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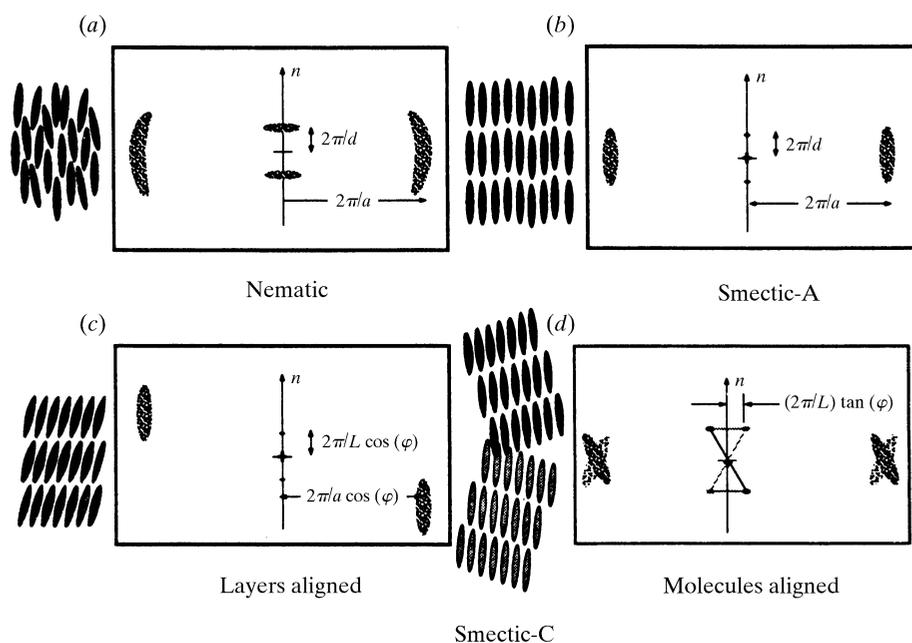
Fig. 4.4.1.2. Schematic illustration of the real-space molecular order and the scattering cross sections in reciprocal space for the: (*a*) nematic; (*b*) smectic-A; and (*c*), (*d*) smectic-C phases. The scattering cross sections are enclosed in the boxes. Part (*c*) indicates the smectic-C phase for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

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

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 ($NCCH_2CH_2CN$) 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

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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 (DB$_6$); lyotropic liquid crystals: (*d*) sodium dodecyl sulfate, (*e*) 1,2-dipalmitoyl-L-phosphatidylcholine (DPPC); and a discotic liquid crystal: (*f*) benzenehexayl 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 **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, **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

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

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

marks the transition temperature from the isotropic phase, when $A > 2B^2/9D$ and the only minimum is at $S = 0$ with $\Delta F = 0$, to the nematic case when $A < 2B^2/9D$ and the absolute minimum with $\Delta F < 0$ is slightly shifted from $S = -2B/3D$. The symmetry properties of second-rank tensors imply that there will usually be a nonvanishing value for B, and this implies that the transition from the isotropic to nematic transition will be first order with a discontinuous jump in the nematic order parameter $S_{i,j}$. Although most nematic systems are uniaxial, biaxial nematic order is theoretically possible (Freiser, 1971; Alben, 1973; Lubensky, 1987) and it has been observed in certain lyotropic nematic liquid crystals (Neto *et al.*, 1985; Hendrikx *et al.*, 1986; Yu & Saupe, 1980) and in one thermotropic system (Malthête *et al.*, 1986).

The X-ray scattering cross section of an oriented monodomain sample of the nematic phase with rod-like molecules usually exhibits a diffuse spot like that illustrated in Fig. 4.4.1.2(a), where the maximum of the cross section is along the average molecular axis $\langle \mathbf{n} \rangle$ at a value of $|\mathbf{q}| \approx 2\pi/d$, where $d \approx 20.0$ to 40.0 Å is of the order of the molecular length L. This is a precursor to the smectic-A order that develops at lower temperatures for many materials. In addition, there is a diffuse ring along the directions normal to $\langle \mathbf{n} \rangle$ at $|\mathbf{q}| \approx 2\pi/a$, where $a \approx 4.0$ Å is comparable to the average radius of the molecule. In some nematic systems, the near-neighbour correlations favour antiparallel alignment and molecular centres tend to form pairs such that the peak of the scattering cross section can actually have values anywhere in the range from $2\pi/L$ to $2\pi/2L$. There are also other cases where there are two diffuse peaks, corresponding to both $|\mathbf{q}_1| \approx 2\pi/L$ and $|\mathbf{q}_2| \approx |\mathbf{q}_1|/2$ which are precursors of a richer smectic-A morphology (Prost & Barois, 1983; Prost, 1984; Sigaud *et al.*, 1979; Wang & Lubensky, 1984; Hardouin *et al.*, 1983; Chan, Pershan *et al.*, 1985). In some cases, $|\mathbf{q}_2| \not\approx \frac{1}{2}|\mathbf{q}_1|$ and competition between the order parameters at incommensurate wavevectors gives rise to modulated phases. For the moment, we will restrict the discussion to those systems for which the order parameter is characterized by a single wavevector.

On cooling, many nematic systems undergo a second-order phase transition to a smectic-A phase and as the temperature approaches the nematic to smectic-A transition the widths of these diffuse peaks become infinitesimally small. De Gennes (1972) demonstrated that this phenomenon could be understood by analogy with the transitions from either normal fluidity to superfluidity in liquid helium or normal conductivity to superconductivity in metals. Since the electron density of the smectic-A phase is (quasi-)periodic in one dimension, he represented it by the form:

$$\rho(\mathbf{r}) = \langle \rho \rangle + \mathrm{Re}\{\Psi \exp[i(2\pi/d)z]\},$$

where d is the thickness of the smectic layers lying in the xy plane. The complex quantity $\psi = |\psi| \exp(i\varphi)$ is similar to the superfluid wavefunction except that in this analogy the amplitude $|\psi|$ describes the electron-density variations normal to the smectic layers, and the phase φ describes the position of the layers along the z axis. De Gennes proposed a mean-field theory for the transition in which the free-energy difference between the nematic and smectic-A phase $\Delta F(\Psi)$ was represented by

$$\Delta F(\psi) = \frac{A}{2}|\psi|^2 + \frac{D}{4}|\psi|^4 + \frac{E}{2}\left[\left|\left\{\frac{\partial}{\partial z} - i\left(\frac{2\pi}{d}\right)\right\}\psi\right|^2 \right.$$
$$\left. + \left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2\right]. \qquad (4.4.2.3)$$

This mean-field theory differs from the one for the isotropic to nematic transition in that the symmetry for the latter allowed a term that was cubic in the order parameter, while no such term is allowed for the nematic to smectic-A transition. In both cases, however, the

coefficient of the leading term is taken to have the form $a(T - T^*)$. If $D > 0$, without the cubic term the free energy has only one minimum when $T > T^*$ at $|\psi| = 0$, and two equivalent minima at $|\psi| = \{a(T^* - T)/D\}^{0.5}$ for $T < T^*$. On the basis of this free energy, the nematic to smectic-A transition can be second order with a transition temperature $T_{\mathrm{NA}} = T^*$ and an order parameter that varies as the square root of $(T_{\mathrm{NA}} - T)$. There are conditions that we will not discuss in detail when D can be negative. In that case, the nematic to smectic-A transition will be first order (McMillan, 1972, 1973a,b,c). McMillan pointed out that, by allowing coupling between the smectic and nematic order parameters, a more general free energy can be developed in which D is negative. McMillan's prediction that for systems in which the difference $T_{\mathrm{IN}} - T_{\mathrm{NA}}$ is small the nematic to smectic-A transition will be first order is supported by experiment (Ocko, Birgeneau & Litster, 1986; Ocko *et al.*, 1984; Thoen *et al.*, 1984). Although the mean-field theory is not quantitatively accurate, it does explain the principal qualitative features of the nematic to smectic-A transition.

The differential scattering cross section for X-rays can be expressed in terms of the Fourier transform of the density–density correlation function $\langle \rho(\mathbf{r})\rho(0) \rangle$. The expectation value is calculated from the thermal average of the order parameter that is obtained from the free-energy density $\Delta F(\psi)$. If one takes the transform

$$\Psi(\mathbf{Q}) \equiv \frac{1}{(2\pi)^3}\int \mathrm{d}^3\mathbf{r}\exp[i(\mathbf{Q}\cdot\mathbf{r})]\rho(\mathbf{r}), \qquad (4.4.2.4)$$

the free-energy density in reciprocal space has the form

$$\Delta F(\psi) = \frac{A}{2}|\psi|^2 + \frac{D}{4}|\psi|^4$$
$$+ \frac{E}{2}\{[Q_z - (2\pi/d)]^2 + Q_x^2 + Q_y^2\}|\psi|^2 \qquad (4.4.2.5)$$

and one can show that for $T > T_{\mathrm{NA}}$ the cross section obtained from the above form for the free energy is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \approx \frac{\sigma_0}{A + E\{[Q_z - (2\pi/d)]^2 + Q_x^2 + Q_y^2\}}, \qquad (4.4.2.6)$$

where the term in $|\psi|^4$ has been neglected. The mean-field theory predicts that the peak intensity should vary as $\sigma_0/A \approx 1/(T - T_{\mathrm{NA}})$ and that the half width of the peak in any direction should vary as $(A/E)^{1/2} \approx (T - T_{\mathrm{NA}})^{1/2}$. The physical interpretation of the half width is that the smectic fluctuations in the nematic phase are correlated over lengths $\xi = (E/A)^{1/2} \sim (T - T_{\mathrm{NA}})^{-1/2}$.

One of the major shortcomings of all mean-field theories is that they do not take into account the difference between the average value of the order parameter $\langle \psi \rangle$ and the instantaneous value $\psi = \langle \psi \rangle + \delta\psi$, where $\delta\psi$ represents the thermal fluctuations (Ma, 1976). The usual effect expected from theories for this type of critical phenomenon is a 'renormalization' of the various terms in the free energy such that the temperature dependence of correlation length has the form $\xi(t) \propto t^{-\nu}$, where $t \equiv (T - T^*)/T^*$, $T^* = T_{\mathrm{NA}}$ is the second-order transition temperature, and ν is expected to have some universal value that is generally not equal to 0.5. One of the major unsolved problems of the nematic to smectic-A phase transition is that the width along the scattering vector $\mathbf{q}$ varies as $1/\xi_\parallel \propto t^{\nu_\parallel}$ with a temperature dependence different from that of the width perpendicular to $\mathbf{q}$, $1/\xi_\perp \propto t^{\nu_\perp}$; also, neither $\nu_\parallel$ nor $\nu_\perp$ have the expected universal values (Lubensky, 1983; Nelson & Toner, 1981).

The correlation lengths are measured by fitting the differential scattering cross sections to the empirical form:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\sigma}{1 + (Q_z - |\mathbf{q}|)^2\xi_\parallel^2 + Q_\perp^2\xi_\perp^2 + c(Q_\perp^2\xi_\perp^2)^2}. \qquad (4.4.2.7)$$

Table 4.4.2.1. *Summary of critical exponents from X-ray scattering studies of the nematic to smectic-A phase transition*

Molecule	γ	$\nu_\parallel$	$\nu_\perp$	Reference
4O.7	1.46	0.78	0.65	(a)
$\bar{8}$S5	1.53	0.83	0.68	(b), (g)
CBOOA	1.30	0.70	0.62	(c), (d)
4O.8	1.31	0.70	0.57	(e)
8OCB	1.32	0.71	0.58	(d), (f)
$\bar{9}$S5	1.31	0.71	0.57	(b), (g)
8CB	1.26	0.67	0.51	(h), (i)
10$\bar{}$S5	1.10	0.61	0.51	(b), (g)
9CB	1.10	0.57	0.39	(g), (j)

References: (a) Garland *et al.* (1983); (b) Brisbin *et al.* (1979); (c) Djurek *et al.* (1974); (d) Litster *et al.* (1979); (e) Birgeneau *et al.* (1981); (f) Kasting *et al.* (1980); (g) Ocko *et al.* (1984); (h) Thoen *et al.* (1982); (i) Davidov *et al.* (1979); (j) Thoen *et al.* (1984).

The amplitude $\sigma \propto t^{-\gamma}$, where the measured values of γ are empirically found to be very close to the measured values for the sum $\nu_\parallel + \nu_\perp$. Most of the systems that have been measured to date have values for $\nu_\parallel > 0.66 > \nu_\perp$ and $\nu_\parallel - \nu_\perp \approx 0.1$ to 0.2. Table 4.4.2.1 lists sources of the observed values for γ, $\nu_\parallel$ and $\nu_\perp$. The theoretical and experimental studies of this pretransition effect account for a sizeable fraction of all of the liquid-crystal research in the last 15 or 20 years, and as of this writing the explanation for these two different temperature dependences remains one of the major unresolved theoretical questions in equilibrium statistical physics.

It is very likely that the origin of the problem is the QLRO in the position of the smectic layers. Lubensky attempted to deal with this by introducing a gauge transformation in such a way that the thermal fluctuations of the transformed order parameter did not have the logarithmic divergence. While this approach has been informative, it has not yet yielded an agreed-upon understanding. Experimentally, the effect of the phase can be studied in systems where there are two competing order parameters with wavevectors that are at $\mathbf{q}_2$ and $\mathbf{q}_1 \approx 2\mathbf{q}_2$ (Sigaud *et al.*, 1979; Hardouin *et al.*, 1983; Prost & Barois, 1983; Wang & Lubensky, 1984; Chan, Pershan *et al.*, 1985). On cooling, mixtures of 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB$_6$) and *N,N'*-(1,4-phenylenedimethylene)bis(4-butylaniline) (also known as terephthal-bis-butyl-aniline, TBBA) first undergo a second-order transition from the nematic to a phase that is designated as smectic-A$_1$. The various smectic-A and smectic-C morphologies will be described in more detail in the following section; however, the smectic-A$_1$ phase is characterized by a single peak at $q_1 = 2\pi/d$ owing to a one-dimensional density wave with wavelength d of the order of the molecular length L. In addition, however, there are thermal fluctuations of a second-order parameter with a period of $2L$ that give rise to a diffuse peak at $q_2 = \pi/L$. On further cooling, this system undergoes a second second-order transition to a smectic-A$_2$ phase with QLRO at $q_2 \approx \pi/L$, with a second harmonic that is exactly at $q = 2q_2 \approx 2\pi/L$. The critical scattering on approaching this transition is similar to that of the nematic to smectic-A$_1$, except that the pre-existing density wave at $q_1 = 2\pi/L$ quenches the phase fluctuations of the order parameter at the subharmonic $q_2 = \pi/L$. The measured values of $\nu_\parallel = \nu_\perp \approx 0.74$ (Chan, Pershan *et al.*, 1985) agree with those expected from the appropriate theory (Huse, 1985). A mean-field theory that describes this effect is discussed in Section 4.4.3.2 below.

It is interesting to note that even those systems for which the nematic to smectic-A transition is first order show some pretransitional lengthening of the correlation lengths $\xi_\parallel$ and $\xi_\perp$. In these cases, the apparent T^* at which the correlation lengths would diverge is lower than T_{NA} and the divergence is truncated by the first-order transition (Ocko *et al.*, 1984).

4.4.3. Smectic-A and smectic-C phases

4.4.3.1. *Homogeneous smectic-A and smectic-C phases*

In the smectic-A and smectic-C phases, the molecules organize themselves into layers, and from a naive point of view one might describe them as forming a one-dimensional periodic lattice in which the individual layers are two-dimensional liquids. In the smectic-A phase, the average molecular axis $\langle \mathbf{n} \rangle$ is normal to the smectic layers while for the smectic-C it makes a finite angle. It follows from this that the smectic-C phase has lower symmetry than the smectic-A, and the phase transition from the smectic-A to smectic-C can be considered as the ordering of a two-component order parameter, *i.e.* the two components of the projection of the molecular axis on the smectic layers (De Gennes, 1973). Alternatively, Chen & Lubensky (1976) have developed a mean-field theory in which the transition is described by a free-energy density of the Lifshitz form. This will be described in more detail below; however, it corresponds to replacing equation (4.4.2.5) for the free energy $\Delta F(\psi)$ by an expression for which the minimum is obtained when the wavevector $\mathbf{q}$, of the order parameter $\psi \propto \exp[i\mathbf{q} \cdot \mathbf{r}]$, tilts away from the molecular axis.

The X-ray cross section for the prototypical aligned monodomain smectic-A sample is shown in Fig. 4.4.1.2(b). It consists of a single sharp spot along the molecular axis at $|\mathbf{q}|$ somewhere between $2\pi/2L$ and $2\pi/L$ that reflects the QLRO along the layer normal, and a diffuse ring in the perpendicular direction at $|\mathbf{q}| \approx 2\pi/a$ that reflects the SRO within the layer. The scattering cross section for an aligned smectic-C phase is similar to that of the smectic-A except that the molecular tilt alters the intensity distribution of the diffuse ring. This is illustrated in Fig. 4.4.1.2(c) for a monodomain sample. Fig. 4.4.1.2(d) illustrates the scattering pattern for a polydomain smectic-C sample in which the molecular axis remains fixed, but where the smectic layers are randomly distributed azimuthally around the molecular axis.

The naivety of describing these as periodic stacks of two-dimensional liquids derives from the fact that the sharp spot along the molecular axis has a distinct temperature-dependent shape indicative of QLRO that distinguishes it from the Bragg peaks due to true LRO in conventional three-dimensional crystals. Landau and Peierls discussed this effect for the case of two-dimensional crystals (Landau, 1965; Peierls, 1934) and Caillé (1972) extended the argument to the mesomorphic systems.

The usual treatment of thermal vibrations in three-dimensional crystals estimates the Debye–Waller factor by integrating the thermal expectation value for the mean-square amplitude over reciprocal space (Kittel, 1963):

$$W \simeq \frac{k_B T}{c^3} \int_0^{k_D} \frac{k^{(d-1)}}{k^2} \, dk, \qquad (4.4.3.1)$$

where c is the sound velocity, $\omega_D \equiv ck_D$ is the Debye frequency and $d = 3$ for three-dimensional crystals. In this case, the integral converges and the only effect is to reduce the integrated intensity of the Bragg peak by a factor proportional to $\exp(-2W)$. For two-dimensional crystals $d = 1$, and the integral, of the form of dk/k, obtains a logarithmic divergence at the lower limit (Fleming *et al.*, 1980). A more precise treatment of thermal vibrations, necessitated by this divergence, is to calculate the relative phase of X-rays

scattered from two points in the sample a distance $|\mathbf{r}|$ apart. The appropriate integral that replaces the Debye–Waller integral is

$$\langle[u(\mathbf{r}) - u(0)]^2\rangle \simeq \frac{k_B T}{c^3} \int \sin^2(\mathbf{k} \cdot \mathbf{r}) \frac{\mathrm{d}k}{k} \mathrm{d}\{\cos(\mathbf{k} \cdot \mathbf{r})\} \quad (4.4.3.2)$$

and the divergence due to the lower limit is cut off by the fact that $\sin^2(\mathbf{k} \cdot \mathbf{r})$ vanishes as $k \to 0$. More complete analysis obtains $\langle[u(\mathbf{r}) - u(0)]^2\rangle \simeq (k_B T/c^2) \ln(|\mathbf{r}|/a)$, where $a \approx$ atomic size. If this is exponentiated, as for the Debye–Waller factor, the density–density correlation function can be shown to have the form $\langle\rho(\mathbf{r})\rho(0)\rangle \simeq |\mathbf{r}/a|^{-\eta}$, where $\eta \simeq |\mathbf{q}|^2(k_B T/c^2)$ and $|\mathbf{q}| \simeq 2\pi/a$. In place of the usual periodic density–density correlation function of three-dimensional crystals, the periodic correlations of two-dimensional crystals decay as some power of the distance. This type of positional order, in which the correlations decay as some power of the distance, is the quasi-long-range order (QLRO) that appears in Tables 4.4.1.1 and 4.4.1.2. It is distinguished from true long-range order (LRO) where the correlations continue indefinitely, and short-range order (SRO) where the positional correlations decay exponentially as in either a simple fluid or a nematic liquid crystal.

The usual prediction of Bragg scattering for three-dimensional crystals is obtained from the Fourier transform of the three-dimensional density–density correlation function. Since the correlation function is made up of periodic and random parts, it follows that the scattering cross section is made up of a δ function at the Bragg condition superposed on a background of thermal diffuse scattering from the random part. In principle, these two types of scattering can be separated empirically by using a high-resolution spectrometer that integrates all of the δ-function Bragg peak, but only a small part of the thermal diffuse scattering. Since the two-dimensional lattice is not strictly periodic, there is no formal way to separate the periodic and random parts, and the Fourier transform for the algebraic correlation function obtains a cross section that is described by an algebraic singularity of the form $|\mathbf{Q} - \mathbf{q}|^{\eta-2}$ (Gunther et al., 1980). In 1972, Caillé (Caillé, 1972) presented an argument that the X-ray scattering line shape for the one-dimensional periodicity of the smectic-A system in three dimensions has an algebraic singularity that is analogous to the line shapes from two-dimensional crystals.

In three-dimensional crystals, both the longitudinal and the shear sound waves satisfy linear dispersion relations of the form $\omega = ck$. In simple liquids, and also for nematic liquid crystals, only the longitudinal sound wave has such a linear dispersion relation. Shear sound waves are overdamped and the decay rate $1/\tau$ is given by the imaginary part of a dispersion relation of the form $\omega = i(\eta/\rho)k^2$, where η is a viscosity coefficient and ρ is the liquid density. The intermediate order of the smectic-A mesomorphic phase, between the three-dimensional crystal and the nematic, results in one of the modes for shear sound waves having the curious dispersion relation $\omega^2 = c^2k_\perp^2 k_z^2/(k_\perp^2 + k_z^2)$, where $k_\perp$ and k_z are the magnitudes of the components of the acoustic wavevector perpendicular and parallel to $\langle\mathbf{n}\rangle$, respectively (De Gennes, 1969a; Martin et al., 1972). More detailed analysis, including terms of higher order in $k_\perp^2$, obtains the equivalent of the Debye–Waller factor for the smectic-A as

$$W \simeq k_B T \int_0^{k_D} \frac{k_\perp \mathrm{d}k_\perp \mathrm{d}k_z}{Bk_z^2 + Kk_\perp^4}, \quad (4.4.3.3)$$

where B and K are smectic elastic constants, $k_\perp^2 = k_x^2 + k_y^2$, and k_D is the Debye wavevector. On substitution of $u^2 = (K/B)k_\perp^2 + k_z^2$, the integral can be manipulated into the form $\int \mathrm{d}u/u$, which diverges logarithmically at the lower limit in exactly the same way as the integral for the Debye–Waller factor of the two-dimensional crystal. The result is that the smectic-A phase has a sharp peak, described by an algebraic cusp, at the place in reciprocal space where one would expect a true δ-function Bragg cross section from a truly periodic one-dimensional lattice. In fact, the lattice is not truly periodic and the smectic-A system has only QLRO along the direction $\langle\mathbf{n}\rangle$.

X-ray scattering experiments to test this idea were carried out on one thermotropic smectic-A system, but the results, while consistent with the theory, were not adequate to provide an unambiguous proof of the algebraic cusp (Als-Nielsen et al., 1980). One of the principal difficulties was due to the fact that, when thermotropic samples are oriented in an external magnetic field in the higher-temperature nematic phase and then gradually cooled through the nematic to smectic-A phase transition, the smectic-A samples usually have mosaic spreads of the order of a fraction of a degree and this is not sufficient for detailed line-shape studies near to the peak. A second difficulty is that, in most of the thermotropic smectic-A phases that have been studied to date, only the lowest-order peak is observed. It is not clear whether this is due to a large Debye–Waller-type effect or whether the form factor for the smectic-A layer falls off this rapidly. Nevertheless, since the factor η in the exponent of the cusp $|\mathbf{Q} - \mathbf{q}|^{\eta-2}$ depends quadratically on the magnitude of the reciprocal vector $|\mathbf{q}|$, the shape of the cusp for the different orders would constitute a severe test of the theory.

Fortunately, it is common to observe multiple orders for lyotropic smectic-A systems and such an experiment, carried out on the lyotropic smectic-A system formed from a quaternary mixture of sodium dodecyl sulfate, pentanol, water and dodecane, confirmed the theoretical predictions for the Landau–Peierls effect in the smectic-A phase (Safinya, Roux et al., 1986). The problem of sample mosaic was resolved by using a three-dimensional powder. Although the conditions on the analysis are delicate, Safinya et al. demonstrated that for a perfect powder, for which the microcrystals are sufficiently large, the powder line shape does allow unambiguous determination of all of the parameters of the anisotropic line shape.

The only other X-ray study of a critical property on the smectic-A side of the transition has been a measurement of the temperature dependence of the integrated intensity of the peak. For three-dimensional crystals, the integrated intensity of a Bragg peak can be measured for samples with poor mosaic distributions, and because the differences between QLRO and true LRO are only manifest at long distances in real space, or at small wavevectors in reciprocal space, the same is true for the 'quasi-Bragg peak' of the smectic-A phase. Chan et al. measured the temperature dependence of the integrated intensity of the smectic-A peak across the nematic to smectic-A phase transition for a number of liquid crystals with varying exponents $\nu_\parallel$ and $\nu_\perp$ (Chan, Deutsch et al., 1985). For the Landau–De Gennes free-energy density (equation 4.4.2.5), the theoretical prediction is that the critical part of the integrated intensity should vary as $|t|^x$, where $x = 1 - \alpha$ when the critical part of the heat capacity diverges according to the power law $|t|^{-\alpha}$. Six samples were measured with values of α varying from 0 to 0.5. Although for samples with $\alpha \approx 0.5$ the critical intensity did vary as $x \approx 0.5$, there were systematic deviations for smaller values of α, and for $\alpha \approx 0$ the measured values of x were in the range 0.7 to 0.76. The origin of this discrepancy is not at present understood.

Similar integrated intensity measurements in the vicinity of the first-order nematic to smectic-C transition cannot easily be made in smectic-C samples since the magnetic field aligns the molecular axis $\langle\mathbf{n}\rangle$, and when the layers form at some angle φ to $\langle\mathbf{n}\rangle$ the layer normals are distributed along the full 2π of azimuthal directions around $\langle\mathbf{n}\rangle$, as shown in Fig. 4.4.1.2(d). The X-ray scattering pattern for such a sample is a partial powder with a peak-intensity distribution that forms a ring of radius $|\mathbf{q}|\sin(\varphi)$. The opening of the single spot along the average molecular axis $\langle\mathbf{n}\rangle$ into a ring can be used to study either the nematic to smectic-C or the smectic-A to smectic-C transition (Martinez-Miranda et al., 1986).

The statistical physics in the region of the phase diagram surrounding the triple point, where the nematic, smectic-A and smectic-C phases meet, has been the subject of considerable theoretical speculation (Chen & Lubensky, 1976; Chu & McMillan, 1977; Benguigui, 1979; Huang & Lien, 1981; Grinstein & Toner, 1983). The best representation of the observed X-ray scattering structure near the nematic to smectic-A, the nematic to smectic-C and the nematic/smectic-A/smectic-C (NAC) multicritical point is obtained from the mean-field theory of Chen and Lubensky, the essence of which is expressed in terms of an energy density of the form

$$\Delta F(\psi) = \frac{A}{2}|\psi|^2 + \frac{D}{4}|\psi|^4 + \frac{1}{2}[E_{\parallel}(Q_{\parallel}^2 - Q_0^2)^2 + E_{\perp}Q_{\perp}^2$$
$$+ E_{\perp\perp}Q_{\perp}^4 + E_{\perp\parallel}Q_{\perp}^2(Q_{\parallel}^2 - Q_0^2)]|\psi(\mathbf{Q})|^2, \qquad (4.4.3.4)$$

where $\psi = \psi(\mathbf{Q})$ is the Fourier component of the electron density:

$$\psi(\mathbf{Q}) \equiv \frac{1}{(2\pi)^3}\int d^3\mathbf{r}\exp[i(\mathbf{Q}\cdot\mathbf{r})]\rho(\mathbf{r}). \qquad (4.4.3.5)$$

The quantities $E_{\parallel}$, $E_{\perp\perp}$, and $E_{\perp\parallel}$ are all positive definite; however, the sign of A and $E_{\perp}$ depends on temperature. For $A > 0$ and $E_{\perp} > 0$, the free energy, including the higher-order terms, is minimized by $\psi(\mathbf{Q}) = 0$ and the nematic is the stable phase. For $A < 0$ and $E_{\perp} > 0$, the minimum in the free energy occurs for a nonvanishing value for $\psi(\mathbf{Q})$ in the vicinity of $Q_{\parallel} \approx Q_0$, corresponding to the uniaxial smectic-A phase; however, for $E_{\perp} < 0$, the free-energy minimum occurs for a nonvanishing $\psi(\mathbf{Q})$ with a finite value of $Q_{\perp}$, corresponding to smectic-C order. The special point in the phase diagram where two terms in the free energy vanish simultaneously is known as a 'Lifshitz point' (Hornreich et al., 1975). In the present problem, this occurs at the triple point where the nematic, smectic-A and smectic-C phases coexist. Although there have been other theoretical models for this transition, the best agreement between the observed and theoretical line shapes for the X-ray scattering cross sections is based on the Chen–Lubensky model. Most of the results from light-scattering experiments in the vicinity of the NAC triple point also agree with the main features predicted by the Chen–Lubensky model; however, there are some discrepancies that are not explained (Solomon & Litster, 1986).

The nematic to smectic-C transition in the vicinity of this point is particularly interesting in that, on approaching the nematic to smectic-C transition temperature from the nematic phase, the X-ray scattering line shapes first appear to be identical to the shapes usually observed on approaching the nematic to smectic-A phase transition; however, within approximately 0.1 K of the transition, they change to shapes that clearly indicate smectic-C-type fluctuations. Details of this crossover are among the strongest evidence supporting the Lifshitz idea behind the Chen–Lubensky model.

4.4.3.2. Modulated smectic-A and smectic-C phases

Previously, we mentioned that, although the reciprocal-lattice spacing $|\mathbf{q}|$ for many smectic-A phases corresponds to $2\pi/L$, where L is the molecular length, there are a number of others for which $|\mathbf{q}|$ is between π/L and $2\pi/L$ (Leadbetter, Frost, Gaughan, Gray & Mosley, 1979; Leadbetter et al., 1977). This suggests the possibility of different types of smectic-A phases in which the bare molecular length is not the sole determining factor of the period d. In 1979, workers at Bordeaux optically observed some sort of phase transition between two phases that both appeared to be of the smectic-A type (Sigaud et al., 1979). Subsequent X-ray studies indicated that in the nematic phase these materials simultaneously displayed critical fluctuations with two separate periods (Levelut et

al., 1981; Hardouin et al., 1980, 1983; Ratna et al., 1985, 1986; Chan, Pershan et al., 1985, 1986; Safinya, Varady et al., 1986; Fontes et al., 1986) and confirmed phase transitions between phases that have been designated smectic-A$_1$ with period $d \approx L$, smectic-A$_2$ with period $d \approx 2L$ and smectic-A$_d$ with period $L < d < 2L$. Stimulated by the experimental results, Prost and co-workers generalized the De Gennes mean-field theory by writing

$$\rho(\mathbf{r}) = \langle\rho\rangle + \mathrm{Re}\{\Psi_1\exp(i\mathbf{q}_1\cdot\mathbf{r}) + \Psi_2\exp(i\mathbf{q}_2\cdot\mathbf{r})\},$$

where 1 and 2 refer to two different density waves (Prost, 1979; Prost & Barois, 1983; Barois et al., 1985). In the special case that $\mathbf{q}_1 \approx 2\mathbf{q}_2$ the free energy represented by equation (4.4.2.3) must be generalized to include terms like

$$(\Psi_2^*)^2\Psi_1\exp[i(\mathbf{q}_1 - 2\mathbf{q}_2)\cdot\mathbf{r}] + \mathrm{c.c.}$$

that couple the two order parameters. Suitable choices for the relative values of the phenomenological parameters of the free energy then result in minima that correspond to any one of these three smectic-A phases. Much more interesting, however, was the observation that even if $|\mathbf{q}_1| < 2|\mathbf{q}_2|$ the two order parameters could still be coupled together if $\mathbf{q}_1$ and $\mathbf{q}_2$ were not collinear, as illustrated in Fig. 4.4.3.1(a), such that $2\mathbf{q}_1\cdot\mathbf{q}_2 = |\mathbf{q}_1|^2$. Prost et al. predicted the existence of phases that are modulated in the direction perpendicular to the average layer normal with a period $4\pi/[|\mathbf{q}_2|\sin(\varphi)] = 2\pi/|\mathbf{q}_m|$. Such a modulated phase has been observed and is designated as the smectic-Ã (Hardouin et al., 1981). Similar considerations apply to the smectic-C phases and the modulated phase is designated smectic-C̃; (Hardouin et al., 1982; Huang et al., 1984; Safinya, Varady et al., 1986).

4.4.3.3. Surface effects

The effects of surfaces in inducing macroscopic alignment of mesomorphic phases have been important both for technological applications and for basic research (Sprokel, 1980; Gray & Goodby, 1984). Although there are a variety of experimental techniques that are sensitive to mesomorphic surface order (Beaglehole, 1982; Faetti & Palleschi, 1984; Faetti et al., 1985; Gannon & Faber, 1978; Miyano, 1979; Mada & Kobayashi, 1981; Guyot-Sionnest et al.,
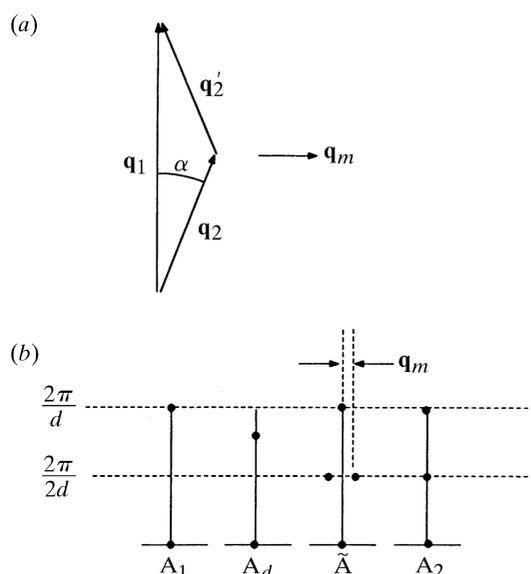
Fig. 4.4.3.1. (a) Schematic illustration of the necessary condition for coupling between order parameters when $|\mathbf{q}_2| < 2|\mathbf{q}_1|$; $|\mathbf{q}| = (|\mathbf{q}_2|^2 - |\mathbf{q}_1|^2)^{1/2} = |\mathbf{q}_1|\sin(\alpha)$. (b) Positions of the principal peaks for the indicated smectic-A phases.

1986), it is only recently that X-ray scattering techniques have been applied to this problem. In one form or another, all of the techniques for obtaining surface specificity in an X-ray measurement make use of the fact that the average interaction between X-rays and materials can be treated by the introduction of a dielectric constant $\varepsilon \approx 1 - (4\pi\rho e^2/m\omega^2) = 1 - \rho r_e \lambda^2/\pi$, where ρ is the electron density, r_e is the classical radius of the electron, and ω and λ are the angular frequency and the wavelength of the X-ray. Since $\varepsilon < 1$, X-rays that are incident at a small angle to the surface θ_0 will be refracted in the material toward a smaller angle $\theta_T \approx (\theta_0^2 - \theta_c^2)^{1/2}$, where the 'critical angle' $\theta_c \approx (\rho r_e \lambda^2/\pi)^{1/2} \approx 0.003$ rad ($\approx 0.2°$) for most liquid crystals (Warren, 1968). Although this is a small angle, it is at least two orders of magnitude larger than the practical angular resolution available in modern X-ray spectrometers (Als-Nielsen et al., 1982; Pershan & Als-Nielsen, 1984; Pershan et al., 1987). One can demonstrate that for many conditions the specular reflection $R(\theta_0)$ is given by

$$R(\theta_0) \approx R_F(\theta_0)|\rho^{-1} \int \mathrm{d}z \exp(-iQz)\langle\partial\rho/\partial z\rangle|^2,$$

where $Q \equiv (4\pi/\lambda)\sin(\theta_0)$, $\langle\partial\rho/\partial z\rangle$ is the normal derivative of the electron density averaged over a region in the surface that is defined by the coherence area of the incident X-ray, and

$$R_F(\theta_0) \approx \left(\frac{\theta_0 - \sqrt{\theta_0^2 - \theta_c^2}}{\theta_0 + \sqrt{\theta_0^2 - \theta_c^2}}\right)^2$$

is the Fresnel reflection law that is calculated from classical optics for a flat interface between the vacuum and a material of dielectric constraint ε. Since the condition for specular reflection, that the incident and scattered angles are equal and in the same plane, requires that the scattering vector $\mathbf{Q} = \hat{z}(4\pi/\lambda)\sin(\theta_0)$ be parallel to the surface normal, it is quite practical to obtain, for flat surfaces, an unambiguous separation of the specular reflection signal from all other scattering events.

Fig. 4.4.3.2(a) illustrates the specular reflectivity from the free nematic–air interface for the liquid crystal 4′-octyloxybiphenyl-4-carbonitrile (8OCB) 0.050 K above the nematic to smectic-A phase-transition temperature (Pershan & Als-Nielsen, 1984). The dashed line is the Fresnel reflection $R_F(\theta_0)$ in units of $\sin(\theta_0)/\sin(\theta_c)$,
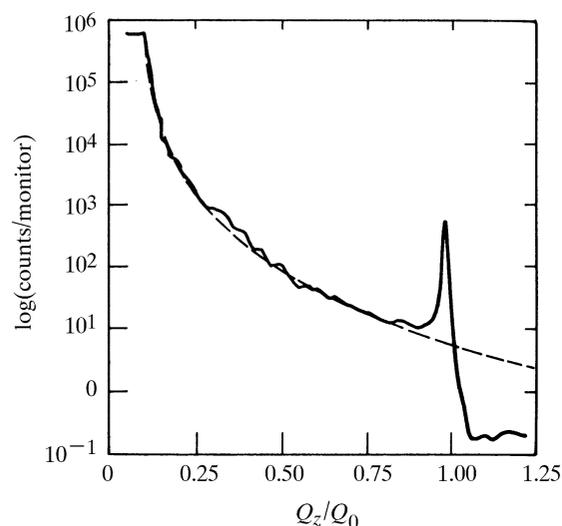
where the peak at $\theta_c = 1.39°$ corresponds to surface-induced smectic order in the nematic phase: i.e. the selection rule for specular reflection has been used to separate the specular reflection from the critical scattering from the bulk. Since the full width at half maximum is exactly equal to the reciprocal of the correlation length for critical fluctuations in the bulk, $2/\xi_\parallel$ at all temperatures from $T - T_{\mathrm{NA}} \approx 0.006$ K up to values near to the nematic to isotropic transition, $T - T_{NA} \approx 3.0$ K, it is clear this is an example where the gravitationally induced long-range order in the surface position has induced mesomorphic order that has long-range correlations parallel to the surface. Along the surface normal, the correlations have only the same finite range as the bulk critical fluctuations. Studies on a number of other nematic (Gransbergen et al., 1986; Ocko et al., 1987) and isotropic surfaces (Ocko, Braslau et al., 1986) indicate features that are specific to local structure of the surface.

4.4.4. Phases with in-plane order

Although the combination of optical microscopy and X-ray scattering studies on unoriented samples identified most of the mesomorphic phases, there remain a number of subtle features that were only discovered by spectra from well oriented samples (see the extensive references contained in Gray & Goodby, 1984). Nematic phases are sufficiently fluid that they are easily oriented by either external electric or magnetic fields, or surface boundary conditions, but similar alignment techniques are not generally successful for the more ordered phases because the combination of strains induced by thermal expansion and the enhanced elasticity that accompanies the order creates defects that do not easily anneal. Other defects that might have been formed during initial growth of the phase also become trapped and it is difficult to obtain well oriented samples by cooling from a higher-temperature aligned phase. Nevertheless, in some cases it has been possible to obtain crystalline-B samples with mosaic spreads of the order of a fraction of a degree by slowing cooling samples that were aligned in the nematic phase. In other cases, mesomorphic phases were obtained by heating and melting single crystals that were grown from solution (Benattar et al., 1979; Leadbetter, Mazid & Malik, 1980).

Moncton & Pindak (1979) were the first to realize that X-ray scattering studies could be carried out on the freely suspended films that Friedel (1922) described in his classical treatise on liquid crystals. These samples, formed across a plane aperture (i.e. approximately 1 cm in diameter) in the same manner as soap bubbles, have mosaic spreads that are an order of magnitude smaller. The geometry is illustrated in Fig. 4.4.4.1(a). The substrate in which the aperture is cut can be glass (e.g. a microscope cover slip), steel or copper sheeting, etc. A small amount of the material, usually in the high-temperature region of the smectic-A phase, is spread around the outside of an aperture that is maintained at the necessary temperature, and a wiper is used to drag some of the material across the aperture. If a stable film is successfully drawn, it is detected optically by its finite reflectivity. In particular, against a dark background and with the proper illumination it is quite easy to detect the thinnest free films.

In contrast to conventional soap films that are stabilized by electrostatic effects, smectic films are stabilized by their own layer structure. Films as thin as two molecular layers can be drawn and studied for weeks (Young et al., 1978). Thicker films of the order of thousands of layers can also be made and, with some experience in depositing the raw material around the aperture and the speed of drawing, it is possible to draw films of almost any desired thickness (Moncton et al., 1982). For films thinner than approximately 20 to 30 molecular layers (i.e. 600 to 1000 Å), the thickness is determined from the reflected intensity of a small helium–neon laser. Since the

Fig. 4.4.3.2. Specular reflectivity of ∼8 keV X-rays from the air–liquid interface of the nematic liquid crystal 8OCB 0.05 K above the nematic to smectic-A transition temperature. The dashed line is the Fresnel reflection law as described in the text.
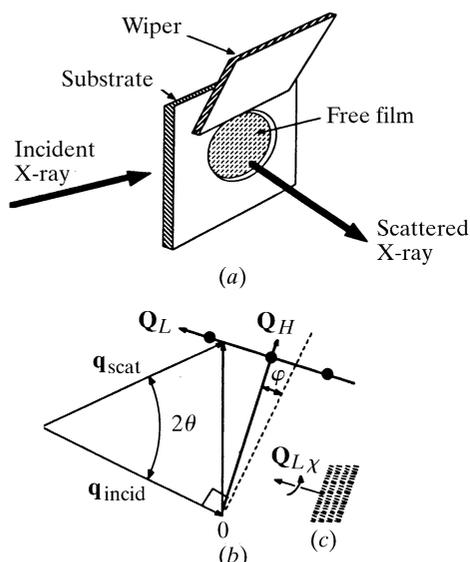
Fig. 4.4.4.1. (*a*) Schematic illustration of the geometry and (*b*) kinematics of X-ray scattering from a freely suspended smectic film. The insert (*c*) illustrates the orientation of the film in real space corresponding to the reciprocal-space kinematics in (*b*). If the angle $\varphi = \theta$, the film is oriented such that the scattering vector is parallel to the surface of the film, *i.e.* parallel to the smectic layers. A 'Q_L scan' is taken by simultaneous adjustment of φ and 2θ to keep $(4\pi/\lambda)\sin(\theta)\cos(\theta - \varphi) = (4\pi/\lambda)\sin(\theta_{100})$, where θ_{100} is the Bragg angle for the 100 reflection. The different in-plane Bragg reflections can be brought into the scattering plane by rotation of the film by the angle χ around the film normal.

Fig. 4.4.4.2. Typical Q_L scans from the crystalline-B phases of (*a*) a free film of 7O.7, displayed on a logarithmic scale to illustrate the reduced level of the diffuse scattering relative to the Bragg reflection and (*b*) a bulk sample of 4O.8 oriented by a magnetic field.

reflected intensities for films of 2, 3, 4, 5, . . . layers are in the ratio of 4, 9, 16, 25, . . ., the measurement can be calibrated by drawing and measuring a reasonable number of thin films. The most straightforward method for thick films is to measure the ellipticity of the polarization induced in laser light transmitted through the film at an oblique angle (Collett, 1983; Collett *et al.*, 1985); however, a subtler method that makes use of the colours of white light reflected from the films is also practical (Sirota, Pershan, Sorensen & Collett, 1987). In certain circumstances, the thickness can also be measured using the X-ray scattering intensity in combination with one of the other methods.

Fig. 4.4.4.1 illustrates the scattering geometry used with these films. Although recent unpublished work has demonstrated the possibility of a reflection geometry (Sorensen, 1987), all of the X-ray scattering studies to be described here were performed in transmission. Since the in-plane molecular spacings are typically between 4 and 5 Å, while the layer spacing is closer to 30 Å, it is difficult to study the 00*L* peaks in this geometry.

Fig. 4.4.4.2 illustrates the difference between X-ray scattering spectra taken on a bulk crystalline-B sample of *N*-[4-(*n*-butyloxy)-benzylidene]-4-*n*-octylaniline (4O.8) that was oriented in an external magnetic field while in the nematic phase and then cooled through the smectic-A phase into the crystalline-B phase (Aeppli *et al.*, 1981), and one taken on a thick freely suspended film of *N*-[4-(*n*-heptyloxy)benzylidene]-4-*n*-heptylaniline (7O.7) (Collett *et al.*, 1982, 1985). Note that the data for 7O.7 are plotted on a semi-logarithmic scale in order to display simultaneously both the Bragg peak and the thermal diffuse background. The scans are along the Q_L direction, at the appropriate value of Q_H to intersect the peaks associated with the intralayer periodicity. In both cases, the widths of the Bragg peaks are essentially determined by the sample mosaicity and as a result of the better alignment the ratio of the
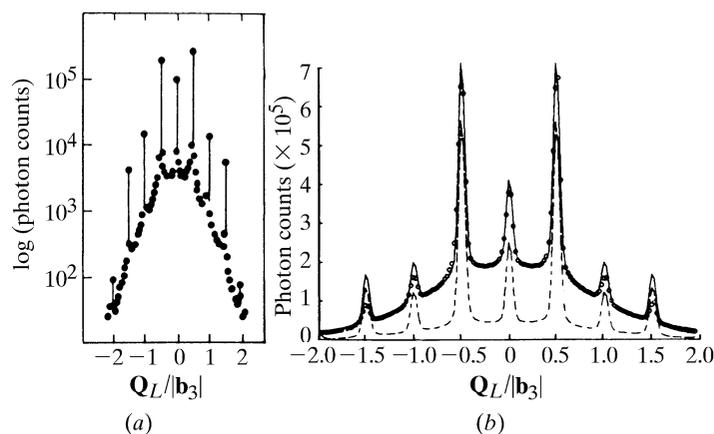
thermal diffuse background to the Bragg peak is nearly an order of magnitude smaller for the free film sample.

4.4.4.1. *Hexatic phases in two dimensions*

The hexatic phase of matter was first proposed independently by Halperin & Nelson (Halperin & Nelson 1978; Nelson & Halperin 1979) and Young (Young, 1979) on the basis of theoretical studies of the melting process in two dimensions. Following work by Kosterlitz & Thouless (1973), they observed that since the interaction energy between pairs of dislocations in two dimensions decreases logarithmically with their separation, the enthalpy and the entropy terms in the free energy have the same functional dependence on the density of dislocations. It follows that the free-energy difference between the crystalline and hexatic phase has the form $\Delta F = \Delta H - T\Delta S \approx T_c S(\rho) - T S(\rho) = S(\rho)(T_c - T)$, where $S(\rho) \approx \rho\log(\rho)$ is the entropy as a function of the density of dislocations ρ and T_c is defined such that $T_c S(\rho)$ is the enthalpy. Since the prefactor of the enthalpy term is independent of temperature while that of the entropy term is linear, there will be a critical temperature, T_c, at which the sign of the free energy changes from positive to negative. For temperatures greater than T_c, the entropy term will dominate and the system will be unstable against the spontaneous generation of dislocations. When this happens, the two-dimensional crystal, with positional QLRO, but true long-range order in the orientation of neighbouring atoms, can melt into a new phase in which the positional order is short range, but for which there is QLRO in the orientation of the six neighbours surrounding any atom. The reciprocal-space structures for the two-dimensional crystal and hexatic phases are illustrated in Figs. 4.4.4.3(*b*) and (*c*), respectively. That of the two-dimensional solid consists of a hexagonal lattice of sharp rods (*i.e.* algebraic line shapes in the plane of the crystal). For a finite size sample, the reciprocal-space structure of the two-dimensional hexatic phase is a hexagonal lattice of diffuse rods and there are theoretical predictions for the temperature dependence of the in-plane line shapes (Aeppli & Bruinsma, 1984). If the sample were of infinite size, the QLRO of the orientation would spread the six spots continuously around a circular ring, and the pattern would be indistinguishable from that of a well correlated liquid, *i.e.* Fig. 4.4.4.3(*a*). The extent of the patterns along the rod corresponds to the molecular form factor. Figs. 4.4.4.3(*a*), (*b*) and (*c*) are drawn on the assumption that the molecules are normal to the two-

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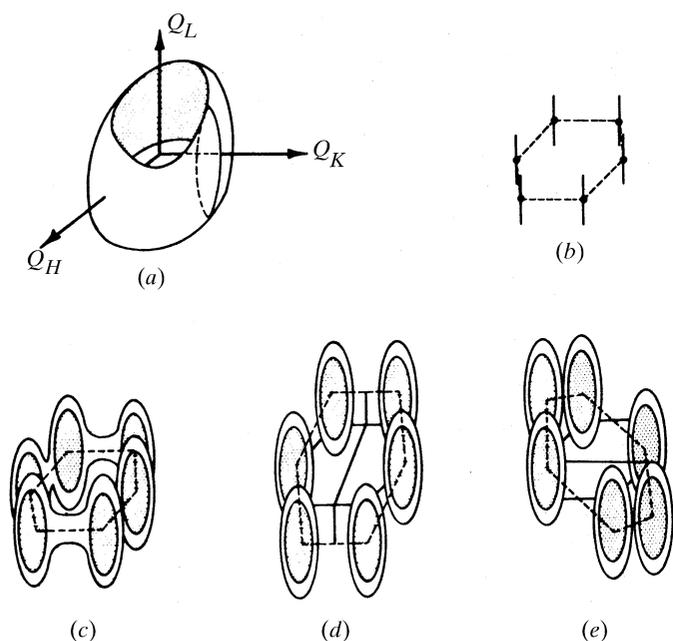
Fig. 4.4.4.3. Scattering intensities in reciprocal space from two-dimensional: (*a*) liquid; (*b*) crystal; (*c*) normal hexatic; and tilted hexatics in which the tilt is (*d*) towards the nearest neighbours as for the smectic-I or (*e*) between the nearest neighbours as for the smectic-F. The thin rods of scattering in (*b*) indicate the singular cusp for peaks with algebraic line shapes in the *HK* plane.

dimensional plane of the phase. If the molecules are tilted, the molecular form factor for long thin rod-like molecules will shift the intensity maxima as indicated in Figs. 4.4.4.3(*d*) and (*e*). The phase in which the molecules are normal to the two-dimensional plane is the two-dimensional *hexatic-B phase*. If the molecules tilt towards the position of their nearest neighbours (in real space), or in the direction that is between the lowest-order peaks in reciprocal space, the phase is the two-dimensional *smectic-I*, Fig. 4.4.4.3(*d*). The other tilted phase, for which the tilt direction is between the nearest neighbours in real space or in the direction of the lowest-order peaks in reciprocal space, is the *smectic-F*, Fig. 4.4.4.3(*e*).

Although theory (Halperin & Nelson, 1978; Nelson & Halperin, 1979; Young, 1979) predicts that the two-dimensional crystal can melt into a hexatic phase, it does not say that it must happen, and the crystal can melt directly into a two-dimensional liquid phase. Obviously, the hexatic phases will also melt into a two-dimensional liquid phase. Fig. 4.4.4.3(*a*) illustrates the reciprocal-space structure for the two-dimensional liquid in which the molecules are normal to the two-dimensional surface. Since the longitudinal (*i.e.* radial) width of the hexatic spot could be similar to the width that might be expected in a well correlated fluid, the direct X-ray proof of the transition from the hexatic-B to the normal liquid requires a hexatic sample in which the domains are sufficiently large that the sample is not a two-dimensional powder. On the other hand, the elastic constants must be sufficiently large that the QLRO does not smear the six spots into a circle. The radial line shape of the powder pattern of the hexatic-B phase can also be subtly different from that of the liquid and this is another possible way that X-ray scattering can detect melting of the hexatic-B phase (Aeppli & Bruinsma, 1984).

Changes that occur on the melting of the tilted hexatics, *i.e.* smectic-F and smectic-I, are usually easier to detect and this will be discussed in more detail below. On the other hand, there is a fundamental theoretical problem concerning the way of understanding the melting of the tilted hexatics. These phases actually have the same symmetry as the two-dimensional tilted fluid phase, *i.e.* the smectic-C. In two dimensions they all have QLRO in the tilt orientation, and since the simplest phenomenological argument says that there is a linear coupling between the tilt order and the near-neighbour positional order (Nelson & Halperin, 1980; Bruinsma & Nelson, 1981), it follows that the QLRO of the smectic-C tilt should induce QLRO in the near-neighbour positional order. Thus, by the usual arguments, if there is to be a phase transition between the smectic-C and one of the tilted hexatic phases, the transition must be a first-order transition (Landau & Lifshitz, 1958). This is analogous to the three-dimensional liquid-to-vapour transition which is first order up to a critical point, and beyond the critical point there is no real phase transition.

4.4.4.2. *Hexatic phases in three dimensions*

Based on both this theory and the various X-ray scattering patterns that had been reported in the literature (Gray & Goodby, 1984), Litster & Birgeneau (Birgeneau & Litster, 1978) suggested that some of the three-dimensional systems that were previously identified as mesomorphic were actually three-dimensional hexatic systems. They observed that it is not theoretically consistent to propose that the smectic phases are layers of two-dimensional crystals randomly displaced with respect to each other since, in thermal equilibrium, the interactions between layers of two-dimensional crystals must necessarily cause the layers to lock together to form a three-dimensional crystal.* On the other hand, if the layers were two-dimensional hexatics, then the interactions would have the effect of changing the QLRO of the hexagonal distribution of neighbours into the true long-range-order orientational distribution of the three-dimensional hexatic. In addition, interactions between layers in the three-dimensional hexatics can also result in interlayer correlations that would sharpen the width of the diffuse peaks in the reciprocal-space direction along the layer normal.

4.4.4.2.1. *Hexatic-B*

Although Leadbetter, Frost & Mazid (1979) had remarked on the different types of X-ray structures that were observed in materials identified as 'smectic-B', the first proof for the existence of the hexatic-B phase of matter was the experiment by Pindak *et al.* (1981) on thick freely suspended films of the liquid crystal *n*-hexyl 4′-pentyloxybiphenyl-4-carboxylate (65OBC). A second study on free films of the liquid crystal *n*-butyl 4′-*n*-hexyloxybiphenyl-4-carboxylate (46OBC) demonstrated that, as the hexatic-B melts into the smectic-A phase, the position and the in-plane width of the X-ray scattering peaks varied continuously. In particular, the in-plane correlation length evolved continuously from 160 Å, nearly 10 K below the hexatic to smectic-A transition, to only 17 Å, a few degrees above. Similar behaviour was also observed in a film only two layers thick (Davey *et al.*, 1984). Since the observed width of the peak along the layer normal corresponded to the molecular form factor, these systems have negligible interlayer correlations.

4.4.4.2.2. *Smectic-F, smectic-I*

In contrast to the hexatic-B phase, the principal reciprocal-space features of the smectic-F phase were clearly determined before the theoretical work that proposed the hexatic phase. Demus *et al.* (1971) identified a new phase in one material, and subsequent X-ray studies by Leadbetter and co-workers (Leadbetter, Mazid & Richardson, 1980; Leadbetter, Gaughan *et al.*, 1979; Gane &

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* Prior to the paper by Birgeneau & Litster, it was commonly believed that some of the smectic phases consisted of uncorrelated stacks of two-dimensional crystals.
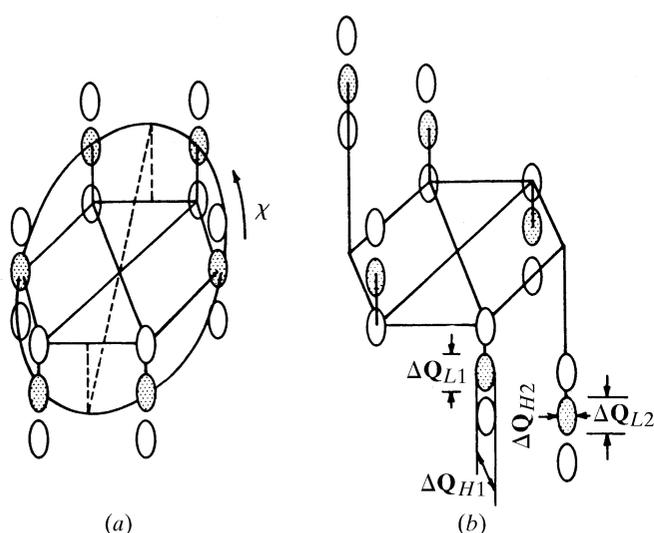
Fig. 4.4.4.4. Scattering intensities in reciprocal space from three-dimensional tilted hexatic phases: (*a*) the smectic-I and (*b*) the smectic-F. The variation of the intensity along the Q_L direction indicates interlayer correlations that are absent in Figs. 4.4.4.1(*d*) and (*e*). The peak widths $\Delta\mathbf{Q}_{L1,2}$ and $\Delta\mathbf{Q}_{H1,2}$ correspond to the four inequivalent widths in the smectic-F phase. Similar inequivalent widths exist for the smectic-I phase. The circle through the shaded points in (*a*) indicates the reciprocal-space scan that directly measures the hexatic order. A similar scan in the smectic-C phase would have intensity independent of χ.

Fig. 4.4.4.5. The phase diagram for free films of 7O.7 as a function of thickness and temperature. The phases *ABAB*, *AAA*, OR_{m1}, OR_{m2}, OR'_{m1}, *M* and *ABAB* are all crystalline-B with varying interlayer stacking, or long-wavelength modulations; CrG, SmF and SmI are crystalline-G, smectic-F and smectic-I, respectively (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987; Sirota, Pershan, Sorensen & Collett, 1987).

Leadbetter, 1981) and by Benattar and co-workers (Benattar *et al.*, 1978, 1980, 1983; Guillon *et al.*, 1986) showed it to have the reciprocal-space structure illustrated in Fig. 4.4.4.4(*b*). There are interlayer correlations in the three-dimensional smectic-F phases, and as a consequence the reciprocal-space structure has maxima along the diffuse rods. Benattar *et al.* (1979) obtained monodomain smectic-F samples of the liquid crystal *N,N'*-(1,4-phenylenedimethylene)bis(4-*n*-pentylaniline) by melting a single crystal that was previously precipitated from solution. One of the more surprising results of this work was the demonstration that the near-neighbour packing was very close to what would be expected from a model in which rigid closely packed rods were simply tilted away from the layer normal. In view of the facts that the molecules are clearly not cylindrical, and that the molecular tilt indicates that the macroscopic symmetry has been broken, it would have been reasonable to expect significant deviations from local hexagonal symmetry when the system is viewed along the molecular axis. The fact that this is not the case indicates that this phase has a considerable amount of rotational disorder around the long axis of the molecules.

Other important features of the smectic-F phase are, firstly, that the local molecular packing is identical to that of the tilted crystalline-G phase (Benattar *et al.*, 1979; Sirota *et al.*, 1985; Guillon *et al.*, 1986). Secondly, there is considerable temperature dependence of the widths of the various diffuse peaks. Fig. 4.4.4.4(*b*) indicates the four inequivalent line widths that Sirota and co-workers measured in freely suspended films of the liquid crystal *N*-[4-(*n*-heptyloxy)benzylidene]-4-*n*-heptyl aniline (7O.7). Parenthetically, bulk samples of this material do not have a smectic-F phase; however, the smectic-F is observed in freely suspended films as thick as ~ 200 layers. Fig. 4.4.4.5 illustrates the thickness–temperature phase diagram of 7O.7 between 325 and 342 K (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987). Bulk samples and thick films have a first-order transition from the crystalline-B to the smectic-C at 342 K. Thinner films indicate a surface phase above

342 K that will be discussed below. Furthermore, although there is a strong temperature dependence of the widths of the diffuse scattering peaks, the widths are independent of film thickness. This demonstrates that, although the free film boundary conditions have stabilized the smectic-F phase, the properties of the phase are not affected by the boundaries. Finally, the fact that the widths $\Delta\mathbf{Q}_{L1}$ and $\Delta\mathbf{Q}_{L2}$ along the **L** direction and $\Delta\mathbf{Q}_{H1}$ and $\Delta\mathbf{Q}_{H2}$ along the in-plane directions are not equal indicates that the correlations are very anisotropic (Brock *et al.*, 1986; Sirota *et al.*, 1985). We will discuss one possible model for these properties after presenting other data on thick films of 7O.7. From the fact that the positions of the intensity maxima for the diffuse spots of the smectic-F phase of 7O.7 correspond exactly to the positions of the Bragg peaks in the crystalline-G phase, we learn that the local molecular packing must be identical in the two phases. The major difference between the crystalline-G and the tilted hexatic smectic-F phase is that, in the latter, defects destroy the long-range positional order of the former (Benattar *et al.*, 1979; Sirota *et al.*, 1985). Although this is consistent with the existing theoretical model that attributes hexatic order to a proliferation of unbounded dislocations, it is not obvious that the proliferation is attributable to the same Kosterlitz–Thouless mechanism that Halperin & Nelson and Young discussed for the transition from the two-dimensional crystal to the hexatic phase. We will say more on this point below.

The only identified difference between the two tilted hexatic phases, the smectic-F and the smectic-I, is the direction of the molecular tilt relative to the near-neighbour positions. For the smectic-I, the molecules tilt towards one of the near neighbours, while for the smectic-F they tilt between the neighbours (Gane & Leadbetter, 1983). There are a number of systems that have both smectic-I and smectic-F phases, and in all cases of which we are aware the smectic-I is the higher-temperature phase (Gray & Goodby, 1984; Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987).

Optical studies of freely suspended films of materials in the *n*O.*m* series indicated tilted surface phases at temperatures for which the bulk had uniaxial phases (Farber, 1985). As mentioned above,

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X-ray scattering studies of 7O.7 demonstrated that the smectic-F phase set in for a narrow temperature range in films as thick as 180 layers, and that the temperature range increases with decreasing layer number. For films of the order of 25 layers thick, the smectic-I phase is observed at approximately 334 K, and with decreasing thickness the temperature range for this phase also increases. Below approximately 10 to 15 layers, the smectic-I phase extends up to ~ 342 K where bulk samples undergo a first-order transition from the crystalline-B to the smectic-C phase. Synchrotron X-ray scattering experiments show that, in thin films (five layers for example), the homogeneous smectic-I film undergoes a first-order transition to one in which the two surface layers are smectic-I and the three interior layers are smectic-C (Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987). The fact that two phases with the same symmetry can coexist in this manner tells us that in this material there is some important microscopic difference between them. This is reaffirmed by the fact that the phase transition from the surface smectic-I to the homogeneous smectic-C phase has been observed to be first order (Sorensen *et al.*, 1987).

In contrast to 7O.7, Birgeneau and co-workers found that in racemic 4-(2-methylbutyl)phenyl 4′-octyloxybiphenyl-4-carboxy-late (8OSI) (Brock *et al.*, 1986), the X-ray structure of the smectic-I phase evolves continuously into that of the smectic-C. By applying a magnetic field to a thick freely suspended sample, Brock *et al.* were able to obtain a large monodomain sample. They measured the X-ray scattering intensity around the circle in the reciprocal-space plane shown in Fig. 4.4.4.4(*b*) that passes through the peaks. For higher temperatures, when the sample is in the smectic-C phase, the intensity is essentially constant around the circle; however, on cooling, it gradually condenses into six peaks, separated by 60°. The data were analysed by expressing the intensity as a Fourier series of the form

$$S(\chi) = I_0 \left[\frac{1}{2} + \sum_{n=1}^{\infty} C_{6n} \cos 6n(90° - \chi) \right] + I_B,$$

where I_0 fixes the absolute intensity and I_B fixes the background. The temperature variation of the coefficients scaled according to the relation $C_{6n} = C_6^{\sigma n}$ where the empirical relation $\sigma_n = 2.6(n - 1)$ is in good agreement with a theoretical form predicted by Aharony *et al.* (1986). The only other system in which this type of measurement has been made was the smectic-C phase of 7O.7 (Collett, 1983). In that case, the intensity around the circle was constant, indicating the absence of any tilt-induced bond orientational order (Aharony *et al.*, 1986).

It would appear that the near-neighbour molecular packing of the smectic-I and the crystalline-J phases is the same, in just the same way as for the packing of the smectic-F and the crystalline-G phases. The four smectic-I widths analogous to those illustrated in Fig. 4.4.4.4(*a*) are, like that of the smectic-F, both anisotropic and temperature dependent (Sirota *et al.*, 1985; Sirota, Pershan, Sorensen & Collett, 1987; Brock *et al.*, 1986; Benattar *et al.*, 1979).

4.4.4.3. *Crystalline phases with molecular rotation*

4.4.4.3.1. *Crystal-B*

Recognition of the distinction between the hexatic-B and crystalline-B phases provided one of the more important keys to understanding the ordered mesomorphic phases. There are a number of distinct phases called crystalline-B that are all true three-dimensional crystals, with resolution-limited Bragg peaks (Moncton & Pindak, 1979; Aeppli *et al.*, 1981). The feature common to them all is that the average molecular orientation is normal to the layers, and within each layer the molecules are distributed on a triangular lattice. In view of the 'blade-like' shape of the molecule, the hexagonal site symmetry implies that the

molecules must be rotating rapidly (Levelut & Lambert, 1971; Levelut, 1976; Richardson *et al.*, 1978). We have previously remarked that this apparent rotational motion characterizes all of the phases listed in Table 4.4.1.1 except for the crystalline-E, -H and -K. In the most common crystalline-B phase, adjacent layers have *ABAB*-type stacking (Leadbetter, Gaughan *et al.*, 1979; Leadbetter, Mazid & Kelly, 1979). High-resolution studies on well oriented samples show that in addition to the Bragg peaks the crystalline-B phases have rods of relatively intense diffuse scattering distributed along the 10*L* Bragg peaks (Moncton & Pindak, 1979; Aeppli *et al.*, 1981). The widths of these rods in the reciprocal-space direction, parallel to the layers, are very sharp, and without a high-resolution spectrometer their widths would appear to be resolution limited. In contrast, along the reciprocal-space direction normal to the layers, their structure corresponds to the molecular form factor.

If the intensity of the diffuse scattering can be represented as proportional to $\langle \mathbf{Q} \cdot \mathbf{u} \rangle^2$, where $\mathbf{u}$ describes the molecular displacement, the fact that there is no rod of diffuse scattering through the 00*L* peaks indicates that the rods through the 10*L* peaks originate from random disorder in 'sliding' displacements of adjacent layers. It is likely that these displacements are thermally excited phonon vibrations; however, we cannot rule out some sort of non-thermal static defect structure. In any event, assuming this diffuse scattering originates in a thermal vibration for which adjacent layers slide over one another with some amplitude $\langle \mathbf{u}^2 \rangle^{1/2}$, and assuming strong coupling between this shearing motion and the molecular tilt, we can define an angle $\varphi = \tan^{-1}(\langle \mathbf{u}^2 \rangle^{1/2}/d)$, where d is the layer thickness. The observed diffuse intensity corresponds to angles φ between 3 and 6° (Aeppli *et al.*, 1981).

Leadbetter and co-workers demonstrated that in the *n*O.*m* series various molecules undergo a series of restacking transitions and that crystalline-B phases exist with *ABC* and *AAA* stacking as well as the more common *ABAB* (Leadbetter, Mazid & Richardson 1980; Leadbetter, Mazid & Kelly, 1979). Subsequent high-resolution studies on thick freely suspended films revealed that the restacking transitions were actually subtler, and in 7O.7, for example, on cooling the hexagonal *ABAB* phase one observes an orthorhombic and then a monoclinic phase before the hexagonal *AAA* (Collett *et al.*, 1982, 1985). Furthermore, the first transition from the hexagonal *ABAB* to the monoclinic phase is accompanied by the appearance of a relatively long wavelength modulation within the plane of the layers. The polarization of this modulation is along the layer normal, or orthogonal to the polarization of the displacements that gave rise to the rods of thermal diffuse scattering (Gane & Leadbetter, 1983).

It is also interesting to note that the *AAA* simple hexagonal structure does not seem to have been observed outside liquid-crystalline materials and, were it not for the fact that the crystalline-B hexagonal *AAA* is always accompanied by long wavelength modulations, it would be the only case of which we are aware.

Figs. 4.4.4.6(*a*) and (*b*) illustrate the reciprocal-space positions of the Bragg peaks (dark dots) and modulation-induced side bands (open circles) for the unmodulated hexagonal *ABAB* and the modulated orthorhombic phase (Collett *et al.*, 1984). For convenience, we only display one 60° sector. Hirth *et al.* (1984) explained how both the reciprocal-space structure and the modulation of the orthorhombic phase could result from an ordered array of partial dislocations. They were not, however, able to provide a specific model for the microscopic driving force for the transition. Sirota, Pershan & Deutsch (1987) proposed a variation of the Hirth model in which the dislocations pair up to form a wall of dislocation dipoles such that within the wall the local molecular packing is essentially identical to the packing in the crystalline-G phase that appears at temperatures just below the crystalline-B phase. This model explains: (1) the macroscopic symmetry of the
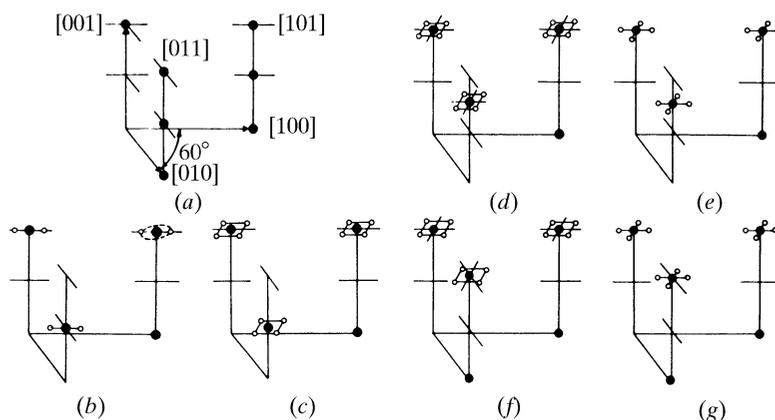
Fig. 4.4.4.6. Location of the Bragg peaks in one 60° section of reciprocal space for the three-dimensional crystalline-B phases observed in thick films of 7O.7. (*a*) The normal hexagonal crystalline-B phase with *ABAB* stacking. (*b*) The one-dimensional modulated phase with orthorhombic symmetry. The closed circles are the principal Bragg peaks and the open circles indicate side bands associated with the long-wavelength modulation. (*c*) The two-dimensional modulated phase with orthorhombic symmetry. Only the lowest-order side bands are shown. They are situated on the corners of squares surrounding the Bragg peak. The squares are oriented as shown and the amplitude of the square diagonal is equal to the distance between the two side bands illustrated in (*b*). (*d*) The two-dimensional modulated phase with monoclinic symmetry. Note that the *L* position of one of the peaks has shifted relative to (*c*). (*e*) A two-dimensional modulated phase with orthorhombic symmetry that is only observed on heating the quenched phase illustrated in (*g*). (*f*) The two-dimensional modulated phase with hexagonal symmetry and *AAA* layer stacking. (*g*) A two-dimensional hexagonal phase with *AAA* layer stacking that is only observed on rapid cooling from the phase shown in (*c*).

phase; (2) the period of the modulation; (3) the polarization of the modulation; and (4) the size of the observed deviations of the reciprocal-space structure from the hexagonal symmetry of the *ABAB* phase and suggests a microscopic driving mechanism that we will discuss below.

On further cooling, there is a first-order transition in which the one-dimensional modulation that appeared at the transition to orthorhombic symmetry is replaced by a two-dimensional modulation as shown in Fig. 4.4.4.6(*c*). On further cooling, there is another first-order transition in which the positions of the principal Bragg spots change from having orthorhombic to monoclinic symmetry as illustrated in Fig. 4.4.4.6(*d*). On further cooling, the Bragg peaks shift continually until there is one more first-order transition to a phase with hexagonal *AAA* positions as illustrated in Fig. 4.4.4.6(*f*). On further cooling, the *AAA* symmetry remains unchanged, and the modulation period is only slightly dependent on temperature, but the modulation amplitude increases dramatically. Eventually, as indicated in the phase diagram shown in Fig. 4.4.4.5, the system undergoes another first-order transition to the tilted crystalline-G phase. The patterns in Figs. 4.4.4.6(*e*) and (*g*) are observed by rapid quenching from the temperatures at which the patterns in Fig. 4.4.4.6(*b*) are observed.

Although there is not yet an established theoretical explanation for the origin of the 'restacking-modulation' effects, there are a number of experimental facts that we can summarize, and which indicate a probable direction for future research. Firstly, if one ignores the long wavelength modulation, the hexagonal *ABAB* phase is the only phase in the diagram for 7O.7 for which there are two molecules per unit cell. There must be some basic molecular effect that determines this particular coupling between every other layer. In addition, it is particularly interesting that it only manifests itself for a small temperature range and then vanishes as the sample is cooled. Secondly, any explanation for the driving force of the restacking transition must also explain the modulations that accompany it. In particular, unless one cools rapidly, the same modulation structures with the same amplitudes always appear at the same temperature, regardless of the sample history, *i.e.* whether heating or cooling. No significant hysteresis is observed and Sirota argued that the structures are in thermal equilibrium.

There are a number of physical systems for which the development of long-wavelength modulations is understood, and

in each case they are the result of two or more competing interaction energies that cannot be simultaneously minimized (Blinc & Levanyuk, 1986; Safinya, Varady *et al.*, 1986; Lubensky & Ingersent, 1986; Winkor & Clarke, 1986; Moncton *et al.*, 1981; Fleming *et al.*, 1980; Villain, 1980; Frank & van der Merwe, 1949; Bak *et al.*, 1979; Pokrovsky & Talapov, 1979). The easiest to visualize is epitaxic growth of one crystalline phase on the surface of another when the two lattice vectors are slightly incommensurate. The first atomic row of adsorbate molecules can be positioned to minimize the attractive interactions with the substrate. This is slightly more difficult for the second row, since the distance that minimizes the interaction energy between the first and second rows of adsorbate molecules is not necessarily the same as the distance that would minimize the interaction energy between the first row and the substrate. As more and more rows are added, the energy price of this incommensurability builds up, and one possible configuration that minimizes the global energy is a modulated structure.

In all known cases, the very existence of modulated structures implies that there must be competing interactions, and the only real question about the modulated structures in the crystalline-B phases is the identification of the competing interactions. It appears that one of the more likely possibilities is the difficulty in packing the 7O.7 molecules within a triangular lattice while simultaneously optimizing the area per molecule of the alkane tails and the conjugated rings in the core (Carlson & Sethna, 1987; Sadoc & Charvolin, 1986). Typically, the mean cross-sectional area for a straight alkane in the all-*trans* configuration is between 18 and 19 Å^2, while the mean area per molecule in the crystalline-B phase is closer to 24 Å^2. While these two could be reconciled by assuming that the alkanes are tilted with respect to the conjugated core, there is no reason why the angle that reconciles the two should also be the same angle that minimizes the internal energy of the molecule. Even if it were the correct angle at some temperature by accident, the average area per chain is certainly temperature dependent. Even without attempting to include the rotational dynamics that are necessary to understanding the axial site symmetry, it is obvious that there can be a conflict in the packing requirements of the two different parts of the molecule.

A possible explanation of these various structures might be as follows: at high temperatures, both the alkane chain, as well as the

other degrees of freedom, have considerable thermal motions that make it possible for the conflicting packing requirements to be simultaneously reconciled by one or another compromise. On the other hand, with decreasing temperature, some of the thermal motions become frozen out, and the energy cost of the reconciliation that was possible at higher temperatures becomes too great. At this point, the system must find another solution, and the various modulated phases represent the different compromises. Finally, all of the compromises involving inhomogeneities, like the modulations or grain boundaries, become impossible and the system transforms into a homogeneous crystalline-G phase.

If this type of argument could be made more specific, it would also provide a possible explanation for the molecular origin of the three-dimensional hexatic phases. The original suggestion for the existence of hexatic phases in two dimensions was based on the fact that the interaction energy between dislocations in two dimensions was logarithmic, such that the entropy and the enthalpy had the same functional dependence on the density of dislocations. This gave rise to the observation that above a certain temperature two-dimensional crystals would be unstable against thermally generated dislocations. Although Litster and Birgeneau's suggestion that some of the observed smectic phases might be stacks of two-dimensional hexatics is certainly correct, it is not necessary that the observed three-dimensional hexatics originate from entropy-driven thermally excited dislocations. For example, the temperature–layer-number phase diagram for 7O.7 that is shown in Fig. 4.4.4.5 has the interesting property that the temperature region over which the tilted hexatic phases exist in thin films is almost the same as the temperature region for which the modulated phases exist in thick films and in bulk samples.

From the fact that molecules in the nO.m series that only differ by one or two —CH$_2$— groups have different sequences of mesomorphic phases, we learn that within any one molecule the difference in chemical potentials between the different meso-morphic phases must be very small (Leadbetter, Mazid & Kelly, 1979; Doucet & Levelut, 1977; Leadbetter, Frost & Mazid, 1979; Leadbetter, Mazid & Richardson, 1980; Smith *et al.*, 1973; Smith & Garland, 1973). For example, although in 7O.7 the smectic-F phase is only observed in finite-thickness films, both 5O.6 and 9O.4 have smectic-F phase in bulk. Thus, in bulk 7O.7 the chemical potential for the smectic-F phase must be only slightly larger than that of the modulated crystalline-B phases, and the effect of the surfaces must be sufficient to reverse the order in samples of finite thickness.

As far as the appearance of the smectic-F phase in 7O.7 is concerned, it is well known that the interaction energy between dislocation pairs is very different near a free surface from that in the bulk (Pershan, 1974; Pershan & Prost, 1975). The origin of this is that the elastic properties of the surface will usually cause the stress field of a dislocation near to the surface either to vanish or to be considerably smaller than it would in the bulk. Since the interaction energy between dislocations depends on this stress field, the surface significantly modifies the dislocation–dislocation interaction. This is a long-range effect, and it would not be surprising if the interactions that stabilized the dislocation arrays to produce the long-wavelength modulations in the thick samples were sufficiently weaker in the samples of finite thickness that the dislocation arrays are disordered. Alternatively, there is evidence that specific surface interactions favour a finite molecular tilt at temperatures where the bulk phases are uniaxial (Farber, 1985). Incommensurability between the period of the tilted surface molecules and the crystalline-B phases below the surface would increase the density of dislocations, and this would also modify the dislocation–dislocation interactions in the bulk.

Sirota *et al.* (1985) and Sirota, Pershan, Sorensen & Collett (1987) demonstrated that, while the correlation lengths of the smectic-F phase have a significant temperature dependence, the

lengths are independent of film thickness, and this supports the argument that although the effects of the surface are important in stabilizing the smectic-F phase in 7O.7, once the phase is established it is essentially no different from the smectic-F phases observed in bulk samples of other materials. Brock *et al.* (1986) observed anisotropies in the correlation lengths of thick samples of 8OSI that are similar to those observed by Sirota.

These observations motivate the hypothesis that the dislocation densities in the smectic-F phases are determined by the same incommensurability that gives rise to the modulated crystalline-B structures. Although all of the experimental evidence supporting this hypothesis was obtained from the smectic-F tilted hexatic phase, there is no reason why this speculation could not apply to both the tilted smectic-I and the untilted hexatic-B phase.

4.4.4.3.2. *Crystal-G, crystal-J*

The crystalline-G and crystalline-J phases are the ordered versions of the smectic-F and smectic-I phases, respectively. The positions of the principal peaks illustrated in Fig. 4.4.4.4 for the smectic-F(I) are identical to the positions in the smectic-G(J) phase if small thermal shifts are discounted. In both the hexatic and the crystalline phases, the molecules are tilted with respect to the layer normals by approximately 25 to 30° with nearly hexagonal packing around the tilted axis (Doucet & Levelut, 1977; Levelut *et al.*, 1974; Levelut, 1976; Leadbetter, Mazid & Kelly, 1979; Sirota, Pershan, Sorensen & Collett, 1987). The interlayer molecular packing appears to be end to end, in an *AAA* type of stacking (Benattar *et al.*, 1983; Benattar *et al.*, 1981; Levelut, 1976; Gane *et al.*, 1983). There is only one molecule per unit cell and there is no evidence for the long-wavelength modulations that are so prevalent in the crystalline-B phase that is the next higher temperature phase above the crystalline-G in 7O.7.

4.4.4.4. *Crystalline phases with herringbone packing*

4.4.4.4.1. *Crystal-E*

Fig. 4.4.4.7 illustrates the intralayer molecular packing proposed for the crystalline-E phase (Levelut, 1976; Doucet, 1979; Levelut *et al.*, 1974; Doucet *et al.*, 1975; Leadbetter *et al.*, 1976; Richardson *et al.*, 1978; Leadbetter, Frost, Gaughan & Mazid, 1979; Leadbetter, Frost & Mazid, 1979). The molecules are, on average, normal to the
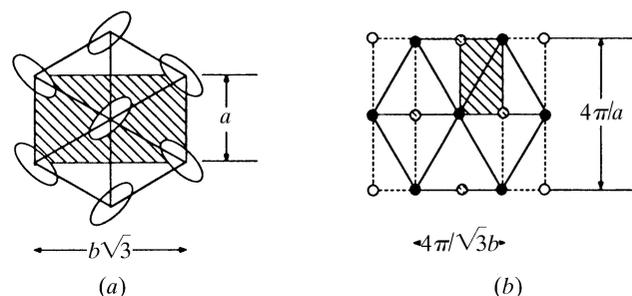
Fig. 4.4.4.7. (*a*) The 'herringbone' stacking suggested for the crystalline-E phase in which molecular rotation is partially restricted. The primitive rectangular unit cell containing two molecules is illustrated by the shaded region. The lattice has rectangular symmetry and $a \neq b$. (*b*) The position of the Bragg peaks in the plane in reciprocal space that is parallel to the layers. The dark circles indicate the principal Bragg peaks that would be the only ones present if all molecules were equivalent. The open circles indicate additional peaks that are observed for the model illustrated in (*a*). The cross-hatched circles indicate peaks that are missing because of the glide plane in (*a*).

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layers; however, from the optical birefringence it is apparent that the site symmetry is not uniaxial. X-ray diffraction studies on single crystals by Doucet and co-workers demonstrated that the biaxiality was not attributable to molecular tilt and subsequent work by a number of others resulted in the arrangement shown in Fig. 4.4.4.7(*a*). The most important distinguishing reciprocal-space feature associated with the intralayer 'herringbone' packing is the appearance of Bragg peaks at $\sin(\theta)$ equal to $\sqrt{7}/2$ times the value for the lowest-order in-plane Bragg peak for the triangular lattice (Pindak *et al.*, 1981). These are illustrated by the open circles in Fig. 4.4.4.7(*b*). The shaded circles correspond to peaks that are missing because of the glide plane that relates the two molecules in the rectangular cell.

Leadbetter, Mazid & Malik (1980) carried out detailed studies on both the crystalline-E phase of isobutyl 4-(4-phenylbenzylidene-amino)cinnamate (IBPBAC) and the crystalline phase immediately below the crystalline-E phase. Partially ordered samples of the crystalline-E phase were obtained by melting the lower-temperature crystalline phase. Although the data for the crystalline-E phase left some ambiguity, they argued that the phase they were studying might well have had molecular tilts of the order of 5 or 6°. This is an important distinction, since the crystalline-H and crystalline-J phases are essentially tilted versions of the crystalline-E. Thus, one important symmetry difference that might distinguish the crystalline-E from the others is the presence of a mirror plane parallel to the layers. In view of the low symmetry of the individual molecules, the existence of such a mirror plane would imply residual molecular motions. In fact, using neutron diffraction Leadbetter *et al.* (1976) demonstrated for a different liquid crystal that, even though the site symmetry is not axially symmetric, there is considerable residual rotational motion in the crystalline-E phase about the long axis of the molecules. Since the in-plane spacing is too small for neighbouring molecules to be rotating independently of each other, they proposed what might be interpreted as large partially hindered rotations.

4.4.4.4.2. *Crystal-H, crystal-K*

The crystalline-H and crystalline-K phases are tilted versions of the crystalline-E. The crystalline-H is tilted in the direction between the near neighbours, with the convenient mnemonic that on cooling the sequence of phases with the same relative orientation of tilt to near-neighbour position is F → G → H. Similarly, the tilt direction for the crystalline-K phase is similar to that of the smectic-I and crystalline-J so that the expected phase sequence on cooling might be I → J → K. In fact, both of these sequences are only intended to indicate the progression in lower symmetry; the actual transitions vary from material to material.

4.4.5. Discotic phases

In contrast to the long thin rod-like molecules that formed most of the other phases discussed in this chapter, the discotic phases are formed by molecules that are more disc-like [see Fig. 4.4.1.3(*f*), for example]. There was evidence that mesomorphic phases were formed from disc-like molecules as far back as 1960 (Brooks & Taylor, 1968); however, the first identification of a discotic phase was by Chandrasekhar *et al.* (1977) with benzenehexyl hexa-*n*-alkanoate compounds. Disc-like molecules can form either a fluid nematic phase in which the disc normals are aligned, without any particular long-range order at the molecular centre of mass, or more-ordered 'columnar' (Helfrich, 1979) or 'discotic' (Billard *et al.*, 1981) phases in which the molecular positions are correlated such that the discs stack on top of one another to form columns. Some of the literature designates this nematic phase as N_D to distinguish it from the phase formed by 'rod-like' molecules
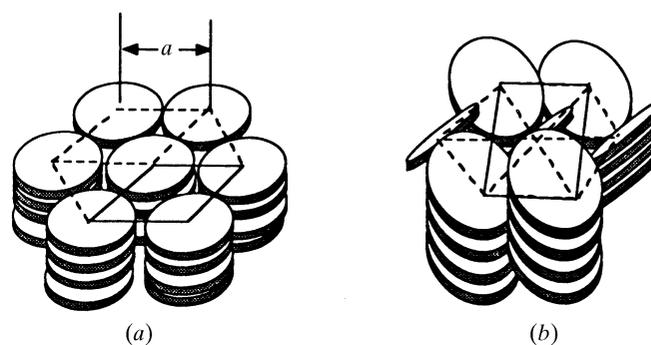
Fig. 4.4.5.1. Schematic illustration of the molecular stacking for the discotic (*a*) D_2 and (*b*) D_1 phases. In neither of these two phases is there any indication of long-range positional order along the columns. The hexagonal symmetry of the D_1 phase is broken by 'herringbone-like' correlations in the molecular tilt from column to column.

(Destrade *et al.*, 1983). In the same way that the appearance of layers characterizes order in smectic phases, the order for the discotic phases is characterized by the appearance of columns. Chandrasekhar (1982, 1983) and Destrade *et al.* (1983) have reviewed this area and have summarized the several notations for various phases that appear in the literature. Levelut (1983) has also written a review and presented a table listing the space groups for columnar phases formed by 18 different molecules. Unfortunately, it is not absolutely clear which of these are mesomorphic phases and which are crystals with true long-range positional order.

Fig. 4.4.5.1 illustrates the molecular packing in two of the well identified discotic phases that are designated as D_1 and D_2 (Chandrasekhar, 1982). The phase D_2 consists of a hexagonal array of columns for which there is no intracolumnar order. The system is uniaxial and, as originally proposed, the molecular normals were supposed to be along the column axis. However, recent X-ray scattering studies on oriented free-standing fibres of the D_2 phase of triphenylene hexa-*n*-dodecanoate indicate that the molecules are tilted with respect to the layer normal (Safinya *et al.*, 1985, 1984). The D_1 phase is definitely a tilted phase, and consequently the columns are packed in a rectangular cell. According to Safinya *et al.*, the D_1 to D_2 transition corresponds to an order–disorder transition in which the molecular tilt orientation is ordered about the column axis in the D_1 phase and disordered in the D_2 phase. The reciprocal-space structure of the D_1 phase is similar to that of the crystalline-E phase shown in Fig. 4.4.4.7(*b*).

Other discotic phases that have been proposed would have the molecules arranged periodically along the column, but disordered between columns. This does not seem physically realistic since it is well known that thermal fluctuations rule out the possibility of a one-dimensional periodic structure even more strongly than for the two-dimensional lattice that was discussed above (Landau, 1965; Peierls, 1934). On the other hand, in the absence of either more high-resolution studies on oriented fibres or further theoretical studies, we prefer not to speculate on the variety of possible true discotic or discotic-like crystalline phases that might exist. This is a subject for future research.

4.4.6. Other phases

We have deliberately chosen not to discuss the properties of the cholesteric phase in this chapter because the length scales that characterize the long-range order are of the order of micrometres and are more easily studied by optical scattering than by X-rays (De Gennes, 1974; De Vries, 1951). Nematic phases formed from chiral

molecules develop long-range order in which the orientation of the director $\langle \mathbf{n} \rangle$ varies in a plane-wave-like manner that can be described as $\mathbf{x}\cos(2\pi z/\lambda) + \mathbf{y}\sin(2\pi z/\lambda)$, where $\mathbf{x}$ and $\mathbf{y}$ are unit vectors and $\lambda/2$ is the cholesteric 'pitch' that can be anywhere from 0.1 to 10 µm depending on the particular molecule. Even more interesting is that for many cholesteric systems there is a small temperature range, of the order of 1 K, between the cholesteric and isotropic phases for which there is a phase known as the 'blue phase' (Coates & Gray, 1975; Stegemeyer & Bergmann, 1981; Meiboom *et al.*, 1981; Bensimon *et al.*, 1983; Hornreich & Shtrikman, 1983; Crooker, 1983). In fact, there is more than one 'blue phase' but they all have the property that the cholesteric twist forms a three-dimensional lattice twisted network rather than the plane-wave-like twist of the cholesteric phase. Three-dimensional Bragg scattering from blue phases using laser light indicates cubic lattices; however, since the optical cholesteric interactions are much stronger than the usual interactions between X-rays and atoms, interpretation of the results is subtler.

Gray and Goodby discuss a 'smectic-D' phase that is otherwise omitted from this chapter (Gray & Goodby, 1984). Gray and co-workers first observed this phase in the homologous series of $4'$-*n*-alkoxy-$3'$-nitrobiphenyl-4-carboxylic acids (Gray *et al.*, 1957). In the hexadecyloxy compound, this phase exists for a region of about 26 K between the smectic-C and smectic-A phases: smectic-C (444.2 K) smectic-D (470.4 K) smectic-A. It is optically isotropic and X-ray studies by Diele *et al.* (1972) and by Tardieu & Billard (1976) indicate a number of similarities to the 'cubic–isotropic' phase observed in lyotropic systems (Luzzati & Riess-Husson, 1966; Tardieu & Luzzati, 1970). More recently, Etherington *et al.* (1986) studied the 'smectic-D' phase of $3'$-cyano-$4'$-*n*-octadecyloxy-biphenyl-4-carboxylic acid. Since this material appears to be more stable than some of the others that were previously studied, they were able to perform sufficient measurements to determine that the space group is cubic $P23$ or $Pm3$ with a lattice parameter of 86 Å. Etherington *et al.* suggested that the 'smectic-D' phase that they studied is a true three-dimensional cubic crystal of micelles and noted that the designation of 'smectic-D' is not accurate. Guillon & Skoulios (1987) have proposed a molecular model for this and related phases.

Fontell (1974) has reviewed the literature on the X-ray diffraction studies of lyotropic mesomorphic systems and the reader is referred there for more extensive information on those cubic systems. The mesomorphic structures of lyotropic systems are much richer than those of the thermotropic and, in addition to all structures mentioned here, there are lyotropic systems in which the smectic-A lamellae seem to break up into cylindrical rods which seem to have the same macroscopic symmetry as some of the discotic phases. On the other hand, it is also much more difficult to prepare a review for the lyotropic systems in the same type of detail as for the thermotropic. The extra complexity associated with the need to control water concentration as well as temperature has made both theoretical and experimental progress more difficult, and, since there has not been very much experimental work on well oriented samples, detailed knowledge of many of these phases is also limited. Aside from the simpler lamellae systems, which seem to have the same symmetry as the thermotropic smectic-A phase, it is not at all clear which of the other phases are three-dimensional crystals and which are true mesomorphic structures. For example, dipalmitoylphosphatidylcholine has an L_β phase that appears for temperatures and (or) water content that is lower than that of the smectic-A L_α phase (Shipley *et al.*, 1974; Small, 1967; Chapman *et al.*, 1967). The diffraction pattern for this phase contains sharp large-angle reflections that may well correspond to a phase that is like one of the crystalline phases listed in Tables 4.4.1.1 and 4.4.1.2, and Fig. 4.4.1.1. On the other hand, this phase could also be hexatic and we do not have sufficient information to decide. The interested reader is referred to the referenced articles for further detailed information.

4.4.7. Notes added in proof to first edition

4.4.7.1. *Phases with intermediate molecular tilt: smectic-L, crystalline-M,N*

Following the completion of this manuscript, Smith and co-workers [G. S. Smith, E. B. Sirota, C. R. Safinya & N. A. Clark (1988). *Phys. Rev. Lett.* **60**, 813–816; E. B. Sirota, G. S. Smith, C. R. Safinya, R. J. Plano & N. A. Clark (1988). *Science*, **242**, 1406–1409] published an X-ray scattering study of the structure of a freely suspended multilayer film of hydrated phosphatidylcholine in which the phase that had been designated $L_{B'}$ in the literature on lipid phases [M. J. Janiak, D. M. Small & G. G. Shipley (1979). *J. Biol. Chem.* **254**, 6068–6078; V. Luzzati (1968). In *Biological Membranes: Physical Fact and Function*, Vol. 1, edited by D. Chapman, pp. 71–123; A. Tardieu, V. Luzzati & F. C. Reman (1973). *J. Mol. Biol.* **75**, 711–733] was shown to consist of three separate two-dimensional phases in which the positional order in adjacent layers is uncoupled. The three phases are distinguished by the direction of the alkane-chain tilt relative to the nearest neighbours, and in one of these phases the orientation varies continuously with increasing hydration. At the lowest hydration, they observe a phase in which the tilt is towards the second-nearest neighbour; in analogy to the smectic-F phase, they designate this phase $L_{\beta F}$. On increasing hydration, they observe a phase in which the tilt direction is intermediate between the nearest- and next-nearest-neighbour directions, and which varies continuously with hydration. This is a new phase that was not previously known and they designate it $L_{\beta L}$. On further hydration, they observe a phase in which the molecular tilt is towards a nearest neighbour and this is designated $L_{\beta I}$. At maximum hydration, they observe the phase with long-wavelength modulation that was previously designated P_β [M. J. Janiak, D. M. Small & G. G. Shipley (1979). *J. Biol. Chem.* **254**, 6068–6078]. J. V. Selinger & D. R. Nelson [*Phys. Rev. Lett.* (1988), **61**, 416–419] have subsequently developed a theory for the phase transitions between phases with varying tilt orientation and have rationalized the existence of phases with intermediate tilt. To be complete, both Fig. 4.4.1.1 and Table 4.4.1.1 should be amended to include this type of hexatic order which is now referred to as the smectic-L. Extension of the previous logic suggests that the crystalline phases with intermediate tilt should be designated M and N, where N has 'herringbone' type of intermolecular order.

4.4.7.2. *Nematic to smectic-A phase transition*

At the time this manuscript was prepared, there was a fundamental discrepancy between theoretical predictions for the details of the critical properties of the second-order nematic to smectic-A phase transition. This has been resolved. W. G. Bouwan & W. H. de Jeu [*Phys. Rev. Lett.* (1992), **68**, 800–803] reported an X-ray scattering study of the critical properties of octyloxy-phenylcyanobenzyloxybenzoate in which the data were in good agreement with predictions of the three-dimensional xy model [T. C. Lubensky (1983). *J. Chim. Phys.* **80**, 31–43; J. C. Le Guillou & J. Zinn-Justin (1985). *J. Phys. Lett.* **52**, L-137–L-141]. The differences between this experiment and others that were discussed previously, and which did not agree with theory, are firstly that this material is much further from the tricritical point that appears to be ubiquitous for most liquid-crystalline materials and, secondly, that they used the Landau–De Gennes theory to argue that the critical temperature dependence for the $\mathbf{Q}_\perp^4$ term in the differential cross section given in equation (4.4.2.7) is not that of the $c\xi_\perp^4$ term but

rather should vary as $[(T - T_{\mathrm{NA}})/T]^{-\gamma/4}$, where γ is the exponent that describes the critical-temperature dependence of the smectic order parameter $|\Psi|^2 \simeq [(T - T_{\mathrm{NA}})/T]^{-\gamma}$. The experimental results are in good agreement with the Monte Carlo simulation of the $N-S_A$ transition that was reported by C. Dasgupta [*Phys. Rev. Lett.* (1985), **55**, 1771–1774; *J. Phys. (Paris)*, (1987), **48**, 957–970].

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