

## 4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

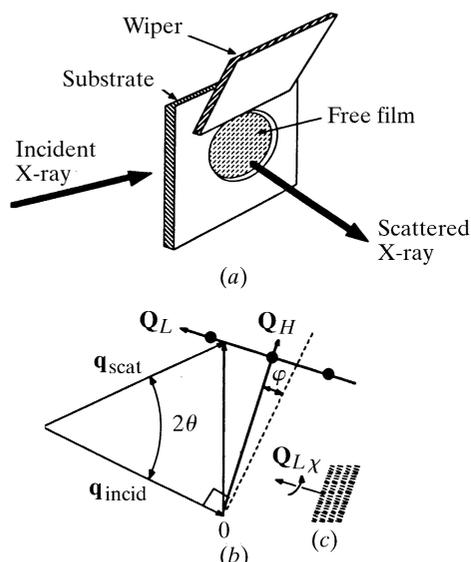


Fig. 4.4.4.1. (a) Schematic illustration of the geometry and (b) kinematics of X-ray scattering from a freely suspended smectic film. The insert (c) illustrates the orientation of the film in real space corresponding to the reciprocal-space kinematics in (b). If the angle  $\varphi = \theta$ , the film 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  $\varphi$  and  $2\theta$  to keep  $(4\pi/\lambda) \sin(\theta) \cos(\theta - \varphi) = (4\pi/\lambda) \sin(\theta_{100})$ , where  $\theta_{100}$  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  $\chi$  around the film normal.

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 Although recent unpublished work has demonstrated the possibility of a reflection geometry (Sorensen, 1987), all of the X-ray scattering studies to be described here were performed in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 00L 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

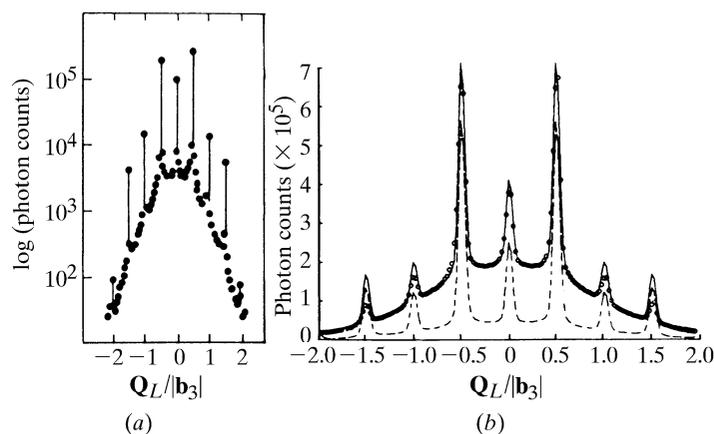


Fig. 4.4.4.2. Typical  $Q_L$  scans from the crystalline-B phases of (a) a free film of 7O.7, displayed on a logarithmic scale to illustrate the reduced level of the diffuse scattering relative to the Bragg reflection and (b) a bulk sample of 4O.8 oriented by a magnetic field.

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  $\Delta F = \Delta H - T\Delta S \approx T_c S(\rho) - TS(\rho) = S(\rho)(T_c - T)$ , where  $S(\rho) \approx \rho \log(\rho)$  is the entropy as a function of the density of dislocations  $\rho$  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-

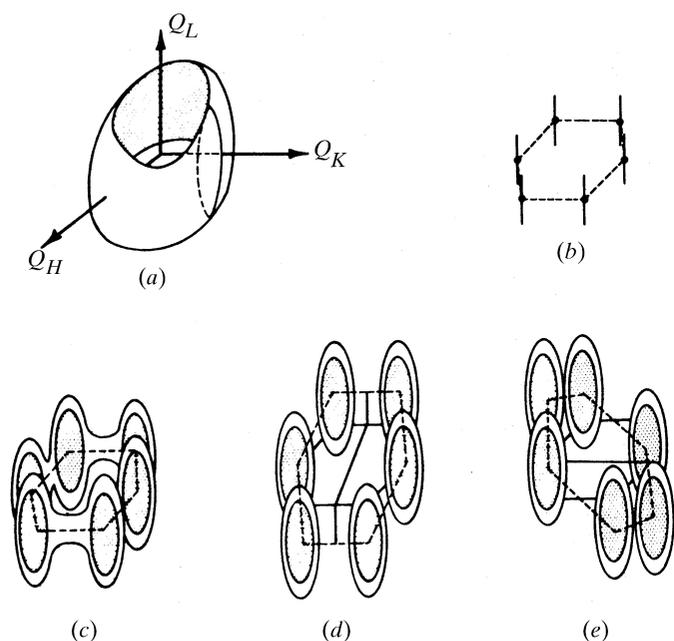


Fig. 4.4.4.3. Scattering intensities in reciprocal space from two-dimensional: (a) liquid; (b) crystal; (c) normal hexatic; and tilted hexatics in which the tilt is (d) towards the nearest neighbours as for the smectic-I or (e) between the nearest neighbours as for the smectic-F. The thin rods of scattering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