

4.4. SCATTERING FROM MESOMORPHIC STRUCTURES

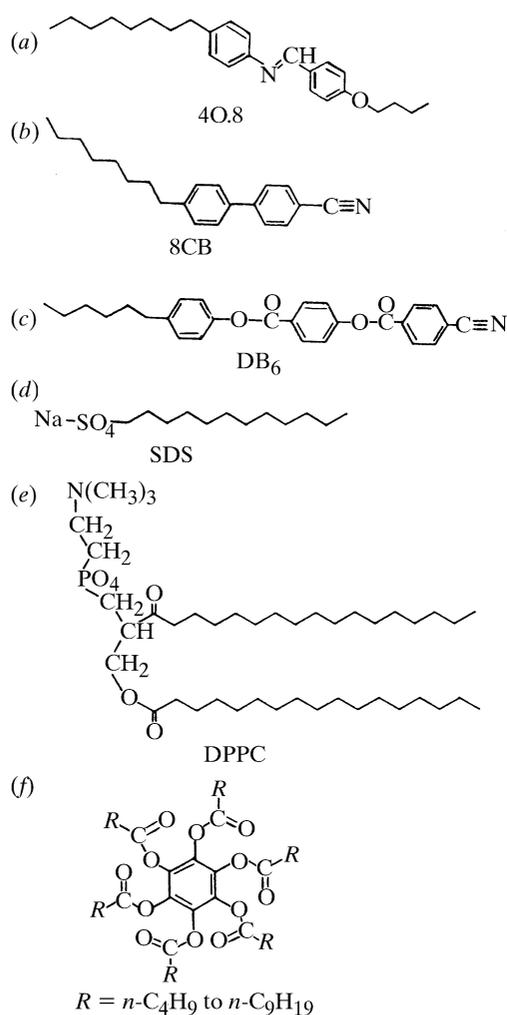


Fig. 4.4.1.3. Chemical formulae for some of the molecules that form thermotropic liquid crystals: (a) *N*-[4-(*n*-butyloxy)benzylidene]-4-*n*-octylaniline (4O.8), (b) 4'-*n*-octylbiphenyl-4-carbonitrile (8CB), (c) 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB₆); lyotropic liquid crystals: (d) sodium dodecyl sulfate, (e) 1,2-dipalmitoyl-L-phosphatidylcholine (DPPC); and a discotic liquid crystal: (f) benzenehexyl hexa-*n*-alkanoates.

that form thermotropic liquid-crystalline phases have hydrophilic and hydrophobic parts, the disparity in the affinity of these parts for either water or oil is much less and most of these molecules are relatively insoluble in water. These molecules are called thermotropic because their phase transformations are primarily studied only as a function of temperature. This is not to say that there are not numerous examples of interesting studies of the concentration dependence of phase diagrams involving mixtures of thermotropic liquid crystals.

Fig. 4.4.1.3 displays some common examples of molecules that form lyotropic and thermotropic phases. In spite of the above remarks, it is interesting to observe that different parts of typical thermotropic molecules do have some of the same features as the lyotropic molecules. For example, although the rod-like thermotropic molecules always have an alkane chain at one or both ends of a more rigid section, the chain lengths are rarely as long as those of the lyotropic molecules, and although the solubility of the parts of the thermotropic molecules, when separated, are not as disparate as those of the lyotropic molecules, they are definitely different. We suspect that this may account for the subtler features of the phase transformations between the mesomorphic phases to be discussed

below. On the other hand, the inhomogeneity of the molecule is probably not important for the nematic phase.

4.4.2. The nematic phase

The nematic phase is a fluid for which the molecules have long-range orientational order. The phase as well as its molecular origin can be most simply illustrated by treating the molecules as long thin rods. The orientation of each molecule can be described by a symmetric second-rank tensor $s_{i,j} = (n_i n_j - \delta_{i,j}/3)$, where \mathbf{n} is a unit vector along the axis of the rod (De Gennes, 1974). For disc-like molecules, such as that shown in Fig. 4.4.1.3(f), or for micellar nematic phases, \mathbf{n} is along the principal symmetry axis of either the molecule or the micelle (Lawson & Flautt, 1967). Since physical quantities such as the molecular polarizability, or the moment of inertia, transform as symmetric second-rank tensors, either one of these could be used as specific representations of the molecular orientational order. The macroscopic order, however, is given by the statistical average $S_{i,j} = \langle s_{i,j} \rangle = S(\langle n_i \rangle \langle n_j \rangle - \delta_{i,j}/3)$, where $\langle \mathbf{n} \rangle$ is a unit vector along the macroscopic symmetry axis and S is the order parameter of the nematic phase.

The microscopic origin of the phase can be understood in terms of steric constraints that occur on filling space with highly asymmetric objects such as long rods or flat discs. Maximizing the density requires some degree of short-range orientational order, and theoretical arguments can be invoked to demonstrate long-range order. Onsager presented quantitative arguments of this type to explain the nematic order observed in concentrated solutions of the long thin rods of tobacco mosaic viruses (Onsager, 1949; Lee & Meyer, 1986), and qualitatively similar ideas explain the nematic order for the shorter thermotropic molecules (Maier & Saupe, 1958, 1959).

The existence of nematic order can also be understood in terms of a phenomenological mean-field theory (De Gennes, 1969*b*, 1971; Fan & Stephen, 1970). If the free-energy difference ΔF between the isotropic and nematic phases can be expressed as an analytic function of the nematic order parameter $S_{i,j}$, one can expand $\Delta F(S_{i,j})$ as a power series in which the successive terms all transform as the identity representation of the point group of the isotropic phase, *i.e.* as scalars. The most general form is given by:

$$\Delta F(S_{i,j}) = \frac{A}{2} \sum_{ij} S_{ij} S_{ji} + \frac{B}{3} \sum_{ijk} S_{ij} S_{jk} S_{ki} + \frac{D}{4} \left| \sum_{ij} S_{ij} S_{ji} \right|^2 + \frac{D'}{4} \sum_{ijkl} S_{ij} S_{jk} S_{kl} S_{li}. \quad (4.4.2.1)$$

The usual mean-field treatment assumes that the coefficient of the leading term is of the form $A = a(T - T^*)$, where T is the absolute temperature and T^* is the temperature at which $A = 0$. Taking a , D and $D' > 0$, one can show that for either positive or negative values of B , but for sufficiently large T , the minimum value of $\Delta F = 0$ occurs for $S_{i,j} = 0$, corresponding to the isotropic phase. For $T < T^*$, ΔF can be minimized, at some negative value, for a nonzero $S_{i,j}$ corresponding to nematic order. The details of how this is derived for a tensorial order parameter can be found in the literature (De Gennes, 1974); however, the basic idea can be understood by treating $S_{i,j}$ as a scalar. If we write

$$\Delta F = \frac{1}{2} A S^2 + \frac{1}{3} B S^3 + \frac{1}{4} D S^4 = \left\{ \frac{A}{2} - \frac{B^2}{9D} \right\} S^2 + \frac{D}{4} \left(S + \frac{2B}{3D} \right)^2 \quad (4.4.2.2)$$

and if T_{NI} is defined by the condition $A = a(T_{\text{NI}} - T^*) = 2B^2/9D$, then $\Delta F = 0$ for both $S = 0$ and $S = -2B/3D$. This value for T_{NI}

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marks the transition temperature from the isotropic phase, when $A > 2B^2/9D$ and the only minimum is at $S = 0$ with $\Delta F = 0$, to the nematic case when $A < 2B^2/9D$ and the absolute minimum with $\Delta F < 0$ is slightly shifted from $S = -2B/3D$. The symmetry properties of second-rank tensors imply that there will usually be a nonvanishing value for B , and this implies that the transition from the isotropic to nematic transition will be first order with a discontinuous jump in the nematic order parameter $S_{i,j}$. Although most nematic systems are uniaxial, biaxial nematic order is theoretically possible (Freiser, 1971; Alben, 1973; Lubensky, 1987) and it has been observed in certain lyotropic nematic liquid crystals (Neto *et al.*, 1985; Hendriks *et al.*, 1986; Yu & Saupe, 1980) and in one thermotropic system (Malthête *et al.*, 1986).

The X-ray scattering cross section of an oriented monodomain sample of the nematic phase with rod-like molecules usually exhibits a diffuse spot like that illustrated in Fig. 4.4.1.2(a), where the maximum of the cross section is along the average molecular axis $\langle \mathbf{n} \rangle$ at a value of $|\mathbf{q}| \approx 2\pi/d$, where $d \approx 20.0$ to 40.0 Å is of the order of the molecular length L . This is a precursor to the smectic-A order that develops at lower temperatures for many materials. In addition, there is a diffuse ring along the directions normal to $\langle \mathbf{n} \rangle$ at $|\mathbf{q}| \approx 2\pi/a$, where $a \approx 4.0$ Å is comparable to the average radius of the molecule. In some nematic systems, the near-neighbour correlations favour antiparallel alignment and molecular centres tend to form pairs such that the peak of the scattering cross section can actually have values anywhere in the range from $2\pi/L$ to $2\pi/2L$. There are also other cases where there are two diffuse peaks, corresponding to both $|\mathbf{q}_1| \approx 2\pi/L$ and $|\mathbf{q}_2| \approx |\mathbf{q}_1|/2$ which are precursors of a richer smectic-A morphology (Prost & Barois, 1983; Prost, 1984; Sigaud *et al.*, 1979; Wang & Lubensky, 1984; Hardouin *et al.*, 1983; Chan, Pershan *et al.*, 1985). In some cases, $|\mathbf{q}_2| \approx \frac{1}{2}|\mathbf{q}_1|$ and competition between the order parameters at incommensurate wavevectors gives rise to modulated phases. For the moment, we will restrict the discussion to those systems for which the order parameter is characterized by a single wavevector.

On cooling, many nematic systems undergo a second-order phase transition to a smectic-A phase and as the temperature approaches the nematic to smectic-A transition the widths of these diffuse peaks become infinitesimally small. De Gennes (1972) demonstrated that this phenomenon could be understood by analogy with the transitions from either normal fluidity to superfluidity in liquid helium or normal conductivity to superconductivity in metals. Since the electron density of the smectic-A phase is (quasi-)periodic in one dimension, he represented it by the form:

$$\rho(\mathbf{r}) = \langle \rho \rangle + \text{Re}\{\Psi \exp[i(2\pi/d)z]\},$$

where d is the thickness of the smectic layers lying in the xy plane. The complex quantity $\psi = |\psi| \exp(i\varphi)$ is similar to the superfluid wavefunction except that in this analogy the amplitude $|\psi|$ describes the electron-density variations normal to the smectic layers, and the phase φ describes the position of the layers along the z axis. De Gennes proposed a mean-field theory for the transition in which the free-energy difference between the nematic and smectic-A phase $\Delta F(\Psi)$ was represented by

$$\Delta F(\psi) = \frac{A}{2}|\psi|^2 + \frac{D}{4}|\psi|^4 + \frac{E}{2} \left[\left| \left\{ \frac{\partial}{\partial z} - i \left(\frac{2\pi}{d} \right) \right\} \psi \right|^2 + \left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2 \right]. \quad (4.4.2.3)$$

This mean-field theory differs from the one for the isotropic to nematic transition in that the symmetry for the latter allowed a term that was cubic in the order parameter, while no such term is allowed for the nematic to smectic-A transition. In both cases, however, the

coefficient of the leading term is taken to have the form $a(T - T^*)$. If $D > 0$, without the cubic term the free energy has only one minimum when $T > T^*$ at $|\psi| = 0$, and two equivalent minima at $|\psi| = \{a(T^* - T)/D\}^{0.5}$ for $T < T^*$. On the basis of this free energy, the nematic to smectic-A transition can be second order with a transition temperature $T_{\text{NA}} = T^*$ and an order parameter that varies as the square root of $(T_{\text{NA}} - T)$. There are conditions that we will not discuss in detail when D can be negative. In that case, the nematic to smectic-A transition will be first order (McMillan, 1972, 1973a,b,c). McMillan pointed out that, by allowing coupling between the smectic and nematic order parameters, a more general free energy can be developed in which D is negative. McMillan's prediction that for systems in which the difference $T_{\text{IN}} - T_{\text{NA}}$ is small the nematic to smectic-A transition will be first order is supported by experiment (Ocko, Birgeneau & Litster, 1986; Ocko *et al.*, 1984; Thoen *et al.*, 1984). Although the mean-field theory is not quantitatively accurate, it does explain the principal qualitative features of the nematic to smectic-A transition.

The differential scattering cross section for X-rays can be expressed in terms of the Fourier transform of the density-density correlation function $\langle \rho(\mathbf{r})\rho(0) \rangle$. The expectation value is calculated from the thermal average of the order parameter that is obtained from the free-energy density $\Delta F(\psi)$. If one takes the transform

$$\Psi(\mathbf{Q}) \equiv \frac{1}{(2\pi)^3} \int d^3\mathbf{r} \exp[i(\mathbf{Q} \cdot \mathbf{r})] \rho(\mathbf{r}), \quad (4.4.2.4)$$

the free-energy density in reciprocal space has the form

$$\Delta F(\psi) = \frac{A}{2}|\psi|^2 + \frac{D}{4}|\psi|^4 + \frac{E}{2} \{ [Q_z - (2\pi/d)]^2 + Q_x^2 + Q_y^2 \} |\psi|^2 \quad (4.4.2.5)$$

and one can show that for $T > T_{\text{NA}}$ the cross section obtained from the above form for the free energy is

$$\frac{d\sigma}{d\Omega} \approx \frac{\sigma_0}{A + E \{ [Q_z - (2\pi/d)]^2 + Q_x^2 + Q_y^2 \}}, \quad (4.4.2.6)$$

where the term in $|\psi|^4$ has been neglected. The mean-field theory predicts that the peak intensity should vary as $\sigma_0/A \approx 1/(T - T_{\text{NA}})$ and that the half width of the peak in any direction should vary as $(A/E)^{1/2} \approx (T - T_{\text{NA}})^{1/2}$. The physical interpretation of the half width is that the smectic fluctuations in the nematic phase are correlated over lengths $\xi = (E/A)^{1/2} \sim (T - T_{\text{NA}})^{-1/2}$.

One of the major shortcomings of all mean-field theories is that they do not take into account the difference between the average value of the order parameter $\langle \psi \rangle$ and the instantaneous value $\psi = \langle \psi \rangle + \delta\psi$, where $\delta\psi$ represents the thermal fluctuations (Ma, 1976). The usual effect expected from theories for this type of critical phenomenon is a 'renormalization' of the various terms in the free energy such that the temperature dependence of correlation length has the form $\xi(t) \propto t^{-\nu}$, where $t \equiv (T - T^*)/T^*$, $T^* = T_{\text{NA}}$ is the second-order transition temperature, and ν is expected to have some universal value that is generally not equal to 0.5. One of the major unsolved problems of the nematic to smectic-A phase transition is that the width along the scattering vector \mathbf{q} varies as $1/\xi_{\parallel} \propto t^{\nu_{\parallel}}$ with a temperature dependence different from that of the width perpendicular to \mathbf{q} , $1/\xi_{\perp} \propto t^{\nu_{\perp}}$; also, neither ν_{\parallel} nor ν_{\perp} have the expected universal values (Lubensky, 1983; Nelson & Toner, 1981).

The correlation lengths are measured by fitting the differential scattering cross sections to the empirical form:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{1 + (\mathbf{Q}_z - |\mathbf{q}|)^2 \xi_{\parallel}^2 + \mathbf{Q}_{\perp}^2 \xi_{\perp}^2 + c(\mathbf{Q}_{\perp}^2 \xi_{\perp}^2)^2}. \quad (4.4.2.7)$$

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

Molecule	γ	ν_{\parallel}	ν_{\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)
10S5	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 , ν_{\parallel} and ν_{\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 (DB₆) and *N,N'*-(1,4-phenylenedimethylene)bis(4-butylaniline) (also known as terephthal-bis-butylaniline, TBBA) first undergo a second-order transition from the nematic to a phase that is designated as smectic-A₁. The various smectic-A and smectic-C morphologies will be described in more detail in the following section; however, the smectic-A₁ 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-A₂ 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-A₁, 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 ξ_{\parallel} and ξ_{\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 (\mathbf{n}) 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):

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

where c is the sound velocity, $\omega_D \equiv ck_D$ 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 $d = 2$, 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