

Chapter 1

Liquid Crystal States of Matter

1.1. LIQUID CRYSTAL STATES

As we know, there are three basic states of matter, solid, liquid, and gaseous states. These states of matter can be transformed into each other at appropriate conditions. In the solid state (generally meaning the crystalline state), the building blocks, such as atoms, or molecules, or clusters of molecules are packed closely and regularly, forming a crystal lattice. The X-ray diffraction of the state shows many regular diffraction spots. Over 95% of matter on the earth exist in the form of the crystalline state. The types of crystal structure are enormous. The physical properties of crystals are basically anisotropic. The crystals have a constant melting temperature (except for amorphous solids). Two different crystal planes make a constant angle. As the temperature of matter increases the thermal movement of atoms or molecules become so severe that the crystal lattice is dissolved and fluidity appears. At this temperature, matter does not have a regular shape and anisotropic properties any more. It becomes a liquid. In the liquid state, the atoms or molecules are no longer arranged in a regular order, but they are still bonded to each other tightly, though not in the tightest packing. Compared with the crystal state, the volume change of a liquid is not great but the liquid does not have a regular shape and can flow. Because of gravity the surface of liquids is usually flat. Increasing the temperature further up beyond the melting point, matter is transformed to the gaseous state. In the gaseous state, no short-range order exists. The interaction between the constituent molecules is extremely weak. Due to thermal excitation the molecules fill the container uniformly and hence the

gas no longer has a flat surface. Generally, as the temperature increases progressively, matter at first appears in the form of a crystal solid, and then a liquid and finally the gaseous state. Exceptionally, a few materials may be heated directly from the solid into the gas state, that is, by sublimation, such as for iodine. Conversely, some substances may be transformed directly from gas to solid, which is called sublimation as well. Water vapor condensing to ice is an example of sublimation.

As the understanding about the states of matter became deeper, people had found that in addition to the above mentioned well-known three states, there exist other states of matter in nature, such as the plasma state, amorphous solid, liquid crystal state, superconductor, neutron state, etc. Among them the liquid crystal state is the subject of this book.

The liquid crystal state is a kind of state whose order is between the crystal solid and isotropic liquid states. In the crystal state, there is a long range order in position and orientation, while in the liquid state there are no long range ordering in either of them. Figure 1.1 is a comparison of the crystal (a), the liquid crystal (b) and the liquid (c) states.

The liquid crystal was once considered a rare state in the nature, but so far over eighty thousand liquid crystalline compounds have actually been found, making them a great family of matter.

The discovery of the liquid crystal state should be traced back to a story taking place one hundred years ago. Austria botanist F. Reinitzer observed a peculiar phenomenon in 1888—under a microscope (Reinitzer, 1888), cholesteryl nonanoate melted into a cloudy liquid at 145.5°C ; as the temperature rose to 178.5°C , it suddenly became clear. When cooling down, the substance briefly appeared violet-blue just before becoming an

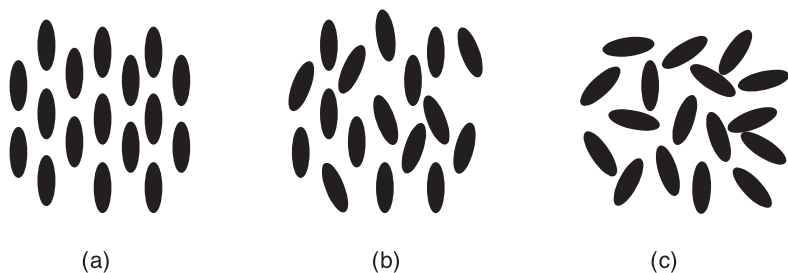


Figure 1.1. The schematics of (a) crystal, (b) liquid crystal and (c) liquid.

opaque liquid, and then finally a white solid crystal. Reinitzer was puzzled about what he observed: why were there two melting points between the crystal (solid) and clear (liquid) states. He sent the sample together with his observation to German physicist Otto Lehmann who later made detailed observations by means of the polarizing microscope equipped with a heat stage. He at last concluded that cholesteryl nonanoate in the temperature range of 145.5°C and 178.5°C must be in a new state of matter. After a few years of hesitation, he finally named this state of matter, the **liquid crystal** (Lehmann, 1900). Later somebody proposed that the term “mesogenic state” might be an appropriate nomenclature for the new state, because it may avoid possible confusion. In spite of this problem, people have seemed to prefer the term liquid crystal due to its vivid description and the term liquid crystal has since been widely adopted, while the term mesogen or mesogenic is now used for a compound that is able to show the liquid crystal state. Contemporary knowledge tells us that cholesteryl nonanoate actually exhibits two liquid crystal phases in the temperature range of 178.5°C and 145.5°C . As the temperature decreases, the first blue color is that of the blue phase of the liquid crystal, and the second violet-blue color results from the cholesteric phase of the liquid crystal. More than twenty liquid crystal phases have since been discovered. The blue phase and cholesteric phase are two of them.

One enlightenment that can be drawn from the discovery of the liquid crystal is that despite the fact that Reinitzer and Lehmann pursued different fields and were in different countries, the cooperation between them inaugurated a new field of science—the liquid crystal. Actually the whole development of the field of the liquid crystal has demonstrated this type of cooperation.

As early as 1850, a German scientist discovered, in fact, the possibility of the liquid crystal when he found that natural fats exhibited two melting points. With increasing temperature, the substance starts to become cloudy at around 52°C and is completely opaque at 58°C , and then becomes clear at 62.5°C . This observation should be the earliest record of the “discovery” of the liquid crystal. At around the same time, the cholesterol derivative exhibited a striking color when it cooled from the isotropic liquid state. Unfortunately, these phenomena were not given enough attention or correctly explained. The researchers themselves did not realize that they were approaching the entrance of a new field of science. Therefore, the discovery of the liquid crystal should be attributed to Reinitzer and Lehmann.

1.2. APPEARANCE AND LIGHT SCATTERING OF LIQUID CRYSTALS

The liquid crystal state is a state of matter which is different from the liquid and solid states. Liquid crystals can flow as a liquid does. Typically, the viscosity of the liquid crystals such as the nematic liquid crystal is in the order of magnitude of 1×10^{-2} Pa.s., a value greater than that of water whose viscosity is about 1×10^{-3} Pa.s. Some liquid crystals, such as high order modifications—smectic liquid crystals, are very viscous. A liquid is transparent, but a liquid crystal is normally milky. This is because the fluctuation of the orientation of the molecular long axes of the liquid crystals causes strong light scattering. The scattering of liquid crystals is as high as one million times that of conventional isotropic liquids. The milky appearance becomes one of the identifications of the liquid crystals.

As we know, the scattering of matter is caused by the fluctuation of their refractive index (or optical dielectric constant). The local compression or dilution of mass density in bulk isotropic liquids modifies in turn the local refractive index. The change can be expressed in the form of the dielectric constant as

$$\varepsilon(\mathbf{r}) = \varepsilon + \varepsilon' \phi(\mathbf{r}), \quad (1.1)$$

where ε is the average dielectric constant, $\phi(\mathbf{r})$ is the bulk compressibility and \mathbf{r} is the distance vector of a point in the material, ε' is the fluctuation of the dielectric constant. According to light scattering rules, the cross-section of light scattering of isotropic liquids, σ_I , is given by

$$\sigma_I \propto \varepsilon'^2 \langle |\phi(\mathbf{k})|^2 \rangle, \quad (1.2)$$

where $\phi(\mathbf{k})$ is the Fourier transformation of $\phi(\mathbf{r})$, and $\langle \dots \rangle$ indicates the statistical average. The average in the bracket can be written as

$$\langle |\phi(\mathbf{k})|^2 \rangle = \frac{Vk_B T}{B}, \quad (1.3)$$

where V is the volume of the sample, $1/B$ is the isothermal compressibility coefficient, and k_B is the Boltzmann constant.

Liquid crystals are optically anisotropic media with the exception of the cubic phases, such as the D-phase and blue phase. The refractive index or dielectric constant of liquid crystals varies according to the orientation of the molecular axes (or the optical axes). For example, the nematic liquid crystals are optically uniaxial and exhibit remarkable birefringence, that

is, their refractive indices of ordinary and extraordinary light, n_o and n_e , are different. The difference of these two refractive indices, the birefringence denoted as $\Delta n = n_e - n_o$, is generally great, say, about 0.1. Due to the thermal fluctuation, the optical axes of nematic molecules always vary from point to point and from time to time. The effect of this phenomenon is much more significant than the density fluctuation. Little energy is required for causing the fluctuation of the optical axes of nematic molecules, so that the thermal fluctuation of the refractive index is significant even at the ambient temperature. This effect results in strong light scattering. The cross-section of light scattering in the nematics is expressed by

$$\sigma_N \propto \varepsilon_a^2 \langle |\delta \mathbf{n}(\mathbf{k})|^2 \rangle, \quad (1.4)$$

where ε_a is the optical dielectric anisotropy ($\varepsilon_{\parallel} - \varepsilon_{\perp}$), *i.e.*, the difference of dielectric constants parallel and perpendicular to the optical axis. $\delta \mathbf{n}(\mathbf{k})$ is the Fourier transformation of the optical axis fluctuation $\delta \mathbf{n}(\mathbf{r})$. The detailed calculation gives the statistical average of $\langle |\delta \mathbf{n}(\mathbf{k})|^2 \rangle$ as follows

$$\langle |\delta \mathbf{n}(\mathbf{k})|^2 \rangle \propto \frac{V k_B T}{K q^2}, \quad (1.5)$$

where K is an elastic constant associated with the change of optical axis. According to the estimate made by de Gennes (1973) $K \sim U/a$ and $B \sim U/a^3$ (a is the molecular dimension, about 1 nm, U is the binding energy), q is the difference between the incident and scattering wave-vectors of light. $2\pi/q$ is about the order of visible light's wavelength. Suppose $\varepsilon' \sim \varepsilon_a \sim 1$, thus the ratio of scattering cross-sections of nematic liquid crystal and isotropic liquid is

$$\frac{\sigma_N}{\sigma_I} \propto \left(\frac{\varepsilon_a}{\varepsilon'} \right)^2 \cdot \frac{B}{K q^2} \approx \frac{1}{(aq)^2} \approx 10^5 - 10^6. \quad (1.6)$$

The ratio reaches up to one million times. This explains why the liquid crystal is in fact very turbid while ordinary liquid is transparent. The light scattering varies for different phases of the liquid crystals. For example, owing to the suppression of molecules into layers the light scattering of the smectic A phase is less than the nematic liquid crystal. For the smectic C phase, the fluctuation of the projection of tilted molecules onto smectic layers (the c-vector) causes stronger scattering than that in the smectic A phase.

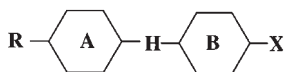
The above analysis is one example of the anisotropic properties of liquid crystals. It is these anisotropic properties that make liquid crystals and provide for its wide applications.

1.3. CHEMICAL STRUCTURE OF LIQUID CRYSTALS

1.3.1. Basic molecular structure of rodic liquid crystals

Most liquid crystalline molecules are highly anisotropic, and to a good approximation they can be regarded as rigid rods or ellipsoids of revolution with lengths l greater than their widths d . The molecular weight ranges from a few hundreds Daltons for low molecular mass liquid crystals to hundreds of thousands Daltons for polymeric liquid crystals.

The basic structure of low molecular mass liquid crystals or monomers of liquid crystalline polymers is schematically shown below



where X is a side group, R is a terminal group, A and B are aromatic rings, and H is a linking group.

1. Side group:

The following side chains are extensively studied: alkyl group (C_nH_{2n+1}); alkoxy group ($C_nH_{2n+1}O$) and alkenyl (C_nH_{2n-1}) or alkenyloxy ($C_nH_{2n-1}O$) group. The length and flexibility of the side chain affect the type of liquid crystal phases and the phase transition. In general, for homologues, the compounds with small n show no mesogenic phase. As n increases, the monotropic liquid crystal phase appears. As n further increases the nematic phase occurs and thereafter smectic phases may appear. As n varies the even-odd alternation occurs: the compounds in odd carbon numbers in the side chains have the higher transition temperature whereas compounds in even numbers have lower transition temperatures.

2. Terminal group:

The terminal group primarily contributes to the dielectric anisotropy and the refractive indices, which in turn affects the threshold voltage and optical properties in display applications, respectively. Common terminal groups are alkyl, alkoxy, cyano, nitro, isocyanate (NCS), sulfide and halides such as F, Cl, CF_3 and OCF_3 .

3. Aromatic rings:

Most liquid crystal compounds consist of two or more aromatic rings. Those aromatic rings can be a totally saturated cyclohexane, a cyclocyclohexane, an unsaturated biphenyl, terphenyl, or combinations of them. Usually, the longer the ring, the higher the melting temperature.

4. Linking group:

The linking group makes an important contribution to the phase transition and physical properties such as the birefringence. The following linking groups have been well studied

- (1) Saturated groups, such as ethylene (C_2H_4)
- (2) Esters
- (3) Unsaturated groups containing a double bond or a triple bond such as stilbene, azoy, schiff base, tolane or acetylene, and diacetylene.

5. Lateral group:

By substituting the hydrogen in the 2-, 3-, or 4-position of a phenyl ring by cyano, fluoro, or chloro polar group, one can modify the physical properties of liquid crystals. In most cases, the lateral substitution will broaden the molecule, thus reducing lateral attractions and lowering the nematic and smectic phase stability. Not only do the nature and size of the substitution affect the liquid crystal properties, but also the position of the group can have a significant effect.

6. Chiral center:

Replace the terminal group by a chiral center and the chiral nematic and smectic phases can be obtained.

The liquid crystal molecules or monomers are generally 2–4 nm in length and 0.4–0.6 nm in width. Experiments and theories demonstrate that for compounds showing the liquid crystal phase, their axial ratio or ratio of length to width (or to diameter) must be greater than a certain value, approximately 4.

1.3.2. Discotic liquid crystals

Disc-like molecules may also exhibit the liquid crystal phase. de Gennes predicted this possibility in his famous book “The Physics of Liquid Crystals”

(1973). A few years later Chandrasekhar (1977) successfully synthesized this kind of discotic liquid crystal. There is a rigid flat aromatic core connected with 3, 4, 6, 8, 9 flexible side chains. Some examples of the discotic liquid crystal molecules are shown in Figure 1.2. Generally, the

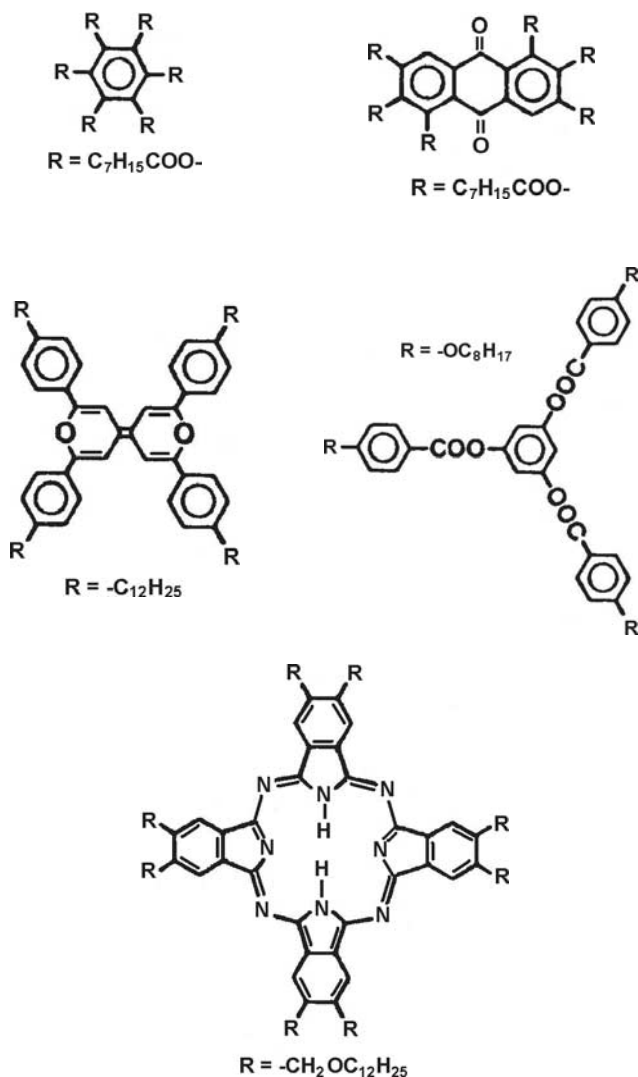


Figure 1.2. Examples of discotic liquid crystal molecules.

discotic liquid crystal molecules are about 1 nm in thickness and a few nm in diameter.

1.3.3. Amphiphilic liquid crystals

Another important member of the liquid crystal family is the solution of amphiphilic molecules. The amphiphilic molecules are tadpole-like. A polar, hydrophilic group is at one end of the amphiphilic molecule while a non-polar, hydrophobic group is at the other end. Two examples are shown in Figure 1.3. Soap in solution, for example, is a liquid crystal. One end of this molecule, $-\text{COO}-\text{Na}^+$ is a polar group and is soluble in water, while the other end is a hydrocarbon paraffin group $\text{CH}_3(\text{CH}_2)_{14}$, dissolved in water.

The liquid crystalline materials exhibit the liquid crystal phase in different ways. Some of them exhibit the liquid crystal phase at a certain range of temperatures, while some exhibit the liquid crystal phase according to their concentration in solution. The former are called thermotropic liquid crystals, and the latter lyotropic liquid crystals. The

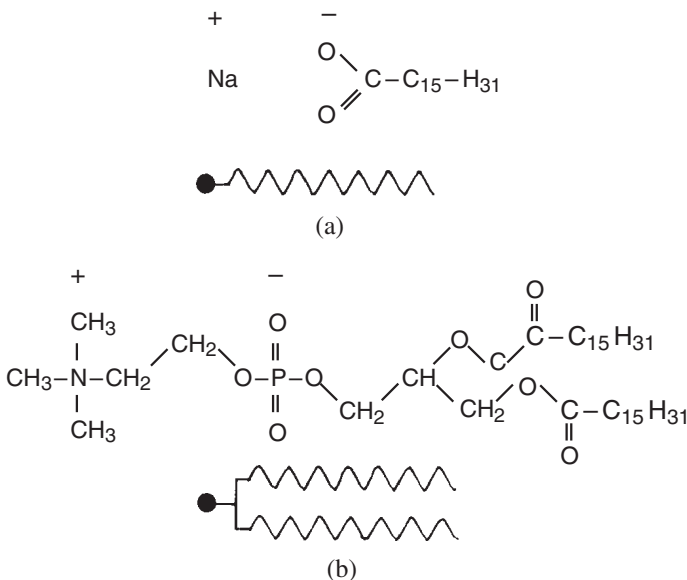


Figure 1.3. Two amphiphilic liquid crystal molecules: (a) sodium laurate; (b) dipalmitoylphosphatidylcholine. (From Collings, 1990.)

above-mentioned rod-like molecules are mainly thermotropic liquid crystals, and the amphiphilic molecules are lyotropic liquid crystals. But, very long, very rigid polymer solutions can exhibit the lyotropic liquid crystal phase.

Liquid crystalline polymers are a kind of polymer that show liquid crystalline phases. They are composed of low molecular mass liquid crystals, which can be either rod-like or disc-like, or rod- and disc-like together in one. The constituent blocks may be of very complicated two-dimensional or three dimensional shape. They may be composed of amphiphilic molecules as well. According to the way the mesogenic units are incorporated into the polymers, the liquid crystalline polymers can be classified as main chain liquid crystalline polymers in which the mesogenic units are connected in the backbone, or side chain liquid crystalline polymers in which the mesogenic units are attached to the backbone as side pendants. The mesogenic units may be incorporated in both ways, that is, a part as the backbone and the other part as side groups attached to the backbone. This kind of liquid crystalline polymer is called the combined liquid crystalline polymer. The side groups may be attached to the backbone through their centers (side-on mode or laterally attached), or through their ends (end-on or terminally attached), or off-center attached (shoulderly attached). Figure 1.4 depicts some examples of liquid crystalline polymers.

Liquid crystalline polymers may be crosslinked to each other to form a network that retains the liquid crystal feature. The liquid crystal networks deform when a stress is applied as rubber does. They exhibit rubber elasticity.

A typical example of a thermotropic liquid crystalline polymers is the polyesters and the mesogen substituted polysiloxane. The aromatic amide, the super strength fiber known commercially as Kevlar belongs to the lyotropic liquid crystalline polymers. The other important lyotropic liquid crystalline polymers are poly(γ -benzyl-L-glutamate), abbreviated as PBLG, cellulose derivatives, the tobacco mosaic virus, *etc.*

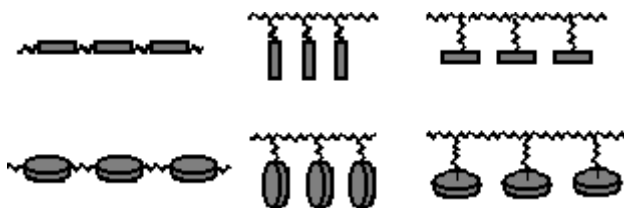
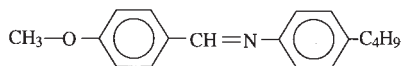


Figure 1.4. The liquid crystalline polymers.

1.4. POLYMORPHISM OF LIQUID CRYSTALS

MBBA, 4-methoxybenzylidene-4'-butylaniline was the first compound which showed the liquid crystal phase at room temperature. The chemical formulae of MBBA is as follows

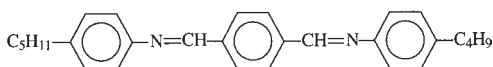


MBBA shows only the nematic liquid crystal phase (denoted as N phase), its phase sequence being

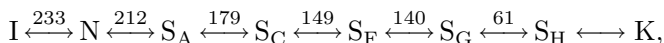


where I denotes the isotropic liquid phase, and K the crystal phase. The figures are the transition temperatures in degrees Celsius between adjacent phases. We will apply this expression when dealing with the phase sequences hereafter.

A few liquid crystals have a more complicated phase behavior, showing more than one liquid crystal phase. The series of terephthalylidene-bis-alkylanilines (TBnA) is particularly interesting in presenting an unusually broad polymorphism. For example, TPBA

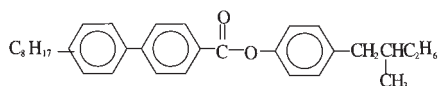


has a phase sequence as follows

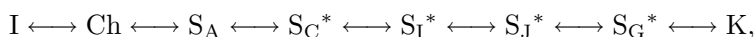


where S_A , S_C , S_F , S_G and S_H denote the smectic A, smectic C, smectic F, smectic G and smectic H phases.

Molecules with non-symmetric carbon atoms may exhibit a chiral structure, *e.g.*, the compound (8SI) of chemical formulae



shows a phase sequence as follows



where Ch or N* denotes the cholesteric phase, and S_I, S_J are the smectic I and J phase. The asterisk denotes the counterpart chiral phases. The names smectic A, B, C, *etc.* were named purely in the chronological sequence in which the phases were discovered. The letter designation does not imply any information about the arrangement of the molecules, the symmetry, or other features.

We now introduce the classification of the liquid crystal phases and their structural features.

There are two fundamental orderings in the materials: positional order and orientational order. At low temperatures, matter exhibits a crystal state. The atoms or molecules are arranged regularly and periodically. Both position and orientation exhibit a long range order. When heated, matter may become an isotropic liquid through two ways, by losing the orientational order first while retaining the translational order, and hence becoming a plastic crystal, or alternatively, by losing the translational order while keeping the orientational order. These latter materials are liquid crystals.

In fact, with increasing temperature, these materials may not completely lose their translational order while retaining their orientational order. All liquid crystals are characterized by their orientational order, but liquid crystal phases show varying amounts of translational order with the only exception of nematics. Apart from the above basic symmetries, there is another important symmetry — bond orientation symmetry. This symmetry is important when dealing with hexatic phases. Liquid crystals are classified in terms of following criterion:

- (1) translational order
- (2) bond orientational order
- (3) correlation between smectic layers
- (4) with chirality?
- (5) cubic structure?

1.4.1. No translational order — Nematics

The nematic liquid crystal, N phase, is the only liquid crystal phase without any long range translational order. Nematics are the most important member in the family of the liquid crystals and are widely used in the display industry.

In nematics, the molecules tend to be parallel to each other. The preferred direction of parallel orientation is characterized by the director,

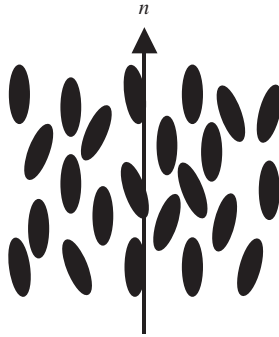


Figure 1.5. The nematic liquid crystals.

denoted by a unit vector \mathbf{n} . The director \mathbf{n} actually has the up and down symmetry. The nematic liquid crystal is shown in Figure 1.5.

This phase has a symmetrical axis C_∞ along the director. In addition, there is a reflection-symmetry plane perpendicular to the axis C_∞ and a mirror-symmetry plane through the C_∞ axis. Therefore, the local symmetry of nematics can be expressed by the $D_{\infty h}$ group. Of course, nematics have three dimensional translational symmetry.

The structural factor of the nematic phase reflects the breaking of the rotational symmetry. The large X-ray scattering angle sphere (short distance) shrinks toward the circle perpendicular to the director while the small scattering angle intensity is compressed along the \mathbf{n} axis. There are two X-ray diffuse spots at $\mathbf{q} = q_0 \mathbf{n}$ with $q_0 = 2\pi/l$ (l the molecular length) and two diffuse rings around $\mathbf{q} = q_1 \mathbf{n} \times \mathbf{k}$ with approximately $q_1 = 2\pi/a$ (a the distance between neighboring molecules).

1.4.2. One-dimensional translational order — Smectic A and C phases

As the temperature is further cooled, the molecules begin to segregate into planes giving rise to a smectic A or smectic C phase. In addition to the orientational order that the nematic phase shows, the smectic A and C phases exhibit a one-dimensional translational order, and can therefore form layered structures. There is a liquid-like motion of the rods in each layer and no correlation of the molecular positions from one layer to the next. In each layer, the mass centers of the molecules are randomly distributed as

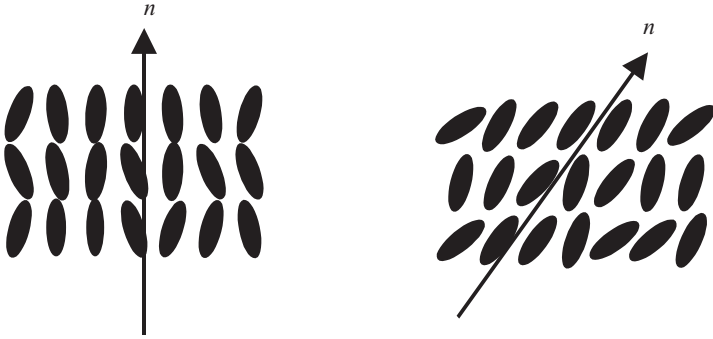


Figure 1.6. The smectic A and C phases.

in isotropic liquids. The layers can easily slide. The molecular arrangement in the smectic A and C phases are schematically shown in Figure 1.6.

In the smectic A phase, molecules tend to be perpendicular to the smectic layers. The layer thickness d is roughly the same as the molecular length l . The thickness of the layers in the case of liquid crystalline polymers is about the order of the monomer's length. But in the smectic C phase, the molecules in the layers are parallel and tilted in arrangement with respect to the normal of the layers by a tilt angle θ . The layer thickness of the smectic C phase is $d = l \cos \theta$. The ordering of the smectic A and C phases are both higher than the nematic phase so that they appear at a lower temperature than the nematics do. The smectic A phase appears first as the temperature decreases if a compound shows both the smectic A and C phases.

The positional correlation in the smectic A phase can be described as a sinusoidal modulation of the average mass density

$$\langle n(\mathbf{r}) \rangle = n_0 + 2n_{q_0} \cos(q_0 z), \quad (1.7)$$

where $q_0 = 2\pi/l$ and the z axis is along the layer normal. The Fourier transformation of this function leads to two Bragg peaks away from $q = 0$ in the structural factor:

$$S(q) \propto |\langle n_{q_0} \rangle|^2 [\delta(q_z - q_0 e_z) + \delta(q_z + q_0 e_z)]. \quad (1.8)$$

The thermal fluctuations destroy the ideal long-range periodic order of the smectic phase and there are power-law singularities rather than the

delta function in $S(\mathbf{q})$ at $\mathbf{q} = \pm q_0 \mathbf{e}_z$. Thus, the peaks in the smectic structural factor are called quasi-Bragg peaks, and the smectics are thus said to be characterized by quasi-long-range order (QLRO) in one dimensional position rather than a true long-range order (LRO). As the smectic phase is approached on cooling from the nematic phase, the diffuse spots in the nematic structural factor are sharpened and eventually become the quasi-Bragg peaks of the smectic phase. The experimental structural factor of the smectic phase has basically confirmed the expectation in Equation (1.8) which has only two quasi-Bragg peaks (at $\pm q_0$).

The local symmetry of smectic A phase is the same as that of the nematics, *i.e.*, its point group is $D_{\infty h}$, while the symmetry of the smectic C phase is C_{2h} (a C_2 symmetry axis plus a reflection plane perpendicular to the axis). In addition, both smectic phases exhibit a one-dimension translational order. Owing to the difference in symmetry, the smectic phases show different optical properties. The smectic A phase is optically uniaxial, but the smectic C phase is optically biaxial.

1.4.3. Two-dimensional translational order within layers with weak correlation along the third dimension — Hexatic phases

There are the smectic B, F and I phases belonging to this kind of liquid crystal, the so-called hexatic phase. The newly discovered smectic M phase is also catalogued to the hexatic liquid crystal phase. These hexatic phases have a six-fold symmetry which can be observed from the X-ray scattering intensity at $q = 2\pi/a$.

In addition to the one-dimensional order which forms the layer structure, there is a two-dimensional translational order within the layers. The molecules of this class of liquid crystals are arranged into a hexatic lattice with a correlation length of tens of nm that is one order of magnitude higher than that in the S_A and S_C phases within layers. In addition, there is two dimensional, long range bond symmetry. In the literature, the S_B , S_F , S_I phases are sometimes called stack hexatic phases.

Assuming θ is the angle that the vector connecting neighboring molecules makes with respect to the x -axis, the hexatic order is defined by

$$\Psi_6 = \exp(6i\theta). \quad (1.9)$$

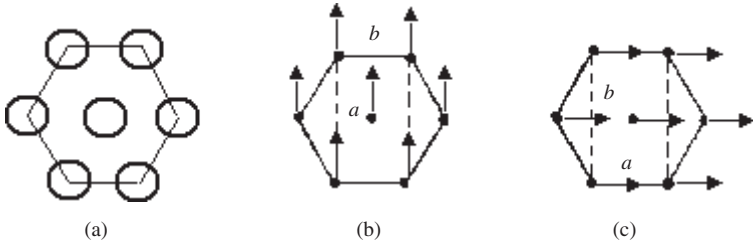


Figure 1.7. The smectic liquid crystal (a) B, (b) F and (c) I phases.

The Fourier transformation of the smectic B phase is characterized by its six-fold bond-orientational order, expressed as a Fourier series in χ

$$S(q) = \sum_p S_{6p}(q_{\parallel}, q_{\perp}) \cos(6p\chi). \quad (1.10)$$

There is a long-range orientational order in the plane but no long-range positional order. In the smectic B phase, only the first harmonic $S_6(q_{\parallel}, q_{\perp})$ is significant. As the temperature is further reduced to that of the smectic crystalline L phase, which is going to be mentioned in a later section, more and more harmonics in χ become important. Figure 1.7 schematizes the three phases.

In the hexatics, there is no chemical bond between neighboring molecules. The hexatic bond order can be viewed as resulting from the loss of the long-range positional but not orientational order of a hexagonal crystal.

The molecular tilt order of the smectic C phase can coexist with the hexatic order, leading to smectic F and I phases depicted in Figure 1.7.

In the smectic B phase, the molecules within the layers are aligned perpendicularly to the layers, but the molecules of the S_F and S_I phases within layers are tilted with respect to the layer normal by a tilt angle. The azimuthal of the tilt direction or the projections onto the smectic layers of the S_F and S_I phases are different. In the former, the projections of molecules onto the layer point to the edge of the hexatic, while in the latter, to the apex. The difference seems not so significant, but S_F and S_I liquid crystals are not miscible, and there is a phase transition between them when the temperature varies.

The S_B phase can be regarded as a hexatic structure. S_F and S_I phases have the base-centered monoclinic structure in the nomenclature

of crystallography even though the correlation between layers in these two smectic phases is weak.

The smectic M phase, discovered in 1990, may be classified as a hexatic phase. The molecules are tilted within layers but are not miscible with the S_F and S_I phases. The structural details are under investigation.

1.4.4. Three-dimensional translational order but correlation is weaker than that in crystals

This class of liquid crystals includes the smectic liquid crystal L, G, and J phases, and the higher ordered ones: the smectic liquid crystal E, H, and K phases.

Compared with the previously mentioned class of liquid crystals, S_B , S_F , S_I , and S_M , this class of liquid crystals exhibits a stronger correlation between smectic layers, the correlation length ranging from tens to hundreds of layers. The way of stacking of successive layers may be either AAA..., ABABAB... or ABCABC.... These six smectic liquid crystals are actually very similar to real crystals, but they do exhibit a significant disorder in both translation and orientation. Dynamic experiments demonstrated that they exhibit rather different characteristics from real crystals, such as the dielectric relaxation and the Mossbauer spectrum. The X-ray diffraction of these liquid crystals shows reflections of only less than five orders. In addition, as the transition to a real crystal happens, a relatively large amount of transition enthalpy and volume change occurs. These variations are in general one order of magnitude greater than those transitions occurring between liquid crystals.

In the S_L phase, the molecules are perpendicular to layers and are arranged in a hexatic lattice within layers. This symmetry is the same as that of the S_B phase. Both of the S_L and S_B phases are optically uniaxial, their molecules within smectic layers rotate more freely around their long axes or rotate in groups simultaneously. In some of the literature, the S_B phase is called the hexatic B phase while the S_L phase is named the S_B phase or crystal B phase. The molecules within the S_G and S_I phases are tilted with respect to the layers while the molecules of the S_L phase are aligned more or less perpendicularly to the layers. The stacking of molecules within the layer of the S_L , S_G and S_J phases is similar to those shown in Figure 1.7 as well. The crystallography classifications of these three liquid crystal phases are the same as those of the S_B , S_F and S_I phases.

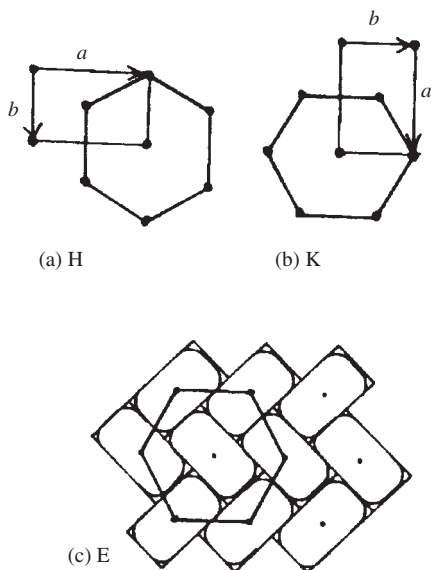


Figure 1.8. The smectic (a) H, (b) K and (c) E phases.

The structural relation of the S_G and S_J phases with the S_L phase is similar to that in the hexatic series, *i.e.* of the S_F and S_I phases with the S_B phase.

The molecules of the S_E phase within the smectic layers tend to be perpendicular to the smectic layers, but they are unable to rotate freely with respect to the long molecular axis. This phenomenon has been verified by X-ray diffraction experiments that demonstrated that the packing of molecules within layers in the S_E phase is too close for them to rotate freely. Incoherent quasi-elastic neutron scattering has illustrated that the molecules of the S_E phase can vibrate at a frequency of 10^{11} Hz within a 180 degree range. Only those molecules with enough energy can go over the energy barrier from one hemi-circle to the other hemi-circle. The molecular packing within the S_E layer is schematically shown in Figure 1.8. In order to demonstrate that the molecules cannot rotate freely they are depicted as ellipses in the figure where the cross-section of the molecules are arranged herringbone-like. The S_E phase is of a monoclinic structure.

The S_H and S_K phases differ from the S_E phase only in their tilted molecules within the layers. The molecules of the S_H phase are tilted to the

edge of the hexatic while in S_K phase to the apex. Both of the S_H and S_K phases are of a monoclinic structure.

1.4.5. Chiral liquid crystals

1.4.5.1. Cholesterics

In this liquid crystal phase, the molecules have non-symmetrical carbon atoms and thus lose mirror symmetry. Otherwise optically active molecules are doped into host nematogenic molecules to induce the chiral liquid crystals. The liquid crystals consisting of such molecules show a helical structure. The most important chiral liquid crystal is the cholesteric liquid crystals. As discussed in Section 1.2, the cholesteric liquid crystal was the first discovered liquid crystal and is an important member of the liquid crystal family. In some of the literature, it is denoted as the N^* phase, the chiral nematic liquid crystal. As a convention, the asterisk is used in the nomenclature of liquid crystals to mean the chiral phase. Cholesteric liquid crystals have beautiful and interesting optical properties, *e.g.*, the selective reflection of circularly polarized light, significant optical rotation, circular dichroism, *etc.*

The molecules in cholesteric liquid crystals are arranged as thin layers. The molecules lie in the layers and are parallel to each other, but the director rotates along the helical axis continuously and uniformly. The helical pitch is much greater than the spacing of successive molecular layers. In general the helical pitch of cholesteric liquid crystals is of the order of visible light's wavelength—about a few hundreds nm. The pitch of those cholesteric liquid crystals induced by doping with optically active molecules is larger, *e.g.*, up to a few microns. A schematic of cholesteric liquid crystals is illustrated in Figure 1.9.

1.4.5.2. Chiral smectic liquid crystals

Almost all the smectic phases, in which the molecules are arranged in layers and are tilted with respect to the layers, have counterpart chiral phases. The most important one of this class is the chiral smectic C phase— S_{C^*} phase. In these chiral liquid crystal phases, the molecules are tilted at a constant angle with respect to the layer normal but the tilt azimuthal rotates uniformly along the chiral axis and forms a helical structure.

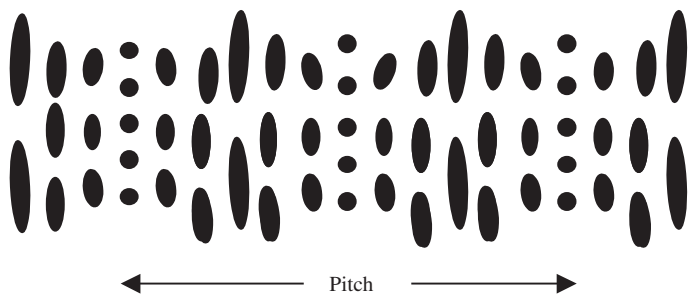


Figure 1.9. The cholesteric liquid crystal.

The local symmetry group of the S_C^* phase is a C_2 group and thus the S_C^* phase has helical electricity. The spontaneous polarization, P_s , is perpendicular to the layer normal and molecular axis. Due to its helical structure P_s changes its direction uniformly, evolving along the helical axis so that the S_C^* phase does not show a measurable ferroelectricity except in the unwinding of its helical structure. The S_C^* phase is one of the very important liquid crystal phases that has a prospective application in fast response display. The detailed structure of the S_C^* phase will be shown in Chapter 6.

Once the helical structure of the S_C^* phase is unwound, ferroelectricity is displayed (see Chapter 6 for the details). In recent years, many experimental studies have revealed that some liquid crystal compounds show new types of smectic phases with complex tilt and dipole order, such as the anti-ferroelectric smectic C phase, S_{CA}^* phase, and the ferroelectric smectic C phase, $S_{C\gamma}^*$ phase. For instance, in the S_{CA}^* phase, the spontaneous polarization P_s is opposite for successive layers. It was found experimentally that the chiral S_O phase is in fact similar to the anti-ferroelectric S_{CA}^* phase.

The twisted-grain-boundary phase, TGB (Renn and Lubensky, 1988) was discovered recently in which topological defects create a new symmetry rather than simply destroy the old one. It occurs in some chiral liquid crystals (Goodby *et al.*, 1988) and is characterized by an array of equally spaced twist-grain boundaries in the smectic A or C liquid crystal as shown in Figure 1.10. In this phase, the average director twists like a cholesteric while regularly spaced molecular planes are configured like a smectic. One

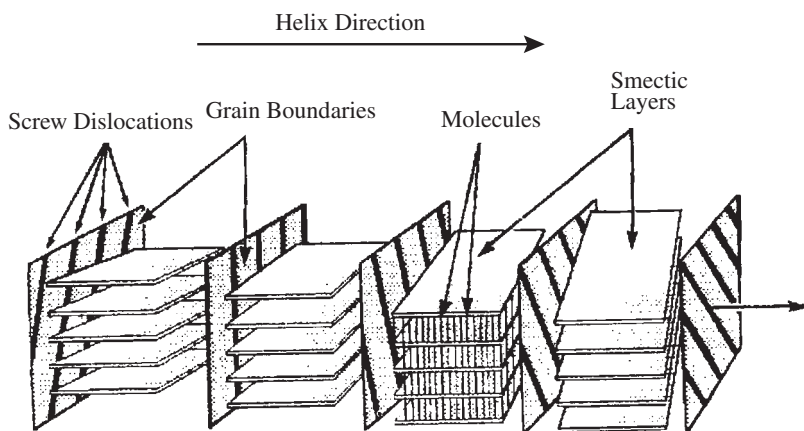


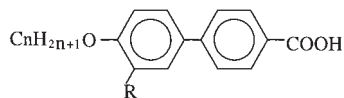
Figure 1.10. The TGB phase of liquid crystals. (From Goodby *et al.*, 1993. Reproduced by permission of Taylor & Francis, <<http://www.tandf.co.uk/journals/tf/02678292.html>>)

would reasonably expect it to appear between the cholesteric and smectic A, or smectic C phases.

1.4.6. Cubic phases

1.4.6.1. D phase

The D phase is the one cubic liquid crystal phase which was discovered independently in 1957 by G. Gray (Gray *et al.*, 1957) and D. Demus (1957) when they were studying the following compounds



where R is either $-\text{NO}_2$ or $-\text{CN}$, and $n = 16$ or 18 . These compounds display a phase between the S_A (or N) and S_C phase and were called the Smectic D, S_D phase. Actually the D phase does not have a layered structure that is characteristic of all smectic phases. The structure has been studied in detail by Etherington *et al.* (Etherington *et al.*, 1985, 1986) through X-ray diffraction, a second-harmonic-generation experiment and modeling. The space group and molecular packing of the phase was proposed. It was thus suggested that it was better to call the S_D phase the D phase.

The D phase had been found in only four compounds until recently (Paschke *et al.*, 1994). The four compounds are the 16 and 18 members of the 4'-n-alkoxy-3'-nitrobiphenyl-4-carboxylic acids (AnBC) synthesized by Gray *et al.* in 1957 and the n = 16 and 18 members of the analogous 3'-cyano compounds (ACBC) prepared by Goodby and Gray (1980). Detail experiments (Etherington *et al.*, 1985, 1986) verified that the compound (CN:18) is of space group P23 or Pm3, and is optically isotropic with no apparent optical rotation. Recently, Paschke *et al.* (1994) found that the D phase appears in more members of the above series of cyano compounds with n = 15 to 22. The temperature range of the D phase becomes wider as n increases.

1.4.6.2. Another D-like cubic phase

Later Demus *et al.* (1984) found that the following compounds exhibits the cubic phase as well



where $n \geq 8$. The cubic phase appears at a temperature below the S_C phase and is not miscible with the above D phase. Recently some CN-substituted analogous compounds were found to show this phase.

It is clear that the cubic unit cell is very large and accommodates more than 100 molecules. It can be assumed that the molecules are aligned in parallel in micelles or in bundles, and the preferred direction is randomly oriented in dynamic equilibrium. The lattice elements form a three-dimensional cubic lattice with a long-range order.

The molecular packing and the mechanism of phase transition of the cubic phases have been attracting much research interest worldwide.

1.4.6.3. Blue phase

Some cholesteric materials show the blue phase as the temperature increases from that of the cholesteric phase and before it reaches that of the isotropic phase. The blue phase is a cubic phase. There have been three blue phases found so far: BP I, BP II and BP III phases. It is now understood that the BP I phase is a body-centered cubic, the BP II phase is a primitive cubic and the BP III phase is a fog phase with no structural symmetry. Generally the temperature range of the blue phase is quite narrow, less than 1 degree

centigrade. The blue phase possesses a helical structure and its pitch is less than that of the corresponding cholesteric phase. It is optically isotropic, but with remarkable optical activity. The molecules in the blue phase are packed into a double helical structure. The networks of defects is believed to play an important role in constructing the structure.

The blue phase has a similar structure to that of the D phase, in spite of the remarkable difference in the lattice parameter. The lattice parameter of the former is hundreds of nm while that of the latter is less than 10 nm.

In general, if all the liquid crystal phases would exist together for a particular material, the phase sequence would be as follows

$$I \longleftrightarrow N \longleftrightarrow BP \longleftrightarrow Ch \longleftrightarrow S_A \longleftrightarrow D \longleftrightarrow S_C \longleftrightarrow S_B \longleftrightarrow S_I \longleftrightarrow S_L \longleftrightarrow S_F \longleftrightarrow S_J \longleftrightarrow S_G \longleftrightarrow S_E \longleftrightarrow S_K \longleftrightarrow S_H \longleftrightarrow K.$$

The chiral counterparts should appear in the sequence immediately following their non-chiral phases *i.e.*, at a lower temperature. The re-entrant phase is an exception. They may appear in reverse order, *e.g.*, as temperature decreases the re-entrant nematic phase appears at a temperature lower than that for the S_A phase

$$N \longleftrightarrow S_A \longleftrightarrow N_{re} \longleftrightarrow S_{Are},$$

where N_{re} and S_{Are} are the re-entrant N and S_A phase, respectively. Only those liquid crystal materials with strong polar group are able to show the re-entrant phases.

1.4.7. Discotic liquid crystals

The liquid crystals discussed so far are composed of rod-like molecules. As discussed in the last section, disc-like molecules may show liquid crystal phases and are called discotic liquid crystals. The first discotic liquid crystal was synthesized by Chandrasekhar (1977) and many more discotic liquid crystals have since been discovered.

The simplest discotic liquid crystal phase is the nematic discotic phase, N_D , in which the normals of the molecular discs tend to align with respect to a preferred direction, *i.e.*, the director, but the mass centers of molecules do not have any positional order. The discs in Figure 1.11 represent the disc-like molecules, the molecules are packed in the way a pile of coins is packed randomly. The discotic nematic phase has its chiral counterpart, *i.e.*, the

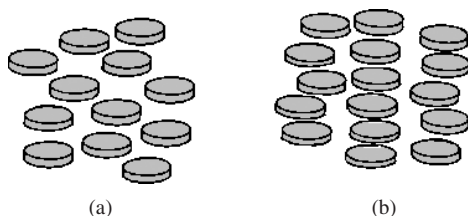


Figure 1.11. The discotic nematic (a) and column phases (b).

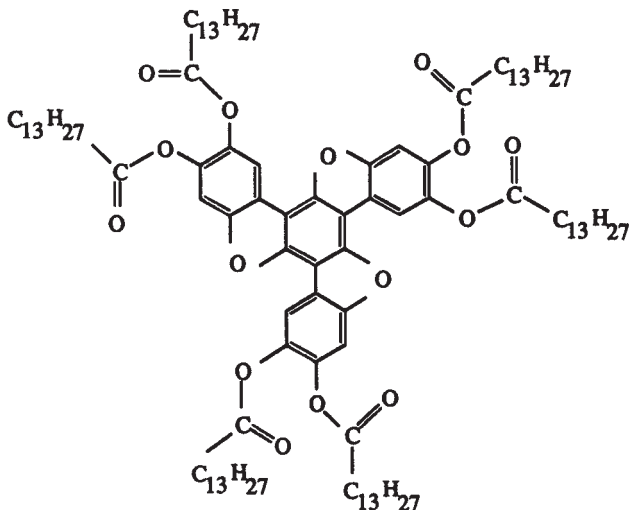


Figure 1.12. An example of a typical disc-like molecule.

N_D^* phase. A phase similar to the rod-like smectic liquid crystal phase is the column phase in which molecules are packed as columns parallel to each other. The columns are arranged in a hexatic or rectangular array. Inside the columns, the spacings of the molecules are either constant or random. The axes of the columns may be tilted with respect to the normal of discotic molecules. Figure 1.12 sketches the chemical formulae of one example of a discotic liquid crystal molecule.

There is another class of liquid crystals, the bowlic liquid crystal phase, whose molecules are bowl-like or pyramid-like, as is shown in Figure 1.13. Because of the breaking down of the up-down symmetry, the bowlic phase shows an even higher order and may be able to show ferroelectricity (Lam, 1986; Wang *et al.*, 1989).

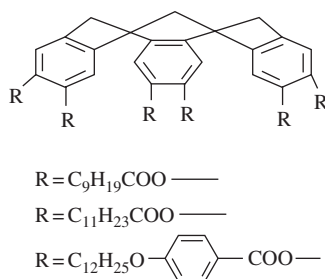


Figure 1.13. A bowlic liquid crystal molecule.

1.4.8. Lyotropic liquid crystals

1.4.8.1. Amphiphilic liquid crystals

Liquid crystal phases also appear in response to changes in the concentration of water, oil, surfactants, or other species in a wide variety of molecular mixtures. These are called lyotropic liquid crystals.

When amphiphilic molecules dissolve in water, their polar heads tend to be close to each other while the non-polar hydrophobic tails are as far away from water as possible. Depending on the concentration, the amphiphilic molecules aggregate to form spheres, or columns, or a laminar structure, see Figure 1.14.

In Figure 1.14 the tadpoles represent amphiphilic molecules, and the solid circles are the polar heads of amphiphilic molecules, *i.e.*, the hydrophilic parts, while the zig-zag lines are the hydrophobic groups. The typical phase diagram is depicted in Figure 1.15.

As the concentration increases, the amphiphilic molecules form micelles and then form columns. The columns are arranged into a hexatic array. As the concentration further increases, the system forms a laminar structure, *i.e.*, a smectic liquid crystal phase. Sometimes, a cubic phase may appear between the micelle and hexatic phases. In fact, the micelles are packed to form a cubic phase. The three phases are all liquid crystal phases: hexatic phase, laminar phase and cubic phase. As seen in the figure, the phase diagram of amphiphilic molecules actually depends on the temperature as well. T_K in Figure 1.15 is the Kraft temperature, below which the system is phase separated into crystal and water.

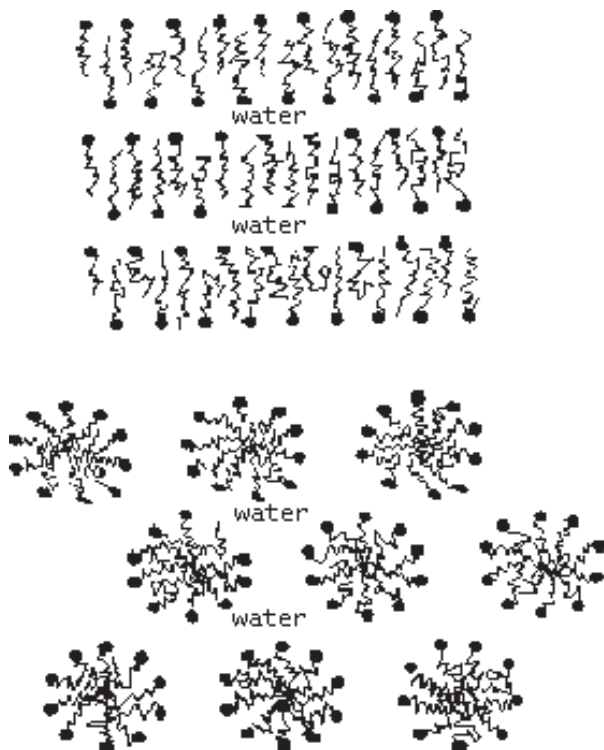


Figure 1.14. The amphiphilic liquid crystals. (From Collings, 1990.)

1.4.8.2. *Lytotropic liquid crystals consisting of long rigid molecules*

A few non-amphiphilic molecules are able to show liquid crystallinity in solution at a certain range of concentration, such as PBLG, DNA, the tobacco mosaic virus, *etc.* They are of great molecular mass, very rigid, rod-like and have a very long anisotropic shape. They are typical macromolecules and are lyotropic liquid crystals. This class of liquid crystals does not aggregate to form sphere, column or laminar structures. These lyotropic systems depend on the properties of the solvent. They are one of major interest of this book and will be discussed in detail later.

1.4.9. Induced liquid crystals

Some materials are themselves not liquid crystals, or do not display the liquid crystal phase at a certain temperature or solvent concentration. But,

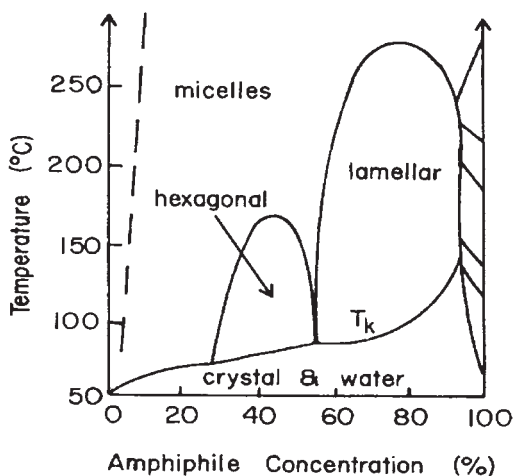


Figure 1.15. The typical phase diagram of amphiphilic molecules. (From Collings, 1990.)

they may become liquid crystals when subjected to certain external conditions, such as pressure, electric field, magnetic field, irradiation, *etc.* The liquid crystal phase may also be induced when two non-liquid crystalline materials are mixed together.

1.5. CONTINUUM THEORY OF LIQUID CRYSTALS

1.5.1. Order parameter

The atoms in crystals are not always fixed in a perfectly ordered position except at the absolute temperature! Due to the thermal movement, atoms more or less deviate from their equilibrium position. For the same reason, the orientational order in liquid crystals is not perfect either. Because of the thermal fluctuation, the orientation and position of liquid crystals vary constantly. If the positions and orientations of liquid crystal molecules are frozen at a moment in time, the picture should look like that shown in Figure 1.5. The molecules tend to align along a preferred direction, but imperfectly. This preferred direction is defined as the director \mathbf{n} . Because the molecules are moving all the time, they are not fixed at a constant

position and do not point in a constant direction, although they have a greater chance of orienting along the director. In other words, at a certain moment more molecules are oriented along the director than otherwise. How close are the molecules aligned along the director? A parameter is needed to quantitatively describe the extent of the molecules' being oriented along the director. This statistical quantity is the order parameter, denoted conventionally as S .

Because the liquid crystals are up and down symmetrical, obviously $\langle \cos \theta \rangle$ (θ is the angle the molecular long axis makes with respect to the director) is not an appropriate candidate for the order parameter. What if $\langle \cos^2 \theta \rangle$ is adopted? If so, for perfect alignment, the order parameter $S = 1$; but for the disordered distribution $S = 1/3$. For the sake of convenience, it is hoped that for the random distribution, *i.e.*, the isotropic phase, $S = 0$, and for the perfect orientation, $S = 1$. Therefore, the statistical average of the second Legendre polynomial P_2 is chosen as the order parameter

$$S = \langle P_2(\cos \vartheta) \rangle = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle. \quad (1.11)$$

If the liquid crystalline molecules are not cylindrically symmetrical, S must be expressed by a tensor (traceless tensor). The nematic liquid crystal state (a uniaxial symmetrical system) is the main concern of the book. For such a phase, the order parameter can be denoted by the scalar in Equation 1.11.

The order parameter S is a very important quantity in a partially ordered system. It is the measure of the extent of the anisotropy of the liquid crystal physical properties, *e.g.*, elastic constants, viscosity coefficients, dielectric anisotropy, birefringence, and so on. S is temperature dependent and decreases as the temperature increases. The typical temperature dependence of S is shown in Figure 1.16.

As the temperature reaches the clear point T_c or isotropization temperature T_i , S jumps abruptly down to zero. The phenomenon implies that the nematic-isotropic transition is of first order.

The combination of S and \mathbf{n} appropriately describes the ordering of liquid crystals. S is the microscopic feature of molecular orientation while \mathbf{n} is the macroscopic characteristic of liquid crystal orientation. In general, the molecular dimension of liquid crystals is about a few nm in length and a few tenth of a nm in width. The range of variation of $\mathbf{n}(\mathbf{r})$ is in the order of the magnitude of microns. $\mathbf{n}(\mathbf{r})$ is in fact the average orientation of a

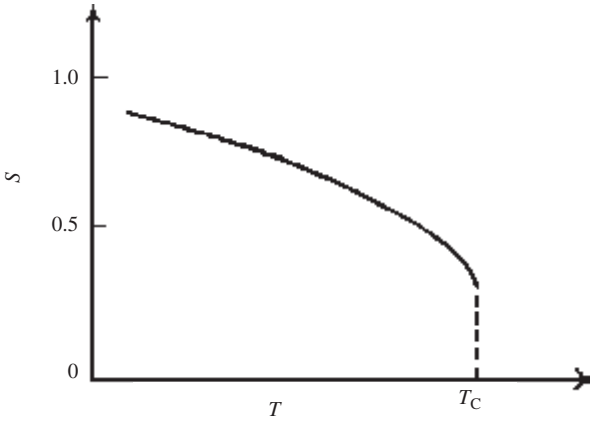


Figure 1.16. The order parameter versus temperature.

small bulk sample of a hundred of thousand molecules, whose scale is much greater than the molecular dimension. When dealing with the orientational distortions and defects in liquid crystals, the analysis of $\mathbf{n}(\mathbf{r})$ is appropriate.

1.5.2. Distortions of liquid crystals

The liquid crystals can be deformed by applying external fields. Even a small electric or magnetic field, shear force, surface anchoring, *etc.*, is able to make significant distortion or deformation to liquid crystals. Thus, \mathbf{n} is actually a function of position \mathbf{r} . According to the symmetry of liquid crystals there exist three kinds of deformations in liquid crystals: splay, twist and bend deformations, shown in Figure 1.17. The short bars in the figure represent the projections of the local directors.

The three kinds of deformations are associated with the variation of \mathbf{n} , *i.e.* $\nabla\mathbf{n}$. For the splay deformation, the divergence of the \mathbf{n} vectors, $\nabla \cdot \mathbf{n}$, is not zero; for the twist deformation, $\mathbf{n} \cdot \nabla \times \mathbf{n} \neq 0$, and for the bend deformation, $\mathbf{n} \times \nabla \times \mathbf{n} \neq 0$. In order to describe the meaning of the three formulae, it is supposed that in the undeformed sample, \mathbf{n} points along the z direction. These three deformations can hence be written in the form of components as follows

$$\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}, \quad \frac{\partial n_y}{\partial x} - \frac{\partial n_x}{\partial y}, \quad \frac{\partial n_y}{\partial z} \mathbf{i} + \frac{\partial n_x}{\partial z} \mathbf{j}. \quad (1.12)$$

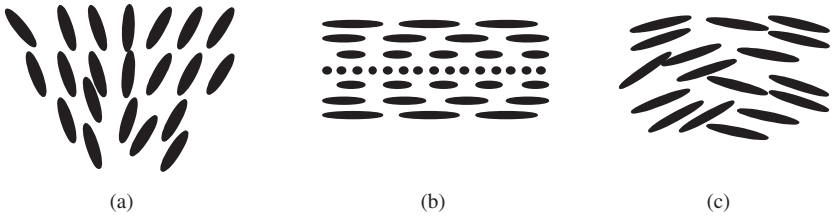


Figure 1.17. Three basic deformations in liquid crystals: (a) splay; (b) twist and (c) bend.

The strain increases the energy of the solid as a stress is applied. The distortion of the director in liquid crystals causes an additional energy in a similar way. The energy is proportional to the square of the deformations and the correspondent coefficients are defined as the splay elastic constant, K_{11} , twisted elastic constant K_{22} and bend elastic constant K_{33} , i.e., the respective energies are the half of

$$K_{11}(\nabla \cdot \mathbf{n})^2; \quad K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2; \quad K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2. \quad (1.13)$$

These three elastic moduli are different in liquid crystals. Generally, K_{11} and K_{33} are greater than K_{22} , which implies that the twist deformation is the easiest one to occur. K_{33} is the largest constant for rod-like polymers while for semi-flexible polymers in a concentrated solution and for thermotropic polymers K_{11} is usually the largest. K_{22} for liquid crystalline polymers is about the same in values as those for small molecular mass liquid crystals. But the above conclusion is not always valid. K_{ii} ($i = 1, 2, 3$) are functions of the temperature. The ratios between them varies with temperature. For example, at temperatures near the transition to the S_A phase, K_{22} may become the greatest term of the three elastic constants. The three elastic constants are all small, that is the reason why liquid crystals deform easily. For the liquid crystal compound MBBA, the three elastic constants at 20°C are: $K_{11} = 5.8 \times 10^{-12}$ N, $K_{22} = 3.3 \times 10^{-12}$ N and $K_{33} = 7.0 \times 10^{-12}$ N. The reorientation of the liquid crystal as a bulk does not give off energy and the spatial orientation of liquid crystals may be determined by an electric or a magnetic field, or by surface alignment agents (SiO, lecithin, B-L films, *etc.*), or by a surface rubbing polyimide and so on.

The elasticity theory of liquid crystals was proposed by Oseen (1933) and Zocher (1933), and then modified by Frank into the form that has since

been accepted (1958). According to the Frank theory, the elastic energy of a deformed nematic liquid crystal can be expressed as

$$F = F_0 + \left(\frac{1}{2}\right) \int_V d^3\mathbf{r} [K_{11}(\nabla \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2], \quad (1.14)$$

where F_0 is the constant term for an undeformed sample.

Because of the spontaneously helical structure in the cholesteric liquid crystals, the second term in the integral must be revised to

$$\frac{1}{2} K_{22} \left(\mathbf{n} \cdot \nabla \times \mathbf{n} + \frac{2\pi}{P_0} \right)^2, \quad (1.15)$$

where P_0 is the intrinsic helical pitch. The supplement favors the molecular twist. The form illustrates that without an external field, the director of liquid crystals is naturally twisted with the period of the helix being the pitch P_0 .

The form of free energy for smectic liquid crystals is different. If there are no defects in the smectic liquid crystals, the curl of \mathbf{n} , $\nabla \times \mathbf{n}$, must be zero. Thus, no twist and bend deformations exist in the smectic liquid crystals. In addition, there is an energy penalty associated with the translational deformation. For example, the displacement of smectic layer \mathbf{u} will cause an additional term of elastic energy

$$\frac{1}{2} B \left(\frac{d\mathbf{u}}{dz} \right)^2, \quad (1.16)$$

where B is the elastic modulus, assuming that the z axis is perpendicular to the layers for the undeformed sample.

The elasticity theory has been used in dealing for example with the response of liquid crystals to external fields (electric, magnetic, mechanical force), defects, *etc.*

The above argument is suitable for polymer liquid crystals as well. In fact, the static properties of polymer liquid crystals are basically the same as those for the low molecular mass liquid crystals. But their dynamics are quite different because of their polymeric structure.

1.5.3. Frederiks transitions

We now apply the elasticity theory of liquid crystals to analyze the deformation of liquid crystals under an external magnetic field.

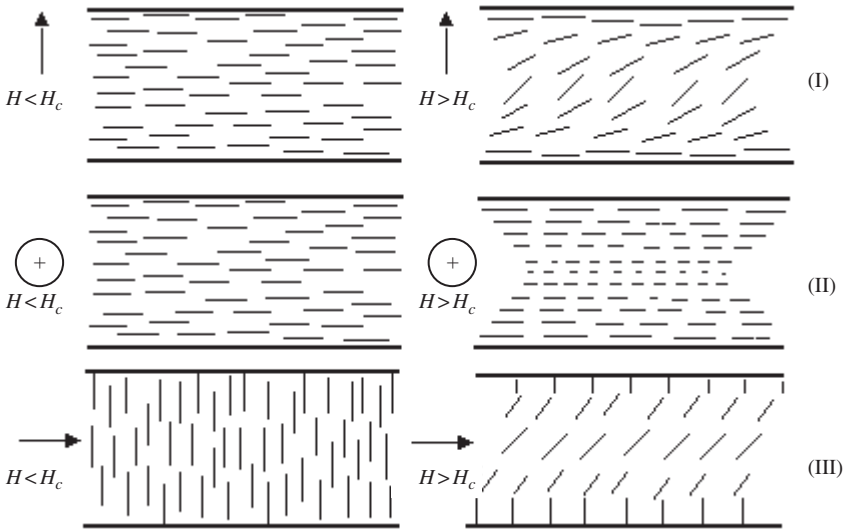


Figure 1.18. The Frederiks transitions I, II and III. The arrows represents the direction of the applied magnetic field \mathbf{H} .

A sheet of nematic liquid crystals sandwiched between two parallel glass plates that have been surface treated to align the liquid crystal molecules on the glass plates in the homogeneous configuration is shown in Figure 1.18(I). The applied magnetic field \mathbf{H} is perpendicular to the director. Because the nematic liquid crystals are paramagnetic, without surface anchoring the liquid crystal molecules would all be reoriented along the magnetic field. In the presence of surface anchoring, the competition between surface anchoring and the external magnetic field will cause the director of the liquid crystal to undergo a deformation.

The magnetic contribution to the free energy density of the liquid crystal has the form

$$-\left(\frac{1}{2}\right)\chi_a(\mathbf{n} \cdot \mathbf{H})^2, \quad (1.17)$$

where χ_a is the anisotropy of magnetic susceptibility. Then the free energy of the liquid crystal is

$$F = \left(\frac{1}{2}\right) \int_V d^3\mathbf{r} [K_{11}(\nabla \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2 - \chi_a(\mathbf{n} \cdot \mathbf{H})^2]. \quad (1.18)$$

Using a coordinate system with the z axis along the \mathbf{H} direction and the x axis along the \mathbf{n} direction of the undeformed sample, the director is written as

$$\mathbf{n} = (\cos \theta, 0, \sin \theta),$$

and the magnetic field as

$$\mathbf{H} = (0, 0, H).$$

Substituting \mathbf{n} and \mathbf{H} into Equation 1.18, the free energy of a unit area of a liquid crystal sheet of thickness d , F_s is

$$F_s = \frac{1}{2} \int_{-d/2}^{d/2} [(K_{11} \cos^2 \theta + K_{33} \sin^2 \theta) \left(\frac{d\theta}{dz}\right)^2 - \chi_a H^2 \sin^2 \theta] dz. \quad (1.19)$$

It is noted that there is no twisted deformation in liquid crystals, thus the K_{22} term does not appear in F_s . If the deformation is not so great, the splay deformation is dominant. When the deformation becomes greater, the bend deformation becomes more important.

The free energy is at its minimum when the liquid crystal is at equilibrium. One can obtain the minimum by means of the Euler-Lagrange functional method.

From the symmetry of the liquid crystal layer the following boundary condition exists

$$z = \pm d/2, \quad \theta = 0;$$

and

$$z = 0, \quad \theta = \theta_m \quad \text{and} \quad \frac{d\theta}{dz} = 0,$$

where θ_m is the deformation angle of the liquid crystal director at the mid-plane of the sample, and, in fact, is the maximum deformation angle of the sample. By substituting them into the Euler-Lagrange differential equation, the dependence of θ_m on the external magnetic field can be implicitly expressed as

$$\int_0^{\theta_m} \sqrt{\frac{K_{11} \cos^2 \theta + K_{33} \sin^2 \theta}{\sin^2 \theta_m - \sin^2 \theta}} d\theta = \sqrt{\chi_a} \cdot \frac{Hd}{2}. \quad (1.20)$$

As θ_m approaches zero, the magnetic threshold field \mathbf{H}_c is then given by

$$H_c = \frac{\pi}{d} \sqrt{\frac{K_{11}}{\chi_a}}. \quad (1.21)$$

Since the applied magnetic field \mathbf{H} is less than \mathbf{H}_c no deformation occurs. If \mathbf{H} is greater than \mathbf{H}_c , θ_m depends on the value of \mathbf{H} . The elastic constant K_{11} may be determined through measuring H_c . The ratio of K_{11} to K_{33} can be evaluated from the curve of θ_m versus H , or accordingly from the transmittance versus H or the electric capacitance versus H .

The reorientation of liquid crystals in this geometrical arrangement is named Frederiks transition I (Frederiks & Zolina, 1933). By appropriately designing the alignment of undeformed liquid crystals and the direction of the magnetic field, as shown in Figure 1.18 II and III, the Frederiks transition II and III occur. From them, K_{22} and K_{33} can be determined through the magnetic threshold field. In fact, K_{22} is more difficult to measure than K_{11} and K_{33} . The Frederiks transition may also occur when an electric field is applied instead. Because of the large dielectric anisotropy of liquid crystals, the electric threshold field is very small, about 0.1 volt/micron. In the above argument, the formulae are valid as long as the liquid crystal sample is pure enough, otherwise the conduction effect will cause other effects.

1.5.4. The twisted — and supertwisted — nematic liquid crystals

The twisted nematic (TN) and supertwisted nematic (STN) liquid crystals are widely used in liquid crystal displays. The former is used in wrist watches and calculators while the latter is used in notebook computers.

The TN cell is schematically shown in Figure 1.19. The liquid crystal sandwiched between two indium-tin-oxide (ITO) coated glass plates is about a few microns in thickness. The liquid crystal molecules on the top and bottom plates are homogeneously aligned and twisted by an angle of $\pi/2$. The liquid crystal molecules have a positive dielectric anisotropy $\varepsilon_a > 0$ so that an electric field will rotate the liquid crystal director up. The threshold voltage is given by

$$V_c = \pi \sqrt{\frac{K_{11} + (K_{33} - 2K_{22})}{4\varepsilon_a}}. \quad (1.22)$$

V_c is typically of order of one volt. Now, polarizers are mounted on the top and bottom glass plates such that their polarization directions are along or normal to the neighboring liquid crystal molecules on both plates. When

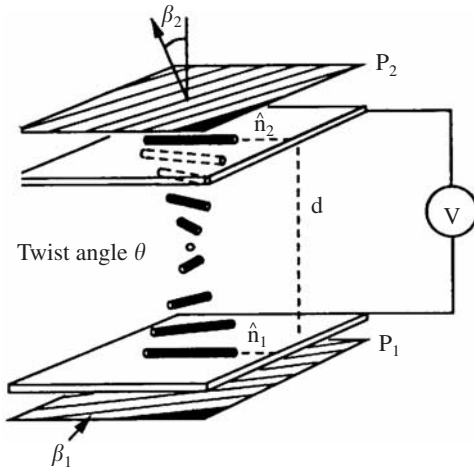


Figure 1.19. The twisted nematic cell. The twist angle $\theta = \pi/2$ and the two polars make an angle $\Psi = 0$ or $\pi/2$.

the voltage is off, the cell is transparent. When the voltage is on, the cell becomes dark.

STN has a twist angle greater than 180 degrees and its electric-optical response is much steeper so that they can be driven in the multiplexing displays such as those found in the SVGA format color notebook computers.

1.6. DEFECTS IN LIQUID CRYSTALS

The local translational and orientational order of atoms or molecules in a sample may be destroyed by singular points, lines or walls. The discontinuities associated with the translational order are the dislocations while the defects associated with the orientational order are the disclinations. Another kind of defect, dispirations, are related to the singularities of the chiral symmetry of a medium. The dislocations were observed long after the research on them began. The dislocations in crystals have been extensively studied because of the requirement in industry for high strength materials. On the contrary, the first disclination in liquid crystals was observed as early as when the liquid crystal was discovered in 1888, but the theoretical treatment on disclinations was quite a recent endeavor.

There is only the orientational order in nematics so that only disclinations may appear with no dislocations. In the other kinds of liquid crystals,

the dislocation may appear because of the discontinuity of the translational order.

1.6.1. The Volterra process

Both dislocation and disclination can be produced by the well-known Volterra process. Take a cylinder of a medium and do the following operations in sequence on it:

- (1) cut off a thin cylinder of diameter r_c along the axis of the cylinder;
- (2) cut a plane via the axis of cylinder and then move two opposite slips of the cut plane by a displacement of either translation \mathbf{b} or rotation $\boldsymbol{\omega}$, or both together. Hence the relative displacement of two slips is

$$\mathbf{d}(\mathbf{r}) = \mathbf{b} + \boldsymbol{\omega} \times \mathbf{r}; \quad (1.23)$$

- (3) If \mathbf{b} or $\boldsymbol{\omega}$ is consistent with the translational or orientational symmetrical element of the matter, the gap resulting from the displacement \mathbf{d} can be filled by a piece of bulk medium and two slips will fit perfectly with the filled piece. If the operation (2) makes the medium overlap, we need to take away an additional piece of medium instead and thus still keep the perfect fit of the two slips.
- (4) The medium will then relax to a new state owing to the internal interactions. Consequently, a singular line L is left.

The six basic Volterra processes are depicted in Figure 1.20, among them the three intrinsic processes on \mathbf{b} produce dislocations while the three intrinsic operations associated with $\boldsymbol{\omega}$ produce disclinations. In Figure 1.20, assuming $\boldsymbol{\sigma}$ is the normal of the cut plane,

- (a) $\mathbf{b} \perp L$, but $\mathbf{b} \parallel \boldsymbol{\sigma}$, the line L is an edge dislocation;
- (b) $\mathbf{b} \perp L$, and $\mathbf{b} \perp \boldsymbol{\sigma}$, L is an edge dislocation;
- (c) $\mathbf{b} \parallel L$, L is a screw dislocation;
- (d) $\boldsymbol{\omega} \parallel L$, L is a wedge disclination;
- (e) $\boldsymbol{\omega} \perp L$, but $\boldsymbol{\omega} \parallel \boldsymbol{\sigma}$, L is a twist disclination;
- (f) $\boldsymbol{\omega} \perp L$, and $\boldsymbol{\omega} \perp \boldsymbol{\sigma}$, L is a twist disclination.

The dislocations have been extensively studied so we limit ourselves mainly to the disclination. Figure 1.21 sketches a sample of nematic liquid crystals, the short bars denoting the directors which all lie on the sheet of paper. Now cut the sample along the normal and via the line L , see

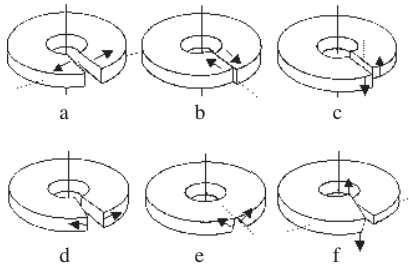


Figure 1.20. The Volterra process.

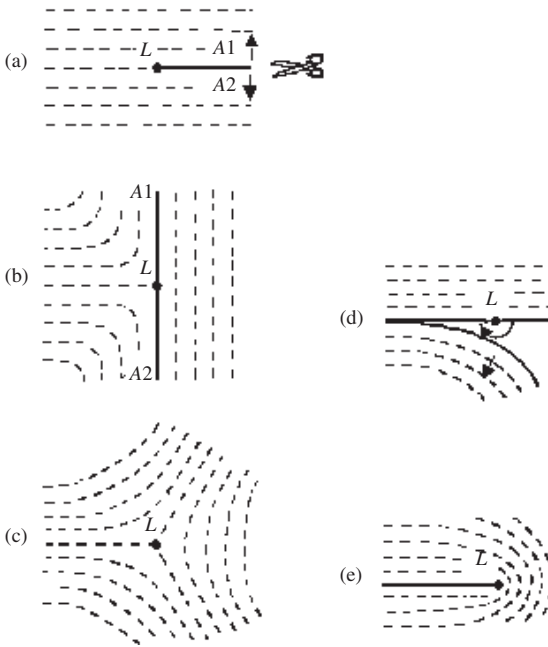
Figure 1.21. The Volterra process generating $\pm 1/2$ disclinations (c and e).

Figure 1.21(a), and rotate the two opposite slips of the cut A1 and A2 by π . π is a symmetry element. Insert a new sample piece of liquid crystals and arrange their director to fit the directors on the A1 and A2 slips, as shown Figure 1.21(b). The liquid crystals then relax themselves to the configuration shown in Figure 1.21(c). A disclination with the strength of $-1/2$

appears. It is a wedge disclination. If the same amount of liquid crystals is needed to be moved, as shown in Figure 1.21(d), the final picture of the director field will look like that shown in Figure 1.21(e). The disclination line L is then $+1/2$ in strength.

There is a simple process to produce a disclination: rotate the directors on two slips respectively by ω_1 and ω_2 and make $\omega_1 - \omega_2 = \omega$. Thus the same disclination line is produced. The process is named the de Gennes-Friedel process. One can prove that the de Gennes-Friedel process is equivalent to the Volterra process for nematic liquid crystals. The operation P_v of the Volterra process can in fact be divided into the translation and rotation steps, *i.e.*, first, translate the directors (T) and then rotate them around themselves (P_g). The latter is actually the de Gennes-Friedel process. In other words

$$P_v = P_g + T. \quad (1.24)$$

Because there is no dislocation in nematics which have only translational symmetry, consequently

$$P_v = P_g. \quad (1.25)$$

1.6.2. Strength of disclination in nematics

The relative rotation of two opposite slips is $\omega = 2m\pi$ where m is the strength of the disclination, which can be either an integer or semi-integer, *i.e.*, $\pm 1/2$, ± 1 , $\pm 3/2$, *etc.*. The general definition of the strength of the disclination is the sum of the deformation angles, in radian measure, made with respect to a laboratory axis when going along a closed contour around the disclination

$$m = \frac{1}{2\pi} \oint_L d\psi, \quad (1.26)$$

where ψ is the angle of the director with respect to a certain direction, *e.g.*, the x axis and L is the closed contour. For convenience, we calculate instead the sum of the angles θ of the directors with respect to the tangents of the closed contour, *i.e.*

$$m = 1 + \frac{1}{2\pi} \oint_L d\theta. \quad (1.27)$$

The sign of m depends on whether \mathbf{n} and the closed contour (*i.e.*, the Burger's circle) have the same direction.

The algebraic sum of the disclinations are not arbitrary, and the sum of all the strengths in a medium is a topological constant, *i.e.*, the Euler

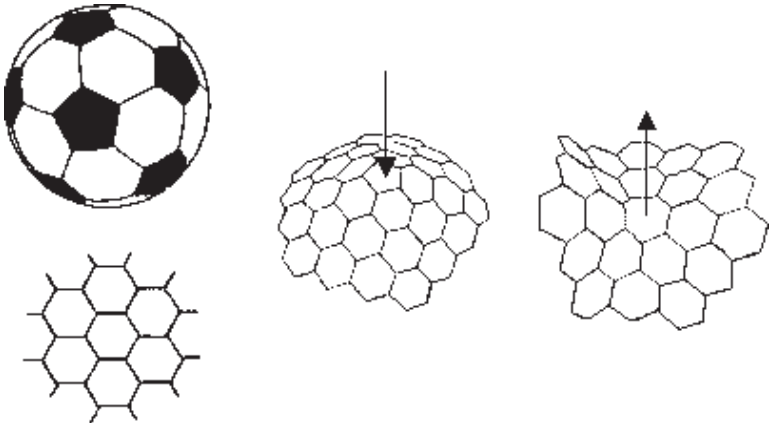


Figure 1.22. The Poincaré theorem on a soccer ball.

characteristic. This is the so-called Poincaré theorem. For example, for a spherical surface or any smooth surface that is topologically equivalent to a spherical surface, the sum of strengths of all disclinations must be equal to 2, the Euler characteristic of a spherical surface. We give some examples to demonstrate the theorem.

For a terrestrial globe, either the longitude or latitude lines' distribution, construct at the south and north poles, a $m = 1$ disclination each. A soccer ball, shown in Figure 1.22, consists of twelve black mosaic pentagons and a number of hexagons. Each pentagon actually corresponds to a $+1/6$ disclination, the total strength of the twelve pentagons counts to $+2$. A $-1/6$ disclination shown in the same figure only produces a locally saddle surface. A buckminster fullerene molecule is a similar example. For a volleyball and a basketball, one observes the same rule. For a bulk sample, the sum of all the disclinations should be about zero. In liquid crystals, $m = \pm 1/2$ and ± 1 disclinations appear frequently but the disclinations with high strength are seldom observed because they cause large energy. The director configuration in the vicinity of various strength disclinations are depicted in Figure 1.23.

Assume the nematic liquid crystals to be a homogeneous planar structure, *i.e.*, the directors lie in the x - y plane, making an angle ϕ with respect to the x axis. For simplicity, we further suppose that all the three elastic constants are equal, *i.e.*, $K_{11} = K_{22} = K_{33} = K$. Thus the energy density

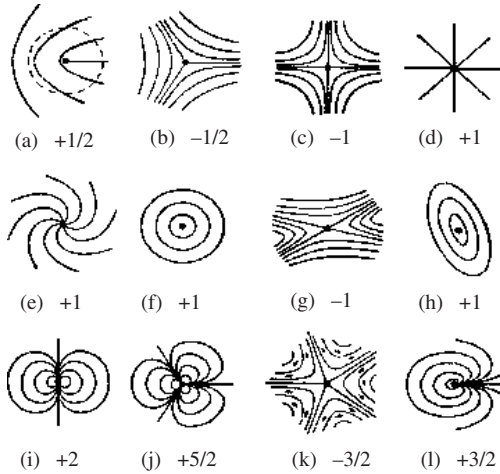


Figure 1.23. The director configurations of disclinations with various strengths.

of the director field is

$$F = \left(\frac{1}{2}\right) K(\nabla \mathbf{n})^2. \quad (1.28)$$

Hence the equilibrium condition is defined by the equation

$$\Delta \phi = 0. \quad (1.29)$$

The solutions may be as follows

$$\phi = 0, \quad \text{the uniform nematic; or} \quad (1.30a)$$

$$\phi = qz + \phi_0, \quad \text{the uniform cholesteric; or} \quad (1.30b)$$

$$\phi = m\theta + \phi_0, \quad \text{the singular solution.} \quad (1.30c)$$

If the disclination line is a wedged one and is along the z axis, then the solution of Equation (1.30c) is

$$\phi = m \cdot tg^{-1} \left(\frac{y}{x} \right) + C \quad (1.31)$$

and if the disclination is along the y axis, then the solution is

$$\phi = m \cdot tg^{-1} \left(\frac{z}{x} \right) + C. \quad (1.32)$$

The configuration of Equation (1.32) is associated with a twist disclination. Both twist and wedge disclinations are shown in Figure 1.24, where the disclination line is normal to this sheet of paper.

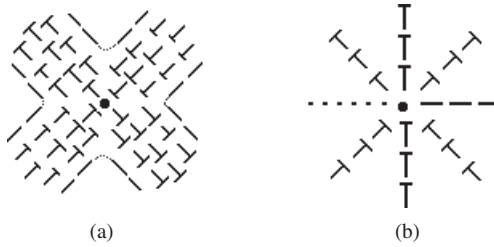


Figure 1.24. A wedge (a) and a twist (b) disclination.

Substitute the solution back into Equation (1.28). The energy per unit length of an isolated disclination in a cylindrical sample of a diameter R is given by

$$F = E_c + \pi K m^2 \ln \left(\frac{R}{r_c} \right), \quad (1.33)$$

where E_c is the core energy of the disclination, whose contribution is not so significant, presumably equal to $\pi K m^2$. This equation indicates that F tends to infinity as R approaches infinity. It is not the case because the disclinations likely appear in pairs with opposite signs. The energy of such a pair is hence

$$F = 2\pi K m^2 \ln \left(\frac{d}{2r_c} \right), \quad (1.34)$$

where d is the separation of the two disclinations. Thus, the deformation area is confined to a limited dimension. The disclinations with the opposite signs tend to approach each other in order to reduce the energy, and may eventually annihilate together. Figure 1.25 shows an example that a $+1$ and a $-1/2$ disclination annihilating to become a $+1/2$ disclination.

An important conclusion obtained from Equation (1.33) is that the deformation energy is proportional to the square of the disclination strength m . The equation is derived for a special case but the above conclusion is universal, with only the coefficient being different. It is expected that a $m = 2$ disclination is likely to divide into two $m = 1$ disclinations or so, in order to achieve a more stable configuration.

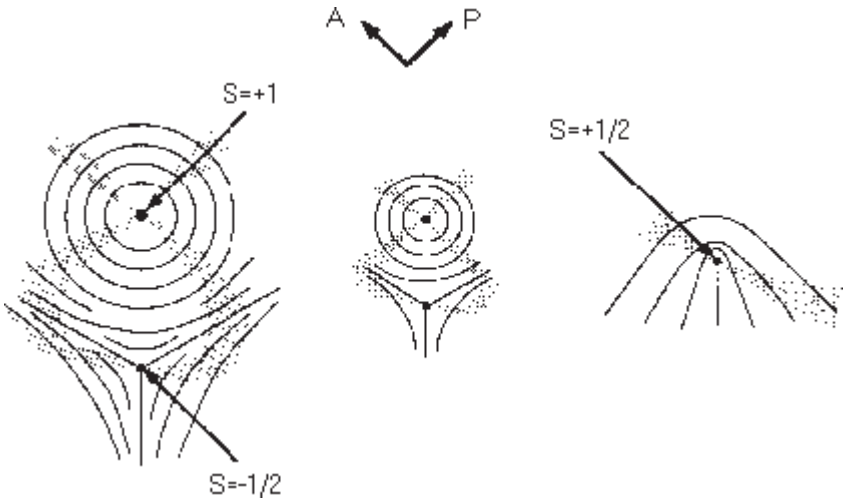


Figure 1.25. A +1 and a $-1/2$ disclinations annihilate to become a $+1/2$ disclination. (From Shiwaku *et al.*, 1995)

1.6.3. Point disclinations

Assume a point disclination located in a nematic droplet of radius R . The point disclination can be classified according to their Poincare characteristic angle α as a knot point ($\alpha = 0$), focus point ($0 < \alpha < \pi/2$), center ($\alpha = \pi/2$), saddle-focus point ($\pi/2 < \alpha < \pi$) or saddle point ($\alpha = \pi/2$). For a knot point, one has a spherically symmetrical radial configuration and then

$$F = 8\pi KR.$$

For a center point, one has a tangential bipolar configuration and

$$F = 5\pi KR.$$

While for a saddle defect, *i.e.*, a hyperbolic configuration

$$F = \left(\frac{8}{5}\right) \pi KR.$$

More complex configurations with a tilted director orientation at the surface have also been reported by Hobdell & Windel (1995) and Madhusudana & Sumathy (1983). It is illustrated that the knot defect has the highest energy while the saddle defect gives the lowest.

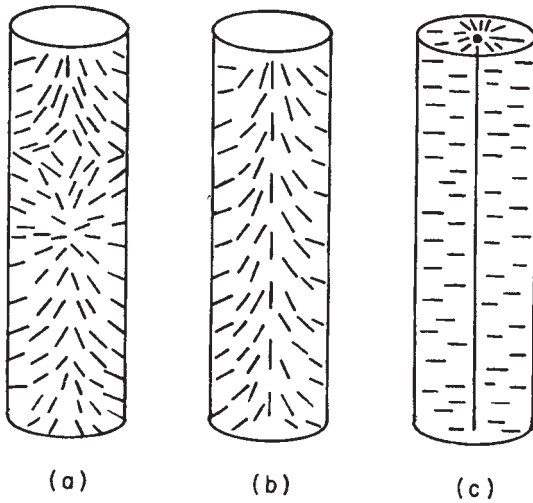


Figure 1.26. A point singularity escape in the third dimension. (From Collings, 1990. Reproduced by permission of Taylor & Francis, <<http://www.tandf.co.uk/journals/tf/02678292.html>>)

The bulk energy of the point defects is proportional to the dimension of the sample. On the other hand, the planar structure of a disclination line contributes to the bulk energy in proportion to the logarithm of the ratio R to r_c . The latter term is much greater than unity if R is large enough for optical observation. In a capillary of radius R , the directors are homeotropically aligned with the wall. The planar solution would lead to a line disclination of $m = +1$, as shown in Figure 1.26(c). But the directors are likely to escape from the center of the disclination $m = 1$ towards a series of point defects of $m = 1$ and $m = -1$, see Figure 1.26(a), the knot and saddle points and may eventually become a non-singular configuration, shown in Figure 1.26(b). It is the so-called escape in the third dimension.

The disclination line of $m = \pm 1/2$ and disclination point of $m = \pm 1$ are frequently observed in liquid crystals. In some cases high strength disclinations may be observed, such as in a thin layer of small molecular mass liquid crystals, polymer liquid crystals, lyotropic liquid crystals, binary thermotropic liquid crystals, *etc.*

If the inequality of the three elastic constants is taken into account, the disclination configurations are slightly different. Even though the energy for same $|m|$ is different. The integration of defects produces the textures of liquid crystals. Owing to the thermal fluctuation of the molecules and

the temperature dependence of the elastic constants and birefringence, the optical textures of liquid crystals are significantly associated with temperature.

The disclinations may split or annihilate due to interactions. The disclinations of the same sign tend to repel each other while those of opposite signs attract each other and may eventually annihilate.

Because of the additional translational order, the dislocations can exist in the cholesteric and smectic liquid crystals, which makes the texture of these liquid crystals even more complicated. Each liquid crystal phase shows characteristic textures and thus the optical texture becomes an important means to differentiate the phase of the liquid crystals. Liquid crystalline polymers have the same topologically stable defects as small molecular mass liquid crystals do, but the textures may be different due to the difference in the energetic stability of the same topological defects in both low molecular mass and polymeric liquid crystals (Kleman, 1991). In Chapter 3 we will discuss the textures in detail.

1.6.4. Defects in smectic A phase

The homotopy group of the smectic A phase is

$$\begin{aligned}\Pi_0(S_A) &= 1, \\ \Pi_1(S_A) &= Z \otimes Z_2, \\ \Pi_2(S_A) &= Z, \\ \Pi_3(S_A) &= Z,\end{aligned}\tag{1.35}$$

where Z is the translational dislocation normal to the smectic layers with the Burger vector being the multiple layer thickness; Z_2 , is a cyclic group of two elements. There is no topological stable singular wall, but there are topological stable singular lines, composed not only of the disclination lines associated with Z_2 but also of the dislocation lines associated with Z . $\Pi_3(S_A) = Z$ implies that there are topological solitons.

The deformations in the smectic A phase liquid crystals are the bending of the smectic layer (accordingly to the splay of the directors) and the dilation or compression of the layers. The energy is thus

$$F = \frac{1}{2}B \left(\frac{\partial u}{\partial z} \right)^2 + \frac{1}{2}K_{11}(\nabla \cdot \mathbf{n})^2,\tag{1.36}$$

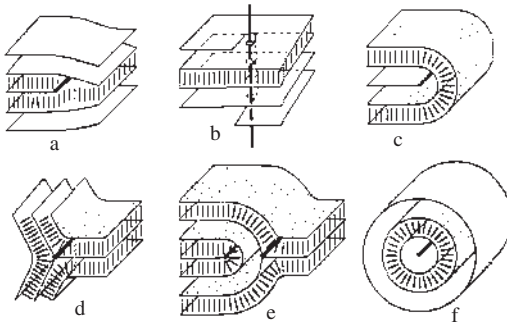


Figure 1.27. Typical dislocations (a, b) and disclinations (c-f) in smectic A liquid crystals. (From Kurik & Lavrentovich, 1988.)

where u is the displacement of the layer and B is the elastic modulus. The equilibrium state is governed by (assuming $\lambda^2 = K_{11}/B$)

$$\frac{\partial^2 u}{\partial z^2} - \lambda^2 \frac{\partial^4 u}{\partial x^4} = 0. \quad (1.37)$$

The typical dislocations (a, b) and disclinations (c-f) are shown in Figure 1.27.

The edge dislocation

Suppose the edge dislocation is along the y axis and the Burger vector has a thickness of one layer. The smectic layer is in the x - y plane. At equilibrium, the displacement u is expressed by

$$u(x, z) = \frac{d}{4} + \frac{d}{4\pi} \int \frac{dq}{iq} \exp(iqx - \lambda|z|q^2) \quad (1.38)$$

and the deformation angle θ between the layer normal and the z axis is given by

$$\theta = \frac{1}{4\sqrt{\pi}} \frac{d}{(\lambda|z|)^{1/2}} \exp\left(-\frac{x^2}{4\lambda|z|}\right). \quad (1.39)$$

It is illustrated that the deformation disappears rapidly in the x -direction and decays slowly in the z -direction. The deformation energy is independent of sample dimension. It is concluded that the dissolution of the dislocation doesn't reduce the energy.

The screw dislocation

There is a helical structure surrounding the screw dislocation line. The screw dislocation is perpendicular to the smectic layer and the deformation is

$$u = \frac{b}{2\pi} tg^{-1} \left(\frac{y}{x} \right). \quad (1.40)$$

The screw dislocation affects neither the lattice dilation nor the bending of the layer. Thus it isn't associated with an energy penalty.

The focal-conic texture

The smectic layers are flexible, *i.e.*, it is relatively easy for bending deformation, but the layers are difficult to compress. The bending of the smectic layers can be expressed by two principal curvatures R_1 and R_2 , *i.e.*,

$$F = \frac{1}{2} K_{11} \int \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2 d\tau. \quad (1.41)$$

For a point on an ellipse, $R_1 \cdot R_2 > 0$; for a point on a hyperbolic, $R_1 \cdot R_2 < 0$.

For a defect point forming a spherical surface, see Figure 1.28(a), where $R = R_1 = R_2 = \infty$, the energy is

$$F = 8\pi K_{11} R.$$

For a Dupin cyclide comprised a circle base and a straight line core, shown in Figure 1.28(b),

$$F = 2\pi^2 K_{11} R \left[\ln \left(\frac{2R}{r_c} \right) - 2 \right].$$

If the base is an ellipse and the core is a hyperbolic curve, shown in Figure 1.28(c), the Dupin cyclide has the energy

$$F = \pi K_{11} (1 - e^2) p \ln(a/r_c),$$

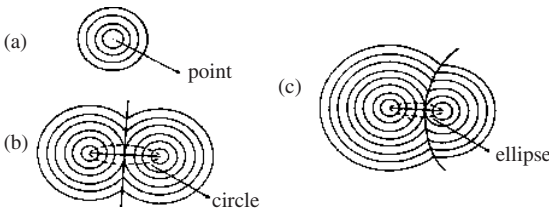


Figure 1.28. The Dupin cyclides (a) a point and sphere; (b) a circle and a straight line; (c) an ellipse and a hyperbolic curve.

where e , p and a are the eccentricity, perimeter and semi-principal diameter. The last case is favorable from the energy point of view. The three possibilities are shown in Figure 1.28. A series of the Dupin cyclides are knitted to each other to construct the focal-conic texture.

1.6.5. Defects in the smectic C phase

The projections of the director on the smectic C layer construct a c -vector (or c -director) field. The distortion of the c -director and the displacement of the layer are two parts of the defects in the smectic C phase. Because the c -director is apolar, there are only the integer disclinations. In addition, there is no escape in the third dimension because the c -director is confined in layers. Neither topological stable singular walls nor points exist in the smectic C sample according to the homotopy argument.

1.6.6. Dispiration in the smectic C* phase

The helical structure of the c -director in the smectic C* phase makes the defects different from those in the smectic C phase. As the Volterra process produces a screw dislocation, for example, along the z axis and the Burger vector $b = d$, it must be accompanied by a parallel wedge disclination in the c -director, in the form

$$\phi = -\frac{b}{p}tg^{-1}\left(\frac{y}{x}\right) + qz. \quad (1.42)$$

It is named the wedge dispiration, designated as $(b, -b/p)$. Similarly, an edge dislocation of the Burger vector b must be accompanied by a partial twist disclination, designated as the twist dispiration $(b, b/p)$.

1.6.7. Defects in the cholesteric phase

The χ -, λ - and τ -disclinations

The order tensor of the cholesteric liquid crystal is a symmetrical matrix, or a set of three orthogonal vectors: \mathbf{n} , \mathbf{q} and $\mathbf{n} \times \mathbf{q}$.

It is known that there is no topological stable singular wall and point but there are topological stable singular lines which are characterized by the Q group, $Q(C0, \overline{C0}, C1, C2, C3)$. The classification of the cholesteric

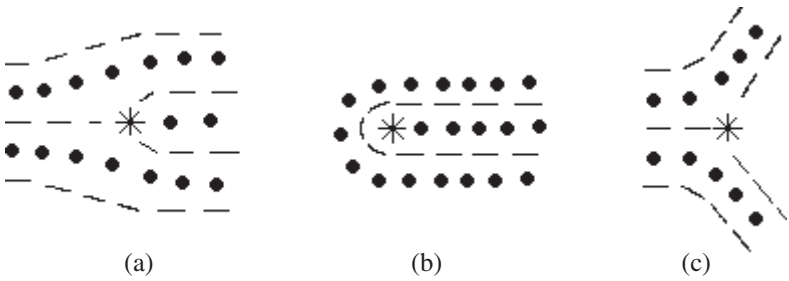


Figure 1.29. The schematics of (a) χ -disclination, (b) λ -disclination and (c) τ -disclination. (Modified from Collings, 1990.)

liquid crystal was made by Kleman & Friedel (1969) as the χ -, λ - and τ -disclinations shown in Figure 1.29:

- (1) χ -disclination: semi-integer turn (*i.e.*, the multiple π rotation) around the helical axis;
- (2) λ -disclination: multiple π rotation around the director;
- (3) τ -disclination: multiple π rotation around $\mathbf{n} \times \mathbf{q}$.

Compared with the homotopy classification, each element in the homotopy Q group corresponds to the above defects in the following way

- $C0$: $\lambda(2n)$, $\tau(2n)$ and $\chi(2n)$
 $\overline{C0}$: $\lambda(2n + 1)$, $\tau(2n + 1)$ and $\chi(2n + 1)$
 $C1$: $\lambda(n + 1/2)$
 $C2$: $\tau(n + 1/2)$
 $C3$: $\chi(n + 1/2)$

It is apparent that the two classifications are consistent, but the homotopy approach is more powerful in further analysis because there is a relation between the group elements, which is associated with the interactions between the defects.

The cholesteric liquid crystal can be regarded as a layered structure so that it also shows the focal-conic texture, especially for large pitch cholesteric liquid crystals.

The texture of cholesteric liquid crystals is rather complicated. Both disclination and dislocation exist together. The typical texture is shown in Figure 1.30.

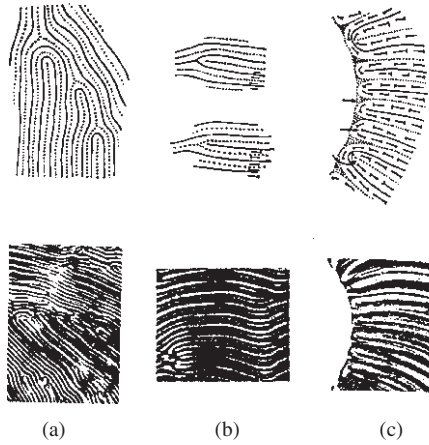


Figure 1.30. Typical finger-print textures in cholesteric liquid crystals: schematics (upper) and images (lower). (From Bouligand & Kleman, 1970.)

The Cano wedge

The Cano wedge can be used to measure the cholesteric pitch. Two substrates are wedged by a small angle 2γ . The cholesteric liquid crystal between the substrates is homogeneously aligned. Under polarized microscopy, the equally spaced disclinations appear at the middle of the wedge. The separation of the lines $2d$ is associated with the pitch P

$$P = 8d \tan \gamma. \quad (1.43)$$

This technique has been applied to measure the pitch of cholesteric liquid crystals.

1.6.8. Textures

Under the polarized optical microscope, the liquid crystal films show colorful patterns, *i.e.*, the optical textures. Each liquid crystal phase shows its typical texture which provides the means to identify the phase of the liquid crystals. The typical textures are the Schlieren, threadlike, homeotropic, homogeneous, marble, finger-print, focal-conic, Dupin cyclide, fan-shape, sanded, mosaic, and so on. They are the integrations of many typical defects mentioned above. Demus & Richter (1978) were the first to review

the textures of liquid crystals in detail. Later, Gray and Goodby (1984) summarized the textures of the smectic liquid crystal phases.

1.6.9. Homotopy classification of defects in liquid crystals

Now we briefly discuss the topological homotopy theory that classifies defects in liquid crystals and judges the stability of the defects according to the symmetry of liquid crystals.

The singularities in the liquid crystals cause the deformation of the director field of liquid crystals and thus affect the symmetry of liquid crystals. This idea provides an approach to analyze the characteristics of the defects. The order vectors (or scalars, or tensors) of various liquid crystals are not the same. The director \mathbf{n} is the order vector of the nematic liquid crystals, but the order for the cholesteric liquid crystals is a symmetric matrix, *i.e.*, a tensor. Because the order vector space is thus a topological one, any configuration of the director field of liquid crystals is thus represented by a point in the order vector space. The order vector space (designated by M) is associated with the symmetry of liquid crystals. The topologically equivalent defects in liquid crystals constitutes the homotopy class. The complete set of homotopy classes constitutes a homotopy group, denoted $\Pi_r(M)$. r is the dimension of the sub-space surrounding a defect, which is related to the dimension of the defect (point, line or wall) d' , and the dimension of the liquid crystal sample d by

$$d' = d - r - 1. \quad (1.44)$$

For a three-dimensional nematic liquid crystal for example, the $r = 0$ case corresponds for example to a defect with $d' = 2$, which means a disclination wall; for $r = 1$, $d' = 1$ corresponds to a disclination line; for $r = 2$, $d = 0$ corresponds to a disclination point. It is known that the order vector space of three dimensional nematic liquid crystals is the projection plane P_2 . Its homotopy group of the zero rank ($r = 0$) is

$$\Pi_0(P_2) = 1.$$

In the other words, there is no topologically stable disclination wall.

The homotopy group of the first rank ($r = 1$) is

$$\Pi_1(P_2) = Z_2.$$

This is a cycle group of two elements, one of two elements is in fact the disclination line of $|m| = 1/2$, the other element corresponds to the $|m| = 1$ disclination line, which is not topologically stable.

The homotopy group of the second rank is

$$\Pi_2(P_2) = Z,$$

where Z is the integer group and corresponds to the topologically stable disclination points of integer strength.

The conclusions are consistent with our knowledge of the defects in nematic liquid crystals.

Similarly, homotopy theory can be applied to other liquid crystal phases, such as the cholesteric and smectic liquid crystals (Mermin, 1979; Wang, 1986).