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Some Remarks on the Polymorphism of Smectics

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Some Remarks on the Polymorphism of Smectics†

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Abstract—We discuss the nature of the order in the main smectic phases (A, C, and B) together with the related phase transitions. (1) The B phase may correspond to a plastic crystal, *or* to a system of weakly coupled solid layers: to discriminate between these two models, acoustical studies using shear waves appear to be most promising, (2) the transitions $A \leftrightarrow \mathrm{N}$, $C \leftrightarrow \mathrm{N}$, $C \leftrightarrow A$ (where N stands for nematic) *may* be of second order in certain cases, which will allow for a number of interesting experiments. The $C \leftrightarrow A$ transition should be very similar to the λ transition of helium, and some critical exponents which are not accessible in helium could be measured here. The $\mathrm{N} \leftrightarrow A$ transition is similar to the onset of superconductivity in a metal. A bend (or twist) deformation tends to suppress the A phase just as a magnetic field destroys superconductivity. In the N phase the twist and bend elastic constants should show pretransitional anomalies. The $C \leftrightarrow \mathrm{N}$ transition is more complex. A tentative calculation suggests that here all three elastic constants should show pretransitional anomalies.

1. Introduction and Comments on the *B* Phase

All smectic phases are layered systems, with an amount of transitional order which is less than that for a three-dimensional solid. Many distinct phases, conforming more or less to this definition, have been observed recently, largely through the efforts of Sackmann and Demus.(1) Among these, three types appear to be both frequent and unambiguously characterized:

—Type A, where the layers are liquid and the molecules are aligned (on the average) with their axis normal to the layers: the system is optically uniaxial.

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—Type *C*; again, the layers are liquid, but now the molecules are tilted, by an angle ω: the system is biaxial.

—Type *B*; here we find peaks in the X-ray scattering which suggest an ordering inside the layers. The system may be either uniaxial (B_A) or biaxial (B_C).

With smectics *A* and *C*, an ideal single domain can easily be deformed into a " focal conic " texture.$^{(2)}$ On the other hand, for smectics *B*, no such deformation is observed. The usual " mosaic " texture of smectics *B* has flat layers and is reminiscent of the texture observed in plastic crystals.$^{(3)}$ Thus it may be that the *B* phase should not be classified as smectic: it could have long range crystalline order—the centers of gravity of the molecules being ordered on a three-dimensional lattice—together with a certain amount of orientational disorder. This analogy with plastic crystals would also account for the large heat of transition observed at the solid ↔ B transition.

However, this is not the only possible assignment for a smectic *B*. Another, quite different, model for this phase has been proposed recently,$^{(4)}$ assuming strong forces inside each layer (which favor a two-dimensional solid-like arrangement) and weak forces between

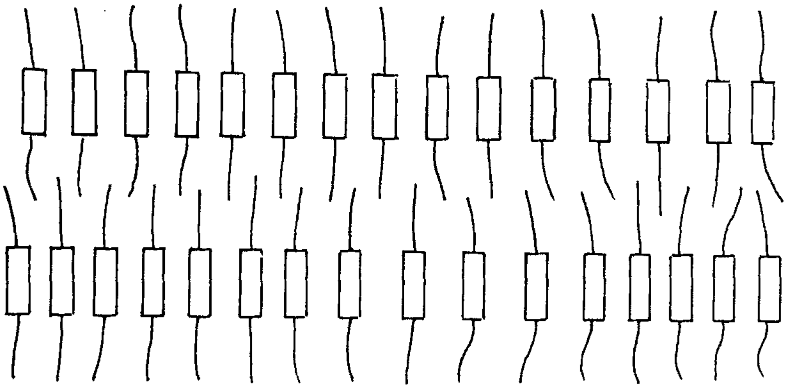

Figure 1. The second model for the *B* phase of smectics. Each molecule has an aromatic part (represented as a rectangle) and two aliphatic chains, in flexible (fluid like) conformation. The aromatic parts are grouped in two-dimensional layers. Each layer is locally ordered. But, because of its two-dimensional character, it shows long range fluctuations—in the *B* phase, the fluctuations of successive layers are essentially uncoupled.

layers. At low temperatures, T, this gives a conventional crystal. But when T increases, the shear modulus associated with relative slipping of adjacent layers drops rapidly. Finally at a certain temperature T_{CB} we reach a state where the layers can slip freely on top of each other (Fig. 1) while still retaining a two-dimensional ordered structure.

Why would the interlayer interactions be so weak? In soaps and other lyotropic systems, we know that the aliphatic chains which build up the hydrophobic parts may exist either in an ordered (" crystalline ") or in a disordered (" fluid ") condition. In most of the thermotropic materials of interest here, we also find aliphatic chains attached at both ends of an aromatic part. The ordering inside one layer will be due to contact interactions between the aromatic parts of neighboring molecules. But the correlations between successive layers must be mediated by the aliphatic chains, and will be weak if the layers are in the molten state. This remark leads to a possible variant for the model of Ref. 4: in this variant, the picture of the B phase is unchanged, but the solid $\leftrightarrow B$ transition is interpreted as the melting point of the chains, leading to weak interplane interactions (Fig. 1).

To summarize: the B phase might correspond either to a three-dimensional crystal with rotational disorder, or to a set of two-dimensional crystals which can slip on each other.

A crucial test, to distinguish between the two models, would be to measure X-ray scattering intensities, on a single domain of the B phase, in the vicinity of a nominal Bragg position. For a plastic crystal one would expect a delta function peak in reciprocal space, plus some diffuse scattering due to phonons and to rotational disorder. With the second model, on the other hand, there is no δ function peak, but the diffuse scattering has a (weaker) singularity at the nominal Bragg position (Fig. 2). X-ray studies on single domains have been performed recently⁽⁵⁾ and have shown some remarkable chain-like correlations between molecules. But these studies, based on photographic techniques, do not allow for a direct comparison with Fig. 2.

Another experimental approach could be based on the propagation of ultrasonic shear waves along the normal to the layers. In a plastic crystal the velocity of propagation stays finite; the rotational

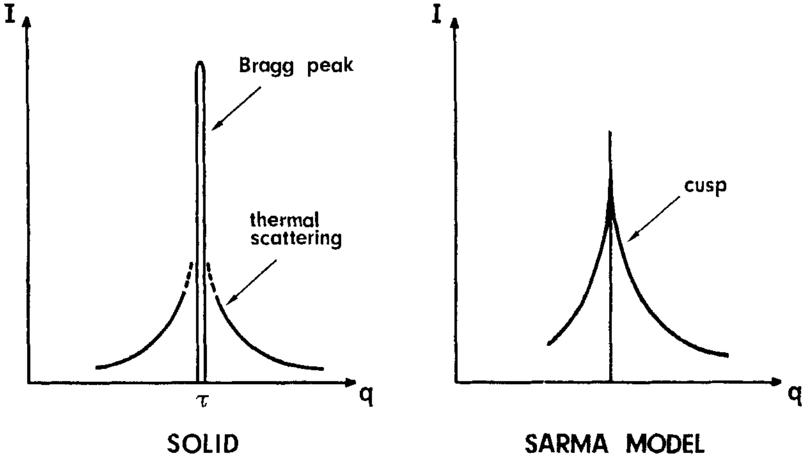

Figure 2. X-ray scattering in two different models of the *B* phase.

disorder simply gives a contribution to the damping. But in the model of Ref. 4, the velocity vanishes and the acoustic properties (for shear waves) are completely different.

Such experiments have not been performed yet (because of the difficulties involved in preparing large size single domains of the *B* phase) and we cannot decide whether either of these two models works; possibly a combination of both—or even a completely different idea—will be required. For this reason, in the present paper, we shall concentrate mainly on the simpler phases of the smectics (*A* and *C*) for which the symmetry properties are reasonably clear, and where detailed predictions can be made.

We shall be particularly concerned with the possible transitions between smectic *A*, smectic *C*, and nematic (N), phases: experimentally, many of these transitions are found to be of first order. However, from the point of view of the Landau rules⁽⁶⁾ all of them *may* be of second order. These second-order transitions, although less frequent, are of great interest because they are always announced by pretransitional anomalies, which are interesting:

(a) from the point of view of statistical mechanics, the smectic phases give us a whole new class of critical phenomena, where the ideas developed in connection with simpler systems (ferromagnets, superfluids,...) can be transposed and subjected to new tests.

(b) from the point of view of applications, in the nematic phase, the onset of quasi smectic features may lead to a drastic change in certain important constants (elastic coefficients, transport properties, etc.). For instance, it has been shown recently by Rondelez$^{(7)}$ that the ratio of the parallel/perpendicular electric conductivities $\sigma_{\parallel}/\sigma_{\perp}$ which is usually larger than unity in nematic, may become significantly smaller than unity in the vicinity of a smectic transition (because the charge carriers do not cross the layers easily). The electrohydrodynamic effects on which many display devices are based, depend critically on $(\sigma_{\parallel}/\sigma_{\perp}-1)$: materials with positive dielectric anisotropy, which could not be used efficiently when $\sigma_{\parallel}/\sigma_{\perp}>1$, may become of technical interest in this pre-smectic regime.

Our discussion of transitions between mesomorphic phases will constantly rely on analogies with other systems, where detailed experimental data—together with some theoretical background—are available. For instance we shall see that in the transition from smectic A to smectic C (Sec. 3) the new order parameter which occurs is a complex number, just as in superfluid helium, and the symmetry properties of both systems are equivalent: If the $C \leftrightarrow A$ transition is continuous† it is then highly plausible to assume that it will show critical properties identical to those of the λ point in helium. We expect, for instance, the specific heat to show a logarithmic divergence. The transition from nematic to smectic A is also approached through an analogy—the analog of the A phase is a superconducting metal (i.e., a charged superfluid)—this brings in a number of remarkable effects and is explained in Sec. 4. The $\mathrm{N} \leftrightarrow C$ transition is more complex and does not compare directly to any commonly known system. One unusual feature is that the relevant order parameter has an infinite number of components. A tentative theoretical scheme for this delicate case is sketched in Sec. 5.

2. The $C \leftrightarrow A$ Transition

The transition from tilted smectic (C) to uniaxial smectic (A) has

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† To define a transition without latent heat, we use both denominations "continuous" or "second-order." The first one is slightly preferable on fundamental grounds, but the second one is more widespread.

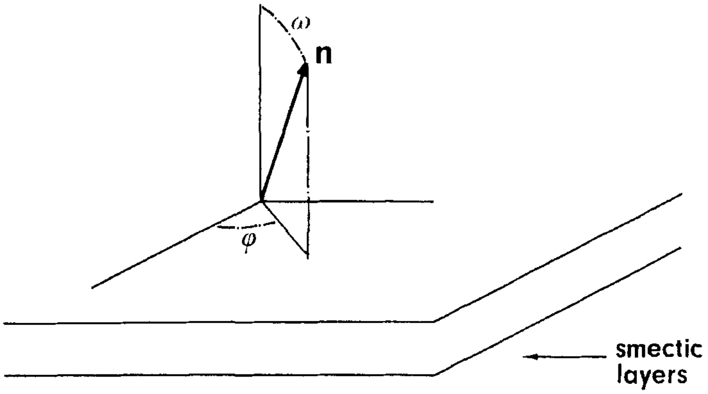

Figure 3. Definition of the tilt parameters in a smectic C: **n** is the direction of the longest principal axis of the dielectric ellipsoid.

been studied on a few typical materials such as TBBA.(8) This particular compound appears to have a continuous (or nearly continuous) transition of the type in which we are interested.

For a given set of layers, to describe the ordered (C) state, one must specify the magnitude ω of the tilt angle, and also the azimuthal direction of tilt, specified by an angle ϕ. The meaning of these two angles is explained on Fig. 3. The precise definition of ω and ϕ must be based on a given tensorial property. For instance we choose to consider the dielectric tensor measured at one reference frequency in the optical spectrum (e.g., at the yellow line of sodium). Then ω and ϕ are the polar angles defining that principal axis of the dielectric tensor which is associated with the largest dielectric constant (or refracting index). Once we know this axis **n** the two other axes are unambiguously defined because the (**n**, z) plane is a plane of symmetry. (z is the normal to the layers.)

Of course, instead of using the dielectric constants, we could have based our definition of ω and ϕ on some other tensor property—for instance on the magnetic susceptibilities. This would lead us to the same ϕ value, but not exactly to the same ω value; in a biaxial crystal, different tensors need not have the same principal axes. However, in the vicinity of a continuous $A \leftrightarrow C$ transition (i.e., for small values of ω) this does not create any serious difficulty. A change from dielectric to magnetic tensors in the definition of ω will simply multiply ω by a constant factor.

In our earlier studies on nematics⁽⁹⁾ we found it preferable to base the definition of the order parameter on magnetic, rather than on dielectric properties—because magnetic susceptibilities are somewhat simpler to relate to the microscope alignment properties. But, for smectics A, it appears wiser to use the optical constants as the basic parameters, since they are by far the simplest probe for the molecular tilt.

To summarize the discussion, we can characterize the onset of order by two real parameters ω and ϕ, or equivalently by the complex number

$$\psi = \omega e^{i\phi} \tag{2.1}$$

This brings in a remarkable analogy with superfluid helium.⁽¹⁰⁾ In helium, what we have is a Bose condensation⁽¹¹⁾ and a macroscopic number of helium atoms are occupying one quantum state, described by a wave function $\psi(\mathbf{r})$. This is the order parameter and it is complex.

The role of the phase parameter ϕ is essentially the same for superfluids and for smectics C:

(1) For a *homogeneous* state (ω and ϕ independent of position) the free energy is independent of ϕ. For the superfluid case, this property is called gauge invariance.

(2) For a *distorted* state, where ω and ϕ do depend on $\mathbf{r}$, the situation is slightly more complex in a smectic C than in a superfluid. This can be understood from the structure of the gradient terms F_g in the free energy:

(a) In a superfluid, F_g must be invariant by rotations of the angle ϕ. This leads to the form:

$$F_g = \frac{1}{2M}\left|\nabla\psi\right|^2$$

where M is a certain " mass tensor ".

(b) In a liquid crystal, F_g is invariant only by simultaneous rotations of the molecular axes (i.e., of ϕ), and of the molecular centers of gravity. Introducing a director:

$$\mathbf{n} = \begin{pmatrix} \omega\cos\phi \\ \omega\sin\phi \\ 1 \end{pmatrix} = \begin{pmatrix} \omega_x \\ \omega_y \\ 1 \end{pmatrix} \qquad (\omega \ll 1)$$

we may write the distortion free energy in the form which is standard for nematics:

$$F_g = \tfrac{1}{2}K_1(\operatorname{div}\mathbf{n})^2 + \tfrac{1}{2}K_2(\mathbf{n}\cdot\operatorname{curl}\mathbf{n})^2 + \tfrac{1}{2}K_3(\mathbf{n}\times\operatorname{curl}\mathbf{n})^2$$

$$= \frac{K_1}{2}\left(\frac{\partial\omega_x}{\partial x} + \frac{\partial\omega_y}{\partial y}\right)^2 + \frac{K_2}{2}\left(\frac{\partial\omega_x}{\partial y} - \frac{\partial\omega_y}{\partial x}\right)^2 + \frac{K_3}{2}\left[\left(\frac{\partial\omega_x}{\partial z}\right)^2 + \left(\frac{\partial\omega_y}{\partial z}\right)^2\right]$$

There are three elastic constants involved, as first pointed out by O. Parodi.† But this numerical complication does not modify the qualitative properties of the phase variable, and the resulting physical features for the C–A transition, which are discussed in Ref. 10 and listed below:

(a) the transition $C \leftrightarrow A$ *may* be continuous; if it is (as we shall assume in all that follows) the specific heat will show a logarithmic singularity at the transition point T_{CA};

(b) below T_{CA}, the tilt angle will vary according to the law

$$\omega = \text{const.}\ |\Delta T|^{\beta} \tag{2.2}$$

where $\Delta T = T = T_{CA}$ and $\beta \cong 0.35$.

(c) above T_{CA}, if we can apply a magnetic field H which is *oblique* with respect to the optical axis (Oz) of the smectic phase (e.g., in the xz plane), we expect to induce a tilt angle

$$\omega = C\frac{\chi_a H_x H_z}{k_B T_{CA}}\left(\frac{T_{CA}}{\Delta T}\right)^{\gamma} \tag{2.3}$$

where C is a numerical constant of order unity, χ_a is the diamagnetic anisotropy per molecule, and the critical exponent γ should be close to 1.30. The tilt predicted by Eq. (2.3) is small, because the diamagnetic energy $\chi_a H^2$ is very weak when compared to $k_B T_{CA}$, but it could be measured by suitable optical methods, at least close to T_{CA}.

(d) again starting from the smectic A phase, and decreasing T towards T_{CA}, we expect to see the onset of a strong (depolarized) light scattering due to fluctuations in the tilt angle. In the (usual) situation where the wavelength of light is larger than the size ξ of the fluctuating domains, the scattered intensity I should be of the form

$$I = I_0 + I_1\left(\frac{T_{AC}}{\Delta T}\right)^{\gamma} \tag{2.4}$$

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† Private communication.

where I_0 is the normal scattering by the smectic A phase, and is small (except for very special circumstances⁽¹²⁾) and I_1 is of comparable magnitude. Thus Eq. (2.4) allows in principle for another measurement of γ.

The determination of β and γ are particularly interesting because these exponents are not accessible in helium (the amplitude of the condensate wave function ψ is not directly observable).

Apart from the static critical effects, we can also think of various *dynamical* experiments which probe the critical exponents. The dynamical theory is much more conjectural than the static theory, but the resulting predictions are still interesting. For the case at hand, it is plausible to assume that the order parameter ψ relaxes according to the law

$$f\frac{\partial\psi}{\partial t} = -\frac{\partial F}{\partial\psi^*} \tag{2.5}$$

where ψ^* is the complex conjugate of ψ, and $-(\partial F/\partial\psi^*)$ is the thermodynamic force driving ψ towards equilibrium. (The free energy $F(\omega, \phi)$ is here written as a function of ψ and ψ^*). f has the dimensions of viscosity. Studies of specific models with rotating, tilted molecules suggest that $f(T)$ should be independent of $|\psi|$ near T_{CA}.⁽¹³⁾ If this is accepted, the following laws result:

(a) above T_{CA} the time constant for the oblique field effect τ is of the form

$$\tau = \tau_0\left(\frac{T_{CA}}{\Delta T}\right)^{\gamma} \tag{2.6}$$

where τ_0 is a microscopic time. The frequency width of the scattering (i.e., the I_1 component of Eq. (2.4)) should be essentially equal to $1/\tau$. The time τ could also be measured in a flow birefringence experiment, where a tilt ω is induced by a shear flow parallel to the smectic planes ($\omega \sim s\tau$ where s is the shear rate);

(b) below T_{CA} we must distinguish two relaxation processes, one for ω and one for ϕ. The relaxation of ω is still expected to follow a law similar to (2.6). On the other hand, the relaxation of ϕ is much slower (because a long wavelength fluctuation of ϕ hardly changes the energy). For a Fourier component of wave vector k the relaxation time is expected to be of the form

$$\frac{1}{\tau_k} = Dk^2 \tag{2.7}$$

In principle, the coefficient D should show a weak singularity near T_{CA}: namely $D \sim \Delta T^{-\eta\nu}$ where $\eta\nu \sim 0.03$. However, our assumptions on the friction coefficient $f(T)$ may not be satisfactory for such weak anomalies.

To summarize, we can say that the $C \leftrightarrow A$ transition offers a very promising field of research. There should be some striking analogies between T_{CA} and the λ point of helium. Certain critical properties are easier to probe in helium (e.g., the specific heat, because the high thermal conductivity allows for very precise temperature definitions). But other properties are accessible much more easily in smectics C (e.g., the exponents γ and β). Also, in spite of the analogy, there are some interesting differences, especially in the dynamical behaviour: below T_C the phase fluctuations in helium are associated with second sound, while in a smectic C they have a purely dissipative behavior, described by Eq. (2.7) and very similar to what we have in a nematic.

3. The $A \leftrightarrow$N Transition

3.1. POSSIBILITY OF HAVING A SECOND-ORDER TRANSITION

The transition between smectic A and nematic is usually discontinuous, with a finite latent heat, etc. But this is not imposed by the symmetry of the problem. As first shown by McMillan⁽¹⁴⁾ on a specific model, with suitable values of the interaction constants one may have a second-order transition. Using a slightly more general formulation we can present the basic ideas as follows:

(a) in the nematic phase the alignment of the molecules around optical axis (z) is described by the conventional parameter

$$S = S_0(T) = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle \tag{3.1}$$

The equilibrium value $S_0(T)$ is rather accurately given by Maier–Saupe mean field calculation.⁽¹⁵⁾

(b) $$\rho(\mathbf{R}) = \rho(z) = \rho_0\left[1 + \frac{1}{\surd 2}|\psi|\cos(q_S z - \Phi)\right] \tag{3.2}$$

where ρ_0 is the average density, and $|\psi|$ measures the strength of the smectic order (the factor $1/\surd 2$ will be convenient). $q_S = 2\pi/d$ is the wave vector of the density wave, d the interlayer distance. Φ is an arbitrary phase the importance of which will be emphasized later.

If the nematic alignment parameter is maintained fixed ($S = S_0(T)$) the free energy (per cm^3) F could be expanded in powers of ψ as follows:

$$F_S = \alpha_0 |\psi|^2 + \beta_0 |\psi|^4 + \dots \tag{3.3}$$

(only even powers of $|\psi|$ may come in). At a certain temperature T^*_{AN} the coefficient α_0 vanishes. Above this temperature it is positive. The coefficient β_0 is constantly positive. With these ingredients alone we could have a second-order transition of $T = T^*_{AN}$.

(c) However, there is some coupling between $|\psi|$ and S: if the alignment measured by S increases, the average attractions between neighboring molecules in a smectic layer will increase. Because of this coupling, the optimal value of S need not coincide with $S_0(T)$. We shall put

$$\delta S = S - S_0(T) \tag{3.4}$$

The coupling term, to lowest order in ψ and S, must have the form

$$F_1 = -C\psi^2 \delta S \tag{3.5}$$

where C is a (positive) constant. Finally we must include in F the nematic free energy F_R, which is a minimum for $\delta S = 0$.

$$F_R = F_R(S_0) + \frac{1}{2\chi} (\delta S)^2 \tag{3.6}$$

Here χ is a response function, which is large (although finite) near the nematic isotropic transition point T_{NI}, but which is small for $T \ll T_{NI}$ (since S_0 is then nearly saturated, and cannot fluctuate very much).

The overall free energy F, obtained by adding F_S, F_1 and F_R must then be minimized with respect to δS, giving

$$\delta S = \chi C \psi^2 \tag{3.7}$$

$$F = F(S_0) + \alpha_0 \psi^2 + \beta \psi^4 \tag{3.8}$$

$$\beta = \beta_0 - \tfrac{1}{2} C^2 \chi \tag{3.9}$$

The order of the transition depends critically on the sign of β (for $T \sim T^*_{AN}$).

(1) If $T^*_{AN} \sim T_{NI}$, $\chi(T^*_{AN})$ is large and β is negative. Then terms in ψ^6 must be added to (3.9) to ensure stability, and the resulting plots of $F(\psi)$ at various temperatures near T^*_{AN} look as shown on Fig. 4. The transition is of first order.

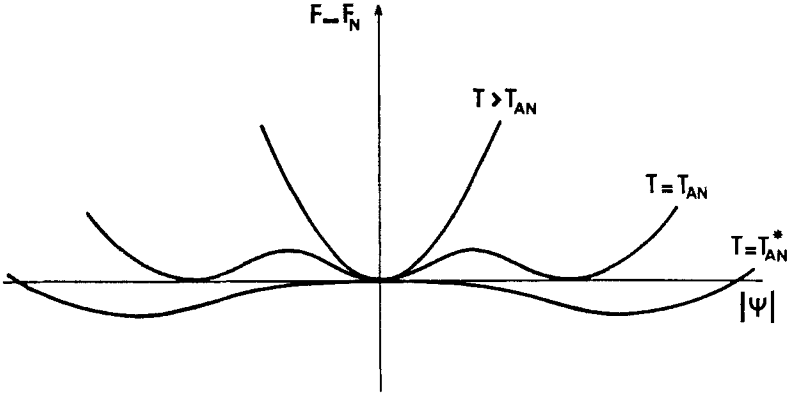

Figure 4. Free energy versus order parameter ψ for a first-order smectic $A \leftrightarrow$ nematic transition. At the temperature $T = T^*_{AN}$ the coefficient of ψ^2 vanishes, but the minimum of F at this temperature occurs for a non zero ψ. The transition is first-order and takes place at higher temperature T_{AN}.

(2) If T^*_{AN} is significantly smaller than T_{NI}, the response function $\chi(T^*_{AN})$ is small and $\beta \sim \beta_0 > 0$. Then the transition is of second order and the transition point is T^*_{AN}.

The change from second to first order is thus induced by a coupling between the order parameter (ψ) and an external variable (S). This is the exact counterpart of the so called Rodbell Bean effect in magnetism.(16) Here the order parameter is the magnetization M, and the external variable is the density (or lattice parameter a). The coupling is due to the dependence of exchange interactions on a. If the magnetic crystal is strongly compressible (large χ) the magnetic transition becomes first-order.

How can we, in practice, arrange for the transition to be second-order? The discussion above suggests that this will occur if χ is small, i.e., when T^*_{AN} is significantly smaller than T_{NI}. We can act on these temperatures by changing the length (l) of the aliphatic chains which hang at the ends of the molecule at hand. Usually an increase in (l) decreases T_{NI} but does not change the limits of the smectic domain very much. Thus the most favorable situation corresponds to (l) small. One series of homologous compounds of variable (l) has been studied recently by Doane and coworkers(17) using NMR measurements of S. They conclude that for the compound with the shortest (l), the transition is of second order as predicted by McMillan. Further tests will be required to clarify completely the situation concerning this particular compound, but in any case the trend shown by the data is clearly favorable.

3.2. PRETRANSITIONAL EFFECTS AND STRUCTURE OF THE FREE ENERGY

In a nematic phase, we may begin to see small domains with stacked layers. This has been recognized first by de Vries(18) who called these domains cybotactic groups (Fig. 5). These groups give rise to intense scattering at small angles. For the smectic $A \leftrightarrow N$ transition, in a single domain N sample, the scattering is concentrated near *two* points in reciprocal space

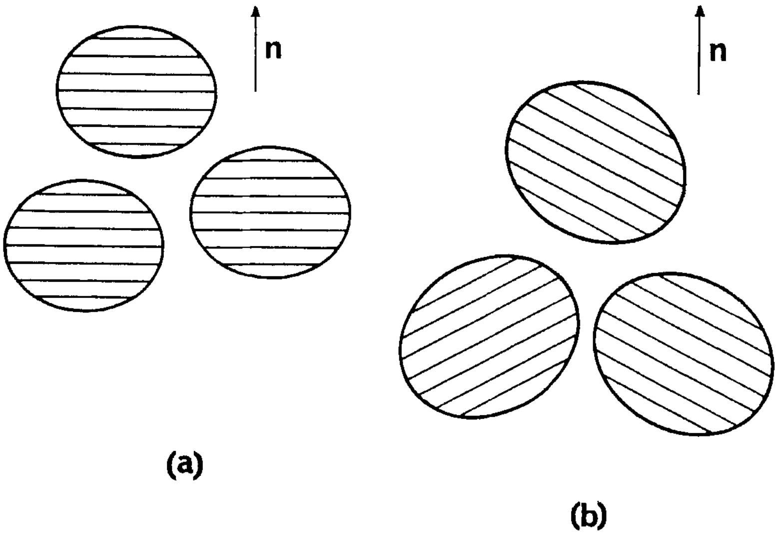

Figure 5. Cybotactic groups in a nematic phase (a) " normal " cybotactic ($A \leftrightarrow N$ transition); (b) " skewed " cybotactic ($C \leftrightarrow N$).

$$\mathbf{k} = \pm q_S \mathbf{n} \tag{3.10}$$

where $\mathbf{n}$ is the director of the nematic phase, while $d = 2\pi/q_S$ is the thickness of the smectic layers. The width of this diffuse peak gives some information on the size of the domains. Actually, because the N phase is anisotropic, we need two parameters to specify this width in reciprocal space. Taking the director along z, we may define them as

$$\left.\begin{aligned} \Delta k_z &= \frac{1}{\xi_v(T)} \\[2ex] \Delta k_x = \Delta k_y &= \frac{1}{\xi_T(T)} \end{aligned}\right\} \qquad (3.11)$$

ξ_v and ξ_T measure the dimension of the cybotactic groups along the optical axis and normal to it. For many qualitative purposes, it is possible to ignore the difference between these two lengths and to put $\xi_v \sim \xi_T \sim \xi$. Here ξ will be called the coherence length.

A more precise definition of these lengths may be obtained in terms of the order parameter and of the associated free energy F. The order parameter for the $A \leftrightarrow \mathrm{N}$ transition appears in the density wave of Eq. (3.2). We must specify both the amplitude $|\psi|$ of the density wave associated with the layers and the phase Φ which tells us where the layers are. Thus the complete order parameter is a complex number $\psi = |\psi| e^{i\Phi}$. This again brings in some analogy with superfluids, as noted independently by W. McMillan$^{(19)}$ and by us.$^{(20)}$ In the disordered phase, ψ vanishes on the average, but there remain fluctuations of the density ρ described by

$$\rho(\mathbf{r}) = \rho_0 \left[1 + \frac{1}{\sqrt{2}} \psi(\mathbf{r}) \exp(-iq_S z) + cc \right]$$

Near the $A \leftrightarrow \mathrm{N}$ transition $\psi(\mathbf{r})$ will be a slowly varying function of $\mathbf{r}$. In the mean field approximation, we can expand the free energy F in terms of ψ, for a fixed director $\mathbf{n}$ (parallel to z) as follows:

$$F_S = \alpha |\psi|^2 + \beta |\psi|^4 + \frac{1}{2M_v} \left(\frac{\partial \psi}{\partial z} \right)^2 + \frac{1}{2M_T} \left[\left(\frac{\partial \psi}{\partial x} \right)^2 + \left(\frac{\partial \psi}{\partial y} \right)^2 \right] \qquad (3.12)$$

The coefficients α and β have been discussed above. The physical meaning of the gradient term displayed in Eq. (3.12) can be understood in at least two ways.

(a) $\underline{T > T_C}$: The thermal averages of the Fourier components $\langle | |\psi| (\mathbf{q}) |^2 \rangle$ give us the X-ray scattering intensity, $I(\mathbf{q}) \sim \langle [|\psi(\mathbf{q} - \mathbf{q}_S)|^2 \rangle$. For small ψ, neglecting the fourth-order terms in (3.12) we have by equipartition

$$\langle|\psi(\mathrm{q})|^2\rangle = \frac{k_B T}{\alpha + (1/2M)q_z^2 + (1/2M_T)(q_x^2 + q_y^2)} \tag{3.13}$$

Thus the widths Δk_z and Δk_x, Δk_y, or the corresponding coherence lengths can be related to M_V, M_T, and α by

$$\xi_v^2 = 1/2M_V\alpha \qquad \xi_T^2 = 1/2M_T\alpha \tag{3.14}$$

In the mean field approximation $\alpha(T)$ varies linearly with $\Delta T = T - T_c$ while the coefficients M_V and M_T are constants.† Thus ξ diverges near T_C.

(b) $\underline{T < T_C}$: Here, for many purposes, we may assume that the magnitude $|\psi|$ of the density modulation takes a fixed value while the phase Φ may still fluctuate significantly. The gradient terms in the free energy F (Eq. (3.12)) then become

$$F_{(\mathrm{grad})} = \frac{\psi_0^2}{2M_V}\left(\frac{\partial\Phi}{\partial z}\right)^2 + \frac{\psi_0^2}{2M_T}\left[\left(\frac{\partial\Phi}{\partial x}\right)^2 + \left(\frac{\partial\Phi}{\partial y}\right)^2\right] \tag{3.15}$$

A constant $\partial\Phi/\partial z$ describes a uniform dilation of layers. $\psi_0^2/2M_V$ is proportional to the corresponding elastic coefficient.‡ A constant $\partial\Phi/\partial x$ represents a rotation of the layers (by an angle $1/q_S\,\partial\Phi/\partial x$, around the y axis) with respect to the long axis of the molecules (which by definition is maintained fixed along z). Thus the last two terms in Eq. (3.15) represent the *energy required to tilt the layers* with respect to the molecules. In the mean field approximation $\rho_S = \psi_0^2/M$ is proportional to $|\alpha|$ and thus linear in $|\Delta T|$. But in reality, a scaling argument due to Josephson(21) shows that ρ_S should be proportional to $1/\xi \sim \Delta T^{\gamma}$, with $\gamma \sim 2/3$.

We have seen that the last two terms in Eq. (3.15) describe a tilting energy for a fixed direction $\mathbf{n}$ (parallel to Z). We shall now modify the free energy F to allow for local fluctuations in $\mathbf{n}$

$$\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}$$

Consider again (for instance) a tilt along the y axis = the rotation angle of the layers is $\partial\Phi/\partial x 1/q_S$. The rotation angle of the molecules is $-\delta n_x$. The physical tilt angle is the difference of the two,

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† In more refined approximations $\alpha \sim \Delta T^{\gamma}$ where $\gamma \sim 1.30$ and $\xi \sim \Delta T^{-\nu}$ where $\nu \sim 2/3$.

‡ In Ref. (12) we use, instead of Φ, the vertical displacement of the layers, u, such that $q_S u = \Phi$. The elastic contribution corresponding to the first term of (3.15) is $\frac{1}{2}\mathbf{B}\left(\frac{\partial u}{\partial z}\right)^2$ with $\mathbf{B} = \frac{\psi_0^2 q_S^2}{M_V}$.

namely $1/q_S(\partial\Phi/\partial x+\delta n_x q_S)$. Thus the generalized form of F, including director fluctuations, is

$$F_{(\mathrm{grad})}=\frac{\psi_0{}^2}{2M_V}\left(\frac{\partial\Phi}{\partial z}\right)^2+\frac{\psi_0{}^2}{2M_T}\left[\left(\frac{\partial\Phi}{\partial x}+q_S\,\delta n_x\right)^2+\left(\frac{\partial\Phi}{\partial y}+q_S\,\delta n_y\right)^2\right] \quad (3.16)$$

Returning to the complete order parameter ψ, we can also rewrite this in a form which is applicable both above and below T_c:†

$$F_s=\alpha\,|\psi|^2+\beta\,|\psi|^4+\frac{1}{2M_V}\left(\frac{\partial\psi}{\partial z}\right)^2+\frac{1}{2M_V}\,|\nabla_T\,\psi+iq_S\,\delta\mathbf{n}\psi|^2 \quad (3.17)$$

Equation (3.17) is strikingly similar to the Landau Ginsburg(22) free energy for a superconductor = for both systems, the complex number ψ is the order parameter. In a superconductor, the gradient terms involve the vector potential A through the combination $\nabla\psi+i(e^*/c)\mathbf{A}\psi$ where e^* is the charge of the Cooper pairs, and curl **A** is the local magnetic field. Equation (3.17) shows that for smectics A, the director **n** is the analog of the vector potential.‡ The vector curl **n**, which is the analog of the magnetic field, represents a distortion of the molecular arrangement (twist if curl **n** is parallel to **n**, and bend if curl **n** is normal to **n**).

This analogy is discussed in some detail in Ref. (20), and we shall present here only the main conclusions together with some comments.

3.3. Transitions in a Deformed Nematic

(a) *Landau Ginsburg parameter*

In a superconductor, Eq. (3.17) allows to define *two* characteristic lengths: one is the coherence length ξ, which is described above. The second length is the penetration depth λ; its meaning for a smectic A is defined on Fig. 6. The equation for λ (ignoring the difference between M_V and M_T) is:

$$\lambda^2=\frac{2MK\beta}{q_S{}^2\,|\alpha|} \quad (3.18)$$

where K is the Frank elastic constant (for twist or bend, depending on the case at hand). We know from theory and experiments on superconductors that a crucial parameter is the ratio of the two lengths

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† In Eq. (3.17), ∇_T represents the components of the gradient operator in the plane of the layers.

‡ This correspondence may also be established through a discussion of line defects in the ordered phase. See Ref. (20).

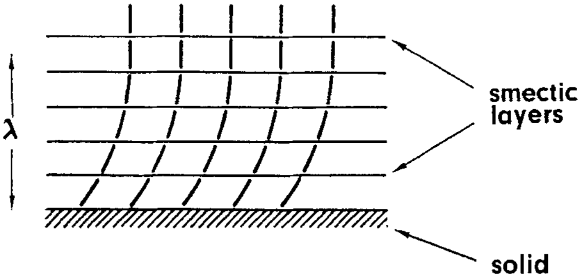

Figure 6. Analog of the penetration depth for a smectic A. A weak bend deformation is imposed at the solid/smectic interface. The director **n** is normal to the layers in the bulk of the smectic phase, but is perturbed in a thickness λ.

$\kappa = \lambda/\xi$. (The so-called Landau Ginsburg parameter). According to Eqs. (3.18) and (3.14) κ^2 is proportional to the coefficient in the quadratic terms of $F(\psi)$ namely β. We have seen, in Eq. (3.9), that β contained 2 contributions of opposite sign—for usual smectogenic compounds, β is negative and the transition is of first order. For compounds with very short terminal chains ($l \to 0$) β may become weakly positive. Then the transition is of second order and this is the case on which we concentrate here: for such a case, β will probably be small, and κ will also be small. Thus we tend to believe that the materials of interest here will have $\kappa < 1$. In the jargon of superconductors, this corresponds to a " type I " situation.

(b) *Type I Behavior*

This observation may have interesting consequences in connection with the $A \leftrightarrow \mathrm{N}$ transition under imposed distortion. This is the analog of a superconducting transition under a magnetic field: under a finite twist, t, for instance (e.g., by starting with a cholesteric rather than with a nematic) one expects the $A \leftrightarrow \mathrm{N}$ transition to become weakly first-order. The transition temperature should decrease with t, and at the transition there may exist an *intermediate state*, i.e., a regular array of coexisting cholesteric and smectic regions. Similar effects could occur in a bent nematic, or more generally in the presence of external fields (e.g., electric fields) inducing a deformation in the nematic alignment—there situations will be in general much more complicated than simple twist, because the distortions are not uniform in the high temperature state—however, they are important in practice, and some of them are currently under study, both experimentally⁽²³⁾ and theoretically.⁽²⁴⁾

3.4. Precritical Anomalies in the Elastic Constants

Let us now look at a deformed nematic, at a temperature just above the smectic ordering point. If the distortion is of the twist, or bend type, the cybotactic groups will not accept it easily. The free energy associated with the deformation will contain two components

$$F = \tfrac{1}{2}K_0(\nabla n)^2 + F_S(\psi) \tag{3.19}$$

where K_0 is the appropriate Frank constant in the absence of any cybotactic groups, while $F_S(\psi)$ is given by Eq. (3.17) and must be averaged of all possible fluctuations ψ. We may estimate roughly the contribution of F_S as follows

$$F_S \to \frac{q_s^2}{M}\langle|\psi|^2\rangle\xi^2(\nabla n)^2 \tag{3.20}$$

where $\xi\nabla n$ is the order of magnitude of the strains in a cybotactic group of size ξ, and (3.20) represents the resulting distortion energies as in Eq. (3.15). Here however instead of the average amplitude ψ_0 squared, which vanishes above T_c, we use the thermal average $\langle|\psi|^2\rangle$. The actual value of $\langle|\psi|^2\rangle$, in the mean field approximation, can be derived from Eq. (3.13), and is

$$\langle\psi^2\rangle \simeq \text{const.}\,\frac{T}{\alpha\xi^3} \tag{3.21}$$

corresponding to correlated fluctuations in a volume $\sim\xi^3$. Equations (3.20, 3.21) then show that the cybotactic groups give a correction to the elastic constants for twist or bend

$$\begin{aligned} K &= K_0 + \delta K \\ \delta K &= \frac{\pi}{3\sqrt{2}}\,\frac{k_B T}{d^2}\,\xi \end{aligned} \tag{3.22}$$

(where we have inserted the correct coefficient). A more rigorous version of this calculation together with extensions of (3.22) allowing for the difference between M_V and M_T, is given in Ref. (20).

Equation (3.22) does show a remarkable anomaly in K_2 (twist) or

K_3 (bend) for $T \to T_c$ since ξ diverges near a second-order transition point. In principle Eq. (3.22) is restricted to the mean field approximation. However, if we depart from mean field, assuming again Eq. (3.20), and replacing (3.21) by the Josephson scaling law for $\psi^2/M^{(21)}$, we are still led to an equation of the form (3.22): then the only difference is that $\xi \sim \Delta T^{-\nu}$ where $\nu = 2/3$ (instead of 1/2).

Unfortunately, at the time of writing, we have no measurements available on the twist or bend electric constants of a nematic just above an $A \leftrightarrow$ N transition. But we may hope to obtain some indirect information on the twist constant K_2 through a study of the temperature dependence of the pitch in a cholesteric phase.† If t is the twist, the free energy for a cholesteric may be written as

$$F = \tfrac{1}{2}K_{20}t^2 - \tfrac{1}{2}K_{20}t_0 t + F_s(\psi) \tag{3.23}$$

where K_{20} and t_0 are respectively the twist constant and the equilibrium twist in the absence of cybotactic groups. The structure of the smectic free energy F_s is not seriously altered by the presence of chirality.‡ Thus the only connection resulting from F_s is the renormalization of the t^2 term, while the term linear in t is unchanged.

$$F \to \tfrac{1}{2}(K_{20} + \delta K_2)t^2 - \tfrac{1}{2}K_{20}t_0 t \tag{3.24}$$

The equilibrium twist, in the presence of cybotactic groups, corresponds to the minimum of F, and is given by

$$t = t_0 \frac{K_{20}}{K_{20} + \delta K_2} \tag{3.25}$$

where δK_2 (given by Eq. (3.22)) is a decreasing function of temperature. Equation (3.25) thus gives rise to a twist $t(T)$ which is increasing with T, in agreement with what is observed in most cholesterics. The well-known experimental rise of $t(T)$ in cholesterol derivatives may thus reflect simply the presence of cybotactic groups: this could be checked by comparing short-range order studies performed with X-rays$^{(25)}$—giving ξ and thus δK_2—to direct data on $t(T)$.

† This possibility was first pointed out to us by Prof. R. B. Meyer. It has also been discussed independently by Dr. Alben (communication at the 4th International Conference on Liquid Crystals).

‡ F_s may contain terms in $\psi^2\, t_0 t$, but this is negligible in comparison with the renormalization of K_2 (giving terms of order $\psi^2\xi^2t^2$).

3.5. *Static critical exponents*

X-ray studies on the " diffuse Bragg peak " just above T_c should yield two critical exponents for smectics *A*—the exponents γ and ν as defined in the usual notation. Since smectics *A* are so similar to superfluids, can we predict that they will show the values of γ and ν which are accepted in Helium II?

We do *not* know the exact answer to this question, for the following reason: in all the ordered phase of a smectic *A*, the fluctuations of the phase ϕ are divergent. This divergence was noticed first by Peierls (see Ref. 6, Chap. 13, and also Ref. 12). It is deeply related to the flexibility of the layers—i.e., to the ability of going from a planar texture to a focal conic arrangement. In our language, the divergence stems from coupled fluctuations of Φ and $\delta\mathbf{n}$, such that the molecules stay normal to the layers: they correspond to the " undulation mode " of Ref. 12, which involves only splay deformations $\delta\mathbf{n}$; the latter have no counterpart in superconductors (where the curl-free part of the vector potential *A* is not a physical degree of freedom). Thus the divergence of $\langle \Phi^2(\mathbf{r}) \rangle$ is a unique feature of smectics *A*.

Of course, it is weak (logarithmic) and suppressed physically by many effects.(12) But it may complicate the analogy between smectics *A* and superfluids: the critical exponents need not be exactly the same for both systems. If a good example of second-order $A \leftrightarrow \mathrm{N}$ transition is found in nature, it will be particularly important to probe the nature of the specific heat anomaly, the magnitude and width of the X-ray peaks above T_c, etc., to see if the difference is serious or not.

3.6. DYNAMICAL EFFECTS

In the smectic *A* phase we expect two branches of acoustical waves:(12) this again shows a similarity with a superfluid such as helium where we have 1st and 2nd sound. Going close to T_{AN}, and always assuming that the transition is of second order, we expect the second sound velocity s_2 to collapse. Another dynamical property of great interest is the Helfrich permeation coefficient, describing how the molecules can flow through the layers—clearly permeation becomes easier when ψ becomes small. These properties have been analyzed recently by F. Brochard, using 2 distinct assumptions on dynamical scaling(26)—they should lead to a number of interesting experiments.

4. The $C \leftrightarrow$N Transition

A direct transition from smectic C to nematic is observed in many mesomorphic systems—for instance with the longer homologs of PAA. This $C \leftrightarrow$N transition may also be of second order from the point of view of the Landau rules (as will become apparent later in this section). Some instances where the $C \leftrightarrow$N heat of transition is particularly low can indeed be found in the literature.(7) Thus, here again, we may expect interesting pretransitional phenomena.

However, from the point of view of statistical mechanics, $C \leftrightarrow$N is much more complex than $A \leftrightarrow$N. Consider for instance the X-ray scattering by a single domain nematic containing some cybotactic groups as defined by de Vries.(18) With " normal " cybotactic groups (A type) the scattering is concentrated around two *points* in reciprocal space $\mathbf{k} = \pm q_s$, $\mathbf{n} = \pm \mathbf{q}_s$. There are two, and only two, Fourier components of the density $\rho(\mathbf{q}_s)$ and $\rho(-\mathbf{q}_s) = \rho^*(\mathbf{q}_s)$ which show large fluctuations near T_c—the natural order parameter is a two-component object ψ—const. $\rho(\mathbf{q}_s)$. On the other hand, with " skewed " cybotactic groups (C type) the scattering intensity is concentrated on two *rings* in reciprocal space, as shown on Fig. 7. All Fourier components $\rho(\mathbf{k})$ for which

$$\begin{aligned} k_z &= q_v (= q_s \cos \omega) \quad (z\text{—optical axis}) \\ k_x^2 + k_y^2 &= q_T^2 \qquad\qquad (q_T = q_s \sin \omega) \end{aligned} \tag{4.1}$$

have large fluctuations near Tc. Thus the natural order parameter† has an infinite number of components $\psi(\phi)$ where ϕ is defined in Fig. 7 and runs from 0 to 2π.

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† Since in the ordered phase only *one* ϕ value occurs for a single domain, one would use a more restricted order parameter, having three components: the magnitude of the density modulation, the phase ϕ, and the angle Φ. This is in some respects simpler than an order parameter with an infinite number of components, but not very convenient computationally. The situation is reminiscent of uniaxial nematics, where 3 real parameters are enough to specify the order, but where a symmetric traceless tensor $Q_{\alpha\beta}$, with 5 independent components, is more practical.(9)

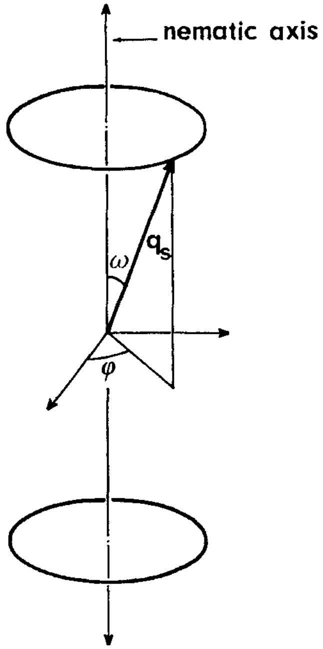

Figure 7. The two rings of critical scattering above a $C \leftrightarrow N$ transition. ω is the tilt angle of the cybotactic groups, $\mathbf{q}_s$ is the wave vector of the density modulation associated with one particular cybotactic group.

$$\psi(\phi) = \rho(k_z = q_v, k_x = q_T \cos\phi, k_y = q_T \sin\phi)$$

The free energy functional for a fixed director ($\mathbf{n} = \mathbf{n}_0$, parallel to Z) now has the form

$$F = \sum_{\phi} \left\{ \alpha |\psi_\phi|^2 + \frac{1}{2M_V}\left(\frac{\partial\psi_\phi}{\partial Z}\right)^2 + \frac{1}{2M_T}(\mathbf{u}\cdot\nabla\psi_\phi)^2 + \frac{1}{M_{VT}}\frac{\partial\psi}{\partial z}\mathbf{u}\cdot\nabla\psi_\phi \right\}$$
$$+ \text{ terms of order } \psi^4 \qquad (4.2)$$

Equation (4.2) must be supplemented by a number of comments:

(a) we have written $\sum_\phi$ rather than $\int d\phi$ to emphasize the role of ϕ as an index for components. (b) Note that the quadratic part does not involve any cross-terms such as $\psi_\phi \psi^*_{\phi'}$. (c) The gradient terms in 4.2 are very different from what we had in a smectic A (Eq. 3.12). The unit vector $\mathbf{u}$ is defined as $(\cos\phi, \sin\phi, 0)$. The gradient terms come into play only for variation in the $(Z, \mathbf{u})$ plane. For variations of ψ along the normal to this plane (i.e., along the direction $\mathbf{v}$ of Fig. 7) we have no terms quadratic in grad ψ—variations of ψ along this direction correspond to a simple shift in the azimuthal angle ϕ. (d) The three coefficients M_v, M_T, and M_{vT} can be derived from a study of the X-ray scattering intensities near the " critical ring " in reciprocal space. (e) It can be shown that there are no terms of order ψ^3 in F—this indicates that the $C \leftrightarrow \mathrm{N}$ transition *may* be of second order (provided that the coefficients of the various ψ^4 terms satisfy some inequalities).

From Eq. (4.2) one can derive the correlations $\langle \psi_\phi{}^*(0)\psi_\phi(R)\rangle$ for $T > T_c$. They are found to extend up to distance $R \sim \xi = (2M\alpha)^{1/2}$ in the Z and $\mathbf{u}$ directions. But in the $\mathbf{v}$ direction their behavior is different. In fact, to get convergent answers, one must add to (4.2) terms of order $(\partial^2\psi_\phi/\partial x_V)^2$. When this is done, one obtains a correlation range along $\mathbf{v}$ which is reduced, and is of order $\sqrt{\xi d}$ (d = layer thickness).

Equation (4.2) is valid only when the director is fixed (along Z). If the director is now allowed to fluctuate, with two independent components δn_u, δn_v the modified form of Eq. (4.2) is, in analogy with (3.17):

$$F_s = \sum_\phi \alpha\psi_\phi{}^2 + (\nabla\psi^* - i\delta\mathbf{q}_s\psi^*)\frac{1}{2\hat{M}}(\nabla\psi + i\delta\mathbf{q}_s\psi) \tag{4.3}$$

where $1/\hat{M}$ is the tensor defined in Eq. (4.2); the analog of the vector potential is thus the vector $\delta\mathbf{q}_s$ with component

$$\begin{aligned} \delta q_{su} &= +q_v\,\delta n_u \\ \delta q_{sv} &= q_v\,\delta n_v \\ \delta q_{sz} &= q_T\,\delta n_u \end{aligned} \tag{4.4}$$

The analog of the magnetic field is the vector

$$\mathbf{h} = \operatorname{curl} \delta\mathbf{q}_s \tag{4.5}$$

Using Eqs. (4.3, 4.4, 4.5) it is then possible to calculate what should be the renormalization of the Frank elastic constants, due to cybotactic groups, above the $C \leftrightarrow \mathrm{N}$ transition point. This calculation is sketched in the Appendix. Here we shall present only some qualitative arguments and results.

(a) The estimate (3.20) for the correction to the elastic energy remains valid, but the formula (3.21) for $\langle|\psi|^2\rangle$ must be modified. As seen above, the correlation volume is $\xi^2\sqrt{\xi d}$ and thus

$$\langle|\psi|^2\rangle \cong \frac{k_B T}{\alpha\xi^2\sqrt{\xi d}} \tag{4.6}$$

Then

$$\delta K \sim q_s^2 \frac{|\psi|^2}{M}\xi^2 \sim \text{const.}\frac{T}{\alpha\xi^{1/2}} \sim \text{const.}\ \xi^{3/2} \tag{4.7}$$

Thus, in the $C \leftrightarrow \mathrm{N}$ case, the renormalization of the elastic constants involves a higher power of the coherence length ξ.

(b) All three electric constants are affected by the presence of skewed cybotactic groups, the shifts being in the ratios

$$\frac{\delta K_1}{3\sin^2\omega} = \frac{\delta K_2}{\sin^2\omega} = \frac{\delta K_3}{4\cos^2\omega} \tag{4.8}$$

With normal (A) cybotactic groups, we had no splay corrections ($\delta K_1 = 0$) but, with a skewed group, even splay becomes difficult.

This may be shown as follows—define the wave vector of the density modulation as

$$\mathbf{q}_s = q_v\mathbf{n} + q_T\mathbf{u} \tag{4.9}$$

The only deformations which maintain a constant interlayer spacing are those for which $\operatorname{curl}\mathbf{q}_s = 0$. (This is shown for instance in Ref. 12.) Let us consider now a situation of pure splay for the director ($\operatorname{curl}\mathbf{n} = 0$, $\operatorname{div}\mathbf{n} = 0$). We shall show that the vector

$$\mathbf{c} = \operatorname{curl}\mathbf{q}_s \equiv q_T \operatorname{curl}\mathbf{u} \tag{4.10}$$

cannot vanish in this case. To see this, let us consider small deviations $\delta\mathbf{u}$, $\delta\mathbf{n}$, and define axes such that the unperturbed vectors $\mathbf{n}_0$ and $\mathbf{u}_0$ are respectively colinear to Z and X. Then we have the conditions $\delta n_z = 0$, $\delta u_x = 0$, $\delta n_x + \delta u_z = 0$. They leave one component δu_y adjustable at will. We have

$$\begin{aligned} c_x &= -\frac{\partial}{\partial x}\delta n_x - \frac{\partial}{\partial z}\delta u_y \\ c_y &= -\frac{\partial}{\partial x}\delta n_x \\ c_z &= \frac{\partial}{\partial z}\delta u_y \end{aligned} \tag{4.11}$$

By a suitable choice of δu_y we can set either c_x or $c_z = 0$. But in any case $c_y \neq 0$.† Thus $|c| \neq 0$ and the layers cannot remain of constant thickness, q.e.d.

Pretransitional effects on K_3 have been observed by Gruler(27) in the higher homologs of PAA. He finds that the ratio K_3/K_1 increases when the temperature decreases and gets close to T_{cn}. This would correspond to our expectations for a smectic A, but not for a C (because of Eq. (4.8)) unless the tilt angle ω be rather small.

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Appendix

TENTATIVE CALCULATION OF THE EFFECT OF SKEWED CYBOTACTIC GROUPS ON THE FRANK CONSTANTS OF A NEMATIC PHASE

Our starting point is the free energy (4.3), where $\delta \mathbf{q}_s$ is related to the director deviations $\delta \mathbf{n}$ by Eq. (4.4). For a given distorted conformation $\delta \mathbf{n}(r)$ we wish to compute the partition function

$$Z = \int D\psi(\mathbf{r}, \phi) \exp\left(-\int F_s d\mathbf{k}/k_B T \right. \tag{A.1}$$

where the symbol $\int D\psi$ represents an integration over all possible forms of $\psi(\mathbf{r}, \phi)$. We keep only quadratic terms in ψ in F_s—this is acceptable only in the mean field approximation. Because F_s is a sum of independent contributions for different angles ϕ, the function Z factorizes and the corresponding thermodynamic potential is an average over ϕ

$$-K_B T \log Z = \sum_\phi \Omega_\phi / \sum_\phi 1 \tag{A.2}$$

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† There is one exception—if $\delta n_x \equiv 0$, i.e., if the cybotactic group (defined by $\mathbf{n}_0$ and $\mathbf{u}_0$) has one particular orientation with respect to the splay plane. But this particular case plays no role after averaging over group orientations.

where Ω_ϕ is the potential for one orientation of the cybotactic groups. Let us thus focus our attention on a single ϕ value. The corresponding component in the free energy (4.3) is the analog of the energy for a quantum mechanical particle of wave function ψ, with a certain effective mass tensor $1/\hat{M}$, a charge equal to 1, in a magnetic field $\mathbf{h} = \text{curl}\ \delta\mathbf{q}_s$. It is crucial to notice that the mass measured along v is infinite, thus the only component of k which will lead to closed orbits and thus to a significant diamagnetism is:

$$h_v = q_v \frac{\partial n_u}{\partial z} + q_T \frac{\partial n_u}{\partial x_u} \tag{A.3}$$

The Landau levels for this orientation of $\mathbf{k}$ are given by

$$E = \frac{h_v}{M}(n+\tfrac{1}{2})\ (n = \text{integer}) \tag{A.4}$$

where $M = \sqrt{M_v M_T - M_{vT}^2}$. From this point, the calculation of Ω_ϕ follows exactly the lines of Ref. 28, and gives

$$\Omega_\phi(h) = \Omega_\phi(0) + \frac{k_B T h_v^2}{2^5 3\pi^2}\int_{-\infty}^{\infty}\frac{dk_v}{\alpha + \Gamma k_v^4} \tag{A.5}$$

where Γk_v^4 is the cutoff term defined in Sec. 4. The integral is equal to $\pi 2^{-1/2}\Gamma^{-1/4}\alpha^{-3/4}$. Since the coherence length is $\xi = (2M\alpha)^{-1/2}$, the contribution to the elastic energy resulting from the cybotactic groups of orientation ϕ is

$$\Omega_\phi(h) - \Omega_\phi(0) = \tfrac{1}{2}S h_v^2 \tag{A.6}$$

where

$$S = \frac{1}{24\pi}\frac{1}{(M\Gamma)^{\frac{1}{4}}}\xi^{3/2} \tag{A.7}$$

Returning to the laboratory frame (xyz) we may write

$$h_v = q_v\left[\cos\phi\frac{\partial n_x}{\partial z} + \sin\phi\frac{\partial n_y}{\partial z}\right] + q_T\left(\cos\phi\frac{\partial}{\partial x} + \sin\phi\frac{\partial}{\partial y}\right)(\cos\phi\, n_x + \sin\phi\, n_y) \tag{A.8}$$

Raising this to the square and taking the appropriate averages

$$\left.\begin{aligned}\overline{\cos^2\phi\sin^2\phi} &= \tfrac{1}{8}\\ \overline{\cos^4\phi} &= \tfrac{3}{8}\end{aligned}\right\}\text{etc.} \tag{A.9}$$

we obtain a correction to the free energy of the form

$$\delta F = \tfrac{1}{2}\delta K_1\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)^2 + \tfrac{1}{2}\delta K_2\left(\frac{\partial n_y}{\partial x} - \frac{\partial n_x}{\partial y}\right)^2 + \tfrac{1}{2}\delta K_3\left[\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right] \tag{A.10}$$

representing a sum of splay, twist, and bend contributions. The coefficients are

$$\left.\begin{aligned} \delta K_1 &= \tfrac{3}{8} S q_T{}^2 \\ \delta K_2 &= \tfrac{1}{8} S q_T{}^2 \\ \delta K_3 &= \tfrac{1}{2} S q_v{}^2 \end{aligned}\right\} \tag{A.11}$$

This corresponds to Eq. (4.8) of the main text.

It should be emphasized that Eqs. (A.11) do not hold for very small tilt angles ($q_T \to 0$): in this limit, the cutoff parameter l' diverges, and the tensor mass expansion of Eq. (4.3) must be revised.

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