

Phases and phase transitions

States of matter intermediate between liquids and solids have recently become of intense interest because of their important applications and their value in studying fundamental problems in statistical physics.

J. David Litster and Robert J. Birgeneau

"Liquid crystals are beautiful and mysterious; I am fond of them for both reasons"—P. G. de Gennes, 1972

In this first sentence of his seminal book "The Physics of Liquid Crystals," Pierre Gilles de Gennes¹ has succinctly stated the appeal that liquid crystals have for all of us working in this field. The term "liquid crystal," in fact, refers to a number of distinct states of matter that have structural order intermediate between that of conventional liquids and solids.

Although liquid crystals have been known for at least 90 years, they have really only attracted major attention from physicists in the last fifteen years. This meteoric rise in interest has occurred for several reasons. First, liquid crystals have precipitated a revolution in the display industry and this in turn has piqued the interest of basic scientists. Second, the liquid-crystalline state is ubiquitous in biologically active systems, including the human anatomy, and thus forms a major thrust in biophysical research. Third, and from our point of view most important, the physical behavior of liquid crystals turns out to be remarkably subtle. Indeed it is only because of the last decade's significant progress on the phase-transition problem that we even know how to begin thinking about some of the basic issues in liquid-crystal physics. As we shall discuss, a number of these fundamental issues remain unsolved.

However, during the past fifteen years great strides have been made in our understanding of the statistical

mechanics of second-order and weakly first-order phase changes. The concept of spontaneously broken symmetry and the resulting appearance of new hydrodynamic modes has been an important one. The ideas of V. L. Ginzburg, Lev D. Landau, and Rudolph Peierls on the importance of thermal fluctuations for various symmetries, range of interactions, and spatial dimensions of ordering have been useful concepts in understanding critical phenomena, and the renormalization-group techniques introduced by Kenneth Wilson and Michael Fisher have enabled calculations of the behavior of strongly fluctuating condensed phases. All of these ideas, combined with the experimental tools that developed concomitantly, have been applied successfully to study phases in liquid crystals. The rich variety of behavior observed is now being used to extend the conceptual tools developed through the study of simpler systems to elucidate in a fundamental way the properties of even more complex materials.

With our interest in understanding phase transitions, we will emphasize here this aspect of liquid crystal physics and the tools for studying it. However, many physical properties of matter are altered by liquid-crystalline order, and a wide variety of experimental techniques, including ultrasonic measurements, nuclear-magnetic resonance, electron-paramagnetic resonance, and linear and nonlinear optics, can fruitfully be used to study them; many physicists can thus use their favorite tools.

Classification

Liquid crystals are broadly classified as nematic, cholesteric and smectic (see figure 1). There are at least nine distinct smectic polytypes bearing the

rather mundane labels smectic A, B, C, ... I, with the phases being labelled not according to any microscopic properties but rather by the chronological order of their discovery. It is clear, however, that it will be most useful to discuss the many liquid-crystal phases in terms of their underlying symmetry properties. Indeed, we shall discover that some of the smectics are actually three-dimensional solids and not distinct liquid-crystal phases at all. To make our discussions quantitative, we introduce a density function $\rho(\mathbf{r})$; $\rho(\mathbf{r})d^3r$ gives the probability of finding an atom in volume d^3r at point $\mathbf{r}$. In liquids $\rho(\mathbf{r})$ is a constant, while in crystalline solids $\rho(\mathbf{r})$ is anisotropic and has a long-range periodicity. Landau pointed out in the late 1930s that the density could still be anisotropic in materials that lacked conventional three-dimensional long-range periodicity; these are liquid crystals.

We discuss first the anisotropy that arises purely from orientational effects. The most obvious way to achieve an anisotropic density is for the liquid to consist of anisotropic molecules that have long-range molecular orientational order; here the anisotropy of $\rho(\mathbf{r})$ represents an orientational ordering of the molecules in the absence of positional ordering. An example is the uniaxial orientational ordering of rod-like molecules that occurs in thermotropic nematic liquid crystals, the phase used in calculator and wrist-watch displays. There is a second and much less obvious way for $\rho(\mathbf{r})$ to be anisotropic even when a material lacks spatial long-range order. It is commonly called "bond orientational" long-range order to distinguish it from "molecular orientational" long-range order. This concept was also discussed by Landau in the context of two dimen-

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sional adsorbed systems. It has only recently been applied to liquid crystals. A state with bond-orientational long-range order may be viewed as one in which the translational ordering of the crystal lattice has been lost but the underlying orientational anisotropy of the intermolecular forces remains. Figure 2 illustrates this idea. We emphasize that there is no actual chemical bond between neighboring molecules but only a registering of the local axes throughout the sample.

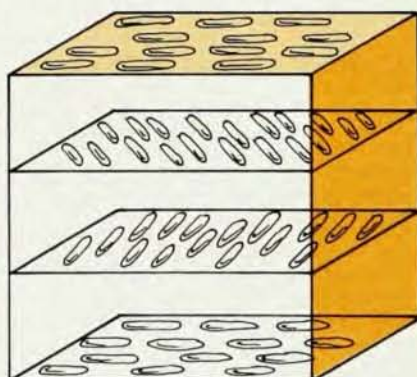
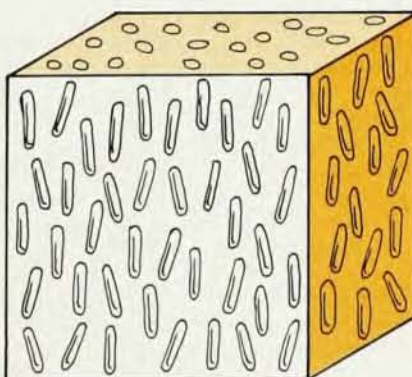
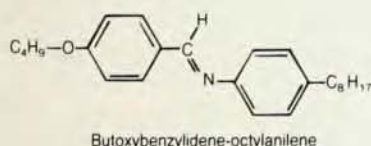
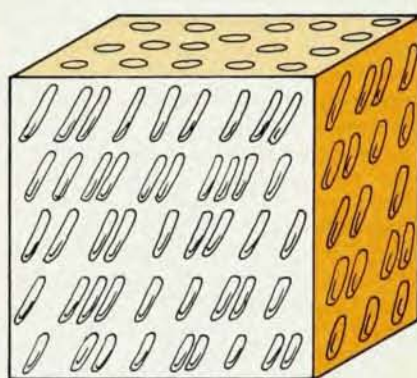
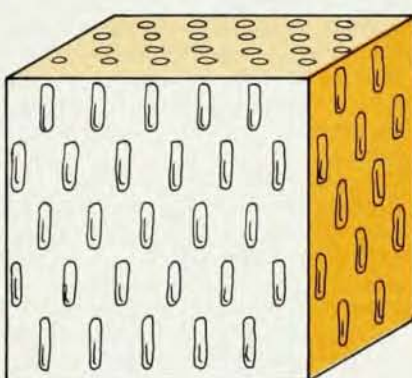
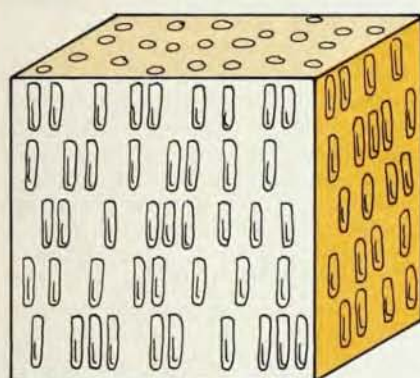
We believe that the concepts of positional, bond-orientational, and molecular-orientational order can serve as a basis to classify the rich variety of liquid crystal phases that exist in nature. In this article we shall discuss a number of these phases, their interest-

ing properties, and how a study of them elucidates problems in statistical physics which are both currently topical and quite fundamental.

Thermotropic liquid-crystal phases are those observed in pure compounds or homogeneous mixtures as the temperature is changed; they are conventionally classified into nematic, cholesteric, and smectic phases (figure 1). As Peter Pershan discusses, in the article on page 34, *lyotropic* liquid-crystal phases are observed when amphiphilic molecules, such as soaps, are dissolved in a suitable solvent, usually water. As Edward Samulski explains in another article (page 40), solutions of polymers also exhibit liquid-crystalline order—the *polymeric* phases. Our knowledge is most complete for the thermotropic

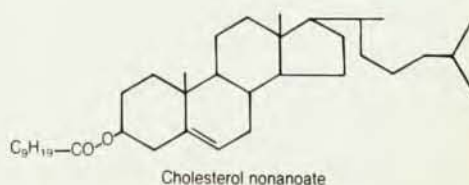
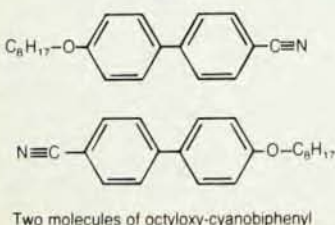
phases and much of this understanding can be transferred to elucidate polymeric and lyotropic phases, but it is not yet clear that it will be sufficient for a complete description of them.

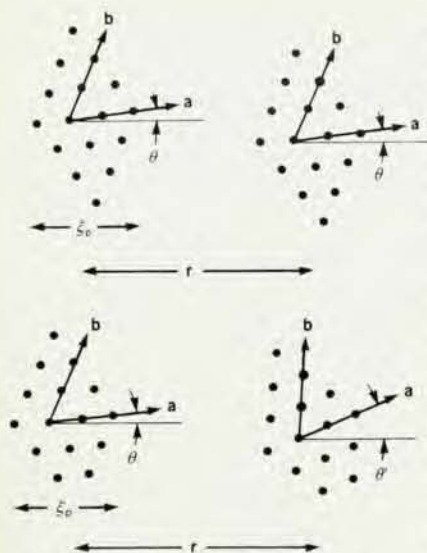
Nematic phase. The simplest phase, which contains only molecular-orientational ordering, is the *nematic*. The word "nematic" derives from the Greek *νημα*, which means thread; it refers to certain thread-like defects commonly observed in these materials. The molecules butoxybenzylidene-octylaniline and octyloxy-cyanobiphenyl in figure 1 both exhibit nematic phases. All known thermotropic nematics have one symmetry axis, called the director $\hat{n}$, and are optically uniaxial with a strong birefringence. The molecules themselves usually lack a center of



Common types of liquid-crystal ordering—nematic, smectic-A, smectic-B, smectic-C and cholesteric. Chemical structure of three liquid-crystal molecules is shown: Butoxybenzylidene-octylaniline has nematic, smectic-A, and lamellar crystalline smectic-B phases; octyloxy-cyanobiphenyl has a nematic phase and a smectic-A phase (in the smectic-A phase the period of the density wave is about 1.4 times the molecular length, which indicates molecules are paired similarly to the two shown here); cholesterol nonanoate is typical of the chiral molecules that have a cholesteric phase.

Figure 1





Bond-orientational order in a triangular two-dimensional lattice. At top, molecular positions are correlated only over a short distance r , while the orientation of the lattice vectors $\mathbf{a}$ and $\mathbf{b}$ is preserved throughout the sample. At bottom, the orientational order of the crystal axes is also only short range. Figure 2

symmetry but the nematic phase has inversion symmetry and the orientational order parameter has quadrupolar rather than dipolar symmetry; there are no ferroelectric nematics. The continuous rotational symmetry of the isotropic liquid phase is broken when the molecules choose a particular direction to orient along in the nematic phase; this is accompanied by the appearance of two new normal modes. In modern language, these are the Goldstone bosons that restore the isotropic symmetry broken by the establishment of the nematic order. (They are thus analogous to spin waves in ferromagnets.) They cost little energy to excite at long wavelengths, and, because they correspond to a local reorientation of the optic axis, they scatter light intensely; the mean distance a photon can travel in a nematic before being scattered by a director fluctuation is about one millimeter, so nematics appear turbid.

The nematic-isotropic phase transition is analogous to the Curie point in a ferromagnet and shows many of the well-known anomalies associated with a critical point. There is, however, an essential difference: In a nematic, positive and negative values of the order parameter correspond to positive and negative birefringence and hence to quite different physical arrangements of the molecules. The sign of the order parameter is important, in contrast to the dipolar symmetry of ferromagnets. In a Landau expansion of the free energy for a nematic, then, there will be a cubic invariant. This, in turn,

means that the transition must be at least weakly first order. In fact, typical latent heats are slightly less than kT per molecule. In general, however, the phase transition behavior of nematics can be readily understood using conventional ideas about critical phenomena, and there do not seem to be any major unsolved problems.

Cholesteric phase. A different thermotropic phase having only molecular orientational order is formed by chiral molecules. This is the *cholesteric* phase, thermodynamically equivalent to a nematic but with a chiral character that causes the director to twist (see figure 1) with a pitch that is comparable to the wavelength of light. The name "cholesteric" derives from the fact that many cholesterol esters exhibit this phase. The strong modulation of the refractive index due to the twist causes Bragg scattering of various colors of light and makes cholesterics the most beautiful of the liquid-crystal phases. The "blue" phase of cholesterics has only recently come to be understood as a stable lattice of defects in the uniform cholesteric structure and is currently very interesting. Because William F. Brinkman and Patricia Cladis treat thin films extensively on page 48, we shall not discuss it any further here.

Smectic phases. The remaining thermotropic phases are all *smectics*. The smectics are distinguished by having an intermediate degree of positional order in addition to molecular orientational and, in some cases, bond-orientational order. The term "smectic" derives from the Greek *σμηγμα*, meaning soap, since the smectic phases tend to have mechanical properties akin to those of soaps. The molecules butoxybenzylidene-octylaniline and octyloxy-cyanobiphenyl shown in Figure 1 also exhibit smectic phases; the former has two (smectic A and smectic B), while the latter has one (smectic A). Smectics have usually been identified by the textures they exhibit under a polarizing microscope and by miscibility studies with known phases. On this basis, at least nine different smectic phases have been identified so far, although not all are truly liquid crystals.

The simplest smectic phase is the smectic-A phase illustrated in figure 3. 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, or equivalently, as stacked two-dimensional fluids; it is more properly described as a one-dimensional density wave in a three-dimensional fluid with the density wave along the nematic director. In typical pictures such as those shown in figure 3 one depicts rather well-defined layers. In fact, in real smectic A materials, x-ray scattering shows that the

higher spatial harmonics of the density wave are surprisingly weak. Thus the dashed lines through the molecules in figure 3 should be interpreted not as lattice planes, but rather as planes of a certain phase of the nearly sinusoidal density wave shown to the right in the figure. The smectic-C phase is similar except the density-wave vector makes a finite angle with the director. In both smectic-A and smectic-C phases there is complete translational symmetry normal to the density-wave vector.

Smectic-A theory

The smectic-A phase has proven to be unusually subtle; indeed we still do not have a proper theoretical description for it or for its phase transition. The most successful phenomenological model is one that is analogous to a Landau-Ginzburg description of a charged superfluid. The order parameter is a complex quantity whose magnitude and phase are the corresponding amplitude and phase of the smectic density wave.

Following reference 2, we can write the density as

$$\rho(\mathbf{r}) = \rho_0 \{ 1 + [\Psi e^{iq_0 z}] \} \quad (1)$$

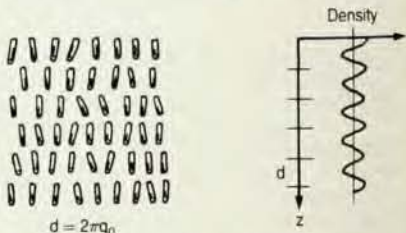
where $2\pi/q_0$ is the layer spacing and $\Psi(\mathbf{r}) = |\Psi| e^{iq_0 u(\mathbf{r})}$. Here $u(x, y, z)$ is the displacement of the layers in the z direction away from this equilibrium position. In terms of Ψ , the free-energy density may be written

$$\begin{aligned} \phi = & \phi_0 + \alpha |\Psi|^2 + \frac{1}{2} \beta |\Psi|^4 \\ & + \frac{1}{2M_{\parallel}} \left| \frac{\partial \Psi}{\partial z} \right|^2 + \frac{1}{2M_{\perp}} \\ & \times \left| \left(\frac{\partial}{\partial x} + i q_0 n_{xy} \right) \Psi \right|^2 + \phi_N \quad (2) \end{aligned}$$

where the nematic free energy ϕ_N is given by

$$\begin{aligned} \phi_N = & \frac{1}{2} [K_1 (\nabla \cdot \hat{n})^2 + K_2 (\hat{n} \cdot \nabla \times \hat{n})^2 \\ & + K_3 (\hat{n} \times \nabla \times \hat{n})^2] \quad (3) \end{aligned}$$

where $\hat{n}$ is the nematic director. Solid-state physicists will immediately recognize equation 2 as being analogous to the Landau free energy for a superconductor, with an anisotropic mass and with $\hat{n}$ playing a role analogous to the



Smectic-A phase consists of a one-dimensional density wave along the average direction of the molecular axis. The sinusoidal shape of the density wave is reflected in the diffraction pattern by the absence of higher-order reflections. Figure 3

magnetic vector potential $\mathbf{A}$. There are, however, some essential differences and it is these differences that have made the smectic-A problem so difficult to solve.

The Goldstone mode of the smectic-A phase, which derives from phase fluctuations in the order parameter, corresponds to fluctuations in the positions of the smectic layers. The elastic constant for compression of the layers is thus analogous to the superfluid density. Nematic-director modes that involve $\nabla \times \hat{\mathbf{n}}$ change the layer spacing and require a much higher energy than in the nematic phase; thus $\nabla \times \hat{\mathbf{n}}$ is suppressed in the smectic-A phase. This is the exact analog of the Meissner effect in a superconductor; one can derive it straightforwardly from equation 2.

The smectic-A phase has highly anisotropic elastic properties that lead to unusual behavior in three dimensions. Indeed, the current edition of Landau and Lifshitz's *Statistical Physics*³ points out, smectic-A and smectic-C liquid crystals technically do not even exist in three dimensions. To see why, consider the Goldstone mode of the smectic-A phase, shown in figure 4; it involves a displacement u of the smectic layers in the z direction or, more properly, gradients of the phase of the density wave. With the wave vector along $\hat{\mathbf{n}}$ (or $q = q_{\parallel}$) as shown in the upper half of figure 4, the displacement is longitudinal and the elastic free energy is of the usual form $\frac{1}{2} B q_{\parallel}^2 u^2(q)$. However, with $\mathbf{q}$ normal to $\hat{\mathbf{n}}$, the displacement is transverse and an additional elastic restoring force arises because the director field $\hat{\mathbf{n}}$ remains normal to the layers; the displacement thus results in a splay distortion ($\nabla \cdot \hat{\mathbf{n}}$) of the director field producing an elastic free energy

$$\frac{1}{2} K_1 q_{\perp}^2 u^2(q) = \frac{1}{2} K_1 q_{\perp}^4 u^2(q)$$

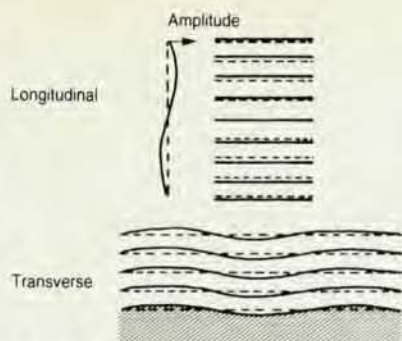
where K_1 is the nematic-phase splay elastic constant (corresponding to a curvature of the smectic layers). The resulting elastic free energy for the displacement is

$$F(\mathbf{q}) = \frac{1}{2} (B q_{\parallel}^2 + K_1 q_{\perp}^4)$$

square displacement $\langle u^2(\mathbf{r}) \rangle$ at a point in space by applying the equipartition theorem and summing the contributions over all q from $2\pi/L$ (where L is the sample size) to q_0 (the smectic density wavevector). This gives

$$\langle u^2(\mathbf{r}) \rangle = (4\pi)^{-1} (BK_1)^{-1/2} kT \ln(q_0 L / 2\pi).$$

Because the fluctuations in layer positions diverge logarithmically with the sample size, the smectic-A phase lacks true long-range order. This is quite reminiscent of a similar logarithmic divergence that is predicted to occur in two-dimensional crystalline solids.³



Anisotropic nature of the Goldstone mode of the smectic-A phase. When the wave-vector is along the director, smectic "layers" are compressed and the energy density is proportional to $q_{\parallel}^2$ as for a normal sound wavevector. When the wavevector is transverse to the molecular orientation, hence in the plane of the layers, the restoring force comes from bending the layers and the energy density is proportional to $q_{\perp}^4$. The dashed lines indicate the equilibrium positions of the layers. Figure 4

The logarithmic divergence is slow and the differences from a system with true long-range order are subtle, although they have both theoretical and experimental importance. To discuss these ideas more quantitatively, it helps to define a correlation function

$$G(\mathbf{r}) = \langle \exp i q_0 (u(0) - u(\mathbf{r})) \rangle$$

Its Fourier transform gives the x-ray scattering intensity from the density wave. A similar function, but with q_0 replaced by a reciprocal lattice vector, would be used to calculate the x-ray scattering from a crystalline solid. In a system with long-range order, $G(\mathbf{r})$ has a constant value equal to the Debye-Waller factor e^{-2u} as r becomes infinite. If there is only short-range order, as in a liquid, $G(r)$ vanishes as $e^{-r/\xi}$ where ξ is the correlation length for the short-range order. For smectic A and C phases in three dimensions as well as solids in two dimensions, a simple calculation⁴ shows that $G(r)$ vanishes algebraically as $r_{\parallel}^{-\eta}$, with η a small number, of order $1/10$. The predicted x-ray scattering for long-range order consists of very sharp Bragg peaks located at reciprocal lattice points; when $G(r)$ decays algebraically, the Bragg peaks are replaced by power-law singularities of the form $(q_{\parallel} - q_0)^{-2+\eta}$.

Technically, there is no elastic scattering and the power-law singularities derive purely from inelastic processes.

Experimentally, it is not trivial to distinguish between the delta-function form characteristic of Bragg scattering and the power-law singularity anticipated for these Landau-Peierls systems; very high angular resolution with steeply dropping tails of the resolution function is necessary. Such an experiment has, however, been performed by Jens Als-Nielsen and his coworkers.⁵ They obtained the appropriate resolution function by using a

monochromatic source of x-rays and perfect-crystal collimators cut to enable each collimator to exhibit three Bragg reflections. In figure 5 we show x-ray scattering from the smectic density wave in the smectic-A phase of octyloxy-cyanobiphenyl. The graph shows the experimental resolution function, which is what would be observed if true long-range order existed, together with the experimental curves for two different temperatures. We note that the exponent η is a function of temperature and has a predicted dependence on K_1 and B .

By fitting the value of η to the data (all other parameters could be independently measured), Als-Nielsen's group was able to deduce the nematic splay constant K_1 and obtain results in excellent agreement with direct measurements. This experiment provided proof that the smectic-A phase in three dimensions lacks true long-range order; it is an example of a system at its lower marginal dimension where thermal fluctuations are just strong enough to prevent the establishment of true long-range order. The experiment also provided the first experimental evidence of an algebraic decay of a correlation function, a concept of broad importance in the statistical mechanics of phase transitions.

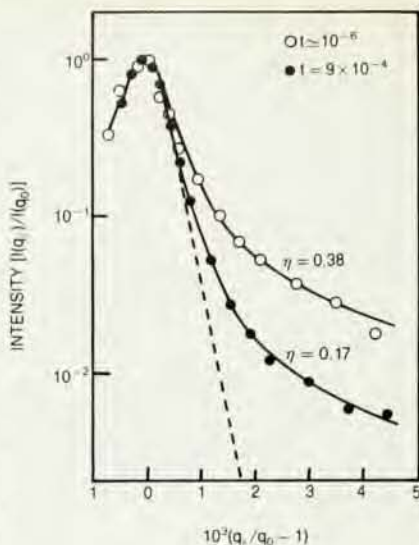
Nematic-smectic transitions

The transition from a smectic-A to a nematic phase is also interesting to study, not only from the viewpoint of critical phenomena, but also because it would appear to be the simplest form of melting to occur in three dimensions. A variety of pretransitional effects in the nematic phase near the second-order transition into the smectic-A phase result from the thermally excited fluctuations in short-range smectic order: A smectic-A density wave appears, but correlated over relatively short distances, and then decays away. It is interesting to note that photon scattering in the optical and x-ray regions probes separately the two important correlation functions in these systems. Specifically the sample-photon interaction derives from the term $\mathbf{P} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{P} + |\mathbf{A}|^2$. In the optical region the $\mathbf{P} \cdot \mathbf{A}$ term dominates, and this couples directly to the director fluctuations; in the x-ray region $|\mathbf{A}|^2$ dominates, and one observes, through Thompson scattering, the smectic mass-density fluctuations. Thus one can measure the correlation lengths of the density waves and the smectic susceptibility $\sigma(q)$ directly from the x-ray profiles and intensities. The smectic-A short-range order also causes an increase in the nematic bend and twist elastic constants. This is the direct analog of the diamagnetism due to fluctuations that one observes above a

superconducting transition: Indeed the result may be derived² from the theory of fluctuation diamagnetism in superconductors essentially by a change in variables in equation 2.

These divergences in K_2 and K_3 can be studied either by light scattering from the nematic director modes or by the threshold for distortion induced by a magnetic field, called a Fredericksz transition.¹ One can use light scattering to study both the dynamical behavior of the fluctuations and the director modes $\hat{n}(\mathbf{q})$ with $q\xi > 1$; a model for nonhydrodynamic behavior of the phase transition then provides an absolute determination of ξ . In figure 6 we show $\xi_{||}$, the correlation length along $\hat{n}$, measured directly by x-ray scattering and indirectly by light scattering⁶ for the nematic-smectic-A transition in butoxybenzylidene-octylaniline; we also show $\xi_{\perp}$ and σ determined from x-ray scattering. It is evident that the agreement is very good, especially at small reduced temperatures. This agreement, of course, also indicates that the coupling of director modes to smectic short-range order as contained in the model of equation 1 is satisfactory. However, there are several ways in which the superconductivity analog fails to describe the nematic-smectic-A transition correctly. The most obvious is that the two correlation lengths—along $\hat{n}$ and perpendicular to $\hat{n}$ —appear to diverge at different rates, with $\xi_{||}/\xi_{\perp}$ diverging as the phase transition is approached, a result that seems to violate conventional wisdom in the field of critical phenomena.

Further valuable information on the nematic-smectic-A phase change has come⁷ from the high-resolution specific-heat measurements pioneered by David Johnson and his collaborators at Kent State University; Carl Garland at MIT has also made important contributions.⁷ The specific heat measures the entropy change associated with thermal fluctuations integrated over the Brillouin zone, and is closely related to the smectic short-range order studied by x-ray and light scattering. If we let $t = |T/T_{NA} - 1|$, where T_{NA} is the nematic-smectic-A transition temperature, then the correlation lengths diverge as $\xi_{||} = \xi_{||}^0 t^{-\nu_{||}}$ and $\xi_{\perp} = \xi_{\perp}^0 t^{-\nu_{\perp}}$, while the specific heat varies as $At^{-\alpha}$. We emphasize that in other phase transitions a single dominant length determines the anomalous thermodynamic behavior and the exponents $\nu_{||}$ and $\nu_{\perp}$ are equal. Typical experimental results for the nematic-smectic-A transition show $\nu_{||} - \nu_{\perp}$ is about 0.13 with $\nu_{||}$ ranging from 0.66 to 0.83 depending on the material studied. This remains a puzzling problem, because we believe that the behavior of a material near a second-order phase transition should



Intensity profile for x-ray scattering from the smectic-A density waves in octyloxy-cyanobiphenyl at two different reduced temperatures. The dashed curve is the measured spectrometer resolution function, as would be seen for true Bragg scattering. The solid curves are a convolution of the resolution function with the theoretical prediction from algebraic decay of the correlation function.

Figure 5

depend only on the symmetry of the phases and the spatial dimensionality; if so, a universal set of exponents should describe the divergences at all nematic-smectic-A transitions. A concept known as two-scale-factor universality, which says in essence that the divergent part of the free energy per correlated volume should be constant near a phase transition, yields the relationship between exponents $\nu_{||} + 2\nu_{\perp} = 2 - \alpha$; this relation appears to be borne out by the experiments, to within their uncertainties; the relative amplitudes of the heat-capacity peaks in different materials are also consistent with this hypothesis. David Nelson and John Toner⁸ at Harvard University recently proposed a model in which the smectic-A phase changes to nematic through a proliferation of defects in the layer structure (analogous to the Kosterlitz-Thouless model⁹ for melting in two-dimensional crystals) predicts that asymptotically $\xi_{||} = \xi_{\perp}$,² and thus $\nu_{||} = 2\nu_{\perp}$. The experiments however all yield $\nu_{||} \leq 1.3\nu_{\perp}$ down to reduced temperatures of 10^{-5} . It is possible that experiments have not yet approached sufficiently close to the transition temperature to test the predictions of the defect theories. However the size of the ordered regions, as measured by $\xi_{||}$, has been observed to grow from 5 Å to over 5 microns when reduced temperature drops from 10^{-1} to 10^{-5} , and we feel that a satisfactory

theory should be able to describe this behavior quantitatively. Tom Lubensky and his coworkers have produced a theory based on a gauge transformation to the pure superconductivity problem; this approach appears quite promising, although it has not yet been compared qualitatively to the data. The smectic-A to nematic transition remains therefore one of the main unsolved problems in critical phenomena. As has been broadly recognized, the difficulties almost certainly originate in the Landau-Peierls nature of the smectic state. It appears that this feature has not yet been incorporated satisfactorily into the theoretical models.

The smectic-C phase (see figure 1) also provides behavior illustrating interesting new concepts in statistical mechanics. In the C phase, director modes that do not alter the angle between the director and the layers cost little energy; consequently they scatter light strongly and a smectic-C material appears as turbid as a nematic phase. It is possible to describe the C phase with a complex order parameter whose magnitude gives the tilt angle between the director and the density wavevector and whose phase corresponds to azimuthal rotation of the molecules about the normal to the layers. The symmetry of this order parameter would permit a second-order phase change from smectic-C to nematic. However, the phase change is always observed to be first order. The mechanism for this ubiquitous first-order character turns out to be quite interesting. S. A. Brazovskii has shown¹⁰ that if a density wave is established with an infinite number of possible characteristic wavevectors in a material, it will always exhibit first-order transitions due to fluctuation effects. Jack Swift has pointed out¹¹ that the azimuthal symmetry of the smectic-C phase provides a ring of points in q -space so that the nematic-smectic-C transition is in the Brazovskii class. Thus the transition is always first-order even though mean-field treatments, which omit such fluctuation effects, predict second-order behavior.

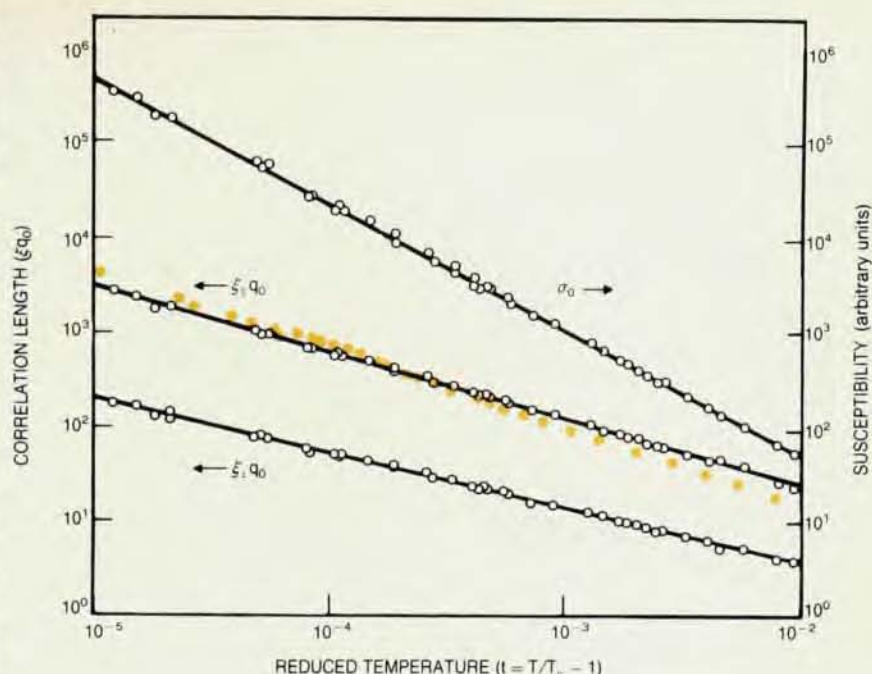
In many materials there are smectic-A-smectic-C phase changes (the A phase is higher in temperature); this transition should be analogous to the superfluid transition in He⁴. Unlike He⁴, however, the observed behavior near the A-C transition in most materials agrees quantitatively with the predictions of a Landau or mean-field approximation to the statistical mechanics. We have just recently come to understand that this is so for reasons first proposed by Ginzburg to explain why the mean-field approximation successfully describes superconductors.¹² If the space dimensionality is less than

four, order-parameter fluctuations in both superfluids and superconductors eventually become so large near the phase transition that the mean-field treatment, which assumes that fluctuations are negligible, fails. However, if the bare characteristic length is large, as in a superconductor, the material may not enter the critical regime until the temperature is very close to T_c . It turns out that in most smectic A-C transitions the bare length is indeed large—chiefly because the molecules are locked parallel to each other by the nematic coupling and one can only tilt large numbers of molecules at a time. Specialists in magnetism will recognize this as the exact analogy of the mechanism causing mean-field behavior in spin reorientation transitions.

By forming solutions of slightly different organic molecules, the interactions tending to produce nematic, smectic-A, or smectic-C order can be modified. In this way complex and interesting phase diagrams result. An example, discovered by David Johnson and his colleagues, which can be realized in several different mixtures is a nematic-smectic-A-smectic-C multicritical point. Multicritical behavior and the interaction between different order parameters is a currently important phase-transition problem. Liquid crystal mixtures afford the opportunity to study order parameters of several symmetries interacting in truly homogeneous systems. A second novel class of multicritical phenomena discovered by Pat Cladis and co-workers is re-entrant nematic behavior.¹³ When octyloxy-cyanobiphenyl (figure 1) is mixed with its hexyloxy homolog it can exhibit the sequence of phases nematic-smectic-A-nematic either as a function of pressure at fixed temperature or as a function of temperature at fixed pressure (see the phase diagram of figure 7.) It turns out that the phase-transition behavior throughout the phase diagram can be quantitatively predicted using standard multicritical theory from current theories of critical phenomena. Thus we have an elaborate phenomenological model for this multicritical behavior using modern concepts, but we still do not have a convincing microscopic model accounting for the mechanism of the re-entrant behavior. This conundrum is characteristic of much of liquid-crystal science.

Exotic smectics

The remaining smectic phases all possess more order than the A and C phases, which, as we mentioned before, lack true long-range order in three dimensions. The "exotic" smectics turn out to provide vivid examples in three dimensions of some of the most exciting recent advances in statistical mechanics has been a theoretical mod-



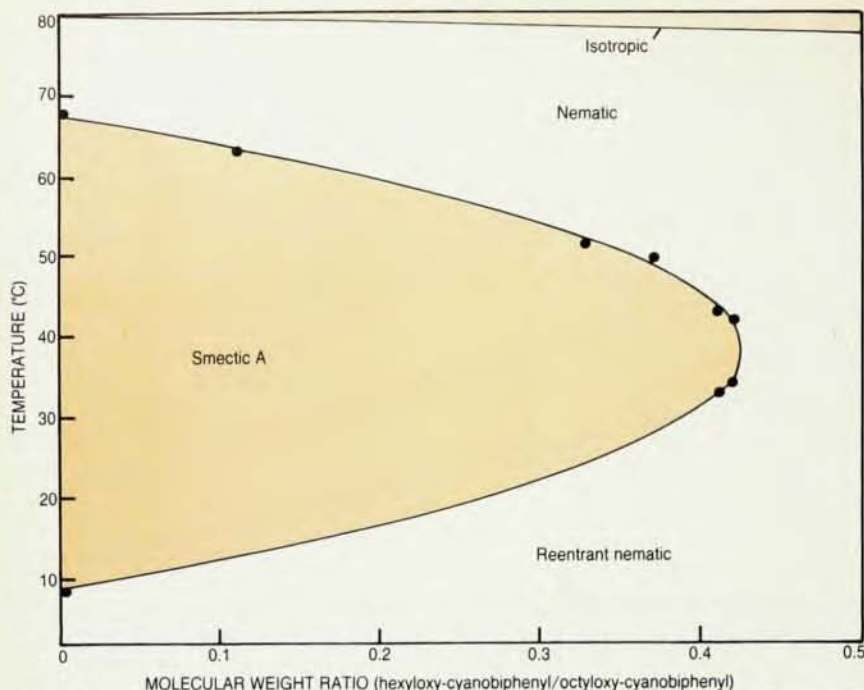
Temperature dependence of susceptibility (σ_0) and the correlation lengths $\xi_{\parallel}$ and $\xi_{\perp}$ for a smectic-A short-range order in the nematic phase of butoxybenzylidene-octylaniline. Open circles were obtained from x-ray scattering measurements; the smectic density wave vector, q_0 , remains essentially constant at $0.222 \text{ \AA}^{-1}$. Colored dots are values of $\xi_{\parallel}$ deduced from light-scattering measurements of the divergence of the nematic bend elastic constant. The solid lines are power-law fits with $\xi_{\parallel}$ diverging at $t^{-0.57}$; $\xi_{\perp}$ increases from about 100 Å to 1.5 micron for the range of t shown.

Figure 6

el⁹ for melting in two dimensions by Michael Kosterlitz and David Thouless, in which the unbinding of pairs of dislocations leads to melting. Recent experiments suggest that this theory correctly describes two dimensional melting when the melting is second order. However, the three-dimensional problem with its more complex topology remains unsolved. The Kosterlitz-Thouless two-dimensional model does not include the orientational anisotropy of the triangular lattice, a situation which was rectified¹⁴ by Bertrand Halperin in working with David Nelson. Their calculations showed that two-dimensional melting could proceed by two stages. The lowest-temperature crystal phase, because of the Landau-Peierls instability we discussed for three dimensional smectic-A phases, has only quasi-long-range positional order and the correlation function $G(r)$ decays algebraically with r . The two-dimensional crystal does, however, have long-range bond-orientational order (figure 2), a point first realized by Landau³ and later developed by David Mermin.¹⁵ This can be discussed quantitatively by defining a correlation function $O(r) = \langle e^{i(\theta(0) - \theta(r))} \rangle$ for a crystal with six-fold symmetry; $\theta(r)$ measures the orientation of one of the crystalline axes at point r . In the two-dimensional crystal, $O(r)$ remains finite as $r \rightarrow \infty$. Then at a higher tempera-

ture, by means of the Kosterlitz-Thouless mechanism, a transition occurs to a phase in which $G(r)$ decays exponentially with distance; that is, the system has short-range positional order whereas $O(r)$ decays algebraically with distance. This phase was christened "hexatic" by Halperin and Nelson. At a still higher temperature there is a second transition that proceeds by unpairing of disclinations in the bond-orientational order to a two-dimensional liquid in which both $G(r)$ and $O(r)$ decay exponentially. The hexatic phase, while an exciting idea, has yet to be observed in two dimensions. Studies of very thin, freely suspended films of liquid crystals may offer the best hope to test these ideas experimentally; this is the subject of a following article by Ronald Pindak and David Moncton (page 56).

We should like to discuss the implications of these ideas for three-dimensional liquid-crystal phases¹⁶. Part of what we say was implicit in a suggestion¹⁷ of de Gennes and G. Sarma, but precise predictions have only become possible since Halperin and Nelson proposed their ideas. The important physical idea in extending these concepts from two to three dimensions is that the algebraic decay of a correlation function means that the associated susceptibility must be infinite; this is a consequence of the fluctuation-dissipation theorem in statistical mechanics.



Phase diagram for mixtures of hexyloxy-cyanobiphenyl and octyloxy-cyanobiphenyl. Smectic-nematic phase boundary can be accurately represented by a parabola. **Figure 7**

Thus when two-dimensional *crystal* phases are stacked, any reasonable interactions between the layers will convert the quasi-long-range positional order into true long-range order and result in a three-dimensional crystal.

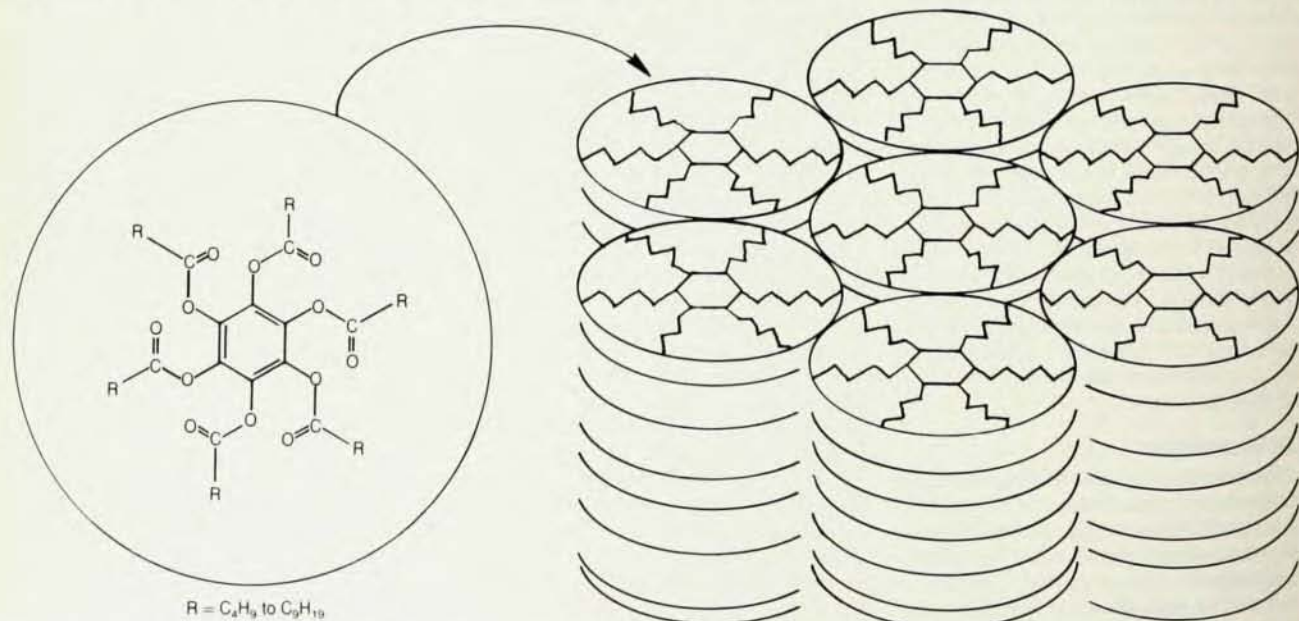
If *hexatic* phases are stacked, the interactions between layers produce long-range bond-orientational order combined with short-range positional order, provided that the interactions between the layers are below a critical value; this phase of stacked hexatics

seems to be the basis for a number of well-ordered smectic liquid-crystal phases. Finally, if two-dimensional *liquids* are stacked together one obtains the smectic-A or smectic-C phases of three-dimensional liquid crystals. These ideas have been tested in recent experiments. Pindak and Moncton present strong evidence for the existence of a hexatic smectic-B phase with the molecules oriented perpendicular to the smectic layers and short-range positional order combined with long-

range bond-orientational order in the plane of the layers. There is also strong evidence that the smectic-I and possibly the smectic-F phases are hexatic smectics with the molecules tilted towards the vertices and sides, respectively, of the triangular in-plane lattice. Thus, although the existence of hexatic phases remains unconfirmed and somewhat controversial in two dimensions, their three-dimensional analog appears to exist. It has, of course, not been proven that these three-dimensional hexatics relate directly to the two-dimensional model of Halperin and Nelson. At the minimum we may know that three-dimensional bond-orientational order is an essential order parameter in describing liquid-crystal phases.

High resolution x-ray studies show that phases that have been classified as smectic-B in many materials are not, in fact, liquid crystals at all but rather lamellar crystals with true long-range positional order in three dimensions. It seems likely that other phases such as smectics E, G and H, which are not yet well-characterized, are also three-dimensional solids. They differ from crystal-B phases in the tilt degree of freedom and in possible distortions from a hexagonal crystal. Study of these phases might more properly be called solid-state rather than liquid-crystal physics; nevertheless they are interesting lamellar phases of matter with a rich behavior and are thus deserving of much more detailed investigation.

The phases we have discussed result from the ordering of rod-like molecules. S. Chandrasekhar and his colleagues¹⁸ have recently discovered nematic-like



Discotic smectic phase discovered by S. Chandrasekhar and co-workers; the disk-shaped molecules are irregularly spaced to form

liquid-like columns, thus giving a two-dimensional smectic density wave. Insert shows a typical molecule. **Figure 8**

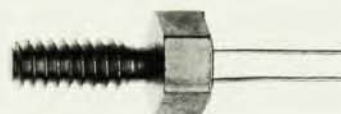
ordering of the symmetry axes of disk-shaped molecules. Some of these materials (we show a typical example in figure 8) also have smectic phases which are in a sense dual to the smectic-A phase formed by rod-like molecules; instead of "layers" the smectic consists of "columns" formed by stacking of the disk molecules. There is only short-range positional order along the columns so this type of smectic corresponds to a two-dimensional density wave in a three-dimensional liquid. This phase has no Landau-Peierls instability in three dimensions and should have long-range order. These "discotic" liquid phases have not yet been as thoroughly studied as other thermotropic phases.

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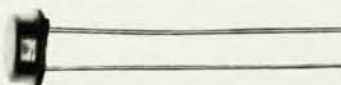
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