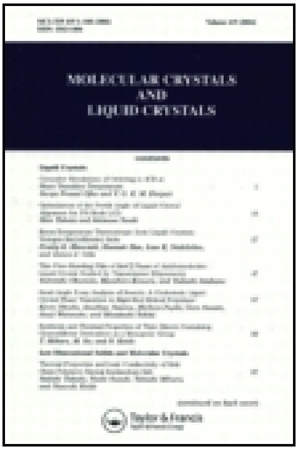

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Basic Liquid Crystal Structures, Polymorphisms and Defects

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BASIC LIQUID CRYSTAL STRUCTURES, POLYMORPHISMS AND DEFECTS

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Abstract A review is given of our present general classification of the liquid crystals. The liquid crystal structures are divided into two main groups: nematic phases with parallel ordering of the long molecular axes and smectic phases having additional layered structure. An interesting phenomenon is that the liquid crystal phases when formed by optical active molecules develop chiral modifications: chiral nematics and chiral smectics. There are four fundamental smectic phases: A, B, L and E having skewed analogues: C for smectic A and F, G, H (with long molecular axes tilted to the side of the hexagon) and I, J, K (tilted to the apex of the hexagon) for smectics B, L and E, respectively. Chiral nematics N^* and chiral modifications of smectics with weak interlayer correlation (C^*, I^* and F^*) form long-range helicoidal structures. We also briefly discuss the main topological defects in liquid crystal structures: dislocations in layered (smectic) or pseudolayered (chiral nematic) phases and disclinations (including focal domains) that are fundamental defects of structures with continuous symmetries.

BASIC LIQUID CRYSTAL STRUCTURES

Liquid crystals can be divided from the thermodynamic point of view into two main classes:

- thermotropic liquid crystals in which the mesomorphic phases arise as intermediate between ordinary crystal and ordinary (isotropic) liquid phases above the melting point of the crystal;
- lyotropic liquid crystals in which the mesomorphic phases arise under action of the solvent on the substance having amphiphilic (polar - nonpolar) character of solubility. The liquid crystal phases in amphiphile - solvent systems exist in certain regions depending upon the concentration and the temperature.

In addition, some mesogenic substances can form the thermotropic as well as the lyotropic phases and thus they can be named amphotropic liquid crystals. Here, the structures, some thermodynamic properties and topological defects will be discussed for thermotropic liquid crystals only.

With respect to the geometrical shape of the molecules, the thermotropic liquid crystals may be divided into:

- calamitic phases when the molecules are rod-like (the name is derived from the greek word καλαμοσ = rod);

- sanidic phases with lath (brick)-like molecules, especially in liquid crystal polymers (from greek σανίζ = lath; see also lath-shaped mineral sanidine K/Na($AlSi_3O_8$);

- discotic phases with disc-like (discotic) molecules.

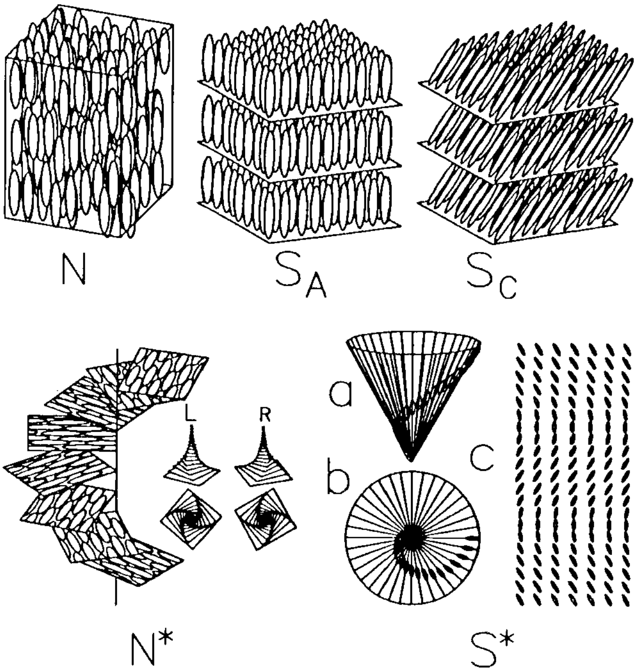

FIGURE 1 The simplest liquid crystal structures: nematic N, smectic A (S_A), smectic C (S_C), chiral nematic N^*, chiral smectic S^* (a - top view of the cone, b - side view of the cone, c - side view of the set of layers)

Calamitic phases represent liquid crystal structures in their "classical" froms. The simplest arrangements of the rod-like molecules in the nematic, smectic, chiral nematic, and chiral smectic phases are presented in Figure 1. In the nematic phase (Fig. 1, N), the long molecular axes are arranged almost parallel without any additional ordering. In this phase, molecules possess freedoms of translation and rotation especially around the long axes. The nematic phase can be further differentiated with regard to their local intermolecular aggregations (associates, cybotactic groups). In the smectic phases, the additional layered ordering arises besides the parallel arrangement of the long molecular axes. The smectic phases are highly differentiated with regard to the type of the ordering inside layers and the variety of the tilted arrangement of the molecules to the layers. The simplest example of the smectic phase is the smectic A (Fig. 1, S_A) in which the long molecular axes are oriented perpendicularly to the layers. It is assumed that the positions of the molecules within layers are random or of low order and that there is no long range correlation between layers. The smectic C (Fig. 1, S_C) is the tilted variation of the phase A preserving the same random distribution of the centers of the molecules.

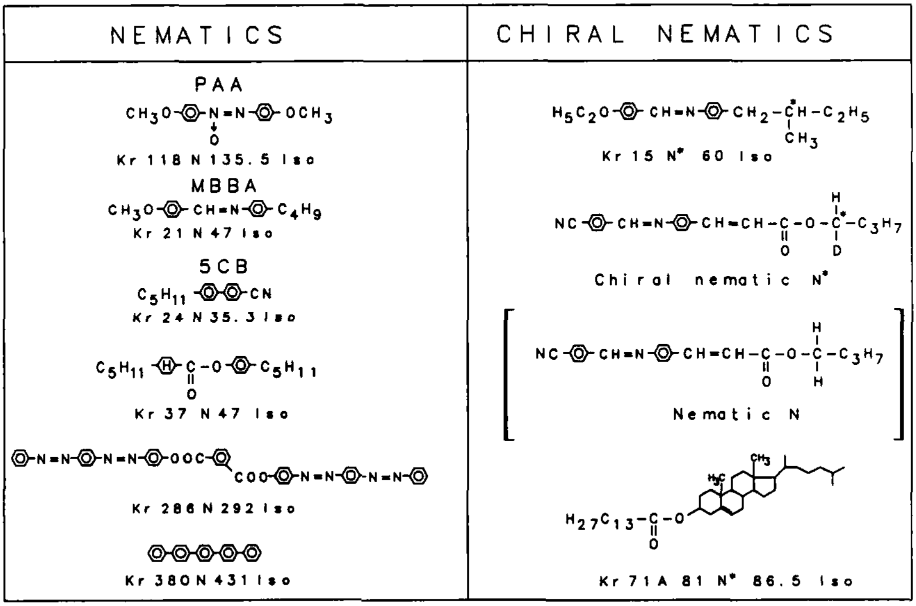

FIGURE 2 Examples of the chemical structures of the calamitic nematics and smectics

Chiral nematics (Fig. 1, N*) can be represented as the stack of nematic pseudo-layers in which the preferred direction of long molecular axes is shifted by a constant angle when coming from one layer to the neighbor. The resultant helicoidal arrangement of the long molecular axes can be left (L) or right (R) handed depending on the chemical structure of the molecules. In the case of chiral smectics (Fig. 1, S*) the helicoidal arrangement is possible only when the correlation between layers is low as, for example, in the case of the chiral smectic C*. Here, the long molecular axes can be considered as placed on some conical surface in which they are shifted by a constant angle coming from one layer to the next such as indicated in Figure 1, S* (a - side view of the cone, b - top view, c - the resultant projections of the long molecular axes).

Typical rod-like molecules of the thermotropic liquid crystals are presented in Figure 2 (nematics and chiral nematics) and in Figure 3 (smectics and chiral smectics).

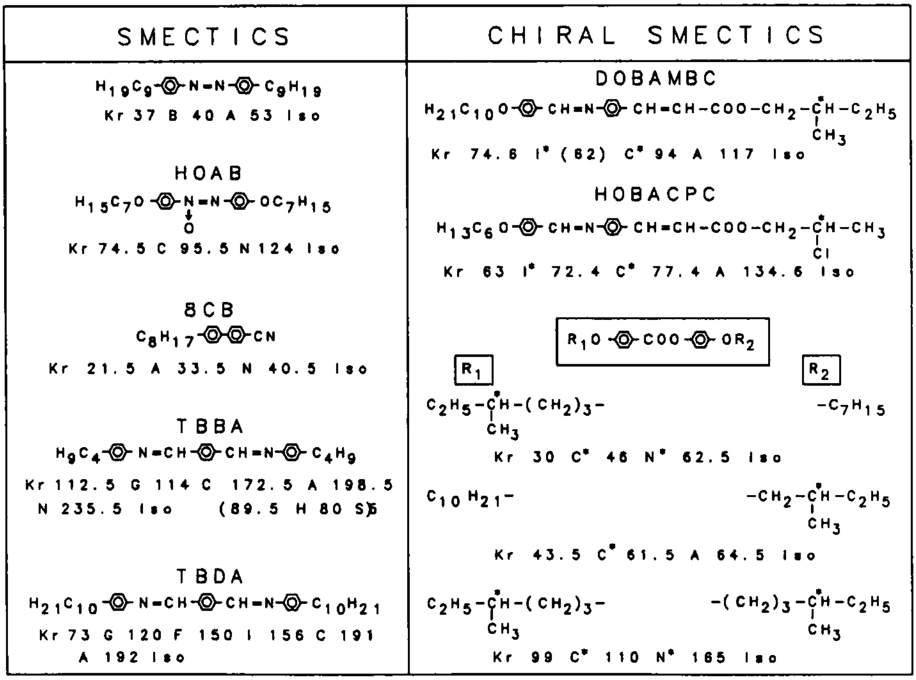

FIGURE 3 Examples of the chemical structures of the calamitic smectics and chiral smectics

Liquid crystal phases can be created also with disc-shaped, named discotic, molecules. There are molecules with 3, 4, 6, 8 and 9 flexible substituents attached symmetrically to the central flat aromatic core as shown in Figure 4 a and b. Such molecules are able to form so-called discotic liquid crystals of two main types: discotic nematics and columnar phases (Fig. 5). In the discotic nematic phase, the molecules are lying parallel to one another without any additional ordering. When the discotic molecules are optically active, the discotic chiral discotic nematic phase N* arises with helicoidal arrangement of the preferred direction.

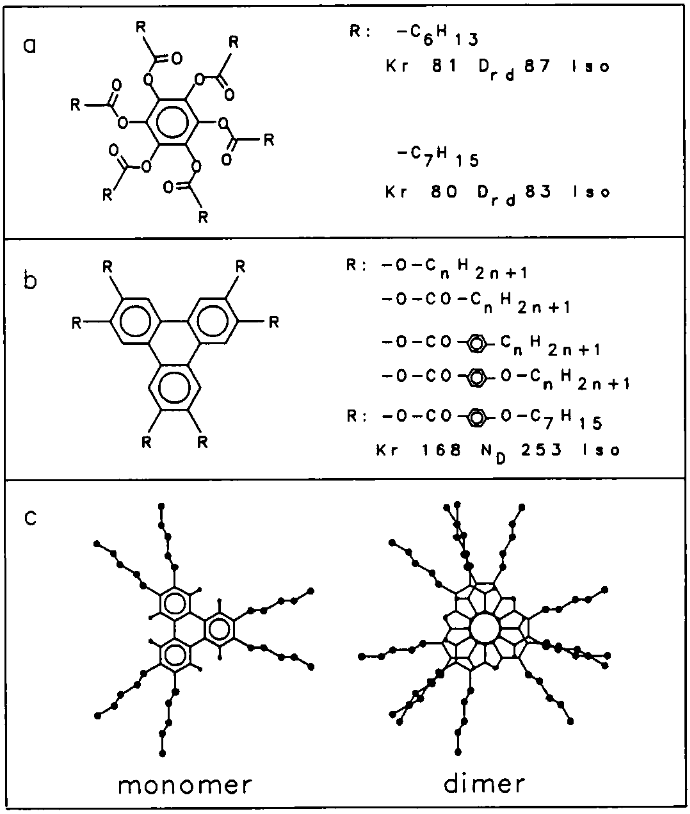

FIGURE 4 Simple examples of discotic molecules: a - hexasubstituted phenylene derivatives, b - hexasubstituted triphenylene derivatives, c - arrangement of the molecules into dimers within columns (M. Cotrait *et al.*, *J. Physique* **43**, 355 (1982)).

In the columnar phases, the discotic molecules are stacked one upon another in the form of columns. The preferential connection of two discotic molecules presented in Figure 4c may serve as an example of the internal arrangement within columns. Along the columns, long range order or disorder in the positions of the centers of molecules can exist. These columns are parallel to each other giving liquid crystal phases with hexagonal or orthorhombic symmetry. The later arises when hindered rotation around long axes of the columns causes a break in the rotational symmetry. Figure 5 shows the simplest discotic phases: nematic N, chiral nematic N* and columnar ordered, disordered, and skewed together with the schematic diagram of the organization of the column sets with hexagonal and orthorhombic symmetries.

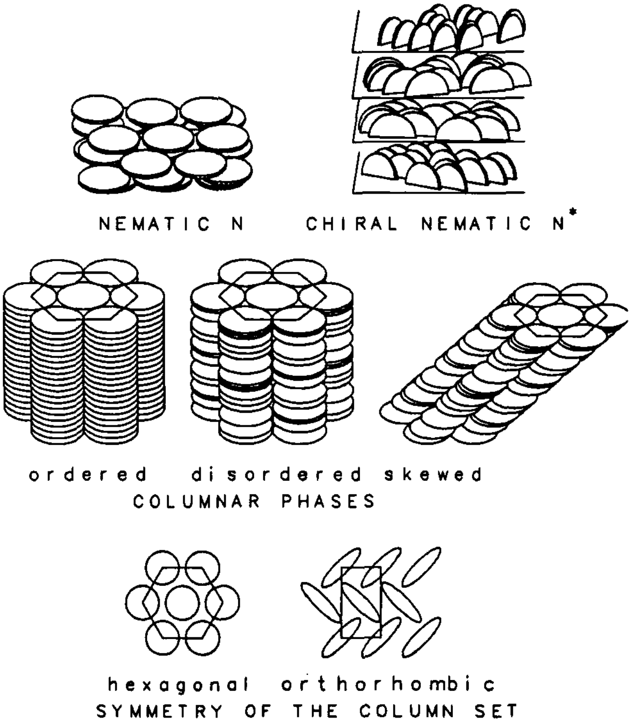

FIGURE 5 Discotic liquid crystal phases: nematic N_D, chiral nematic N_D^*, and columnar D. In addition, two types of the symmetry of the column set, hexagonal and orthorhombic, are presented.

Polymeric liquid crystals arise when rod-like or discotic mesogenic groups are attached to polymer chains as their side-groups or are included as the parts of the main chain. In Figure 6 the examples of molecular structures of both main-chain and side-chain (comb-like) liquid crystal polymers are shown. In the liquid crystal state, the mesogenic groups adopt parallel configuration to form the nematic or smectic phase as is presented in Figure 7. The main polymer chain, however, remains unoriented. In the case of liquid crystal elastomers and thermosets the cross-linking is present between the main polymer chains.

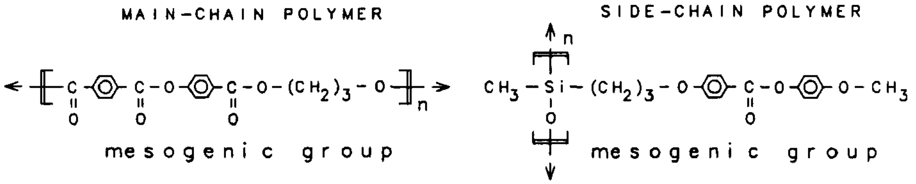

FIGURE 6 Examples of the molecules of both main-chain and side-chain (comb-like) liquid crystal polymers. The arrows indicate the direction of the polymer chains.

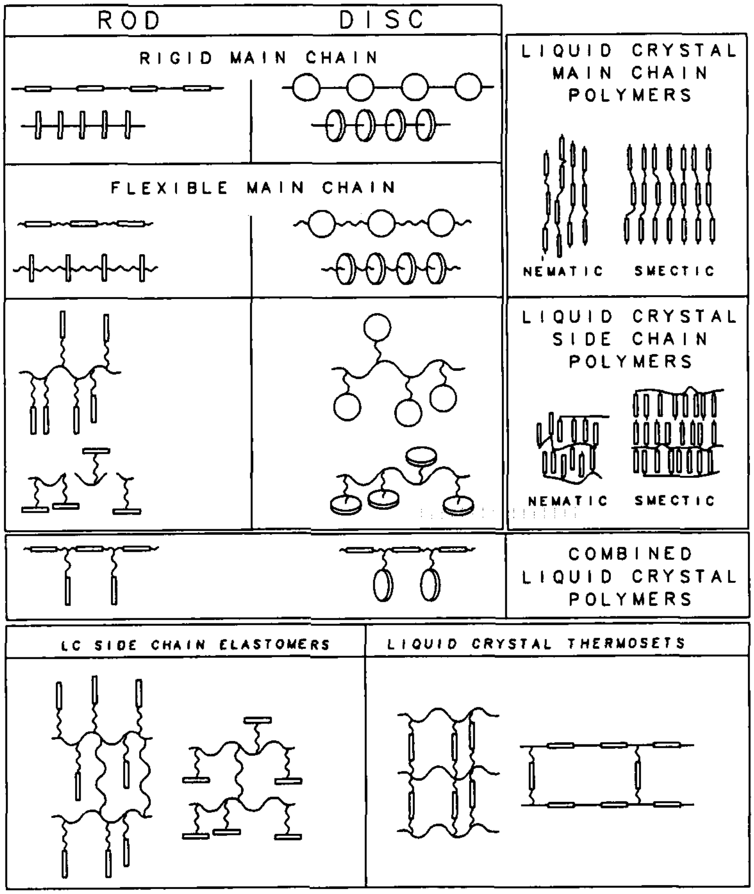

FIGURE 7 Structures of molecules of the liquid crystal polymers. The rod-like and disc-like mesogenic groups can be included as main groups into rigid or flexible polymeric chains or can be attached as the side groups of flexible chains. The cross-linking gives the liquid crystal elastomers or thermosets. The nematic and smectic arrangements of the mesogenic groups are also symbolized.

The schematic diagram of the phases in the thermotropic calamitic liquid crystals is presented in Figure 8. In every basic smectic A, B, L, and E, the long axes of the molecules are oriented perpendicularly to the constituent layers. There are two major differences between these phases. The first is the order of the molecules within layers. In the phases A and B, the molecules posses rotational symmetry around their long axes and their centers are disordered in the A phase whereas in the phase B they are arranged in a hexagonal manner. In the phase L the rotation of the molecules is hindered such that there are six equipotential positions. In the phase E, the rotational hindrance is so strong that only 180° jumps between two favoured positions are allowed. As the result, the so-called "herring-bone" structure arises giving the orthorhombic symmetry in the phase E as shown in Figure 9. The second difference between phases is the interlayer correlation in position of the centers of the molecules. It is assumed that there is no correlation in the phase A and it is of short-range type in the phase B. In the case of the phases L and E, there is long-range interlayer correlation and these phases are named "crystal" in the contrary to the phase B named "hexatic".

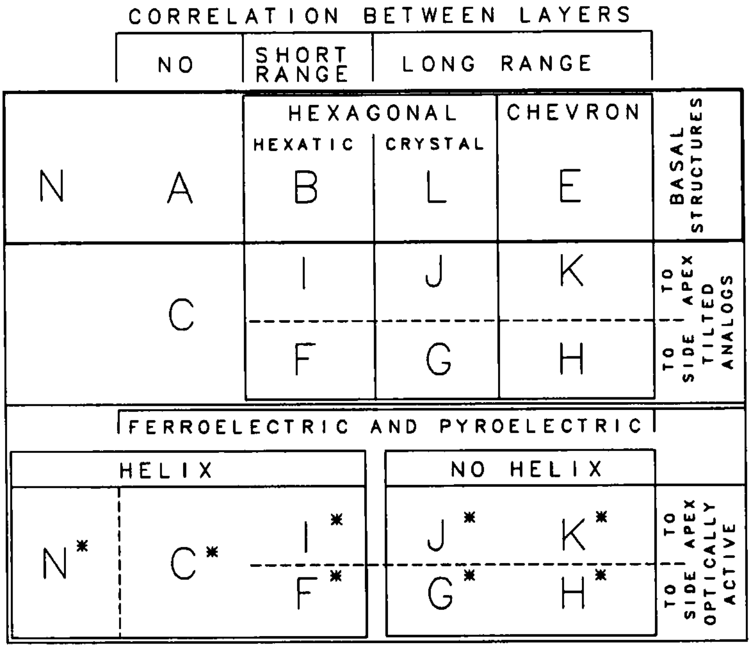

FIGURE 8 Schematic diagram of the basic liquid crystal phases and their chiral analogues.

Every basic smectic phase, A, B, L, and E, has one or two tilted modifications. The phase C is the tilted modification of the phase A. The phase B has two tilted modifications of the pseudo-hexagonal symmetry: the phase I with the tilt to the apex of the hexagon and F tilted to the side of the hexagon. The phase L has analogous pseudohexagonal modifications: J - tilted to the apex and G - tilted to the side. The orthorhombic phase E has two monoclinic modifications: K with the tilt to the shorter side and H tilted to the longer side of the orthorhombic cell.

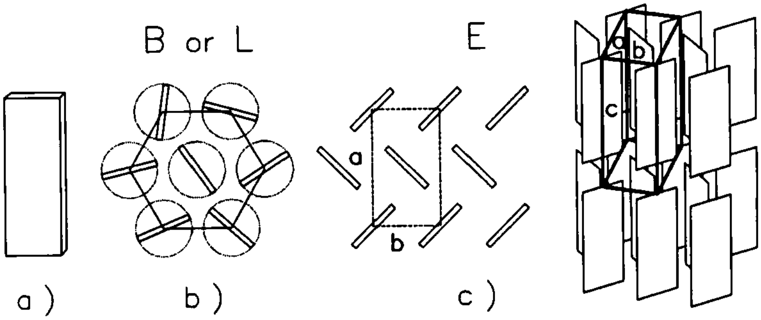

FIGURE 9 Transition from the smectic B (or smectic L) to the smectic E due to the hindrance of rotation around the long molecular axes. a) the simplified shape of a three-axis molecule; b) rotational symmetry (B or L); c) phase E.

In the chiral modifications, the helicoidal arrangement is not present in the phases with long-range interlayer correlations, i.e. in the chiral phases of the tilted analogues of the phases L and E (J^*, G^*, K^*, and H^*).

The phase transitions between liquid crystalline phases are preferentially of the first order however some of them are of second or weak first order. In some substances the neighbor phases are very similar and the transition enthalpies can be as small as a few J/mole. Figure 10 presents some of really observed phase transitions of the first order (solid lines) and the second or weak first order (dashed lines) between liquid crystal phases. Here, the symbol of the actually observed phase is situated inside the large triangle and the symbols of the phases located above the side of the triangle denote the phases from which the phase in the triangle arises. The symbols below the apex of the triangle denote the possible transitions of the phase located inside triangle with decreasing temperature. For example, the phase C can arise immediately from the isotropic phase or from the nematic phase (1st order phase transition) or from the phase

A (2nd or weak 1st order). At lower temperature, the phase C can transform to the phases B, G, E and solid crystal in the 1st order phase transitions or to the phases I and F in the 2nd (or weak 1st) order transitions. As a rule, the liquid crystal phases arise in fixed sequence with decreasing temperature from the isotropic liquid to the crystal state. Neglecting the chiral phases, the sequence rule can be written in generalized form as: Iso - N - A - C - B - I - F - L - J - G - E - K - H - Kr with Iso and Kr standing for

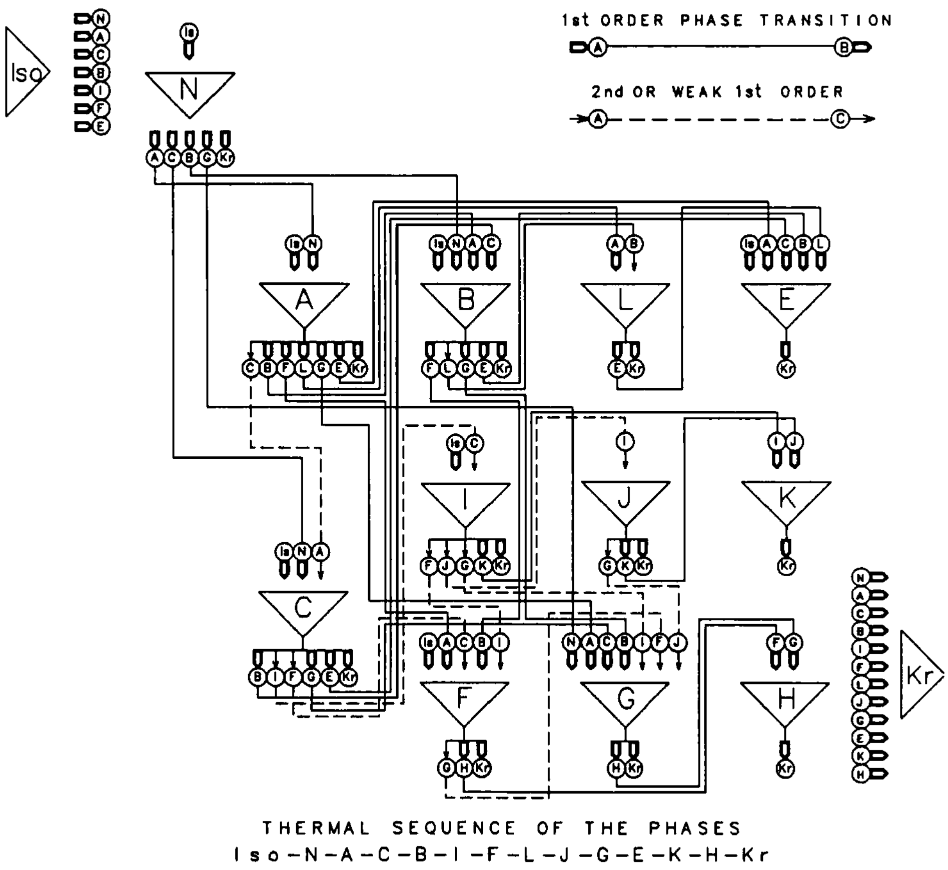

FIGURE 10 Some of really observed phase transitions in the thermotropic liquid crystals. The symbol of the actually observed phase is situated inside the triangle. The phases from which the phase in the triangle arises are placed above the side of the triangle . The symbols below the apex of the triangle denote the possible transitions at lowered temperature. For example, the phase C can arise from the phases Iso or N (1st order phase transition - solid lines) or from the phase A (2nd or weak 1st order - dashed lines). At lower temperature, the phase C can transform to the phases B, G, E or solid crystal in the 1st order phase transitions or to the phases I or F in the 2nd (or weak 1st) order transitions.

the isotropic and crystal phases, respectively. Despite of rather rich polymorphism observed in liquid crystal substances, there is no one known substance in which the entire sequence is registered and the sequence rule, as presented above, has been established from the transition sequences observed in many different substances. In some strongly polar compounds, the "reentrant" phases were discovered which violate the above sequence rule. These phases arise when the molecules form associates which play the role of separate units. On the other hand, if any phase arises not in its own place in the sequence rule, it is regarded as the reentrant phase. Some of the polymorphic paths which have been really observed in liquid crystal substances are presented in Figure 11.

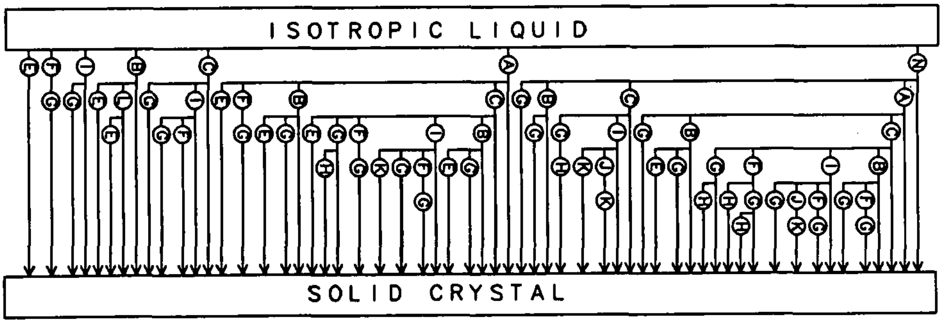

FIGURE 11 Some of experimentally observed polymorphic paths in the thermotropic liquid crystals.

To summarize, it is useful to present the schematic diagram of the liquid crystal phases recapitulating the symmetries of the phases as is shown in Figure 12 together with the thermal sequence of the phases as is presented in Figure 13. The thermal sequence of the liquid crystal phases can be simply obtained when going repeatedly down the columns.

The classification of the thermotropic liquid crystal phases presented here as the set of the basic N, A, B, L, and E phases and their derivatives is phenomenological in nature and is neither complete nor theoretically motivated. An existing attempts to give the theoretical classification of the liquid crystal phases based on the group theory or the elastic properties predict numerous new liquid crystal phases. The modern classification of the liquid crystal phases is presented in many books and review articles, e.g. [1-4].

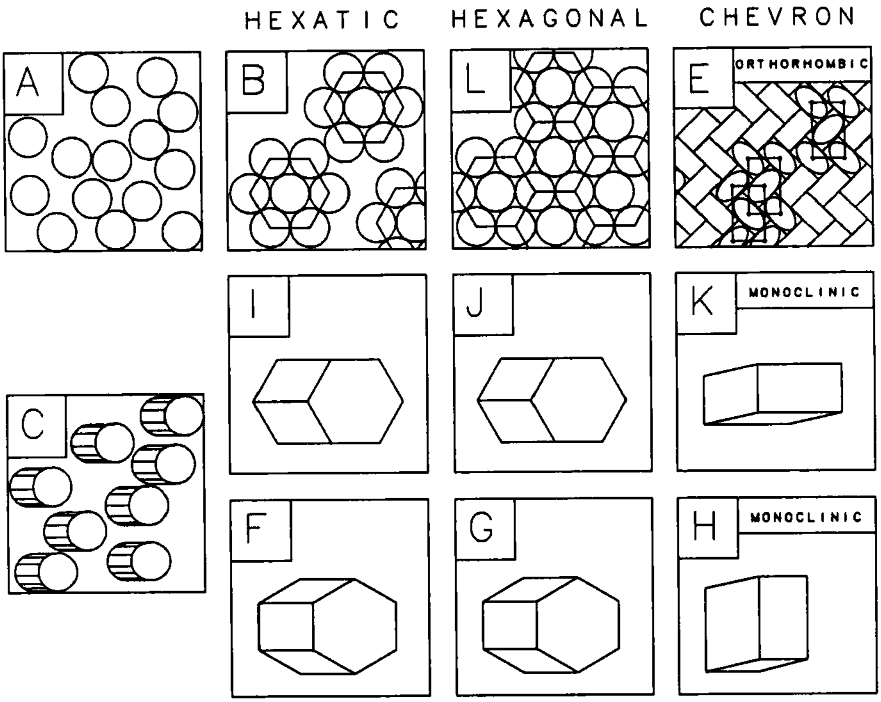

FIGURE 12 Symmetries of the basic liquid crystal phases

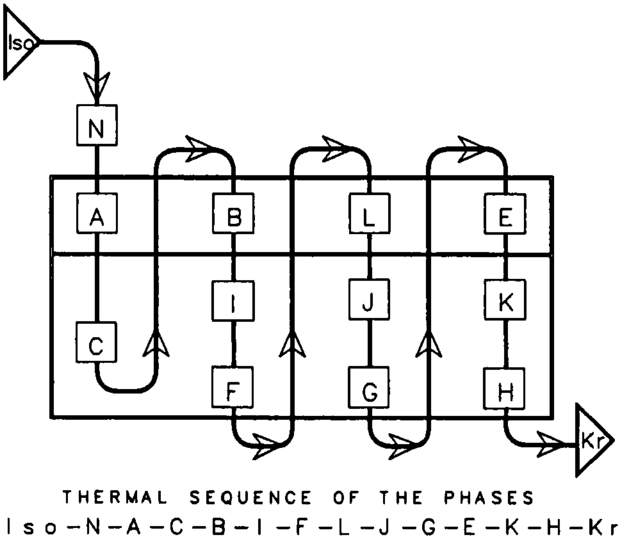

FIGURE 13 The thermal sequence of the phases.

Up to the present, several liquid crystal phases have been observed which can be considered as varieties of the main phases mentioned above and are not discussed here in details. Among such phases, especially interested are: biaxial nematics with brick-like molecules, chiral smectic A^* observed in certain chiral biphenyl derivatives with a helical arrangement of orthogonal blocks of molecules separated from one another by screw dislocations, smectics O and O^* in which the tilt of long axes of the molecules is opposite in neighboring layers to produce an antiferroelectric arrangement, "bowlic" columnar phases with cone-shaped molecules, and the columnar "tubular mesophases" consisting of macrocyclic molecules with central holes. In addition to the ordinary helical phases there are double-twist structures in which the helical arrangements are superimposed in more than one preferential direction. Novel chiral liquid crystal phases, called blue phases, are examples of the double-twist structures. The lyotropic liquid crystals that play very important role in the biological structures are completely omitted here due to their great variety and complexity.

TOPOLOGICAL DEFECTS IN LIQUID CRYSTAL STRUCTURES

The simplest topological defects in liquid crystals are zero-dimensional singular points. The screw and wedge dislocations in the smectic, chiral nematics and chiral smectic phases as well as the disclination lines are the one-dimensional defects. In addition, there are two-dimensional (domain walls) and three-dimensional (bulk inversion walls) defects.

At constant boundary conditions, there is no possibility to obtain liquid crystal droplet without one at least topological defect as shown in Figure 14. Here, the distributions of the long molecular axes are presented for normal boundary conditions in nematic droplets (Fig. 14., a, b), tangential boundary conditions in nematic droplets (Fig. 14., c - f), and tangential boundary conditions in chiral nematic droplets (Fig. 14., g, h). In the hedgehog-type droplets (Fig. 14., a), the singular point is located as the central point of a droplet. In the monopole-type nematic droplets (Fig. 14., c), the isolated singular point (named boojum) is located at the surface. In the bipolar-type nematic (Fig. 14., d) and chiral nematic droplets (Fig. 14., h), two singular points are located at the pole sites of droplets. In the case of chiral nematic monopole droplets, the monopole-type nematic shells are included one into another and shifted to preserve the chiral structure (Fig. 14., g).

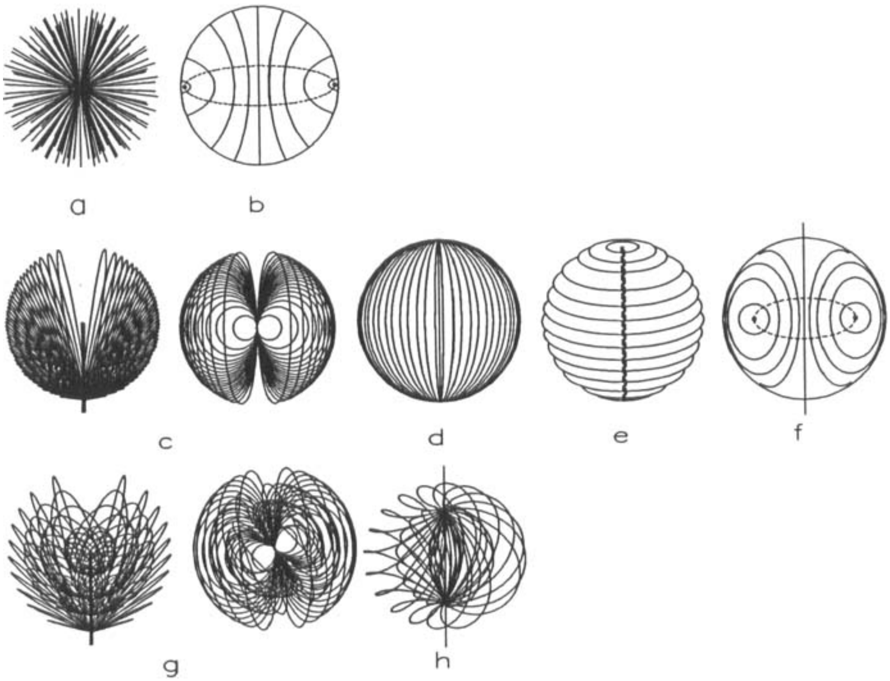

FIGURE 14 The distribution of the long molecular axes inside nematic and chiral nematic droplets with constant boundary conditions.

Some droplets in Figure 14 are organized around singular lines instead of singular points (Fig. 14., b, e, f). These lines, named disclination lines, are composed of singular points of various types. The disclination lines are very frequently observed in the nematic phase as sharply visible threads freely floating inside nematic layers. When the nematic layer is placed between glass plates with special surface treatment, the disclination lines can form short sections connecting perpendicularly the surfaces of the plates. In this case, the dark brushes originating from points can be seen under a polarizing microscope (the so-called schlieren texture). These brushes arise due to the distribution of the long molecular axes around the disclination lines. Such a distribution can be formally described as follow. Consider a nematic layer in which the long molecular axes are confined to the xy plane. If the z axis is normal to the film, then the unit vector **n** describing the preferential local orientation of the long molecular axes has the components $n_x = \cos\varphi$, $n_y = \sin\varphi$, $n_z = 0$. Euler-Lagrange equation which minimizes the free energy density F is of the form

$$\left(\frac{\partial F}{\partial n_{i,j}}\right)_{,j} - \frac{\partial F}{\partial n_i} = 0$$

with

$$F = \frac{1}{2}\left[k_{11}(\nabla\cdot\boldsymbol{n})^2 + k_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + k_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2\right]$$

Using one-constant approximation for the elastic constants $k_{11} = k_{22} = k_{33} = k$, we obtain the Euler-Lagrange equation in the reduced form

$$\nabla^2\varphi = 0$$

The solutions of this equation are $\varphi = 0$, which is of no interest, and

$$\varphi = s\alpha + c,$$

where $\alpha = \tan^{-1}(y/x)$ and c is a constant. The constant *s* is known as the strength of the disclination having values as below:

$$s = \pm 1/2, \pm 1, \pm 3/2, \ldots \text{ with } 0 < c < \pi.$$

The distributions of the long molecular axes around the disclination lines of various strengths are presented in Figure 15. The constant *c* is important only in the case of *s* = 1. For other values of *s*, the change of the constant *c* results only in a rotation of the director field without any changes of its shape.

Three-dimensional view of the molecular field around low-strength disclination lines is presented in Figure 16. Because of high energy density connected with the elastic deformation of the liquid crystal material in the vicinity of the disclination lines, high-strength disclinations are unstable and dissociate into two or more disclinations with lower strengths. This process is demonstrated in Figure 16 in the case of dissociation of the line with s = 1 into two lines with s = +1/2.

In large nematic samples, the algebraic sum of the strengths of all the defects presented is assumed to be zero. Thus, there must be the same number of defects with s positive and negative. The connection of defects of the opposite signs is presented in Figure 17.

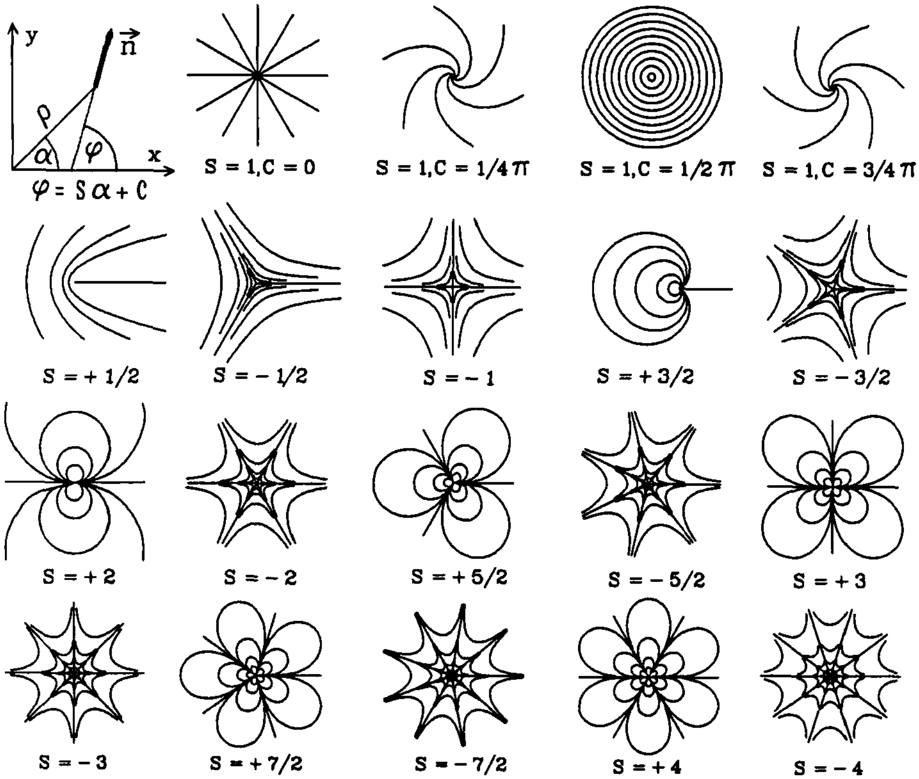

FIGURE 15 The distribution of the long molecular axes around the disclination lines of various strength *s*.

In chiral nematics, the disclination lines are of special geometry due to the helical arrangement of the long molecular axes. These lines are named χ-screw disclination lines and the molecular distributions around lines with s = 1/2 and s = 1 are as shown in Figure 18. Locally, the distribution is similar to those observed for ordinary nematics but it is changed as shown to preserve the helical arrangement of the long molecular axes. The three-dimensional view shows the resultant molecular fields.

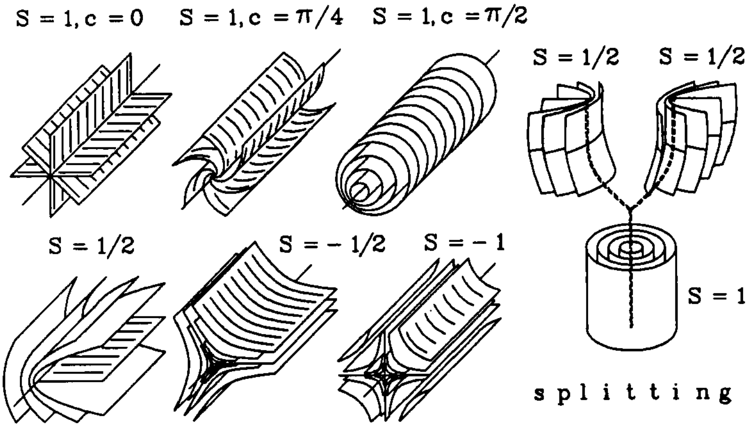

FIGURE 16 Three-dimensional view of the distribution of the long molecular axes around low-strength disclination lines. The splitting of the line with $s = 1$ into two $s = +1/2$ is presented.

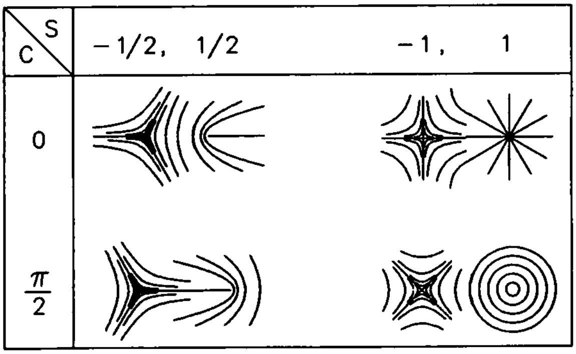

FIGURE 17 The distribution of the long molecular axes for two pairs of unlike disclination lines (+1/2, -1/2) and (+1, -1).

High energy-density around disclination lines connected with the elastic deformation of a nematic can be avoided when the orientation of the long molecular axes "escapes" in the direction parallel to the disclination line. Such "escaped" defects are frequently observed in thin capillaries and in layers under action of the electric field. The "escaped" configurations at the cores of defects with $s = 1$ ($c = 0, \pi/2, \pi/4$) and $s = -1$ are shown in Figure 19.

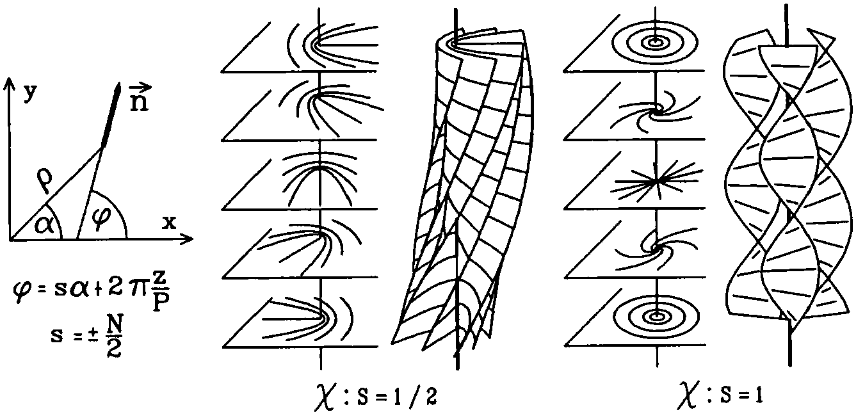

FIGURE 18 The distributions of the long molecular axes around the χ-screw disclinations in chiral nematics.

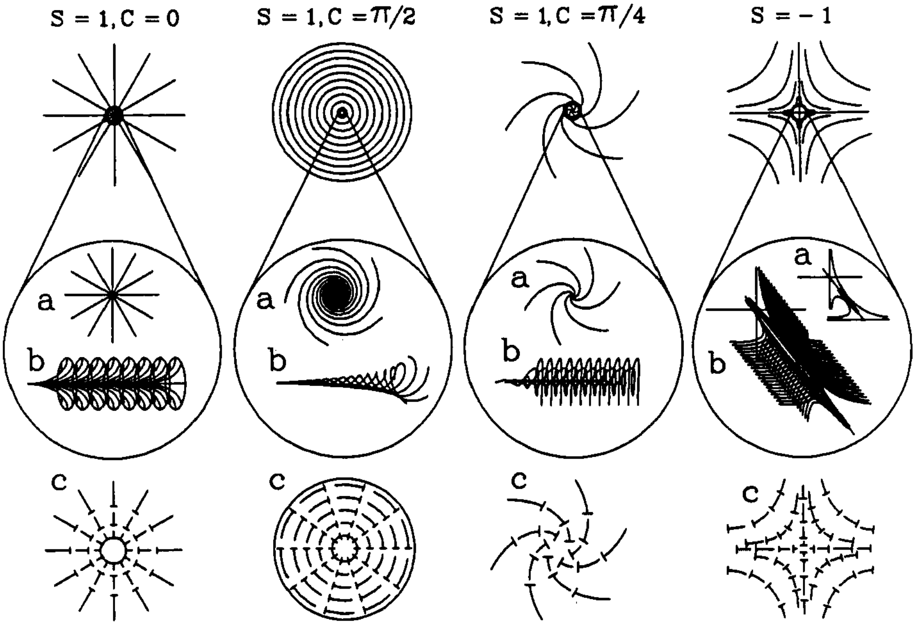

FIGURE 19 "Escaped" configurations of the molecular fields at the cores of defects with s = 1 and s = -1.

The disclination lines in smectic A are shown in Figure 20. The molecular distribution around the lines depends on whether the cut in the so-called Volterra process is made through the end of the molecule or through its center. The resulting disclinations are designated as Ω_a and Ω_b.

In the layered (smectic) and pseudo layered (chiral nematic) liquid crystals there are the edge and screw dislocations quite analogous to the respective dislocations in crystals. The dislocations of both the types are presented in Figure 20 for the case of smectic A. In addition, the transformation of the edge dislocation into set of two disclinations is showed (Fig. 20., A2).

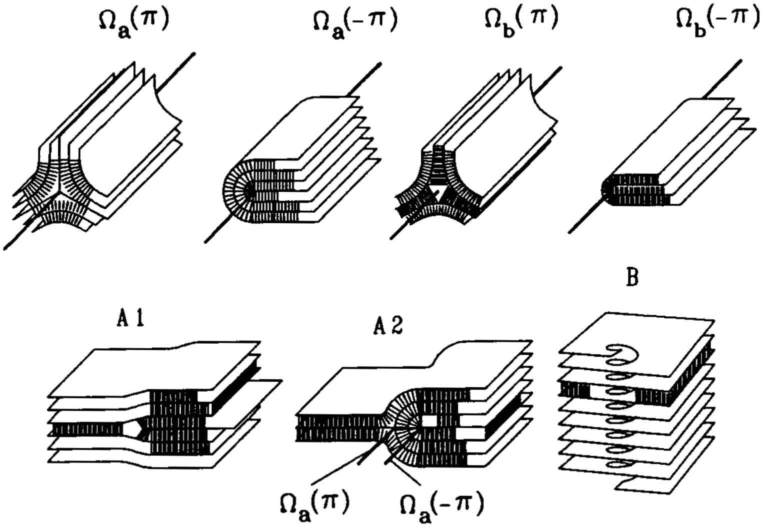

FIGURE 20 Disclination lines Ω_a and Ω_b and the edge (A1) and screw (B) dislocations in smectics A. A2 - transformation of the edge dislocation into two disclinations.

To reduce the curvature elastic energy in the layered (smectic) or pseudolayered (chiral nematic) phases, the droplets and not oriented layers adopt the so-called focal-conic texture. These structures are most commonly seen under microscope in such media. The focal-conic unit is based on two singular lines - ellipse and hyperbola - mutually located in such a manner that the hyperbola comes through the focus of the ellipse and the ellipse through the focus of the hyperbola, their planes are perpendicular and the hyperbola is in plane of the long axis of the ellipse. The creation of the focal-conic unit is presented in Figure 21 for the case of the smectic A. In the initial stage, the smectic layers are wrapped round in concentric cylinders with a singular disclination line along the axis. In the next stage, the cylinder becomes closed to form torus and the disclination line becomes a circle. In this stage, the structure has the new straight singular line through the center of the circle and perpendicular to its plane. Such a configuration is energetically unstable and transforms to the Dupin cyclide. The circle transforms now to an ellipse and the straight line into a hyperbola. The energetical considerations based on the relations between the main curvatures in the Dupin cyclides lead to the conclusion that the focal-conic unit is the most stable configuration for layered liquid crystals not subject to external interactions.

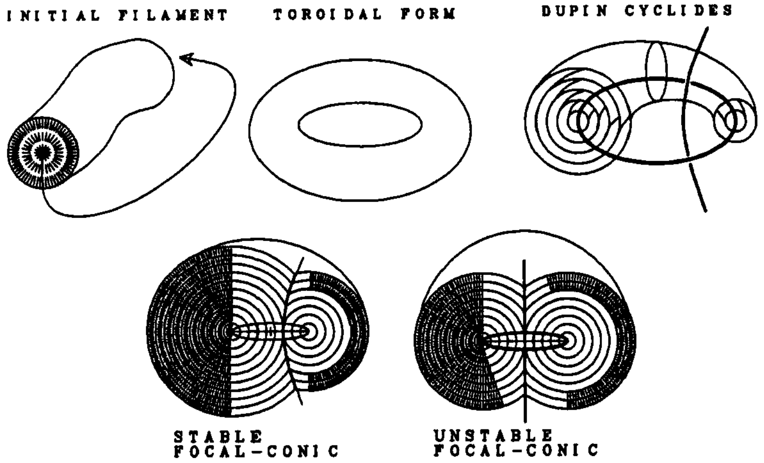

FIGURE 21 The formation of the focal-conic unit

For the general discussion of the textures and topological defects in liquid crystals as well as their energetics see [5-7].

ACKNOWLEDGMENTS

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