4. DIFFUSE SCATTERING AND RELATED TOPICS

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

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

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 $\sin(\theta_0)/\sin(\theta_c)$,
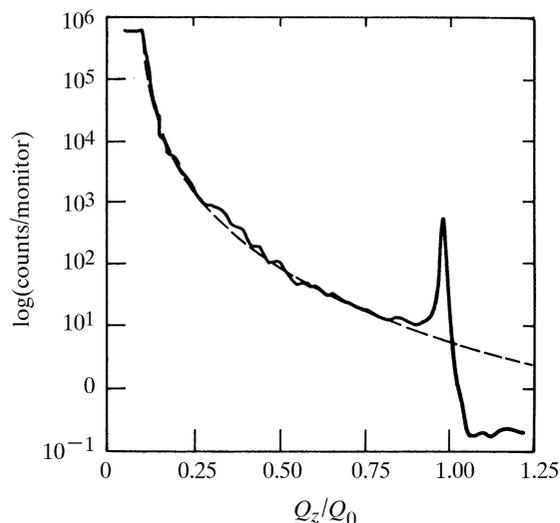
where the peak at $\theta_c = 1.39°$ corresponds to surface-induced smectic order in the nematic phase: *i.e.* the selection rule for specular reflection has been used to separate the specular reflection from the critical scattering from the bulk. Since the full width at half maximum is exactly equal to the reciprocal of the correlation length for critical fluctuations in the bulk, $2/\xi_{\parallel}$ at all temperatures from $T - T_{NA} \approx 0.006$ 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.

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