

4. DIFFUSE SCATTERING AND RELATED TOPICS

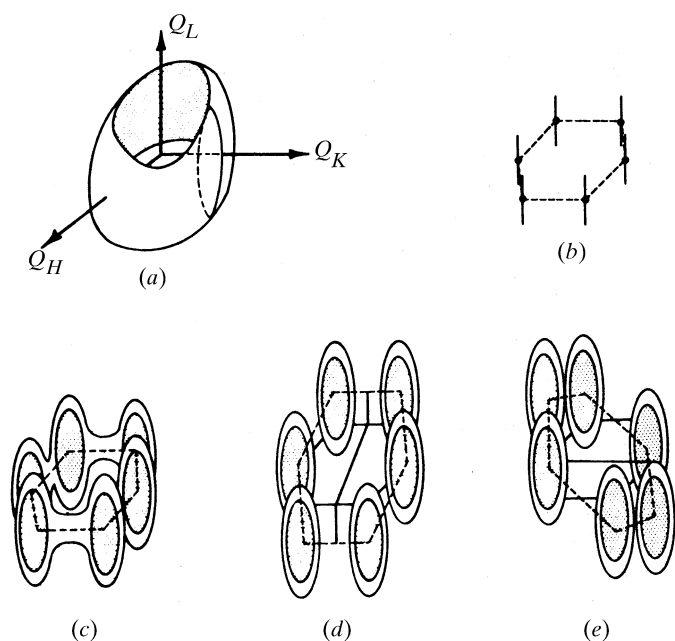


Fig. 4.4.4.3. Scattering intensities in reciprocal space from two-dimensional: (a) liquid; (b) crystal; (c) normal hexatic; and tilted hexatics in which the tilt is (d) towards the nearest neighbours as for the smectic-I or (e) between the nearest neighbours as for the smectic-F. The thin rods of scattering 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 &

* 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.

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

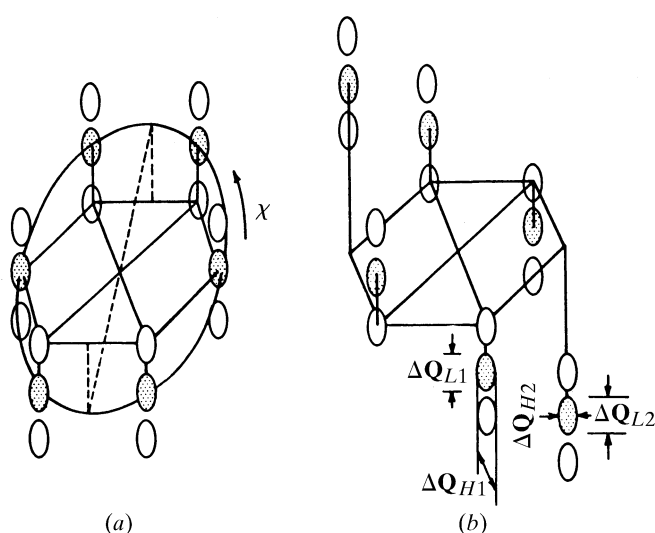


Fig. 4.4.4.4. Scattering intensities in reciprocal space from three-dimensional tilted hexatic phases: (a) the smectic-I and (b) the smectic-F. The variation of the intensity along the Q_L direction indicates interlayer correlations that are absent in Figs. 4.4.4.1(d) and (e). The peak widths $\Delta Q_{L1,2}$ and $\Delta Q_{H1,2}$ 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 .

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 (70.7). 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 70.7 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

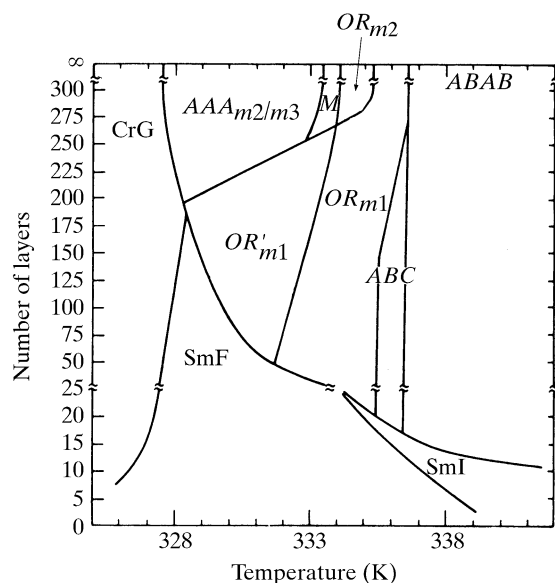


Fig. 4.4.4.5. The phase diagram for free films of 70.7 as a function of thickness and temperature. The phases *ABAB*, *AAA*, *OR_{m1}*, *OR_{m2}*, *OR'_{m1}*, *M* and *ABAB* are all crystalline-B with varying interlayer stacking, or long-wavelength modulations; *CrG*, *SmF* and *SmI* are crystalline-G, smectic-F and smectic-I, respectively (Sirota *et al.*, 1985; Sirota, Pershan & Deutsch, 1987; Sirota, Pershan, Sorensen & Collett, 1987).

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 ΔQ_{L1} and ΔQ_{L2} along the L direction and ΔQ_{H1} and ΔQ_{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 70.7. From the fact that the positions of the intensity maxima for the diffuse spots of the smectic-F phase of 70.7 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 nO_m series indicated tilted surface phases at temperatures for which the bulk had uniaxial phases (Farber, 1985). As mentioned above,

4. DIFFUSE SCATTERING AND RELATED TOPICS

X-ray scattering studies of 70.7 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 70.7, Birgeneau and co-workers found that in racemic 4-(2-methylbutyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (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

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

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 70.7 (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 10L 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 $(\mathbf{Q} \cdot \mathbf{u})^2$, where \mathbf{u} describes the molecular displacement, the fact that there is no rod of diffuse scattering through the 00L peaks indicates that the rods through the 10L 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 $nO.m$ 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 70.7, 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