

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

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

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

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

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

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-A₁ with period $d \approx L$, smectic-A₂ 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

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

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

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

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-A (Hardouin *et al.*, 1981). Similar considerations apply to the smectic-C phases and the modulated phase is designated smectic-C̄; (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.*,

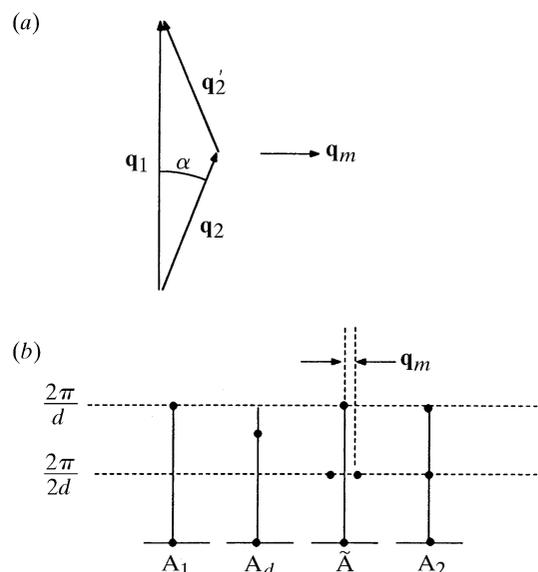


Fig. 4.4.3.1. (a) Schematic illustration of the necessary condition for coupling between order parameters when $|\mathbf{q}_2| < 2|\mathbf{q}_1|$; $|\mathbf{q}| = (|\mathbf{q}_2|^2 - |\mathbf{q}_1|^2)^{1/2} = |\mathbf{q}_1| \sin(\alpha)$. (b) Positions of the principal peaks for the indicated smectic-A 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 ($\approx 0.2^\circ$) 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

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

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 $\sin(\theta_0)/\sin(\theta_c)$,

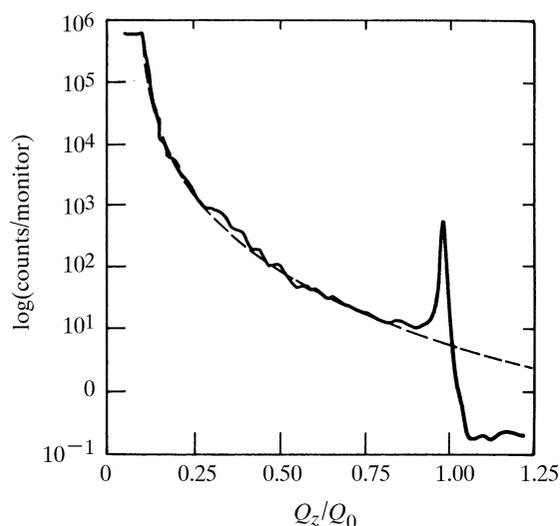


Fig. 4.4.3.2. Specular reflectivity of ~ 8 keV X-rays from the air-liquid interface of the nematic liquid crystal 8OCB 0.05 K above the nematic to smectic-A transition temperature. The dashed line is the Fresnel reflection law as described in the text.

where the peak at $\theta_c = 1.39^\circ$ 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 $T - T_{NA} \approx 0.006$ 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