislocations (namely screw dislocations necessary for the cholesteric twist) allow very different shapes ; one observes concentric layers in the spherulitic germs of these synthetic polypeptides. The formation of δ lines is also difficult to

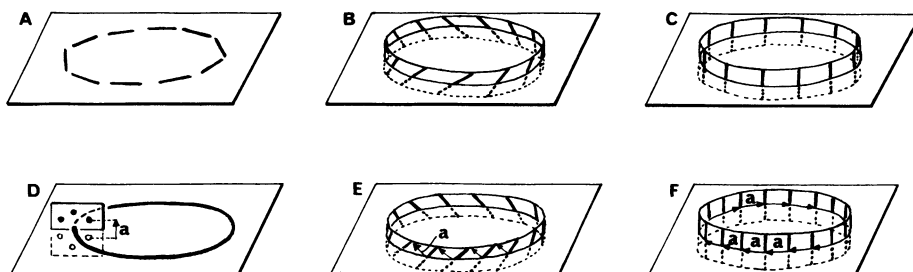


Fig. 22. — A, B, C : *Escape in the third dimension* in the case of a nematic liquid. A configuration of the type $S = 1$ [20] is continuously transformed into a parallel alignment. D, E, F : A similar transformation in hexagonal systems involves translation defects and rotation defects, which change the homotopy class ; \mathbf{a} is one vector allowing to pass from one rod to one of the six first neighbours.

conceive in lyotropic cholesterics, the twist being absent in such defects. One must recall that spherulitic germs of lyotropic cholesterics present a radial screw dislocation. The arrangement of layers around this axis resembles that of a second type of focal line [23]. The layers do not form domes, but a double fold twisted along the radius. The director distribution is continuous all along this defect of the cholesteric arrangement [24]. The folded architecture of the core is compatible with the presence of hexagonal order and developable surfaces in small domains.

It appears therefore, that the hexagonal packing in lyotropic cholesterics, formed by synthetic polypep-

tides, profoundly changes the texture and, especially, prevents the formation of focal lines (with the exception of a very special type of focal lines). This study has shown the importance of the concept of developable surface, not only for the description of caustics in hexagonal liquids, but also for the reticular layers themselves.

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