

LIQUIDS, CRYSTALS AND LIQUID CRYSTALS

Concepts developed to explain melting in two dimensions and multicritical phenomena in three dimensions lead to a detailed model for the growth and structures of smectic liquid crystal materials.

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In thinking about the states of condensed matter, we usually consider two extremes. At one extreme are crystalline solids, in which atoms form a perfectly periodic array that extends to infinity in three directions. At the other extreme are fluids or glasses, in which the atoms or molecules are completely disordered and the system is both orientationally and positionally isotropic—that is, the materials look the same when viewed from any direction.

For many decades, however, physicists have realized that an intermediate state of matter is possible. In such a state the atoms or molecules are distributed at random, as in a fluid or glass, but the system is orientationally anisotropic on a macroscopic scale, as in a crystalline solid. This means that some properties of the fluid are different in different directions. Order of this sort is known as bond-orientational order. Although such phases of matter have long been recognized to be theoretically possible, little work was done on them until recently because there did not appear to be any realizations of them in nature. Indeed, as Rudolph Peierls, one of the pioneers of solid-state physics, recently commented to us, "We knew in the 1930s that it was possible theoretically for the positional

and orientational order to vanish at different temperatures; we just could not think of a scenario in which it would actually happen."

Ironically, it turns out that appropriate physical systems—smectic liquid crystals—not only were known at that time, but also had been discussed extensively even earlier, by Georges Friedel and Karl Herrmann in the 1920s.¹ (See box on page 55 for a discussion of smectic liquid crystals and their phases.) Some 50 years passed, however, before a proper association was made between the smectic liquid crystal phases and the concept of distinct translational and orientational order.² This connection came not directly but indirectly, via the development of a theory of melting in two dimensions.^{3,4} As we shall discuss, the application of these concepts to liquid crystals leads to a natural classification of the smectic phases.

At the same time this theory was under development, synchrotron x-ray studies of freestanding liquid crystal films have provided new, incisive information in two and three dimensions that confirms the basic theory. These successes in turn have led to the development of a detailed model for the growth of two- and three-dimensional bond-orientationally ordered smectic liquid crystals, in which one applies concepts from renormalization-group theories of multicritical phenomena in magnets. We can now use these models to understand in detail the ordering processes in such diverse physical systems as rare earth magnets, thin films on crystalline substrates, lamellar high- T_c superconductors and biological systems such as the one pictured on the cover of this issue. Liquid crystals

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Spiral star defect in a three-layer film of the liquid crystal (S)-4-(2'-methylbutyl)-phenyl-4-*n*-octylbiphenyl-4-carboxylate in the chiral S_1 phase just below the S_C - S_1 transition. (Courtesy of Steven Dierker, AT&T Bell Laboratories.) **Figure 1**

themselves, of course, have broad technological impact in such diverse areas as display devices, solid-state electronics and tertiary oil recovery.

Two-dimensional melting

In the early 1970s J. Michael Kosterlitz and David J. Thouless³ in England and V. L. Berezinski in the Soviet Union proposed a theory of the superfluid transition in two dimensions. In these theories, thermally generated vortices exist in the superfluid wavefunction in bound pairs of opposite vorticity below the transition temperature T_c . Above T_c these vortex pairs unbind, destroying the superfluid state in a manner that Kosterlitz and Thouless were able to describe quantitatively. Kosterlitz, Thouless and Berezinski suggested that similar ideas could be applied to the melting of a two-dimensional crystal, with dislocations taking the place of vortices. Subsequently, quantitative theories of melting based on these ideas were developed by Bertrand I. Halperin and David R. Nelson and by A. Peter Young.⁴

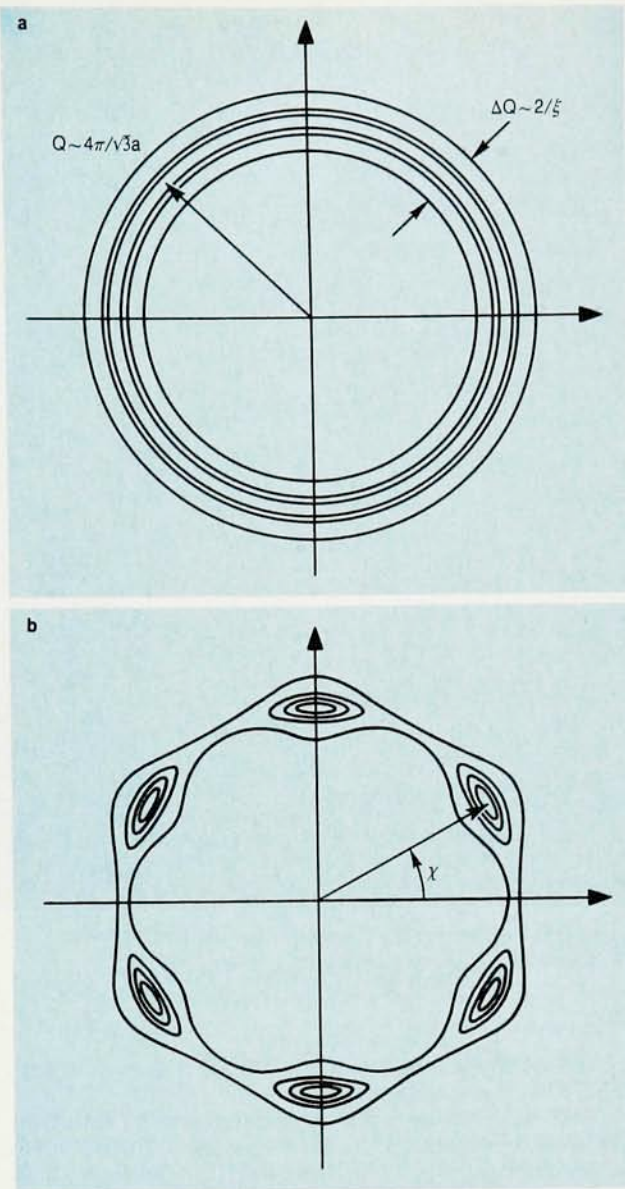
The positional order parameter for a planar crystal is the first Fourier component of the mass density $\rho_{\mathbf{K}}$; for a triangular crystal the magnitude of the reciprocal lattice vector $\mathbf{K}$ is $4\pi/\sqrt{3}a$, where a is the interatomic spacing. In a two-dimensional solid the mass density correlation function $\langle \rho_{-\mathbf{K}}(\mathbf{r}) \rho_{\mathbf{K}}(0) \rangle$ decays with distance (as $r^{-\eta}$) instead of remaining nonzero, as true long-range order requires. In a liquid phase the positional correlations decay as $e^{-r/\xi}$, where ξ is the positional correlation length. As we shall discuss later, in the different smectic

liquid crystal phases ξ can vary from a few to a few hundred lattice spacings.

Following earlier work by David Mermin,⁵ Halperin and Nelson introduced the idea of a bond-orientational parameter $\Psi_6(\mathbf{r}) = \langle e^{i6\theta(\mathbf{r})} \rangle$. Here the 6 implies that one is explicitly considering a system with sixfold rotational symmetry. Imagine a bond between two neighboring atoms. The bond orientation $\theta(\mathbf{r})$ is defined as the angle between this bond direction at position $\mathbf{r}$ and some reference axis $\theta(\mathbf{r})$. The bond-orientational-order parameter is complex because one must specify both the magnitude of the orientational order and the direction of the axes in space; that is, one needs two degrees of freedom. As Lev Landau noted originally and Mermin discussed in detail, two-dimensional solids have true long-range orientational order.

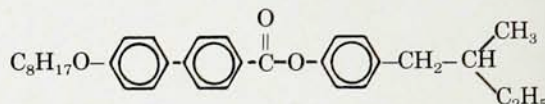
Halperin and Nelson proceeded to make a remarkable prediction: melting in two dimensions could occur in two steps. At one temperature T_M the dislocations would unbind and the positional order would be lost. However, the orientational order would remain, or, more precisely, would be converted from true long-range order to order that decays algebraically, that is, $\langle \Psi_6^*(\mathbf{0}) \Psi_6(\mathbf{r}) \rangle \sim r^{-\eta_6}$. In a system of finite size or in a very small ordering field this new state of matter would have well-defined crystalline axes but no positional order. Such a state of matter is called "hexatic" for two-dimensional systems with hexagonal symmetry.⁴

The second melting transition temperature suggested by Halperin and Nelson is peculiar to the hexatic phase



Scattering functions for isotropic and positionally ordered liquid crystals. **a:** Schematic illustration of the in-plane x-ray scattering function for an isotropic smectic liquid crystal. The six circles are the 20%, 40%, 60%, 60%, 40% and 20% intensity contour lines. The inverse of half the width ΔQ of the diffraction peak measures the distance ξ over which the molecules are positionally ordered. The momentum transfer Q is related to the average molecular separation a as indicated. **b:** The same scattering function for an orientationally ordered hexatic liquid crystal. The contour lines represent the 20%, 40%, 60% and 80% intensities. The hexatic spots are more intense because the total scattered intensity is conserved. **Figure 2**

carboxylate, which is usually given the more convenient name 8OSI. It has the structure



Liquid crystals form many different phases, some of which were quite mysterious for decades. In many of these phases the molecules tend to line up in parallel and then segregate into layers. Such phases are referred to as smectics. By the 1970s researchers had identified at least 11 such phases and had given them the rather mundane labels S_A , S_B , S_C , ..., S_K . There was, indeed, no consensus on what differentiated these phases and, specifically, what different sorts of order they exhibited microscopically.

Bond-orientational order turned out to be the missing idea needed to clarify the order found in smectic phases. Below we describe the development of a detailed model for these phases and their order parameters. The box on page 55 gives the essential structural details of the phases according to this model. In 1978 Birgeneau and Litster suggested that some of the exotic smectic liquid crystal phases might actually be three-dimensional realizations of a bond-orientationally ordered phase. In this view, each smectic layer is an independent, two-dimensional, bond-orientationally ordered system: The S_B phase is the bond-orientationally ordered version of the S_A phase, and the S_I phase is a bond-orientationally ordered version of the S_C phase. The effect of the three-dimensional coupling is to convert the algebraic decay of the Halperin-Nelson hexatic phase to true long-range order. It thus turns out that the three-dimensional S_B , S_F and S_I phases would have true long-range orientational order but only short-range positional order.

Order in freestanding films

Conceptually, an experiment to test the above-mentioned model for the classification of smectic liquid crystals is straightforward. One can draw these materials over an opening in a slide to form freestanding films (that is, flat bubbles); the layers are then oriented parallel to the surface of the film by surface tension. Friedel originally suggested this approach in the 1920s.¹ However, the technique of preparing freely suspended films of liquid crystals was not in fact developed until the late 1970s, in an elegant set of experiments by the liquid crystal group at Harvard.⁷

In such experiments S_A -phase material is piled around the edges of a 6-mm-diameter hole, made in a thin plate of glass, stainless steel or some other inert substance. The S_A material is then drawn across the hole with a wiper blade, creating the freely suspended film. The smectic layers align parallel to the free surfaces. By

and denoted T_H . In a hexatic phase, the defect analogous to a vortex in a superfluid is a "disclination"—a point in space at which the local axes rotate by either $+60^\circ$ or -60° . In the hexatic phase there are no free disclinations; they are always paired. At T_H the disclinations would unbind. The resultant high-temperature phase would be a normal fluid with exponentially decaying positional and orientational order.

The existence of two-dimensional hexatics has now been proven beyond a doubt. Figure 1 shows the optical signature of a spectacular defect in the hexatic phase of a three-layer liquid crystal film near the hexatic-fluid transition. This observation of the defect structure, by Steven Dierker, Ronald Pindak and Robert Meyer at AT&T Bell Laboratories, was part of the first direct proof of the existence of a true two-dimensional hexatic phase.⁶

Liquid crystals

As the theories of melting in two dimensions were being developed, advances were also being made in the understanding of liquid crystals. Liquid crystals are usually long, rod-like organic molecules. An example is racemic 4-(2-methylbutyl)-phenyl-4'-(octyloxy)-(1,1')-biphenyl-4-

Smectic Phases

Smectic liquid crystals are characterized by an intermediate degree of positional order in addition to molecular-orientational order and, in some cases, bond-orientational order. The term "smectic" derives from the Greek *smegma*, meaning soap; the smectic phases tend to have mechanical properties similar to those of the layered phases of soaps. Smectics have historically been identified by the textures they exhibit under a polarizing microscope and by studies of their miscibility with known smectic phases.¹⁶

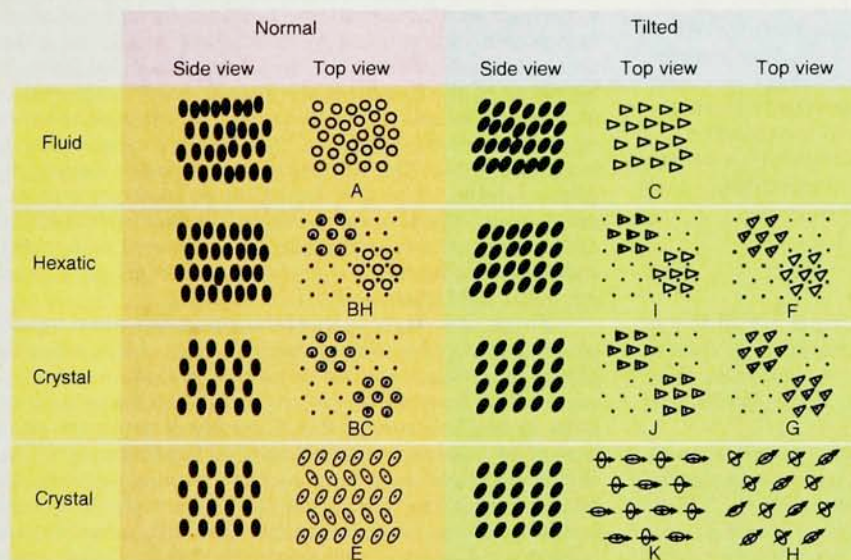
The simplest smectic phase is the smectic A phase, denoted S_A . This phase has traditionally been described as a system that is a solid in the direction along the director and a fluid normal to the director; equivalently, it is a stacked two-dimensional fluid. It is more properly described as a one-dimensional density wave, along the nematic director, in a three-dimensional fluid. In fact, in real S_A materials, x-ray scattering shows that the higher spatial harmonics of the density wave are surprisingly weak. Thus the smectic planes should be interpreted not as lattice planes but rather as planes of a certain phase of a sinusoidal density wave.

The smectic C phase S_C is similar except that the density wave vector makes a nonzero angle with the director; this angle is known as the tilt. In both the S_A and

S_C phases there is complete translational symmetry perpendicular to the density wave vector.

The remaining smectic phases all possess more order than the S_A and S_C phases. One of two phases formerly labeled the smectic B phase is now believed to be an example of a stacked hexatic phase, and is denoted S_{BH} . In each smectic layer of the S_{BH} phase, the director is parallel to the smectic density wave, as in the S_A phase, and there is short-range positional order in the smectic plane; however, there is long-range bond-orientational order in the smectic plane. The S_I and S_F phases are similar to the S_{BH} phase, but, as in the S_C phase, the director makes a finite angle with the density wave vector. The figure below illustrates the distinction between the S_I and S_F phases: The projection of the director onto the smectic planes points toward a near neighbor in the S_I phase and between two near neighbors in the S_F phase.

If order continues to increase, we leave the true liquid crystal phases. The S_{BC} phase is actually a three-dimensional crystal. Similarly, the S_I and S_F phases are crystalline versions of the S_I and S_F phases. Other smectic phases (S_E , S_H , S_K) are arrived at by including additional types of ordering such as herringbone packing.



Microscopic ordering

exhibited by liquid crystal molecules in the principal smectic phases. The molecules are cigar shaped. Thus solid ovals are used to represent the side view; circles, the top view. Triangles and arrows indicate tilt direction. Dots represent periodic lattice points. Open ovals indicate the in-plane packing found when rotation about the long axis of the molecule is not allowed. (Adapted from ref. 15.)

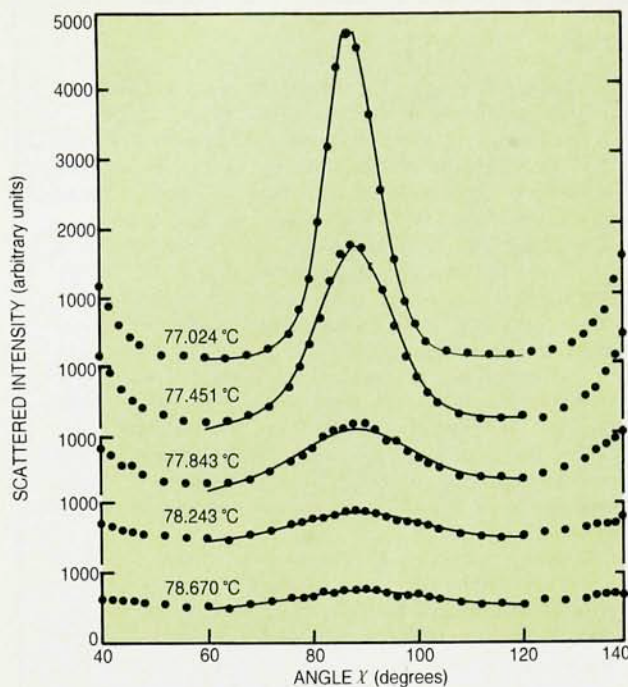
varying the temperature, the rate of motion of the wiper and the amount of S_A material, one can prepare stable films ranging in thickness from two molecular layers to several microns. The variable thickness of the films suggests the possibility of tuning the dimensionality of the sample; the potential for studying the effect of dimension experimentally, however, has only recently been realized.

In 1979 David Moncton and Pindak recognized that in the thin-film limit, freely suspended films of liquid crystal material should provide ideal substrate-free systems in which to study two-dimensional melting.⁸ They began a series of studies on the melting of very thin films at the S_A - S_B phase transition, using synchrotron x-ray sources. Figure 2 illustrates the expected in-plane diffraction patterns for the isotropic (S_A) and hexatic (S_B) fluid structures.

Consider first the normal-fluid isotropic scattering

function shown in figure 2a. There are three features of note. First, one expects a peak at a momentum transfer Q of about $4\pi/(\sqrt{3}a)$, where a is the average molecular separation. Second, if the fluid is isotropic, the intensity and shape of this peak must be independent of direction. Therefore, if one scans the angular variable χ , defined in figure 2b, one should not see any variation in the strength of the scattering. Third, the width ΔQ of the scattering ring should be about $2/\xi$, where ξ is the length scale on which positional correlations between the molecules decay. Such diffraction patterns are seen ubiquitously in fluids.

For the hexatic diffraction pattern (figure 2b) the ring positions and widths ΔQ are the same as they are for the isotropic fluid phase described above. However, in the bond-orientationally ordered hexatic phase, the fluid develops a sixfold modulation in the angular variable χ ; that is, the angular isotropy is broken. The system is still



Thick-film scans. Results are shown from angular x-ray scans made in a thick film of the liquid crystal 8OSI in the immediate vicinity of the S_C - S_I phase transition. The scans were of the type shown in figure 2. At high temperatures, the scattering ring is uniform to within counting statistics. As the sample is cooled, a sinusoidal modulation with a period of 60° develops, indicating a substantial amount of hexatic bond-orientational ordering.¹⁰ **Figure 3**

a fluid, however, because the positional order is still short-range. At a lower temperature the material may freeze, condensing the modulated ring of fluid scattering into sharp spots. Sharp diffraction peaks, or Bragg peaks, are the signature of a crystal.

Moncton and Pindak's first set of experiments showed that, contrary to the Birgeneau-Litster hypothesis, the S_B phase found in the liquid crystal compound *N*-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline has three-dimensional long-range positional order and is therefore a true crystalline phase. Subsequently, however, Pindak and his coworkers,⁹ working with x-ray scattering, observed a hexatic bond-orientationally ordered S_B phase in a freely suspended film of the liquid crystal *n*-hexyl-4'-*n*-pentyloxybiphenyl-4-carboxylate. Thus " S_B " refers to two distinct phases, which are now called the S_{BC} (crystal) and the S_{BH} (hexatic) phases. Although these experiments identified a bond-orientationally ordered phase, Pindak's group was not able to obtain quantitative information on the bond-orientationally ordered phase. The variable number of domains present within the probed area made such quantitative measurements impossible. One needs single-domain hexatic samples to obtain quantitative information on bond-orientationally ordered.

In the past three years major advances have been made on this problem. The first clear demonstration that the S_I phase in very thin films has hexatic bond-orientationally ordered was the elegant experiment of Dierker, Pindak and Meyer referred to above.⁶ A $+2\pi$ point disclination in the director field (the field that

specifies the local average orientation of the molecules) is a common defect in the S_C phase; in this disclination, the orientation of the director follows a circumferential path around the defect core. In the S_I phase, the tight distortion near the defect core produces a large bond-orientationally ordered strain due to coupling between the molecular tilt (the tilt of the director) and the bond-orientationally ordered. This strain can be relaxed, at the expense of director disclination line energy, by creating radial lines of 60° disclinations that separate regions of relatively uniform director orientation. Using depolarized laser reflection microscopy to study a freely suspended film, Dierker and his colleagues observed this defect in a very thin film of the liquid crystal compound racemic 4-(2'-methylbutyl)-phenyl-4-*n*-octylbiphenyl-4-carboxylate. Thus they demonstrated that the S_I phase has hexatic bond-orientationally ordered. Near the hexatic-fluid transition this defect takes on the elaborate geometry illustrated in figure 1.

The second major advance was the discovery that by applying a small magnetic field, the tilt direction of the director in S_C films could be oriented at the S_A - S_C phase transition, and that as the liquid crystal cooled from the S_C phase to the S_I phase, the hexatic axes would develop at fixed angles relative to the molecular tilt (see the box on page 55) and therefore at fixed angles relative to the magnetic field. The net result was a single-domain S_I -phase sample. The first quantitative measurement of a bond-orientationally ordered parameter was a systematic set of synchrotron x-ray diffraction experiments using freely suspended films of the liquid crystal 8OSI in a small magnetic field of about 1 kG.

There are two caveats about using the tilted hexatic phases to study bond-orientationally ordered. First, when the phase transition in the idealized field-free case is a continuous transition, the tilt field introduces a linear term in the free energy that formally destroys the phase transition. (A magnetic field applied to a ferromagnet has the same effect.) As long as the coupling between the bond-orientationally ordered and the molecular tilt is weak, however, there is no serious difficulty; the critical behavior can be extracted by considering the full equation of state. Second, the twofold symmetry of the tilt field destroys the sixfold symmetry of the hexatic axes. The loss of sixfold symmetry may be a more serious complication, and one must observe the scattering on a case-by-case basis to determine whether the loss of sixfold symmetry is significant.

Experiments on thick films

As discussed above, the in-plane x-ray scattering function of the S_A phase is a diffuse ring characteristic of the fluid order in the smectic layers. For the S_C phase, the shape of the diffuse ring is more complex, since its tilt is caused by the tilt of the molecules. There is no fundamental difference, however, and so for simplicity we refer to the more complicated scans required to probe the bond-orientationally ordered in tilted smectics as χ scans. The point to bear in mind is that in an x-ray scattering experiment, any modulation in a χ scan indicates long-range orientational order. The orientation of the bond-orientationally ordered axes must persist over lengths comparable to the

dimensions of the illuminated area; otherwise the orientational structure will average out over different regions of the illuminated area.

Figure 3 shows results¹⁰ from χ scans at several temperatures near the S_C - S_I phase transition in a thick film of 8OSI. At high temperatures the ring is uniform to within counting statistics. As the sample is cooled, a measurable sinusoidal modulation of the ring develops. At a temperature of about 77.5 °C the χ scan shows definite peaks every 60°, indicating a substantial amount of hexatic bond-orientational ordering. At high temperatures longitudinal scans through the same peak show a broad, diffuse scattering profile indicative of short-range positional order. As the sample is cooled, the width of the peak narrows as bond-orientational order develops, suggesting that the enhanced positional correlations are due to a coupling to the bond-orientational order. The peak width never approaches the resolution ΔQ of the spectrometer, which is $2 \times 10^{-4} \text{ \AA}^{-1}$; the positional order is always short range. Thus the material is indeed a bulk hexatic in the S_I phase; that is, it has the positional order of a fluid and the bond-orientational order of a crystalline solid. When the material is cooled below about 73 °C into the S_J phase, the broad peaks of figure 4 and of the corresponding longitudinal scan become sharper than the resolution of the spectrometer. Thus the bulk S_J phase is actually a solid rather than a liquid crystal.

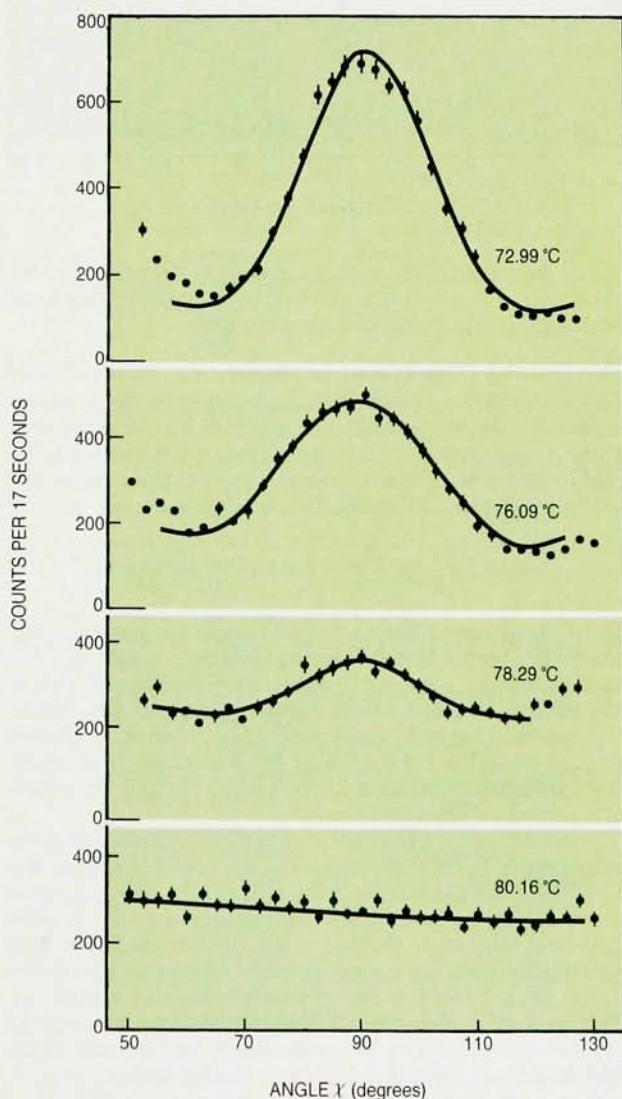
Experiments on thin films

As discussed above, one of the attractive features of the freestanding film technique is that one can prepare stable films whose thicknesses vary from two molecules to macroscopic values. Since the Birgeneau-Litster model for three-dimensional smectic liquid crystals is based on the Halperin-Nelson model for two-dimensional melting, one naturally asks how the bulk smectic states evolve as the film becomes progressively thinner. The first generation of experiments addressing this question were on multidomain hexatic films and were conducted by Pindak and his coworkers at Bell Laboratories and by Eric Sirota, Peter Pershan and Moshe Deutsch at Harvard.¹¹ More recent experiments have used single-domain films of 8OSI with thicknesses of 4 and 22 molecules.¹⁰ Figure 4 shows results for the 22-layer film. At 80.16 °C the material is in the S_C phase and the χ scan is isotropic as expected. As the film is cooled, angular structure develops, demonstrating that the material is going into a bond-orientationally ordered phase. This progression parallels exactly the three-dimensional S_I -phase data shown in figure 3, except that the bond-orientational order is much less well developed. Measurements of the width of the diffraction peak ΔQ (see figure 2) show that the material is positionally disordered; in other words, it is a fluid. The 4-layer film gives identical results. Thus a 22-layer film is already thin enough to act the way this material would in the two-dimensional limit. Again, when the film is cooled below 72 °C, it goes into the crystalline solid S_J phase.

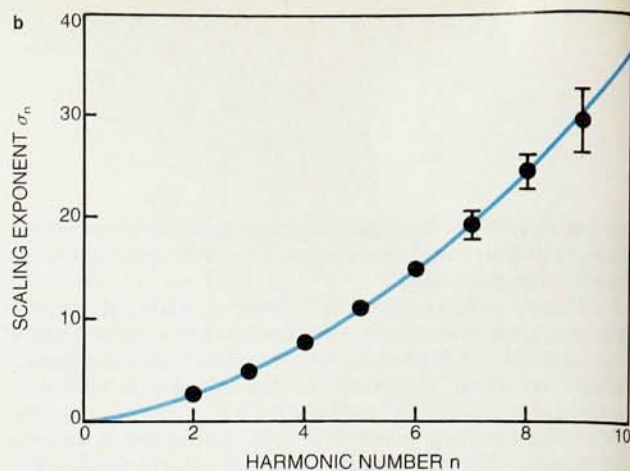
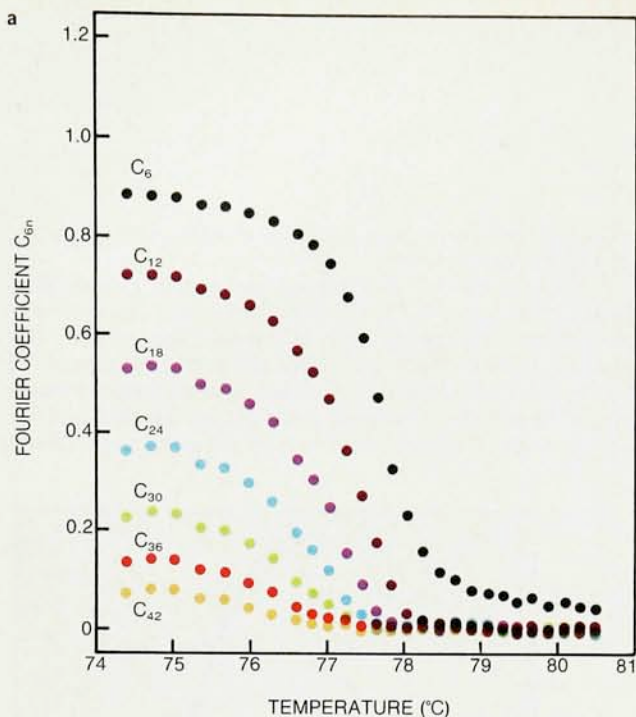
These thin-film experiments complete the picture. They show that the phase sequence predicted by the two-dimensional Halperin-Nelson theory of melting—isotropic liquid, hexatic liquid crystal, crystalline solid—does indeed obtain. Furthermore, in 8OSI these two-dimen-

sional phases evolve into the three-dimensional phases S_C , S_I and S_J , respectively.

Clearly, the introduction of the concept of a stacked hexatic phase has led to the identification of the essential microscopic symmetry that is broken in some of the smectic phases. When molecular tilt and other degrees of freedom are also considered, all the smectic liquid crystals can be classified according to this scheme. The box and figure on page 55 explain this final characterization. Thus,



Thin-film scans. A 22-molecule-thick film of the liquid crystal 8OSI was the medium for the angular x-ray scans that give these data. The sequence shows the evolution from a two-dimensional isotropic fluid (80.16 °C) to a two-dimensional hexatic phase (78.29–72.99 °C). At lower temperatures the material forms a two-dimensional solid.¹⁰ **Figure 4**



Fourier coefficients and the exponents by which they scale. a: The first seven Fourier coefficients (see equation 1, below) describing hexatic ordering in a thick film of the liquid crystal 8OSI. **b:** The scaling exponents σ_n plotted against the harmonic number n . The curve is the best fit to the theoretical functional form $\sigma_n = n + 0.3n(n-1)$.

Figure 5

out of an apparently esoteric model of freezing in two dimensions, the solution to one of the major unsolved problems in liquid crystals has emerged.

Measuring orientational order

The availability of single-domain samples in the S_I phase makes it possible to characterize the bond-orientational order quantitatively. One can do this quite generally by performing a nonlinear least-squares fit of the χ -scan data between 60° and 120° to the Fourier cosine series

$$S(\chi) = I_0 \left\{ \frac{1}{2} + \sum_{n=1}^{\infty} C_{6n} \cos 6n(90^\circ - \chi) \right\} + I_{BG} \quad (1)$$

Here χ is the angle between the in-plane component of the scattering vector $\mathbf{Q}$ and the magnetic field vector $\mathbf{H}$. The coefficients C_{6n} measure the amount of $6n$ -fold ordering in the sample and are called harmonic amplitudes. When the constant term in the equation is $1/2$, each coefficient C_{6n} approaches 1 for perfect bond-orientational order; that is, the equation with $C_{6n} = 1$ is the Fourier transform of a periodic delta function.

In fact, each of the coefficients C_{6n} is a separate bond-orientational-order parameter. Figure 5a shows the temperature dependence of the first seven members of the set of bond-orientational-order parameters $\{C_{6n}\}$. The data show explicitly that all of the coefficients C_{6n} evolve continuously, so the system smoothly develops first 6-fold order, then 12-fold order, then 18-fold order and so on. This lack of a sharp S_C - S_I phase boundary is a consequence of the coupling between the tilt and hexatic fields, which induces hexatic ordering in the S_C phase.

Harmonic scaling

An astonishing result of the above analysis was the empirical discovery¹⁰ of the simple scaling relation $C_{6n} = C_6^n$. Figure 5b gives the average values of the exponents σ_n and their standard deviations. With this scaling, all the quantities C_{6n}^{1/σ_n} up to $n = 7$ fall on the same curve over the complete temperature range to within the fitting error, with no adjustment in the amplitude.

It turns out that one can obtain a complete theoretical understanding of the scaling of the bond-orientational-order parameter harmonics and the series of exponents $\{\sigma_n\}$ using theories of multicritical phenomena developed to explain phase diagrams in magnets. First recall that the bond-orientational-order parameter $\Psi_6(\mathbf{r})$ is a complex number, $\langle e^{i6\theta(\mathbf{r})} \rangle$. All the higher harmonics measured by x-ray scattering are directly related to the fundamental order parameter by¹²

$$C_{6n} = \langle \frac{1}{V} \int d\mathbf{r} \operatorname{Re} \{ \Psi_6^n(\mathbf{r}) \} \rangle \quad (2)$$

Because Ψ_6 is a complex number, the critical properties of this system should be those of a system with a two-component order parameter, such as the superfluid transition or a magnet with two spin components (the XY model). If one writes $\Psi_6 = x + iy$, it is clear from simple algebra that the successive order parameters C_{6n} , with $n = 2, 3, 4, \dots$, scale like $(x^2 - y^2)$, $(x^3 - 3xy^2)$, $4(x^4 + y^4) - 3|\Psi_6|^4$ and so on. Each of these order parameters has a different symmetry and hence, according to current ideas in the theory of critical phenomena, must have a different scaling behavior. Indeed, earlier measurements of each of these behaviors required separate experiments.¹³

In mean-field theory the predicted value of σ_n is n , which manifestly disagrees with the experimental results. The disagreement implies that fluctuation effects are important. These effects can be included via the calculational techniques introduced by Kenneth Wilson and Michael Fisher—the renormalization-group approach. An elaborate renormalization-group calculation gives $\sigma_n \approx n + 0.3n(n-1)$. As one can see in figure 5b, this form describes the measured exponents σ_n remarkably well—indeed, better than the approximations in the theory would seem to justify.

The harmonic scaling results of the hexatic transition theory should also apply to many other systems in which the order parameter is represented by the real part of a complex number. The spiral spin-density wave found in the rare earth metal erbium is an example of such a

system. Using neutron scattering, Sunil Sinha and his coworkers at Ames Laboratory in Iowa were able to measure the temperature dependence of the higher-order harmonics of the *c*-axis moment of the erbium spin-density wave up to the 17th harmonic.¹⁴ Although the erbium data are qualitatively similar to those of figure 5a, no quantitative comparison has been made. Future experiments on similar systems could provide an excellent test of the harmonic scaling theory. Variants of the theory that explicitly include the quasi-two-dimensional nature of the phase transition describe well the thermodynamic properties of the hexatic-fluid transition and should describe equally well the phase transition behavior of the CuO₂ lamellar superconductors.

Extension to two dimensions

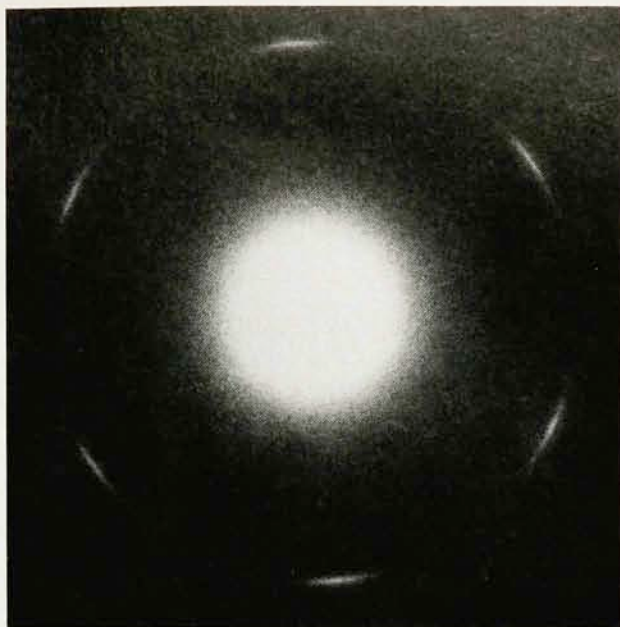
Although the thermodynamic argument for harmonic scaling in the critical region is valid for all dimensions, the form of the scaling may vary. As the number of spatial dimensions is reduced, fluctuations become increasingly important in a reduced volume in phase space. As we have emphasized throughout this article, in two dimensions these fluctuations are so large that they produce an algebraic decay of the (formerly long-range ordered) bond-orientational correlation functions. It is straightforward to demonstrate that an algebraically decaying correlation function implies that the exponents σ_n are proportional to n^2 . This is a consequence of a harmonic theory for the phase fluctuations of the bond-orientational parameter Ψ_6 , and implies that as the system crosses over from three to two dimensions, the higher harmonics of the order parameter "turn off." In other words, the fluctuations eliminate the higher-order Fourier coefficients in equation 1 (page 57). Analysis of the thin-film data in figure 4 indicates the absence of all but the terms for which n is 1 or 2; the data are also consistent with $\sigma_n \sim n^2$.

Ming Cheng and his coworkers at the State University of New York, Buffalo, have also seen two-dimensional behavior.¹⁵ In a beautiful transmission electron diffraction experiment on very thin films, they were able to measure the coefficients C_{6n} for $n = 1, 2, 3$ and 4 in a four-layer-thick hexatic liquid crystal exhibiting S_A and S_{BH} phases. Figure 6 shows one of their S_{BH} -phase electron diffraction patterns, which exhibits clearly the characteristic hexatic diffraction pattern. Further, the profiles are well described by the two-dimensional model as adapted for n -layer systems.

The study of stacked hexatics has yielded a complete classification of the large variety of thermotropic liquid crystal phases. It has also demonstrated the coupling of the order parameters of many different symmetries. Finally, it is an excellent system with which to study experimentally the crossover from two to three dimensions and to explore the interplay between two- and three-dimensional physics.

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The liquid crystal research at MIT has been supported by the National Science Foundation's Materials Research Laboratory Program under contract number DMR 84-18718 and by NSF grant DMR 86-19234; that at Tel Aviv University has been supported by grants from the US-Israel Binational Science Foundation and the Israel Academy of Science and Humanities.



Electron diffraction pattern from a four-layer film made up (by weight) of 25% 4-propionylphenyl-*trans*-(4-pentyl)-cyclohexane-carboxylate in a base of *n*-hexyl-4'-pentyloxybiphenyl-4-carboxylate. (Adapted from ref. 15.) **Figure 6**

References

1. G. Friedel, *Ann. Phys. (Paris)* **18**, 273 (1922). E. Alexander, K. Herrmann, *Z. Kristallogr.* **69**, 285 (1928).
2. R. J. Birgeneau, J. D. Litster, *J. Phys. (Paris) Lett.* **38**, 1399 (1978).
3. J. M. Kosterlitz, D. J. Thouless, *J. Phys. C* **6**, 1181 (1973).
4. B. I. Halperin, D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978). D. R. Nelson, B. I. Halperin, *Phys. Rev. B* **19**, 2457 (1979). A. P. Young, *Phys. Rev. B* **19**, 1855 (1979).
5. N. D. Mermin, *Phys. Rev.* **176**, 250 (1968).
6. S. B. Dierker, R. Pindak, R. B. Meyer, *Phys. Rev. Lett.* **56**, 1819 (1986).
7. C. Y. Young, R. Pindak, N. A. Clark, R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978).
8. D. E. Moncton, R. Pindak, *Phys. Rev. Lett.* **43**, 701 (1979).
9. R. Pindak, D. E. Moncton, S. C. Davey, J. W. Goodby, *Phys. Rev. Lett.* **46**, 1135 (1981).
10. J. D. Brock, A. Aharony, R. J. Birgeneau, K. W. Evans-Lutterodt, J. D. Litster, P. M. Horn, G. B. Stephenson, A. R. Tajbakhsh, *Phys. Rev. Lett.* **57**, 98 (1986). J. D. Brock, D. Y. Noh, B. R. McClain, J. D. Litster, R. J. Birgeneau, A. Aharony, P. M. Horn, J. C. Liang, *Z. Phys. B* **74**, 197 (1989).
11. R. Pindak, D. E. Moncton, S. C. Davey, J. W. Goodby, *Phys. Rev. Lett.* **46**, 1135 (1981). E. B. Sirota, P. S. Pershan, M. Deutsch, *Phys. Rev. A* **36**, 2890 (1987).
12. A. Aharony, R. J. Birgeneau, J. D. Brock, J. D. Litster, *Phys. Rev. Lett.* **57**, 1012 (1986).
13. A. Aharony, in *Phase Transitions and Critical Phenomena*, C. Domb, M. S. Green, eds., Academic, New York (1976), p. 357.
14. M. Habenschuss, C. Stassis, S. K. Sinha, H. W. Deckman, F. H. Spedding, *Phys. Rev. B* **10**, 1020 (1974).
15. M. Cheng, J. T. Ho, S. W. Hui, R. Pindak, *Phys. Rev. Lett.* **59**, 1112 (1987).
16. G. W. Gray, J. W. Goodby, *Smectic Liquid Crystals: Textures and Structures*, Leonard Hill, Glasgow and London (1984). A very recent book on smectic liquid crystals is P. S. Pershan, *Structure of Liquid Crystal Phases*, World Scientific, Singapore (1988).