4.4. Scattering from mesomorphic structures

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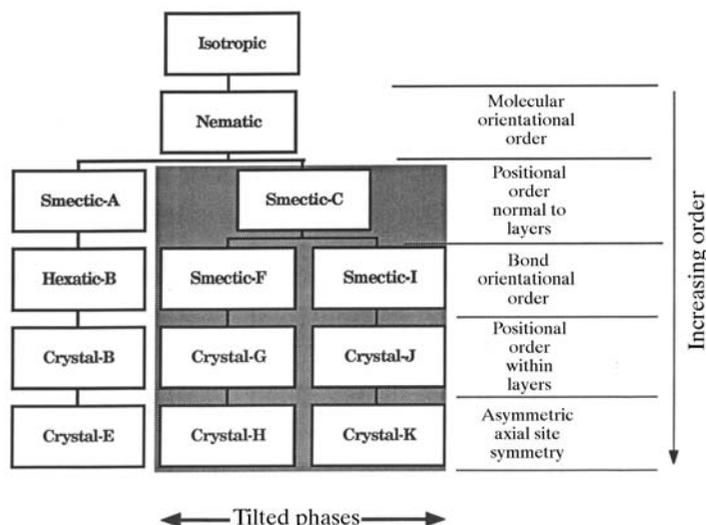
Table 4.4.1.1. *Some of the symmetry properties of the series of three-dimensional phases described in Fig. 4.4.1.1*

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

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.

* 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.*

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