

# 1

## Introduction to liquid crystals

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### 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,  $\mathbf{n}$ , known as the *director*. The degree of order, denoted by the *orientational order parameter*,  $S$ , is the thermal average  $\frac{3}{2} \cos^2 \theta - 1/2$ , where  $\theta$  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:

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

where  $\rho$  is the average electron density,  $\text{Re}$  means real part of,  $\Psi$  is the complex amplitude, and  $\mathbf{k}$  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

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

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

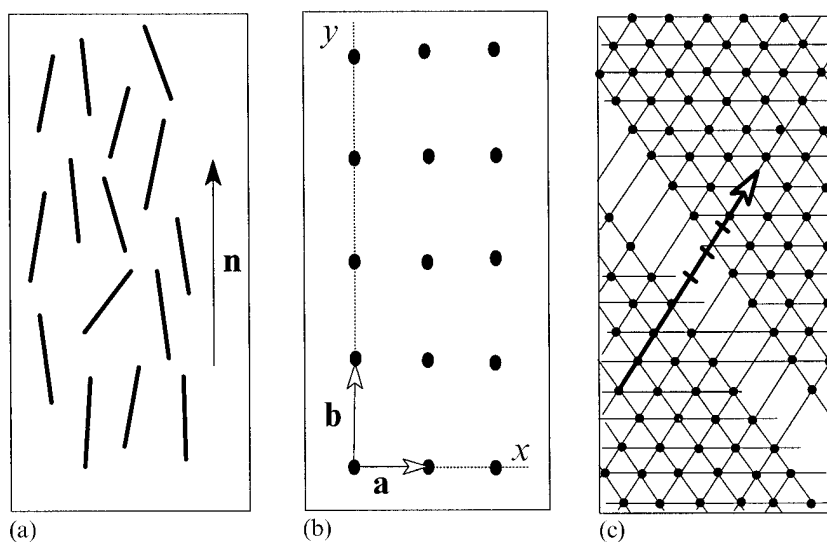


Figure 1.1. Schematic representation of the three basic types of order: (a) orientational order parallel to the director  $\mathbf{n}$ , (b) positional order in two dimensions with lattice vectors  $\mathbf{a}$  and  $\mathbf{b}$ , and (c) bond orientational order. In the last case, translation from 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,  $\psi_6$ , 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  $\phi$  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  $\mathbf{n}$ , 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  $\mathbf{n}$ , 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

	<u>Phase</u>	<u>Type of order</u>	<u>Abbreviation</u>
Temperature 	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	

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  $\mathbf{n}$ ; (c) the direction of  $\mathbf{n}$  in space is arbitrary, and typically imposed by outside forces such as electric/magnetic fields; (d)  $\mathbf{n}$  and  $-\mathbf{n}$  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  $\mathbf{n}$ . This phase possesses two unique directions perpendicular to  $\mathbf{n}$  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

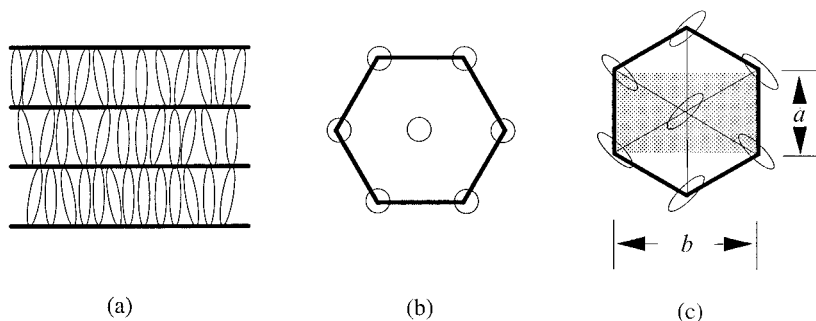


Figure 1.3. Some liquid crystal phases formed by untilted rod-like molecules. (a) The smectic-A phase; note that there is quasi-long range PO normal to the layers, OO with the mean orientation of the molecules perpendicular to the layers and short range PO and BOO within the layers. (b) A view of the 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

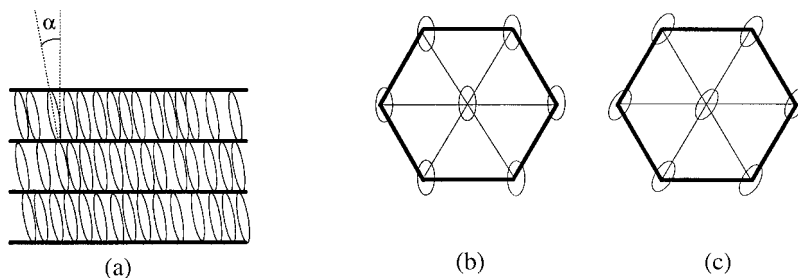


Figure 1.4. Schematic representation of some tilted phases formed by rod-like molecules. (a) The SmC phase; the layers are indicated by the lines and the molecules by the ellipses. Short range order in hexatic smectic-F and hexatic smectic-I phases are shown in (b) and (c) respectively. Here the major 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.,  $\mathbf{n}$  and smectic layer normal are not collinear, Fig. 1.4(a). Furthermore, the tilt angle,  $\alpha$ , 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  $\alpha$  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