

## 4. DIFFUSE SCATTERING AND RELATED TOPICS

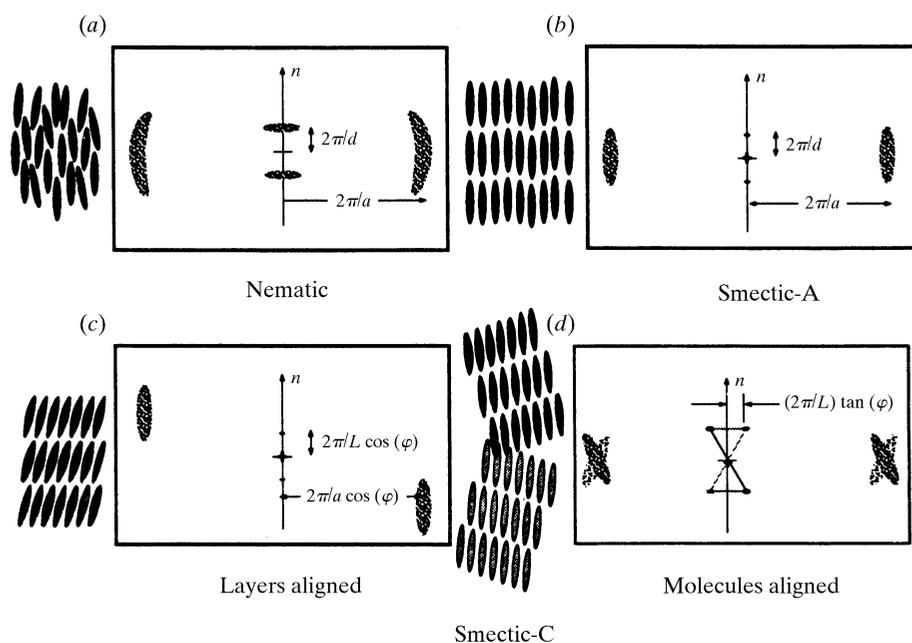


Fig. 4.4.1.2. Schematic illustration of the real-space molecular order and the scattering cross sections in reciprocal space for the: (a) nematic; (b) smectic-A; and (c), (d) smectic-C phases. The scattering cross sections are enclosed in the boxes. Part (c) indicates the smectic-C phase for an oriented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