4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

Table 4.4.2.1. *Summary of critical exponents from X-ray scattering studies of the nematic to smectic-A phase transition*

Molecule	γ	$\nu_\parallel$	$\nu_\perp$	Reference
4O.7	1.46	0.78	0.65	(*a*)
$\bar{8}$S5	1.53	0.83	0.68	(*b*), (*g*)
CBOOA	1.30	0.70	0.62	(*c*), (*d*)
4O.8	1.31	0.70	0.57	(*e*)
8OCB	1.32	0.71	0.58	(*d*), (*f*)
$\bar{9}$S5	1.31	0.71	0.57	(*b*), (*g*)
8CB	1.26	0.67	0.51	(*h*), (*i*)
10$\bar{5}$S5	1.10	0.61	0.51	(*b*), (*g*)
9CB	1.10	0.57	0.39	(*g*), (*j*)

References: (*a*) Garland *et al.* (1983); (*b*) Brisbin *et al.* (1979); (*c*) Djurek *et al.* (1974); (*d*) Litster *et al.* (1979); (*e*) Birgeneau *et al.* (1981); (*f*) Kasting *et al.* (1980); (*g*) Ocko *et al.* (1984); (*h*) Thoen *et al.* (1982); (*i*) Davidov *et al.* (1979); (*j*) Thoen *et al.* (1984).

The amplitude $\sigma \propto t^{-\gamma}$, where the measured values of γ are empirically found to be very close to the measured values for the sum $\nu_\parallel + \nu_\perp$. Most of the systems that have been measured to date have values for $\nu_\parallel > 0.66 > \nu_\perp$ and $\nu_\parallel - \nu_\perp \approx 0.1$ to 0.2. Table 4.4.2.1 lists sources of the observed values for γ, $\nu_\parallel$ and $\nu_\perp$. The theoretical and experimental studies of this pretransition effect account for a sizeable fraction of all of the liquid-crystal research in the last 15 or 20 years, and as of this writing the explanation for these two different temperature dependences remains one of the major unresolved theoretical questions in equilibrium statistical physics.

It is very likely that the origin of the problem is the QLRO in the position of the smectic layers. Lubensky attempted to deal with this by introducing a gauge transformation in such a way that the thermal fluctuations of the transformed order parameter did not have the logarithmic divergence. While this approach has been informative, it has not yet yielded an agreed-upon understanding. Experimentally, the effect of the phase can be studied in systems where there are two competing order parameters with wavevectors that are at $\mathbf{q}_2$ and $\mathbf{q}_1 \approx 2\mathbf{q}_2$ (Sigaud *et al.*, 1979; Hardouin *et al.*, 1983; Prost & Barois, 1983; Wang & Lubensky, 1984; Chan, Pershan *et al.*, 1985). On cooling, mixtures of 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB$_6$) and *N,N'*-(1,4-phenylenedimethylene)bis(4-butylaniline) (also known as terephthal-bis-butyl-aniline, TBBA) first undergo a second-order transition from the nematic to a phase that is designated as smectic-A$_1$. The various smectic-A and smectic-C morphologies will be described in more detail in the following section; however, the smectic-A$_1$ phase is characterized by a single peak at $q_1 = 2\pi/d$ owing to a one-dimensional density wave with wavelength d of the order of the molecular length L. In addition, however, there are thermal fluctuations of a second-order parameter with a period of $2L$ that give rise to a diffuse peak at $q_2 = \pi/L$. On further cooling, this system undergoes a second second-order transition to a smectic-A$_2$ phase with QLRO at $q_2 \approx \pi/L$, with a second harmonic that is exactly at $q = 2q_2 \approx 2\pi/L$. The critical scattering on approaching this transition is similar to that of the nematic to smectic-A$_1$, except that the pre-existing density wave at $q_1 = 2\pi/L$ quenches the phase fluctuations of the order parameter at the subharmonic $q_2 = \pi/L$. The measured values of $\nu_\parallel = \nu_\perp \approx 0.74$ (Chan, Pershan *et al.*, 1985) agree with those expected from the appropriate theory (Huse, 1985). A mean-field theory that describes this effect is discussed in Section 4.4.3.2 below.

It is interesting to note that even those systems for which the nematic to smectic-A transition is first order show some pretransitional lengthening of the correlation lengths $\xi_\parallel$ and $\xi_\perp$. In these cases, the apparent T^* at which the correlation lengths would diverge is lower than T_{NA} and the divergence is truncated by the first-order transition (Ocko *et al.*, 1984).

4.4.3. Smectic-A and smectic-C phases

4.4.3.1. *Homogeneous smectic-A and smectic-C phases*

In the smectic-A and smectic-C phases, the molecules organize themselves into layers, and from a naive point of view one might describe them as forming a one-dimensional periodic lattice in which the individual layers are two-dimensional liquids. In the smectic-A phase, the average molecular axis $\langle \mathbf{n} \rangle$ is normal to the smectic layers while for the smectic-C it makes a finite angle. It follows from this that the smectic-C phase has lower symmetry than the smectic-A, and the phase transition from the smectic-A to smectic-C can be considered as the ordering of a two-component order parameter, *i.e.* the two components of the projection of the molecular axis on the smectic layers (De Gennes, 1973). Alternatively, Chen & Lubensky (1976) have developed a mean-field theory in which the transition is described by a free-energy density of the Lifshitz form. This will be described in more detail below; however, it corresponds to replacing equation (4.4.2.5) for the free energy $\Delta F(\psi)$ by an expression for which the minimum is obtained when the wavevector $\mathbf{q}$, of the order parameter $\psi \propto \exp[i\mathbf{q} \cdot \mathbf{r}]$, tilts away from the molecular axis.

The X-ray cross section for the prototypical aligned monodomain smectic-A sample is shown in Fig. 4.4.1.2(*b*). It consists of a single sharp spot along the molecular axis at $|\mathbf{q}|$ somewhere between $2\pi/2L$ and $2\pi/L$ that reflects the QLRO along the layer normal, and a diffuse ring in the perpendicular direction at $|\mathbf{q}| \approx 2\pi/a$ that reflects the SRO within the layer. The scattering cross section for an aligned smectic-C phase is similar to that of the smectic-A except that the molecular tilt alters the intensity distribution of the diffuse ring. This is illustrated in Fig. 4.4.1.2(*c*) for a monodomain sample. Fig. 4.4.1.2(*d*) illustrates the scattering pattern for a polydomain smectic-C sample in which the molecular axis remains fixed, but where the smectic layers are randomly distributed azimuthally around the molecular axis.

The naivety of describing these as periodic stacks of two-dimensional liquids derives from the fact that the sharp spot along the molecular axis has a distinct temperature-dependent shape indicative of QLRO that distinguishes it from the Bragg peaks due to true LRO in conventional three-dimensional crystals. Landau and Peierls discussed this effect for the case of two-dimensional crystals (Landau, 1965; Peierls, 1934) and Caillé (1972) extended the argument to the mesomorphic systems.

The usual treatment of thermal vibrations in three-dimensional crystals estimates the Debye–Waller factor by integrating the thermal expectation value for the mean-square amplitude over reciprocal space (Kittel, 1963):

$$W \simeq \frac{k_B T}{c^3} \int_0^{k_D} \frac{k^{(d-1)}}{k^2} dk, \qquad (4.4.3.1)$$

where c is the sound velocity, $\omega_D \equiv c k_D$ is the Debye frequency and $d = 3$ for three-dimensional crystals. In this case, the integral converges and the only effect is to reduce the integrated intensity of the Bragg peak by a factor proportional to $\exp(-2W)$. For two-dimensional crystals $d = 1$, and the integral, of the form of dk/k, obtains a logarithmic divergence at the lower limit (Fleming *et al.*, 1980). A more precise treatment of thermal vibrations, necessitated by this divergence, is to calculate the relative phase of X-rays