International Tables for Crystallography (2006). Vol. B, Section 4.4.3.2, p. 455.

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

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

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

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

The quantities $E_\parallel$, $E_{\perp\perp}$, and $E_{\parallel\perp}$ 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-A (Hardouin *et al.*, 1981). Similar considerations apply to the smectic-C phases and the modulated phase is designated smectic-$\tilde{\mathrm{C}}$; (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.*,

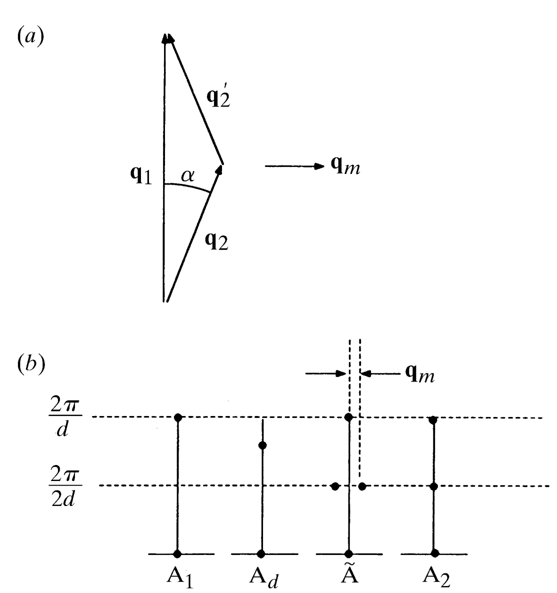

Fig. 4.4.3.1. (*a*) Schematic illustration of the necessary condition for coupling between order parameters when $|\mathbf{q}_2| < 2|\mathbf{q}_1|$; $|\mathbf{q}| = (|\mathbf{q}_2|^2 - |\mathbf{q}_1|^2)^{1/2} = |\mathbf{q}_1|\sin(\alpha)$. (*b*) Positions of the principal peaks for the indicated smectic-A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

references