

4.4. Scattering from mesomorphic structures

BY P. S. PERSHAN

4.4.1. Introduction

The term mesomorphic is derived from the prefix ‘meso-’, which is defined in the dictionary as ‘a word element meaning middle’, and the term ‘-morphic’, which is defined as ‘an adjective termination corresponding to morph or form’. Thus, mesomorphic order implies some ‘form’, or order, that is ‘in the middle’, or intermediate between that of liquids and crystals. The name liquid crystalline was coined by researchers who found it to be more descriptive, and the two are used synonymously. It follows that a mesomorphic, or liquid-crystalline, phase must have more symmetry than any one of the 230 space groups that characterize crystals.

A major source of confusion in the early liquid-crystal literature was concerned with the fact that many of the molecules that form liquid crystals also form true three-dimensional crystals with diffraction patterns that are only subtly different from those of other liquid-crystalline phases. Since most of the original mesomorphic phase identifications were performed using a ‘miscibility’ procedure, which depends on optically observed changes in textures accompanying variation in the sample’s chemical composition, it is not surprising that some three-dimensional crystalline phases were mistakenly identified as mesomorphic. Phases were identified as being either the same as, or different from, phases that were previously observed (Liebert, 1978; Gray & Goodby, 1984), and although many of the workers were very clever in deducing the microscopic structure responsible for the microscopic textures, the phases were labelled in the order of discovery as smectic-A, smectic-B *etc.* without any attempt to develop a systematic nomenclature that would reflect the underlying order. Although different groups did not always assign the same letters to the same phases, the problem is now resolved and the assignments used in this article are commonly accepted (Gray & Goodby, 1984).

Fig. 4.4.1.1 illustrates the way in which increasing order can be assigned to the series of mesomorphic phases in three dimensions listed in Table 4.4.1.1. Although the phases in this series are the most thoroughly documented mesomorphic phases, there are others not included in the table which we will discuss below.

The progression from the completely symmetric isotropic liquid through the mesomorphic phases into the crystalline phases can be described in terms of three separate types of order. The first, or the molecular orientational order, describes the fact that the molecules have some preferential orientation analogous to the spin orientational order of ferromagnetic materials. In the present case, the molecular quantity that is oriented is a symmetric second-rank tensor, like the moment of inertia or the electric polarizability, rather than a magnetic moment. This is the only type of long-range order in the nematic phase and as a consequence its physical properties are those of an anisotropic fluid; this is the origin of the name liquid crystal. Fig. 4.4.1.2(a) is a schematic illustration of the nematic order if it is assumed that the molecules can be represented by oblong ellipses. The average orientation of the ellipses is aligned; however, there is no long-range order in the relative positions of the ellipses. Nematic phases are also observed for disc-shaped molecules and for clusters of molecules that form micelles. These all share the common properties of being optically anisotropic and fluid-like, without any long-range positional order.

The second type of order is referred to as bond orientational order. Consider, for example, the fact that for dense packing of spheres on a flat surface most of the spheres will have six neighbouring spheres distributed approximately hexagonally around it. If a perfect two-dimensional triangular lattice of indefinite size were constructed of these spheres, each hexagon on the lattice would be oriented in the same way. Within the last few years, we have come to recognize that this type of order, in which the hexagons are everywhere parallel to one another, is possible even when there is no lattice. This type of order is referred to as bond orientational order, and bond orientational order in the absence of a lattice is the essential property defining the hexatic phases (Halperin & Nelson, 1978; Nelson & Halperin, 1979; Young, 1979; Birgeneau & Litster, 1978).

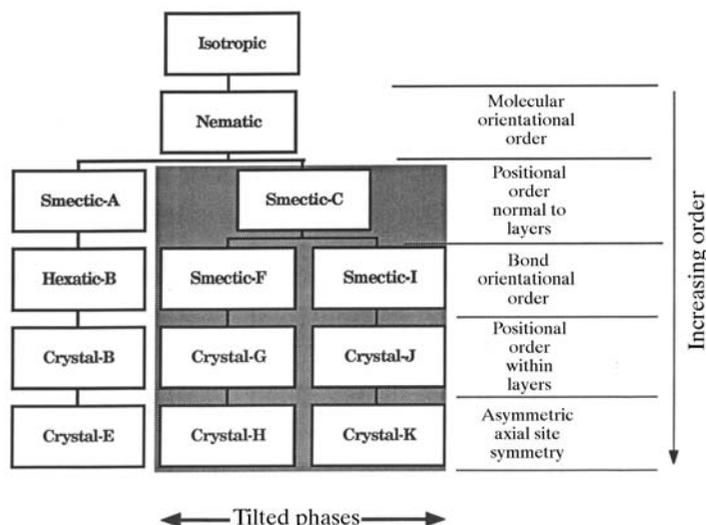


Fig. 4.4.1.1. Illustration of the progression of order throughout the sequence of mesomorphic phases that are based on ‘rod-like’ molecules. The shaded section indicates phases in which the molecules are tilted with respect to the smectic layers.

Table 4.4.1.1. Some of the symmetry properties of the series of three-dimensional phases described in Fig. 4.4.1.1

The terms LRO and SRO imply long-range or short-range order, respectively, and QLRO refers to ‘quasi-long-range order’ as explained in the text.

Phase	Molecular orientation order within layer	Bond orientation order	Positional order	
			Normal to layer	Within layer
Smectic-A (SmA)	SRO	SRO	SRO	SRO
Smectic-C (SmC)	LRO	LRO*	SRO	SRO
Hexatic-B	LRO*	LRO	QLRO	SRO
Smectic-F (SmF)	LRO	LRO	QLRO	SRO
Smectic-I (SmI)	LRO	LRO	QLRO	SRO
Crystalline-B (CrB)	LRO	LRO	LRO	LRO
Crystalline-G (CrG)	LRO	LRO	LRO	LRO
Crystalline-J (CrJ)	LRO	LRO	LRO	LRO
Crystalline-E (CrE)	LRO	LRO	LRO	LRO
Crystalline-H (CrH)	LRO	LRO	LRO	LRO
Crystalline-K (CrK)	LRO	LRO	LRO	LRO

* Theoretically, the existence of LRO in the molecular orientation, or tilt, implies that there must be some LRO in the bond orientation and *vice versa*.

4. DIFFUSE SCATTERING AND RELATED TOPICS

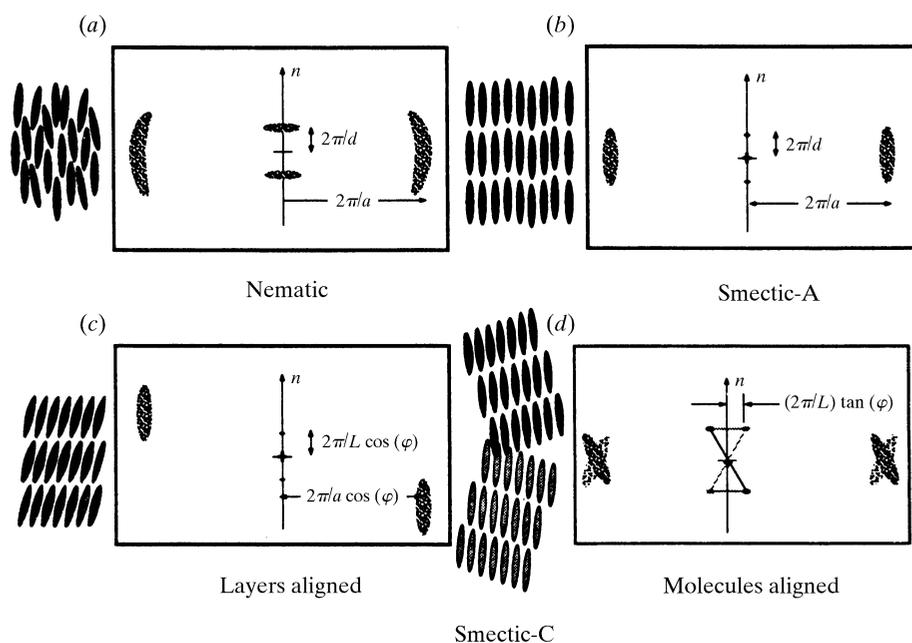


Fig. 4.4.1.2. Schematic illustration of the real-space molecular order and the scattering cross sections in reciprocal space for the: (a) nematic; (b) smectic-A; and (c), (d) smectic-C phases. The scattering cross sections are enclosed in the boxes. Part (c) indicates the smectic-C phase for an oriented monodomain and (d) indicates a polydomain smectic-C structure in which the molecular axes are aligned.

The third type of order is the positional order of an indefinite lattice of the type that defines the 230 space groups of conventional crystals. In view of the fact that some of the mesomorphic phases have a layered structure, it is convenient to separate the positional order into the positional order along the layer normal and perpendicular to it, or within the layers.

Two of the symmetries listed in Tables 4.4.1.1 and 4.4.1.2 are short-range order (SRO), implying that the order is only correlated over a finite distance such as for a simple liquid, and long-range order (LRO) as in either the spin orientation of a ferromagnet or the positional order of a three-dimensional crystal. The third type of symmetry, 'quasi-long-range order' (QLRO), will be explained below. In any case, the progressive increase in symmetry from the isotropic liquid to the crystalline phases for this series of

mesomorphic phases is illustrated in Fig. 4.4.1.1. One objective of this chapter is to describe the reciprocal-space structure of the phases listed in the tables and the phase transitions between them.

Finally, in most of the crystalline phases that we wish to discuss, the molecules have considerable amounts of rotational disorder. For example, one series of molecules that form mesomorphic phases consists of long thin molecules which might be described as 'blade shaped'. Although the cross section of these molecules is quite anisotropic, the site symmetry of the molecule is often symmetric, as though the molecule is rotating freely about its long axis. On cooling, many of the mesomorphic systems undergo transitions to the phases, listed at the bottom of Fig. 4.4.1.1, for which the site symmetry is anisotropic as though some of the rotational motions about the molecular axis have been frozen out. A similar type of transition, in which rotational motions are frozen out, occurs on cooling systems such as succinonitrile ($\text{NCCH}_2\text{CH}_2\text{CN}$) that form optically isotropic 'plastic crystals' (Springer, 1977).

There are two broad classes of liquid-crystalline systems, the thermotropic and the lyotropic, and, since the former are much better understood, this chapter will emphasize results on thermotropic systems (Liebert, 1978). The historical difference between these two, and also the origin of their names, is that the lyotropic are always mixtures, or solutions, of unlike molecules in which one is a normal, or non-mesogenic, liquid. Solutions of soap and water are prototypical examples of lyotropics, and their mesomorphic phases appear as a function of either concentration or temperature. In contrast, the thermotropic systems are usually formed from a single chemical component, and the mesomorphic phases appear primarily as a function of temperature changes. The molecular distinction between the two is that one of the molecules in the lyotropic solution always has a hydrophilic part, often called the 'head group', and one or more hydrophobic alkane chains called 'tails'. These molecules will often form mesomorphic phases as single-component or neat systems; however, the general belief is that in solution with either water or oil most of the phases are the result of competition between the hydrophilic and hydrophobic interactions, as well as other factors such as packing and steric constraints (Pershan, 1979; Safran & Clark, 1987). To the extent that molecules

Table 4.4.1.2. *The symmetry properties of the two-dimensional hexatic and crystalline phases*

Phase	Molecular orientation order within layer	Bond orientation order	Positional order within layer
Smectic-A (SmA)	SRO	SRO	SRO
Smectic-C (SmC)	QLRO	QLRO	SRO
Hexatic-B	QLRO	QLRO	SRO
Smectic-F (SmF)	QLRO	QLRO	SRO
Smectic-I (SmI)	QLRO	QLRO	SRO
Crystalline-B (CrB)	LRO	LRO	QLRO
Crystalline-G (CrG)	LRO	LRO	QLRO
Crystalline-J (CrJ)	LRO	LRO	QLRO
Crystalline-E (CrE)	LRO	LRO	QLRO
Crystalline-H (CrH)	LRO	LRO	QLRO
Crystalline-K (CrK)	LRO	LRO	QLRO

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

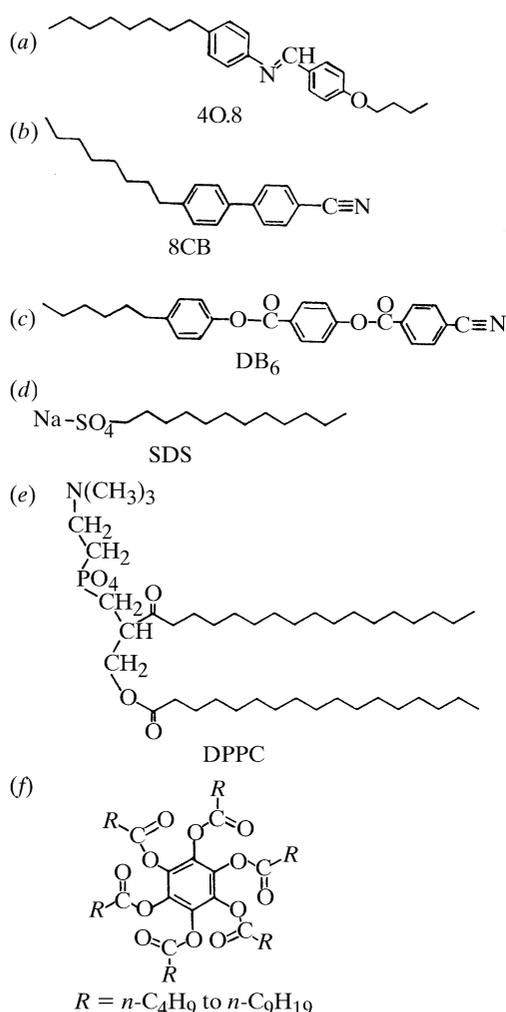


Fig. 4.4.1.3. Chemical formulae for some of the molecules that form thermotropic liquid crystals: (a) *N*-[4-(*n*-butyloxy)benzylidene]-4-*n*-octylaniline (4O.8), (b) 4'-*n*-octylbiphenyl-4-carbonitrile (8CB), (c) 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB₆); lyotropic liquid crystals: (d) sodium dodecyl sulfate, (e) 1,2-dipalmitoyl-L-phosphatidylcholine (DPPC); and a discotic liquid crystal: (f) benzenehexyl hexa-*n*-alkanoates.

that form thermotropic liquid-crystalline phases have hydrophilic and hydrophobic parts, the disparity in the affinity of these parts for either water or oil is much less and most of these molecules are relatively insoluble in water. These molecules are called thermotropic because their phase transformations are primarily studied only as a function of temperature. This is not to say that there are not numerous examples of interesting studies of the concentration dependence of phase diagrams involving mixtures of thermotropic liquid crystals.

Fig. 4.4.1.3 displays some common examples of molecules that form lyotropic and thermotropic phases. In spite of the above remarks, it is interesting to observe that different parts of typical thermotropic molecules do have some of the same features as the lyotropic molecules. For example, although the rod-like thermotropic molecules always have an alkane chain at one or both ends of a more rigid section, the chain lengths are rarely as long as those of the lyotropic molecules, and although the solubility of the parts of the thermotropic molecules, when separated, are not as disparate as those of the lyotropic molecules, they are definitely different. We suspect that this may account for the subtler features of the phase transformations between the mesomorphic phases to be discussed

below. On the other hand, the inhomogeneity of the molecule is probably not important for the nematic phase.

4.4.2. The nematic phase

The nematic phase is a fluid for which the molecules have long-range orientational order. The phase as well as its molecular origin can be most simply illustrated by treating the molecules as long thin rods. The orientation of each molecule can be described by a symmetric second-rank tensor $s_{i,j} = (n_i n_j - \delta_{i,j}/3)$, where \mathbf{n} is a unit vector along the axis of the rod (De Gennes, 1974). For disc-like molecules, such as that shown in Fig. 4.4.1.3(f), or for micellar nematic phases, \mathbf{n} is along the principal symmetry axis of either the molecule or the micelle (Lawson & Flautt, 1967). Since physical quantities such as the molecular polarizability, or the moment of inertia, transform as symmetric second-rank tensors, either one of these could be used as specific representations of the molecular orientational order. The macroscopic order, however, is given by the statistical average $S_{i,j} = \langle s_{i,j} \rangle = S(\langle n_i \rangle \langle n_j \rangle - \delta_{i,j}/3)$, where $\langle \mathbf{n} \rangle$ is a unit vector along the macroscopic symmetry axis and S is the order parameter of the nematic phase.

The microscopic origin of the phase can be understood in terms of steric constraints that occur on filling space with highly asymmetric objects such as long rods or flat discs. Maximizing the density requires some degree of short-range orientational order, and theoretical arguments can be invoked to demonstrate long-range order. Onsager presented quantitative arguments of this type to explain the nematic order observed in concentrated solutions of the long thin rods of tobacco mosaic viruses (Onsager, 1949; Lee & Meyer, 1986), and qualitatively similar ideas explain the nematic order for the shorter thermotropic molecules (Maier & Saupe, 1958, 1959).

The existence of nematic order can also be understood in terms of a phenomenological mean-field theory (De Gennes, 1969*b*, 1971; Fan & Stephen, 1970). If the free-energy difference ΔF between the isotropic and nematic phases can be expressed as an analytic function of the nematic order parameter $S_{i,j}$, one can expand $\Delta F(S_{i,j})$ as a power series in which the successive terms all transform as the identity representation of the point group of the isotropic phase, *i.e.* as scalars. The most general form is given by:

$$\Delta F(S_{i,j}) = \frac{A}{2} \sum_{ij} S_{ij} S_{ji} + \frac{B}{3} \sum_{ijk} S_{ij} S_{jk} S_{ki} + \frac{D}{4} \left| \sum_{ij} S_{ij} S_{ji} \right|^2 + \frac{D'}{4} \sum_{ijkl} S_{ij} S_{jk} S_{kl} S_{li}. \quad (4.4.2.1)$$

The usual mean-field treatment assumes that the coefficient of the leading term is of the form $A = a(T - T^*)$, where T is the absolute temperature and T^* is the temperature at which $A = 0$. Taking a , D and $D' > 0$, one can show that for either positive or negative values of B , but for sufficiently large T , the minimum value of $\Delta F = 0$ occurs for $S_{i,j} = 0$, corresponding to the isotropic phase. For $T < T^*$, ΔF can be minimized, at some negative value, for a nonzero $S_{i,j}$ corresponding to nematic order. The details of how this is derived for a tensorial order parameter can be found in the literature (De Gennes, 1974); however, the basic idea can be understood by treating $S_{i,j}$ as a scalar. If we write

$$\Delta F = \frac{1}{2} A S^2 + \frac{1}{3} B S^3 + \frac{1}{4} D S^4 = \left\{ \frac{A}{2} - \frac{B^2}{9D} \right\} S^2 + \frac{D}{4} \left(S + \frac{2B}{3D} \right)^2 \quad (4.4.2.2)$$

and if T_{NI} is defined by the condition $A = a(T_{NI} - T^*) = 2B^2/9D$, then $\Delta F = 0$ for both $S = 0$ and $S = -2B/3D$. This value for T_{NI}