LIQUID CRYSTALS

Experimental Study of Physical Properties and Phase Transitions

SATYENDRA KUMAR

Author and Editor

with additional contributions by
J. Brock
D. Finotello
M. Fisch
C. Garland
J. Ho
M. Neubert
B. Padulka
P. Photinos
S. Sinha
P. Ukleja

CAMBRIDGE
UNIVERSITY PRESS

Contents

Color plate section facing page 52

1

Introduction to liquid crystals

MICHAEL R. FISCH AND SATYENDRA KUMAR

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

1.1 What is a liquid crystal?

We all remember learning that there are three states of matter: solid, liquid and gas. This, however, is not the whole story. There are situations in which more than just these three phases exist. For now, consider the large class of organic molecules which do not show a single transition from solid to liquid, but rather a series (more than one) of transitions between the solid and the normal (isotropic) liquid as their temperature is raised. These new phases have mechanical, optical, and structural properties between those of the crystalline solid and the corresponding isotropic liquid. For this reason, these phases are referred to as *liquid crystalline* phases, and the materials which form them upon a change in phase are often referred to as thermotropic liquid crystals. A more proper name is mesomorphic (or intermediate) phases.

  Liquid crystalline properties are exhibited by several different types of systems. In addition to certain classes of organic molecules, micellar solutions of surfactants, main and side chain polymers, and a large number of biological systems are known to be liquid crystalline. Several textbooks [1–4] on liquid crystals have discussed these topics to varying degree. The purpose of the present chapter is not to paraphrase what is in these texts but rather to lay the foundation for understanding the topics covered in different chapters of this book. A number of publications which emphasize and review specific topics in significant detail are available and are strongly recommended as supplemental reading [5–10]. Following de Gennes and Prost [1], we will define a liquid crystal as an intermediate phase which (a) has liquid-like order in at least one direction, and (b) possesses a degree of anisotropy, which is characteristic of some sort of order. The latter requirement is typically met if the molecules (and, in our later discussion, other objects such as micelles) which form liquid crystals are anisotropic, either

rod-like (prolate) or disk-like (oblate). However, one must remember that while all liquid crystalline phases are formed by anisotropic objects not all anisotropic molecules form liquid crystalline phases [11, 12].

1.2 Ordering of anisotropic objects

Objects which have shapes other than spherical may possess three types of order giving rise to different liquid crystalline phases. Let us first define the types of order that are necessary to discuss the phases involved. The simplest of these is *orientational order* (OO). This is possible when the symmetry axes of the ordering objects are on average parallel to a well-defined spatial direction, **n**, known as the *director*. The degree of order, denoted by the *orientational order parameter*, S, is the thermal average $\langle 3/2 \cos^2 \theta - 1/2 \rangle$, where θ is the angle between a molecule's symmetry axis and the director. The orientational order parameter is typically a function of temperature.

The second type of order is *positional* or *translational order* (PO). When PO is present, the system remains invariant under translation by an integer number of lattice translation vectors. The arrangement of the basic units (e.g., molecules) and the mass density (and, consequently, the electron density) exhibit periodicity. In the simplest case, this periodicity is one-dimensional, and may be conveniently represented by a density function of the form:

$$\rho(\mathbf{r}) = \langle \rho \rangle + \mathrm{Re}[\Psi \exp(i\mathbf{k} \cdot \mathbf{r})],$$

where $\langle \rho \rangle$ is the average electron density, Re means real part of, Ψ is the complex amplitude, and **k** is the wavevector. It is important to note that a liquid crystal system does not have to possess translational order in all three directions. In particular, for the 'fluid' smectic (-A and-C) phases, which possess positional order only in one dimension, the *smectic order parameter* representing the density variation is written as

$$|\Psi(\mathbf{r})| = \mathrm{Re}[\rho_1 \exp(i2\pi z/d)],$$

where d is the thickness of smectic layers which are assumed to be perpendicular to the z direction [1].

A third type of order is *bond orientational order* (BOO) [13]. A bond, in the present context, is not a chemical bond but a line in space joining two adjacent molecules. If the orientation of these bonds is preserved over a long range, then a system possesses BOO. It is encountered in a category of smectic phases called the *hexatic smectics*. In these phases, the molecules within a smectic plane possess BOO and, since the molecules can best pack
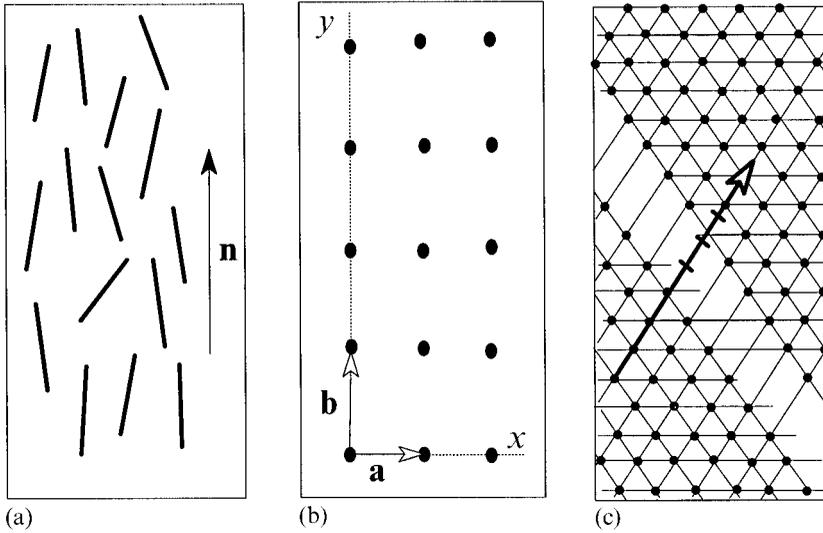
Figure 1.1. Schematic representation of the three basic types of order: (a) orientational order parallel to the director **n**, (b) positional order in two dimensions with lattice vectors **a** and **b**, and (c) bond orientational order. In the last case, translation from one lattice site along the arrow by an integer multiple of lattice spacing shows a lack of translation symmetry.

in a hexagonal fashion, the orientation of *bonds* possess six-fold symmetry. A complex order parameter, ψ_6, similar to the smectics density wave has been used to account for BOO;

$$\psi_6 = \text{Re}[I_6\exp(6i\phi)],$$

where I_6 is a complex amplitude, and ϕ is the azimuthal angle with respect to the layer normal. Systems can possess long range BOO without long range positional order PO, but the reverse is not true. It is possible for PO to become short range due to the presence of dislocations and disclinations which can leave the BOO unperturbed. The three types of order discussed above are shown in two dimensions in Fig. 1.1.

1.3 The concept and use of symmetry in liquid crystals

One of the strongest guiding principles in liquid crystal science has been symmetry, i.e., physical properties of a liquid crystalline phase depend on the symmetry of the liquid crystal phase. Thus, the least ordered phase is the most symmetric *isotropic* (I) phase which exhibits isotropic behavior similar to regular liquids such as water. There is, then, a plethora of mesophases of

lower symmetry than the I phase before the least symmetric crystalline phases belonging to the 230 space groups [14] which characterize crystals are encountered. This progression may be described in terms of the three types of order described above.

Consider imposing the simplest, i.e. orientational, order on a collection of molecules. The resulting structure is known as the *nematic* (N) phase. Such a phase is described by the director and the orientational order parameter defined above. If the molecules are on average parallel to **n**, the value of S is positive and ranges between 0 and 1. On the other hand, if the OO is such that molecules, on average, are perpendicular to **n**, then S is negative and its values range from 0 to $-\frac{1}{2}$. Evidently, a Landau–Ginzburg type expression for its free energy must not be invariant with respect to a change in the sign of S as its positive and negative values represent physically different systems. This is usually ensured by including a cubic term in the free energy. A consequence of this symmetry requirement is that the transition from I to an orientationally ordered state, or the N phase, must be first order. Indeed, the I–N transition is always found to be first order with a large enthalpy of transition. The physical properties of a nematic are described by a symmetric second rank tensor.

The presence of PO in one direction leads to the smectic-A (SmA) phase. However, there can be no long range order in one dimension [15], so this is really a quasi long range order (QLR). Transitions between the isotropic liquid and the SmA phase are first order while transitions between the N and the SmA phase may be either first or second order depending upon the coupling between the OO and PO, which in turn depends on the width of the N phase. A liquid crystal with a wide N phase is more likely to exhibit a second order N–SmA transition. Further discussion of this topic can be found in Chapters 3 and 7.

A smectic phase has at least two unique directions, the director and the layer normal. In the SmA phase, these two directions are collinear. But there are phases in which the director makes an angle with the layer normal as in the smectic-C (SmC) phase. In the chiral smectic-C (SmC*) phase, the director maintains a constant angle with respect to the layer normal while describing a helical path as the sample is traversed along the direction normal to the smectic planes. The chiral phases invariably are ferroelectric in nature. The details of the structure of different phases will be discussed later in this chapter.

Various smectic phases have BOO and PO to varying degree within a smectic plane and it is convenient to consider the extent of order that separates a smectic phase from the rest. The BOO and PO can be either short

Untilted thermotropic liquid crystal phases

Phase	Type of order	Abbreviation
Isotropic		I
Nematic	OO	N
Smectic-A	PO; $\mathbf{n} \perp$ to layers	SmA
Hexatic-B	In-plane: LR-BOO, SR-PO	HexB
Crystal-B	In-plane: LR-PO and BOO (Molecular rotations allowed)	CrB
Crystal-E	In-plane: LR-PO and BOO (Molecular rotations restricted)	CrE

(Temperature increases upward / phase progression downward with increasing order)
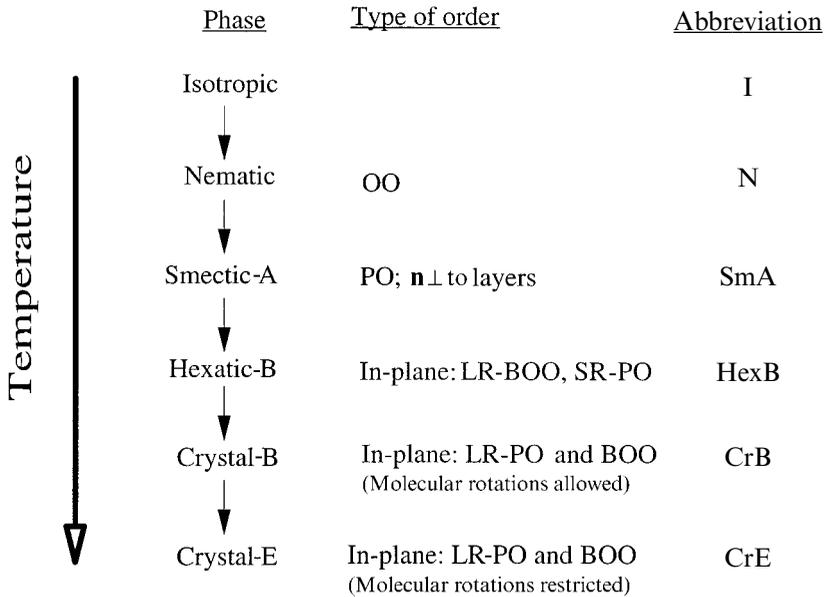
Figure 1.2. An illustration of a possible phase progression in a liquid crystal. The most symmetric and least ordered phase is at the top, and the most ordered and least symmetric phase is at the bottom.

range (SR) as is observed in liquids or long range (LR) as observed in crystals. Three distinct possibilities exist:

1. Both the BOO and PO are short range – such smectics can be considered as fluid smectics, examples being SmA, SmC, and SmC*, etc.
2. Long range BOO but short range PO – these are referred to as the hexatic smectic phases. Smectic-I, -F, and -HexB are some examples.
3. Long range BOO and PO – such phases are very close to being crystalline phases except that the molecules undergo rotational diffusion. They used to be known as smectic-B, -E, etc. but nowadays they are referred to as the crystal-B, -E, -G, etc. phases. (See Section 2.1 for recent terminology.)

Various (untilted) smectic phases, with the director parallel to the layer normal, are given different names as summarized in Fig. 1.2 [8].

The use of symmetry goes beyond noting which phase is more symmetric than another and helping one discern the symmetry of physical properties of the corresponding phase. It also allows one to make analogies to phase transitions in other non-liquid crystalline systems. For example, as

de Gennes [1, 16] has observed, the introduction of the smectic order parameter allows one to draw a strong analogy between the SmA phase and the superconducting phase. The tilted SmC phase has been compared [17] with superfluid helium, and the SmA to SmC transition predicted to exhibit critical behavior similar to that of helium or the XY model. Similarly, the transition between SmA and hexatic-B is described by a two-dimensional order parameter and may similarly be described by the superfluid analogy. The use of symmetry in liquid crystals will become evident in different chapters of this book. Suffice it to state that symmetry has been a crucial and indispensable tool in our understanding of the physics of liquid crystalline phases. At the same time, the field of liquid crystals has been used as a testing ground of theoretical ideas that are not manifest in other systems with such elegance and simplicity.

1.4 Liquid crystal phases formed by rod-like molecules

In this section we will briefly discuss the liquid crystalline phases formed by simple entities: organic molecules which can be viewed as short rigid rods of a length to diameter ratio of roughly 3–8. Such molecules exhibit various mesophases at different temperatures and hence are generically referred to as thermotropic liquid crystals. The chemistry and structure–property relationships of this technologically and scientifically interesting group of materials are discussed in greater detail in Chapter 10 by Neubert. A common feature of all molecules of this type is that they all comprise a central rigid core connected to a flexible alkyl chain at one or both ends.

Without proof or reference we will state some of the physical properties of these phases. A detailed discussion of these properties and how they can be measured will be found in the various chapters of this book and the referenced literature. However, one should note that the size of a typical molecule which forms a thermotropic liquid crystal is such that x-rays work as an ideal and direct probe of the structure of these materials. Thus, a particularly good starting point is Chapter 3 on x-ray scattering by Kumar and the book by Pershan [8].

1.4.1 Non-tilted phases

This is a sub-class of thermotropic liquid crystalline phases which are free from chirality and molecular tilt. However, these phases differ from each other in the type and extent of order and the symmetry they possess.

The nematic phase

As discussed above, the simplest liquid crystalline phase is the nematic phase. There are several types of nematic phases but all of them can, to a first approximation, simply be thought of as liquids which have long range orientational order, OO, but lack PO and BOO. An example of a nematic made of rod-like molecules is shown in Fig. 1.1(a). The various types of nematics have slightly different properties based on the details of their molecular structure and chemical behavior. The two primary types of nematic are uniaxial and biaxial.

The uniaxial nematic is characterized by the following features [2]: (a) no PO, so, no BOO; (b) OO parallel to the director **n**; (c) the direction of **n** in space is arbitrary, and typically imposed by outside forces such as electric/magnetic fields; (d) **n** and −**n** are equivalent; and (e) molecules which form nematics are either archiral (identical to their mirror images) or racemic (contain equal numbers of left and right handed molecules).

The biaxial nematic phase is also characterized by the above properties. However, this liquid crystalline phase does not possess cylindrical symmetry about **n**. This phase possesses two unique directions perpendicular to **n** rendering it biaxial. It should be pointed out that, despite some reports, there are no known thermotropic biaxial nematic phases [18]. The existence of biaxial phases has been confirmed in lyotropic liquid crystals (Section 1.8)

The smectic-A phase

The name 'smectic', was coined by G. Friedel to describe certain mesophases that feel slippery like soap when touched, and was originally associated with what is now known as the smectic-A phase. The important feature which distinguishes smectic phases is that they have a layered structure. In fact, as mentioned above, PO and BOO have all been observed among molecules lying in a smectic plane resulting in over 20 smectic liquid crystalline phases.

The simplest is the SmA phase made of non-chiral and non-polar molecules and characterized by a one-dimensional layered structure (or PO), in which each layer is essentially a two-dimensional liquid as shown in Fig. 1.3(a). However, arguments [15] show that one-dimensional liquids can not exhibit long range PO. Nevertheless, PO almost does exist, and this system is said to exhibit quasi long range order or have Landau–Peierls' instability. This phase is uniaxial, the layers are essentially incompressible, and the long axes of molecules within the layer, on the average, are perpendicular to the layers. The SmA phase is characterized by short range PO and short
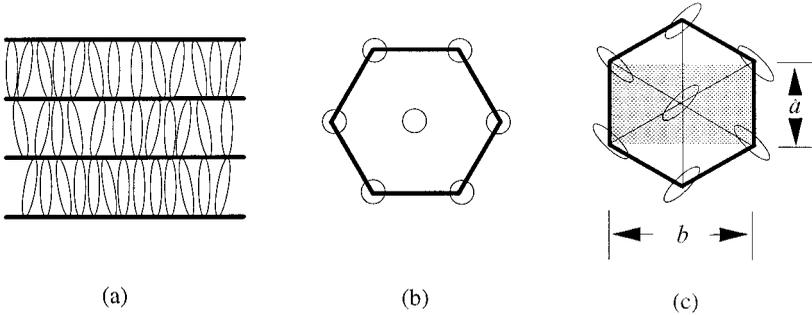
Figure 1.3. Some liquid crystal phases formed by untilted rod-like molecules. (a) The smectic-A phase; note that there is quasi-long range PO normal to the layers, OO with the mean orientation of the molecules perpendicular to the layers and short range PO and BOO within the layers. (b) A view of the short range hexagonal PO of the molecules within a layer of a HexB phase. The molecules are perpendicular to the smectic plane as indicated by the circles. (c) The local herringbone arrangement of molecules in a layer of the crystal-E phase. The ellipses represent a view of the rigid benzene rings in the molecules. The lattice has a rectangular unit cell.

range BOO in the layers, and quasi long range PO perpendicular to the planes. It may be thought of, somewhat crudely, as a stack of two-dimensional fluid layers.

The hexatic-B or hexatic smectic-B phase

These two names for the same phase, abbreviated as HexB, describe a phase which is characterized by a layered structure, just like the SmA phase, *and* long range BOO within the layers. BOO is the essential property of a hexatic phase. This is a very special class of smectics characterized by quasi long range PO in the direction perpendicular to the layers, short range PO within the smectic layers (although typically longer than in the SmA), and most importantly BOO. In the HexB phase, the molecules are locally hexagonally packed, and the resulting six-fold BOO is maintained for macroscopic distances. The HexB is a uniaxial phase. In three dimensions, the transition from SmA to HexB phase is expected to be in the same universality class as superfluid helium. However, this is not the case. The explanation is that there is a strong coupling between the mass density and the hexatic order parameter, and fluctuations in the order parameter influence its behavior near the transition [2]. A schematic of the BOO of a hexatic phase is shown in Fig. 1.1(c). A top view of the molecules within a smectic plane, which indicates that the molecules are perpendicular to the planes, is shown in Fig. 1.3(b).

The hexatic phases have been studied quite extensively in two-dimen-

sional freely suspended films. In these studies, liquid crystal films were drawn over a hole in a metal or glass plate. These films have smectic layers aligned almost perfectly parallel to their physical surface rendering the data interpretation easier than in bulk samples. X-ray diffraction studies of the growth of hexatic order in such films will be discussed in greater detail in Chapter 8 by Brock. The transition between SmA and HexB (in two dimensions) can be second order. The Halperin–Nelson–Young theory [19] has been applied to describe this transition. This theory predicts that in two dimensions dislocations destroy PO but not BOO. This is indeed the case.

The crystal-B phase

There are several crystalline smectic phases; that is, smectics which are very close to three-dimensional crystals. They differ from true crystal phases in one important aspect. The molecules in them have freedom of rotation about their long axis, i.e., their thermal motion is not completely frozen out. Such phases, in which the position of the molecules is fixed but their motion is not arrested, should more correctly be classified as *plastic crystalline* phases. The reader who is interested in greater detail in this area should read Pershan [8] and references therein. The common feature of these phases is that the average molecular orientation is normal to smectic layers and within each layer the molecules are ordered in a triangular lattice and possess long range PO and, of course, BOO. The stacking of these triangular arrays varies from material to material and restacking transitions have been observed.

The crystal-E phase

As in the crystal-B phase, the molecules within a smectic-E plane are arranged on a triangular (or hexagonal) lattice and are perpendicular to the smectic layers. This phase differs from the crystal-B phase in the rotational motion of molecules. In the crystal-E phase, the thermal motion of molecules is reduced to the extent that they arrange themselves in a herringbone pattern within a smectic layer. The intralayer molecular packing is shown in Fig. 1.3(c). With this type of packing their continuous rotational freedom is hindered. NMR [20] studies have concluded that molecules can undergo correlated six-fold jump rotational diffusional motion.

1.4.2 Tilted phases

There is a complete set of smectic phases in which the long axis of molecules (or the director) is not perpendicular to the layer normal, but makes
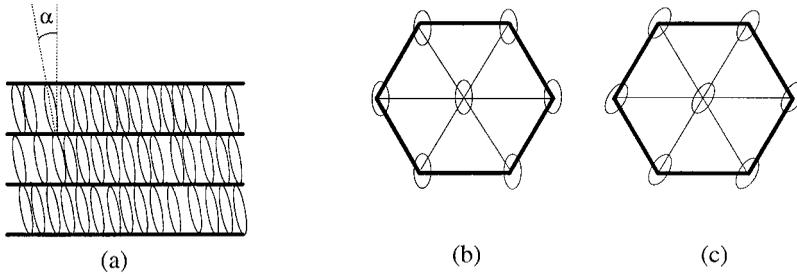
Figure 1.4.   Schematic representation of some tilted phases formed by rod-like molecules. (a) The SmC phase; the layers are indicated by the lines and the molecules by the ellipses. Short range order in hexatic smectic-F and hexatic smectic-I phases are shown in (b) and (c) respectively. Here the major axis of ellipse indicates the molecular tilt direction with respect to the hexagon axes.

a relatively large angle. Just like the untilted phases discussed above, the various tilted phases possess different structures and order.

The smectic-C phase

The smectic-C, SmC, phase is similar to the SmA phase in that it is a layered structure and each layer may be thought of as a two-dimensional liquid film with no BOO or PO. However, in this case the molecules are on the average tilted with respect to the normal to the layers, i.e., **n** and smectic layer normal are not collinear, Fig. 1.4(a). Furthermore, the tilt angle, α, that the molecular long axis makes with the layer normal, is a strong function of temperature. In the case of a transition from SmA to SmC phase at temperature T_{AC}, smectic layer spacing at a temperature T below the transition $d(T) = d(T_{AC}) \cos \alpha$. The angle α which is an order parameter for this phase can range from zero to as high as 45–50° deep in the SmC phase. The temperature dependence of molecular tilt [21] in the SmC phase of terephthal-bis-(4n)-butylaniline (TBBA) is shown in Figure 1.5. Most of the SmA to SmC transitions are second order but first order transitions in fluorinated compounds have recently been observed [22]. A consequence of the tilting of the molecules is that this phase exhibits biaxial optical and physical properties.

The smectic-F and smectic-I phases

Tilted phases with in-plane hexatic order have also been observed. These may be thought of as tilted analogs of the HexB phase. However, with a hexagonal arrangement within smectic planes, the molecules can tilt along two distinct directions with respect to the hexagonal lattice. In the HexF phase, the tilt is in a direction perpendicular to the sides of the hexagon. If molecules
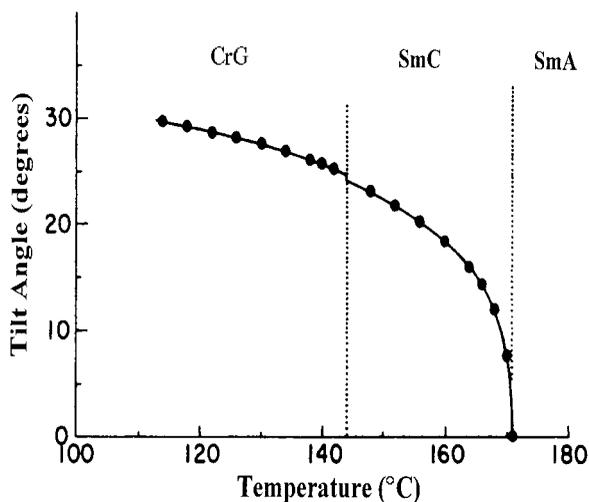
Figure 1.5. Temperature dependence of molecular tilt in the SmC phase of TBBA determined by high-resolution x-ray diffraction.

tilt towards a corner, it is known as the HexI phase. The descriptions of these phases often leave one confused. When both phases are formed by the same material, the HexI is always the higher temperature phase. The short range in-plane order of these three phases is shown in Fig. 1.4(b) and (c). These phases are also the topic of discussion for Chapter 8 on freely suspended film measurements and further details can be found there.

The crystal-G and crystal-J phases

The crystal-G and crystal-J phases are the phases normally obtained at temperatures lower than the HexF and HexI phases. The molecular arrangement within a smectic plane possesses long range PO and BOO. In both these phases and their higher temperature hexatic versions, the molecules are tilted with respect to the layer normals by approximately 25 to 30°. The local order is hexagonal which is distorted due to molecular tilt, with molecules having rotational freedom comparable to the untilted crystal-B phase.

The crystal-H and crystal-K phases

The crystalline H and K phases are tilted versions of the crystal-E phase. The molecules in the crystalline H (K) phase are tilted in a manner similar to the crystal-G (J) and HexF (HexI) phases, i.e., along the direction perpendicular to a side (towards a corner) of the underlying hexagonal structure. The general sequence of tilted phases with decreasing temperature is

Smectic-C

Smectic-F   Smectic-I

Crystal-G   Crystal-J

Crystal-H   Crystal-K
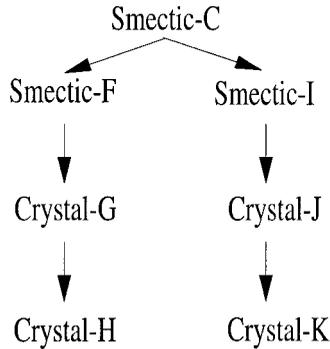
Figure 1.6.   A typical phase sequence for tilted phases of rod-like molecules.

shown in Fig. 1.6. However, the actual order of phases varies from material to material.

1.4.3 Chiral tilted phases

Molecules which are not identical to their mirror image are said to be chiral. Molecular chirality has profound influence on liquid crystal properties. There exists a complete *designer line* of liquid crystal phases with chirality, as discussed in the following pages. The extension of the schemes discussed above on the basis of symmetry properties to the phases formed by chiral molecules is rather straightforward.

The cholesteric or chiral nematic phase

The phase which, in most regards, is similar to the nematic phase but with chiral structure is known as the cholesteric phase. The name is based on the fact that derivatives of the infamous cholesterol were initially found to exhibit this phase. This phase forms if the molecules which form the liquid crystal are either intrinsically chiral or if chiral dopants are added to a non-chiral (regular) nematic. The chirality of the system leads to a helical distortion, in which the director **n** rotates continuously in space along, say, the z-direction, with a spatial period of π/p. Here p is the pitch of the cholesteric which can be positive or negative, corresponding to right or left handedness, and has a magnitude which can be a strong function of temperature. The temperature dependence of their pitch has been exploited in making thermometers. The pitch of a cholesteric can also be increased (unwound) with the help of an applied electric field. It is important to note that for systems which have a small twist (long pitch), locally a cholesteric
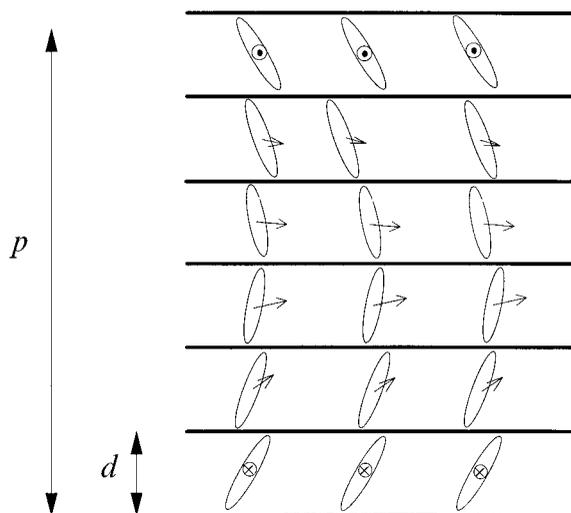
Figure 1.7. A schematic diagram of the SmC* phase showing the precession of the tilt angle as one moves along the layer normal. The arrows attached to the molecules point to represent the direction of the molecular electric dipole moment which renders these phases ferroelectric. d is the layer spacing and p is the pitch.

liquid crystal 'looks' like a nematic. Of course, this picture breaks down for short pitched cholesterics. We will discuss this situation later in the section on defect phases.

Chiral smectic phases

The smectic phases formed by chiral molecules are designated with a * over the letter specifying the analogous non-chiral phase. For example, the chiral smectic-A is abbreviated as SmA*. Many of the physical properties of a chiral phase, e.g., the linear electro-optical effect [14] of the SmA* phase, are not present in the SmA phase. Tilted phases occur for chiral molecules. The simplest is called the fluid smectic-C*, SmC*, phase. This extra degree of freedom obtained from chirality causes a distortion in the SmC structure, and the direction of tilt precesses around the layer normal as one moves from layer to layer. A schematic picture of the SmC* is shown in Fig. 1.7. This phase is ferroelectric in nature as the molecules have a transverse permanent dipole moment. This property has been the basis of many new technologies and the subject of intense study in its own right [23–25]. Ferroelectric phases will be discussed in Section 1.4.5 in more detail.

The precession of tilt angle from layer to layer is also seen in other chiral

smectic and crystalline phases. They generally show the same phase sequence as shown in Fig. 1.6. Because the molecules are chiral in analogy with the SmC* all of these phases are also labeled with a star. Thus we obtain HexF*, HexI*, CrG*, CrJ*, CrH* and CrK* phases.

1.4.4 Frustrated or polar smectics
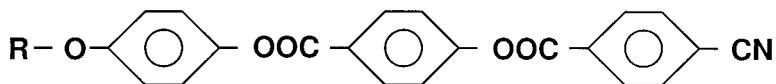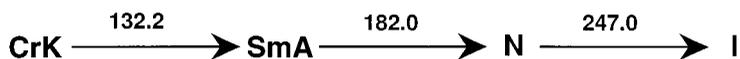
Liquid crystalline compounds with a large longitudinal permanent electric dipole moment exhibit a very rich mesomorphism including several smectic-A phases and reentrant nematic phases. The longitudinal dipole moment arises because of the presence of chemical groups such as NO_2 or CN. Chemical formulae and mesomorphism of some of the often studied materials are given in Fig. 1.8. This behavior was first observed unexpectedly in a mixture by Sigaud and coworkers [26]. The term frustrated stems from a microscopic frustrated spin model of Berker *et al*. [27]. At present, more than ten smectic phases have been observed in these systems.

The molecular arrangement in the four simplest frustrated phases, namely the N, smectic-A_1, -A_2, and -A_d (abbreviated as N, SmA_1, SmA_2, and SmA_d) phases, is shown in Fig. 1.9 along with their characteristic x-ray diffraction patterns. Here, the molecules are drawn as straight lines with an arrowhead at one end to represent the dipole. Two diffuse spots observed in the x-ray diffraction pattern of these nematic phases set them apart from the nematic phase of non-polar materials. The dipoles have no orientational preference in the SmA_1 phase. In the SmA_1 phase, quasi-Bragg reflection and a diffuse peak are observed. The diffuse peak condenses into a sharp reflection in the SmA_2 phase as the antiferroelectric order develops accompanied by a dipole density modulation of periodicity $2l$, l being the molecular length. The dipole density modulation has periodicity of $2l' < 2l$ in the SmA_d phase, in which molecules partially overlap. The two quasi-Bragg reflections in the SmA_d phase appear at slightly higher values of the scattering vectors than in the SmA_2 phase. In this phase, a diffuse peak corresponding to liquid-like short range order at a length scale of l persists.

Prost, Lubensky, and coworkers [28] developed a mean-field theory for these systems using two two-component smectic order parameters Ψ_1 and Ψ_2 [$\Psi_i(\mathbf{r}) \sim \Psi_{i0} \exp(i\mathbf{q_i} \cdot \mathbf{r})$, $i = 1, 2$] that characterize long range head-to-head antiferroelectric order of molecules and mass density modulations, respectively. The wavevectors $\mathbf{q}_1$ and $\mathbf{q}_2$, at which Ψ_1 and Ψ_2 condense, are in general not required to be collinear. The two order parameters would prefer to condense at their natural wavevectors $\mathbf{k}_1$ ($= 2\pi/2l'$) and $\mathbf{k}_2$ ($= 2\pi/l$) in the absence of coupling between them. Here, $2l'$ ($2l' \leq 2l$) is the effective length

R – O⟨○⟩ – OOC ⟨○⟩ OOC ⟨○⟩ CN

DB$_7$OCN : R = C$_7$H$_{15}$

CrK $\xrightarrow{132.2}$ SmA $\xrightarrow{182.0}$ N $\xrightarrow{247.0}$ I

DB$_8$OCN : R = C$_8$H$_{17}$

CrK $\xrightarrow{128.5}$ SmA $\xrightarrow{199.4}$ N $\xrightarrow{242.8}$ I

8OCB

C$_8$H$_{17}$O – ⟨○⟩ ⟨○⟩ – CN

CrK $\xrightarrow{56.0}$ SmA $\xrightarrow{67.1}$ N $\xrightarrow{80.6}$ I

8OBCAB

C$_8$H$_{17}$O – ⟨○⟩ – OOC ⟨○⟩ – N = N – ⟨○⟩ – CN

CrK $\xrightarrow{92.0}$ SmA $\xrightarrow{99.8}$ N $\xrightarrow{258.6}$ I
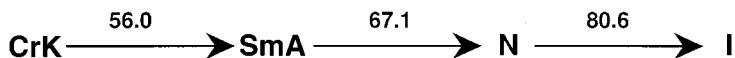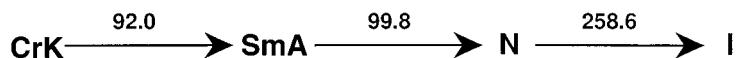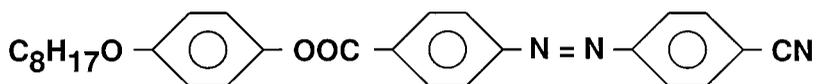
Figure 1.8. Molecular formulae and phase sequence of some frustrated smectic liquid crystals.
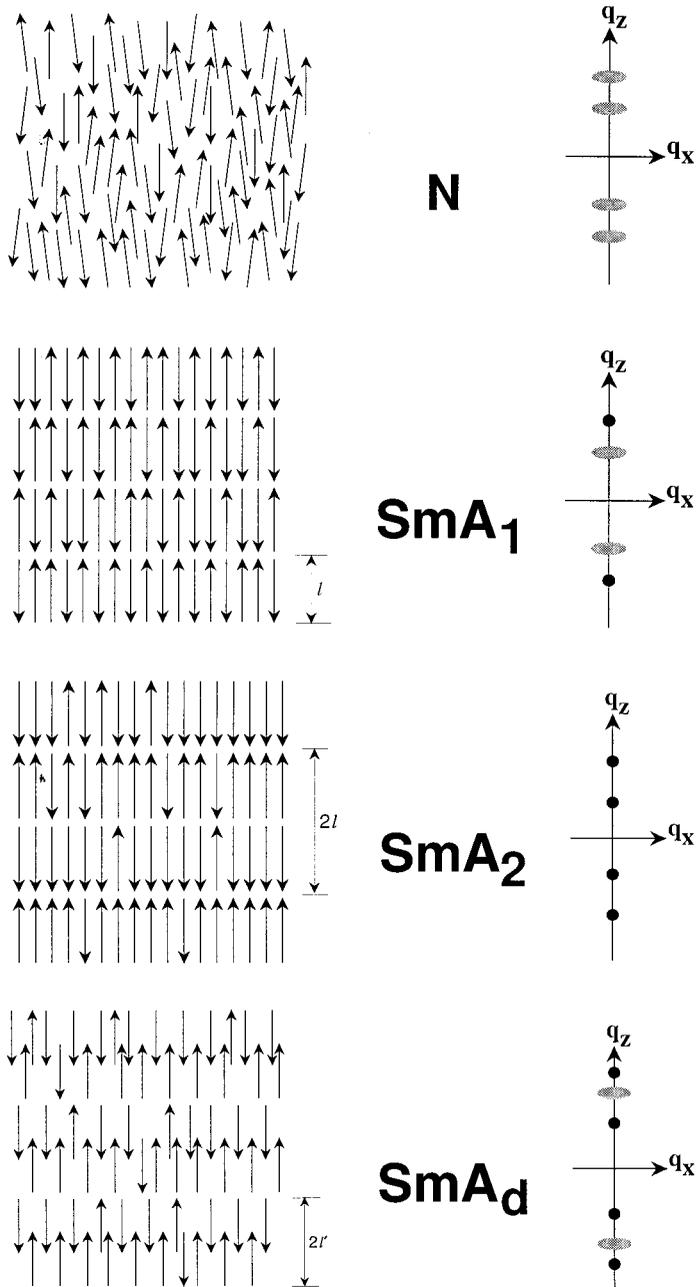
Figure 1.9.   Schematic representation of frustrated liquid crystal phases and corresponding x-ray diffraction patterns.

of an antiferroelectrically ordered pair of molecules which can be thought of as a dimer. The excess free energy density can be written as

$$f - f_0 = a_1(T - T_{c1})|\Psi_1|^2 + D_1|(\Delta + k_1^2)\Psi_1|^2 + C_1|\nabla_\perp\Psi_1|^2 + u_1|\Psi_1|^4$$
$$+ a_2(T - T_{c2})|\Psi_2|^2 + D_2|(\Delta + k_2^2)\Psi_2|^2 + C_2|\nabla_\perp\Psi_2|^2 + u_2|\Psi_2|^4$$
$$+ 2u_{12}|\Psi_1|^2|\Psi_2|^2 - w\mathrm{Re}\Psi_1^2\Psi_2^* - v\mathrm{Re}\Psi_1\Psi_2^*.$$

Here T_{ci} are the two mean-field transition temperatures. The elastic terms with coefficients D_i describe the spatial modulation and favor $q_1^2 = k_1^2$ and $q_2^2 = k_2^2$. The terms with $\nabla_\perp$, a gradient in the plane perpendicular to **n**, favor that $\mathbf{q}_1$, $\mathbf{q}_2$, and **n** be parallel to each other. The terms $\Psi_1\Psi_2^*$ and $\Psi_1^2\Psi_2^*$ favor locking of two wavevectors at $\mathbf{q}_1 = \mathbf{q}_2$ and $\mathbf{q}_1 = \mathbf{q}_2/2$, respectively. These competing tendencies give rise to a variety of phases in mixtures of compounds with very different molecular lengths. In binary mixtures, the quantities Ψ_1 and Ψ_2 depend on the concentration, which influences the strength of coupling terms and the natural wavevectors. The cubic term dominates $l' \sim l$ but the harmonic term becomes most important when $l' \sim l/2$.

The formation of various phases follows quite naturally from this theory. When $\Psi_1 = \Psi_2 = 0$, a nematic phase is obtained which possesses neither a mass density nor a polarization density modulation. It has only short range PO along with the director or, in other words, has smectic order fluctuations corresponding to both wavevectors which appear as two sets of diffuse peaks in x-ray diffraction experiments. In the monolayer SmA_1 phase, only the mass density wave develops, so $\Psi_1 = 0$ and $\Psi_2 \neq 0$. The quasi-Bragg reflection from this phase appears at $2q_0 = 2\pi/l$ and a diffuse nematic-like peak at $2\pi/2l'$. When $\Psi_1 \neq 0 \neq \Psi_2$, a number of interesting cases arise. If both density waves are collinear and $l' \cong l$, then the cubic coupling term enforces commensurability, requiring $q_2 = 2q_1 = 2\pi/2l \, (= q_0, \text{ say})$ and the bilayer SmA_2 phase results. On the other hand, if $l' < l$, as would be the case if molecules were overlapping, no locking of the wavevectors is possible and the partial bilayer SmA_d phase is obtained. Obviously, this theory provides a very satisfactory explanation for the formation of these and several other (SmC_1, SmC_2, etc. when molecules are tilted) phases which we shall not discuss in any detail here.

Numerous other possibilities exist arising from (i) letting the magnitude of the two collinear wavevectors take different relative values giving rise to the possibility of incommensurate SmA phases [29] which have not yet been discovered. Only the existence of incommensurate crystal smectic phase has been confirmed [30], and (ii) letting them become non-collinear permitting the formation of phases in which one of the density waves is in a

direction parallel to the smectic planes. Depending upon whether the molecules are normal or tilted with respect to the smectic layers, the SmÃ or the SmC̃ antiphase forms [31]. The existence of these phases has experimentally been confirmed.

1.4.5 Ferroelectric, antiferrolectric, and ferrielectric smectic phases

One of the more remarkable aspects of the SmC* phase is that it is ferroelectric. In the present context this means that a non-zero spontaneous polarization develops in this phase. Typically the polarization is a very strong function of temperature near the transition (from higher temperature phase) to the SmC* phase and somewhat slower farther from the transition. Recall that the SmC* phase consists of tilted molecules and typically the polarization is coupled to the tilt angle which also is zero at the transition to the (untilted) SmA phase. In fact, one often writes:

$$\theta = \theta_0 (T_C - T)^\alpha,$$
$$P = P_0 (T_C - T)^\beta.$$

where θ is the tilt angle, P is the spontaneous polarization, θ_0 and P_0 are constants, T_c is the transition temperature, T the temperature, and α and β are constants, theoretically predicted to be equal to 0.5. The above is somewhat deceiving. Recall that in our discussion of the SmC* phase we stated that the chirality leads to a twisting of the molecules and hence there is a helical arrangement of the molecules as shown in Fig. 1.7. In a macroscopic sample, without surfaces or external electric fields, the molecular polarization will follow this helix and result in zero total spontaneous polarization. Hence the more correct name is helielectric phases [32]. However, if the helix is unwound, which happens if a strong electric field is applied, there is a spontaneous non-zero polarization which can be measured. Measurement of P is discussed in Chapter 4 on physical properties.

Surface stabilization of the SmC* phase is the basis of surface stabilized ferroelectric liquid crystal (SSFLC) display devices first proposed by Clark and Lagerwall [33]. These cells, which are very thin, use surface anchoring to provide alignment of the liquid crystal. The cell is switched between two equivalent energy states, with very different optical properties when viewed through crossed polarizers, by reversing the direction of the applied electric field. This type of cell has achieved switching speed as fast as 0.1 μs which is three to four orders of magnitude faster than the nematic displays [33]. Other details and a discussion of the chemistry of these materials is available elsewhere [34].
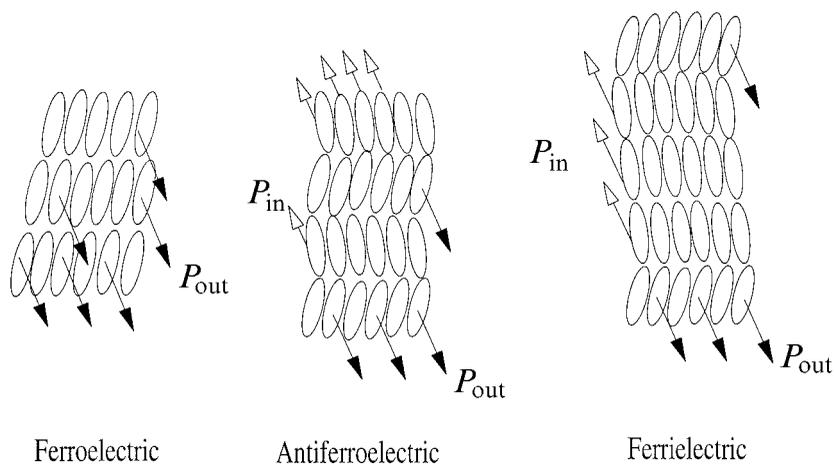
Figure 1.10. Schematic pictures of the ferroelectric SmC* phase, an antiferro-electric SmC* phase and a ferrielectric SmC* phase. The open arrows indicate that the spontaneous polarization of the molecular layer is into the page, the dark arrows indicate that the spontaneous polarization is out of the page.

Recently, two more phases closely related to the SmC* have been discovered. These are somewhat like the frustrated smectic phases in which local dipoles become antiparallel. In these phases, the layer spacing and the polarization direction are not related in the same manner as in the SmC* phase. These phases, by analogy to the situation in magnets, are called antiferroelectric liquid crystals and ferrielectric liquid crystals. Figure 1.10 schematically depicts the SmC* phase, the proposed structure of the antiferroelectric phase, and the simplest ferrielectric phase. All phases possess chirality which has not been shown in Fig. 1.10 to clarify local molecular and dipolar arrangements. The SmC* phase is characterized by the spontaneous polarization of each layer pointing in the same direction. The antiferroelectric phase is characterized by alternating directions of the spontaneous polarization and the molecular tilt in adjacent layers. Thus, the average tilt angle and the average spontaneous polarization in this phase are both zero. A sufficiently strong electric field will switch the anti-ferroelectric phase to the ferroelectric phase. It is significant to note that antiferroelectrics repeat their helical structure every 180° of rotation about the layer normal compared to 360° for the ferrolectric phase. The ferri-electric phase is characterized by an uneven number of layers stacked with tilt to the left and to the right. Thus there is a net but low spontaneous polarization, since there are an uneven number of molecules with polarization in the two opposite directions. Recent work has shown that many shades of

ferrielectric phases exist differing in the proportion of layers with the two different tilt directions. Readers are referred to the literature for more details on these phases [35].

1.4.6 Blue and twist grain boundary phases

One of the advances in recent years in liquid crystal research has been the discovery of defect phases. You might recall that in crystals defects such as vacancies, dislocations, grain boundaries and the like exist, and can sometimes be removed by special preparation of the material. In liquid crystals defects also exist [36]. These defects have several specific geometries, and are energetically unfavored. In most experiments these defects are accidents of sample preparation and one tries to remove them by annealing, careful and clean sample preparation, or other techniques. However, in sufficiently high chirality materials defects form spontaneously and are an essential feature of the liquid crystalline phase. There are two common examples, both of which we will briefly discuss: the blue phases (BP) and the twist grain boundary phases (TGB). The BPs may be thought of as double twist order permeated by a lattice of line defects. The TGB phase occurs when twist is frustrated by layer structures. The resulting structure has periodic grain boundaries.

Recall that the chiral nematic phase is locally a nematic with a slow (on a molecular scale) rotation in the director. This phase occurs when the pitch is large or the chirality is low. At the other extreme, when the chirality is high, this picture is not correct. The presence of the high chirality makes it possible for the system to have a lower energy state by having a double twist structure rather than the single twist. However, this is not the whole story; the free energy can be further reduced by forming many spatially ordered double twist structures. The resulting defect phases possess simple cubic, body centered cubic, and amorphous structures [37, 38]. Usually these phases occur only over a small temperature range between the isotropic and the chiral nematic phases, and are called blue phases because the first discovered phase appears blue in reflected light.

The twist grain boundary phases formed by high chirality molecules have a structure similar to the SmA phase and are more accurately denoted as the TGB_A phases. The layered structure of the SmA excludes twist. However, just as in the blue phases, high chirality subtly changes the energetics of the system leading to a different type of structure. In this case the free energy is minimized by introducing grain boundaries at periodic intervals. This phase was theoretically predicted by Renn and Lubensky [39] and almost simulta-

racemic and homogeneously chiral stacking of the layers, the racemic having the lower free energy; (iv) the coexistence of chiral domains of both handedness which maintain their handedness during switching in response to an applied field; and (v) 'sergeants-and-soldiers' biasing of the global chirality upon addition of chiral dopants. This phase has been observed to form thin films of two or three layers. Currently there are several research groups working on these materials. The structure and nomenclature of these materials have not yet been finalized.

1.6 Liquid crystals formed from disk-shaped molecules

The liquid crystalline phases formed by disk-shaped molecules are referred to as the discotic phases. They were first synthesized and identified in 1977 [2, 43]. Structurally they generally form either nematic or columnar phases. The simplest columnar phase consists of stacked disks, forming a one-dimensional liquid-like structure; the columns themselves form a two-dimensional lattice. Hexagonal, rectangular, and other lattice types have been identified. Tilted phases have also been reported. The discotic nematic phase is denoted by N_D where the subscript D is to avoid confusion with the normal nematic phase. This phase is characterized by the short axis of the molecule aligning parallel to the director. The N_D phase is diamagnetically and optically negative. This is in contrast with the rod-like nematics which are mostly optically and diamagnetically positive. Figure 1.12 illustrates the N_D phase and the columnar phases.

The structure of the columnar phases merits some discussion. There is no PO along the columns. The columns themselves are arranged with PO and form a two-dimensional array which is either a rectangular or a hexagonal lattice. There is orientational order (at least for the cores of these molecules) within the columns. The rectangular or D_r phase has columns which occupy a rectangular lattice. The molecules are oriented away from the column axis in this phase; the resulting tilt forms a herringbone pattern such as shown in Figure 1.12(c). The columns of the hexagonal, D_h, phase are arranged in a hexagonal pattern. The molecules are tilted within the columns, but there is no coordinated azimuthal orientation of the molecules in the columns.

1.7 Polymeric liquid crystals

Another class of thermotropic mesogens is polymer liquid crystals. These structures consist of mesogenic subunits (either rod-like or disk-like) which are connected together with flexible links forming what are known as the
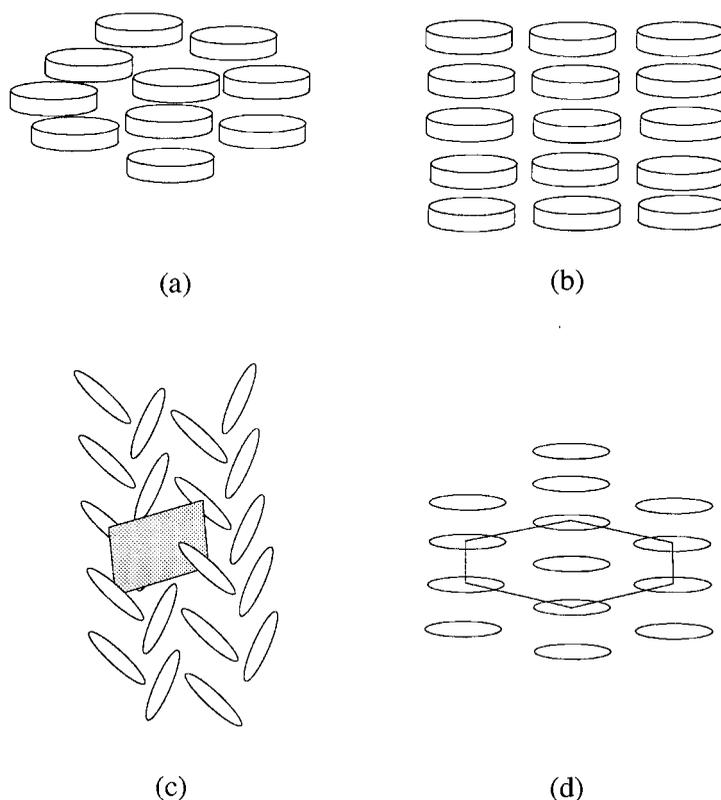
Figure 1.12. The structure of the N_D (a) and columnar (b) phases. In columnar phases there is PO in the columns. The rectangular columnar phase, D_r, is shown in (c) and the hexagonal columnar phase, D_h, is shown in (d). In these two parts of the figure the molecules are tilted. This is illustrated by drawing the disks as ellipses.

main-chain polymer liquid crystals (PLC). Alternatively, the mesogenic subunits can be attached to the polymer chains as side groups or pendates. These are known as the side-chain PLCs. The nature of the liquid crystal-line phases which form depends on the backbone, spacers, flexible links, etc. These are reviewed in several references [4, 44]. A schematic presentation of these PLCs is shown in Fig. 1.13.

1.8 Lyotropic liquid crystals

1.8.1 Colloidal lyotropic phases

Solutions of biomolecules such as proteins and DNA and sufficiently con-centrated solutions of surfactants can form another interesting class of liquid crystals. Since the phase behavior is most easily induced by changes
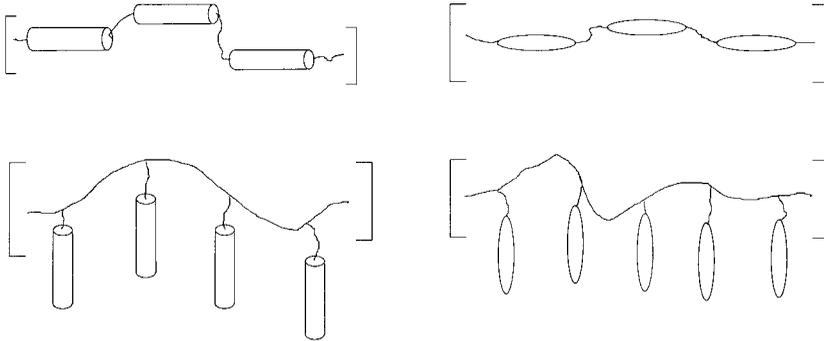
Figure 1.13.   Schematic representation of polymeric liquid crystals. The rods and ellipses represent rod-like and disk-like mesogens, respectively. The wavy lines represent the polymer chains or segments. The brackets, [ ], indicate that the unit is repeated many times. The top two figures represent main-chain PLCs, the bottom two side-chain PLCs.

in concentration (although temperature is still an important variable) these are referred to as lyotropic liquid crystals. These mesophases [1, 2] were first considered by Onsager [45] and Flory [46]. Representative examples are synthetic polypeptides, precipitated metal oxides, and rigid polymers in appropriate solvents. Typically these molecules achieve length to diameter ratios of ∼10–20. Liquid crystal properties of solutions of DNA molecules, some proteins, and viruses have also been extensively studied. Of particular interest is tobacco mosaic virus (TMV) which has a length of approximately 3000 Å and a diameter of 200 Å and is known to form phases analogous to the nematic and smectic phases of thermotropic liquid crystals.

1.8.2 Self-assembled structures

In addition to small molecules, polymer liquid crystals, and large chemically bonded objects such as viruses, another simple class of materials exhibits liquid crystalline phases. This class of materials consists of amphiphilic molecules in a solvent in which they spontaneously form lyotropic micellar systems. An example of such a system is a solution of soap in water. A typical soap molecule consists of a polar head and one or more hydrocarbon tails. When a sufficient number of such molecules is dissolved in a solvent, the lowest free energy state is a state in which the hydrocarbon tails segregate to shield themselves from the polar water environment. This leads to the formation of aggregates of molecules. Molecules in such aggregates, called micelles, are not covalently bonded and can assume several
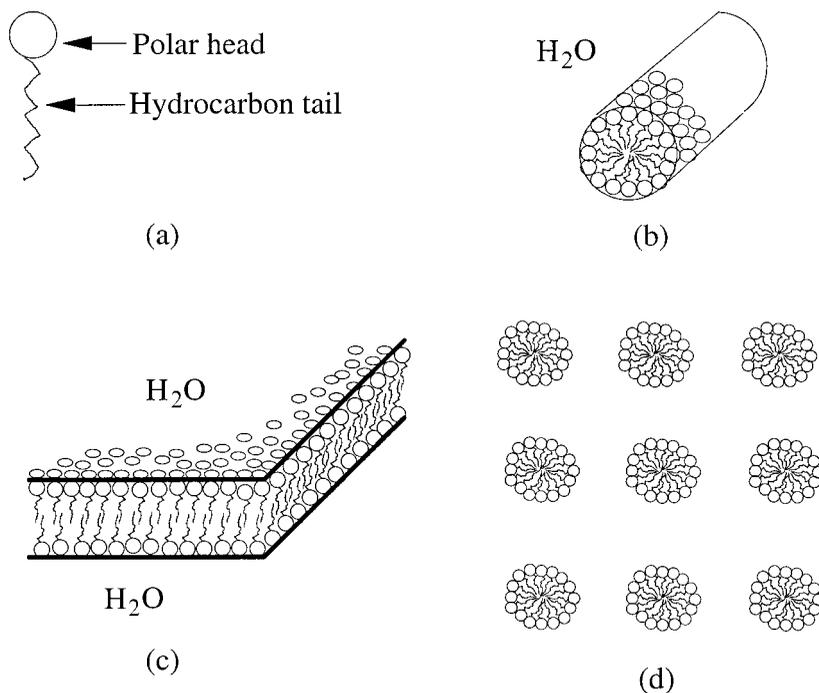
Figure 1.14.   (a) A 'cartoon' of a typical amphiphilic molecule. (b) An example of a rod-like micelle. (c) A slice of a bilayer structure. This is an example of a lamellar phase. (d) A cubic phase formed by spherical aggregates.

different geometries depending on the thermodynamic conditions and chemical nature of the molecules. These aggregates can be rod-like or disk-like which can be orientationally and/or positionally ordered to exhibit a wide range of liquid crystalline phases including isotropic, nematic, lamellar, hexagonal, and cubic phases [1, 5]. A typical surfactant and a few simple phases of amphiphilic materials are shown in Fig. 1.14.

   This area of liquid crystal research, in fact, precedes the age of thermotropic liquid crystals. Early work [47] demonstrated the existence of mesophases with PO in one (lamellar or smectic phases), two (hexagonal and rectangular phases), and three (cubic) dimensions. The observation of the nematic phase came more recently [48]. It typically consists of rod-like or disk-like micelles with their symmetry axis orientationally ordered. This phase is observed between the isotropic phase and a smectic-like phase called the lamellar phase of disk-like micelles. For cylindrical micellar systems, it appears between the isotropic and the hexagonal phase. These phases can be observed over a rather large concentration range typically

from 0.1 to 0.5 weight percent as well as over a wide temperature range. The Onsager theory explains the isotropic to nematic phase transition in these materials rather well. Finally, the nematic composed of rod-like micelles is called the canonic [5] nematic, N_C. A review of research in this field has been prepared by Boden [49].

References

1. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd Edn., Oxford University Press, New York (1993).
2. S. Chandrasekhar, *Liquid Crystals*, 2nd Edn., Cambridge University Press, New York (1992).
3. G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals*, Springer-Verlag, New York (1988).
4. A. Blumstein (Ed.), *Polymeric Liquid Crystals*, Plenum Press, New York (1985).
5. P. J. Collings and J. S. Patel (Eds.), *Handbook of Liquid Crystal Research*, Oxford University Press, New York (1997).
6. R. Blinc and R. Zeks, *Ferroelectric and Antiferroelectric Liquid Crystals and Electro-optic Applications*, World Scientific, New Jersey (1999).
7. S. Kumar, *Liquid Crystals in the Nineties and Beyond*, World Scientific, New Jersey (1995).
8. P. S. Pershan, *Structure of Liquid Crystal Phases*, World Scientific, New Jersey (1988).
9. I.-C. Khoo and S.-T. Wu, *Optics and Nonlinear Optics of Liquid Crystals*, World Scientific, New Jersey (1993).
10. P. Tolédano and A. M. Figueiredo Neto, *Phase Transitions in Complex Fluids*, World Scientific, New Jersey (1998).
11. K. C. Chu and W. L. McMillan, *Phys. Rev. A* **15**, 1181 (1977).
12. E. B. Priestley, P. J. Wojtowicz, and P. Sheng, *Introduction to Liquid Crystals*, Plenum Press, New York (1975).
13. R. J. Birgeneau and J. D. Litster, *J. Phys. (Paris)* **39**, L-399 (1978); A. Aharony, R. J. Birgeneu, J. D. Brock, and J. D. Litster, *Phys. Rev. Lett.* **57**, 1012 (1986).
14. *International Tables for X-ray Crystallography*, Vol. A–C, 2nd Edn., Kluwer Academic Publishers, Netherlands (1999).
15. R. E. Peierls, *Helv. Phys. Acta, Suppl.* **7**, 81 (1934); M. A. Caille, *C. R. Acad. Sci. Ser. B* **274**, 891 (1972).
16. P. G. de Gennes, *Solid State Commun.* **10**, 753 (1972).
17. P. G. de Gennes, *C. R. Acad. Sci.* **274**, 758 (1972) and *Mol. Cryst. Liq. Cryst.* **21**, 49 (1973).
18. M. J. Freiser, *Phys. Rev. Lett.* **24**, 1041 (1970); R. Alben, *Phys. Rev. Lett.* **30**, 778 (1973); D. W. Allender, M. A. Lee, N. Halfiz, *Mol. Cryst. Liq. Cryst.* **124**, 45 (1985); J. Melthete, L. Liebert, A. M. Levelut, and Y. Galerne, *C. R. Acad. Sci.* **303**, 1073 (1986); G. Shinuoda, Y. Shi, and M. E. Neubert, *Mol. Cryst. Liq. Cryst.* **257**, 209 (1994).
19. B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); D. R. Nelson and B. I. Halperin, *Phys. Rev. B* **19**, 2457 (1979); A. P. Young, *Phys. Rev. B* **19**, 1855 (1979).

20. See for instance: B. Deloche, J. Charvolin, L. Liébert, and L. Strzelecki, *J. Phys. (Paris)* **36**, C1-21 (1975), G. J. Krüger, H. Spiesecke, and R. Van Steenwinkel, *J. Phys. (Paris)* **37**, C3-123 (1976), and R. Blinc, M. Luzar, M. Vilfan, and M. Burgar, *J. Chem. Phys.* **63**, 3445 (1975).
21. S. Kumar, *Phys. Rev. A* **23**, 3207 (1981).
22. T. P. Rieker and E. P. Janulis, *Phys. Rev. E* **52**, 2688 (1995); M. Hird and K. J. Toyne, *Mol. Cryst. Liq. Cryst.* **323**, 1 (1998).
23. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett*. **36**, 899 (1980); J. W. Goodby, *Ferroelectric Liquid Crystals: Principles, Properties, and Applications, Ferroelectricity and Related Phenomena* vol. 7, Gordon and Breach Science Publishers, New York (1991).
24. P. Patel, D. Chu, J. W. West, and S. Kumar, *SID Digest* **XXV**, 845 (1994); V. Vorflusev and S. Kumar, *Ferroelectrics* **213**, 117 (1998).
25. X.-Y. Wang, J.-F. Li, E. Gurarie, S. Fan, T. Kyu, M. E. Neubert, S. S. Keast, and C. Rosenblatt, *Phys. Rev. Lett.* **80**, 4478 (1998).
26. G. Sigaud, M. F. Achard, F. Hardouin, and H. Gaspraux, *J. Phys. (Paris) Colloq.* **40**, C3-356 (1979).
27. J. O. Indekeu and A. N. Berker, *Phys. Rev. A* **33**, 1158 (1986); J. O. Indekeu, A. N. Berker, C. Chiang, and C. W. Garland, *ibid*. **35**, 1371 (1987).
28. P. Barois, J. Prost, and T. C. Lubensky, *J. Phys. (Paris)* **46**, 391 (1985); J. Prost, *Adv. Phys.* **33**, 1 (1984), and references therein.
29. P. Patel, S. Kumar, and P. Ukleja, *Liq. Cryst.* **16**, 351 (1994).
30. J. T. Mang, B. Cull, Y. Shi, P. Patel and S. Kumar, *Phys. Rev. Lett.* **74**, 4241 (1995).
31. Y. Shi, G. Nounesis, and S. Kumar, *Phys. Rev. E* **54**, 1570 (1996); C. R. Safinya, W. A. Varady, L. Y. Chiang, and P. Dimon, *Phys. Rev. Lett* **57**, 432 (1986).
32. H. R. Brand, P. E. Cladis, and P. L. Flinn, *Phys. Rev. A.* **31**, 361 (1985).
33. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett*. **36**, 899 (1980); N. A. Clark and S. T. Lagerwall, *Ferroelectrics* **59**, 25 (1984).
34. B. Bahadur (Ed.), *Liquid Crystals Applications and Uses*, 3 vols. World Scientific, New Jersey (1990–1992); J. S. Patel and J. W. Goodby, *Mol. Cryst. Liq. Cryst.* **144**, 117 (1987).
35. See for instance: A. D. Chandani, Y. Ouchi, H. Takezoe, A. Fukuda, K. Terashima, K. Furukawa, and A. Kishi, *Jpn. J. Appl. Phys. Lett.* **28**, 1261 (1989); E. Gorecka, A. D. L. Chandani, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **29**, 131 (1990); S. Inui, S. Kawano, M. Saito, H. Iwane, Y. Takanishi, K. Hiraoka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys. Lett.* **29**, 987 (1990); A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, *J. Mater. Chem*. **4**, 997 (1994).
36. M. Kleman, *Points, Lines and Walls: In Liquid Crystals, Magnetic Systems and Various Ordered Media*, Wiley Interscience, New York (1983).
37. There are many reviews of this area. See for instance: P. P. Crooker, *Liq. Cryst.* **5**, 751 (1989).
38. P. H. Keyes, *Mater. Res. Bull.* **16**, 32 (1991).
39. S. R. Renn and T. C. Lubensky, *Phys. Rev. A.* **38**, 2132 (1988).
40. J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak, J. S. Patel, *J. Am. Chem. Soc.* **111**, 8119 (1989).
41. Y. Matsunaga and S. Miyamoto, *Mol. Cryst. Liq. Cryst.* **237**, 311 (1993); K. J. Semmler, T. J. Dingemans, and E. T. Samulski, *Liq. Cryst.* **24**, 799 (1998); L. C. Chien, private communication.

42. D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblova, and D. M. Walba, *Science* **278**, 1924 (1997).

43. S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana* **9**, 471 (1977); S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusudana, S. Kumar, R. Shashidhar, and G. Venkatesh, *J. Phys. (Paris) Colloq.* **40**, C3-120 (1979).

44. T. Tsuruta (Ed.), *Biopolymers, Liquid Crystalline Polymers and Phase Emulsions*, Advances in Polymer Science Series 126 (1996).

45. L. Onsager, *Ann. NY Acad. Sci.* **51**, 627 (1949).

46. P. J. Flory, *Proc. R. Soc. London Ser. A* **234**, 73 (1956).

47. S. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes*, Addison-Wesley, Reading (1994); G. J. T. Tiddy, *Phys. Rep.* **57**, 1 (1980).

48. There are numerous references, for example: J. Charvolin, *J. Chim. Phys.* **80**, 16 (1983); A. Saupe, S. Y. Xu, S. Plumley, Y. K. Zhu, and P. J. Photinos, *Physica A* **174**, 195 (1991).

49. N. Boden in *Micelles, Membranes, Microemulsions and Monolayers*, W. Gelbart, A. Ben-Shaul, and D. Roux (Eds.) Springer-Verlag, New York, (1994).