

Phase transitions in diskotic liquid crystals

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Phase transitions in diskotic liquid crystals are analyzed in the Landau theory. The thermodynamic coefficients for transitions from the diskotic phase to the nematic phase are estimated.

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1. Mesophases of disk-shaped molecules have been the subject of intense study, both theoretical and experimental, in recent years.¹ The basic thrust of this research, however, has been on specific structures or the thermodynamic properties of mesophases. In the present letter we will analyze the symmetry properties of mesophases of disk-shaped molecules and the characteristics of phase transitions in these systems. We will designate the “diskotic” phase (i.e., the system of liquid columns which form a two-dimensional lattice) by the letter D ; N_D represents the nematic phase (this phase differs from the ordinary nematic phase in the sign of the anisotropy of the dielectric viscoelastic characteristics); I is the isotropic liquid; and K is the solid crystalline phase. The overall phase diagram includes the sequence of transitions

$$K \longleftrightarrow D \longleftrightarrow N_D \longleftrightarrow I.$$

The phase I has a finite-dimensional symmetry group $O(3) \times T(3)$, where $O(3)$ is the rotation group, and $T(3)$ is the three-dimensional translation group. At the transition to N_D , the $T(3)$ symmetry is retained, but the $O(3)$ group is not; it reduces to one of the uniaxial symmetry groups of the nematic phase. If, for example, the molecules are achiral, then the complete symmetry group of the N_D phase is $D_{\infty h} \times T(3)$.

At the following transition to the D phase, a two-dimensional lattice forms. The $T(3)$ symmetry is disrupted, and only the $T(1)$ translational invariance is retained along the direction perpendicular to the plane of the lattice. This symmetry must be matched with the two-dimensional lattice and with the effect of the group $D_{\infty h}$. The physical characteristics of the D and N_D phases are symmetric with respect to the order parameter vector \mathbf{n} : $\psi(-\mathbf{n}) = \psi(\mathbf{n})$. These transitions form the gauge group Z_2 . The joint effects of the gauge and space groups cause a limitation on the type of lattice in the diskotic phase. So far, hexagonal and square lattices have been observed experimentally.

The final crystallization (i.e., the transition $D \leftrightarrow K$) disrupts the one-dimensional translational symmetry $T(1)$ and forms a three-dimensional lattice, one of the 230 crystallographic symmetry groups.

2. Let us examine the general properties of these transitions, working from the Landau expansion for the free energy. We will specify the transition $D \leftrightarrow K$ by the two-component order parameter χ , which corresponds to the formation of a density wave

with a period q_0 along the direction perpendicular to the plane of the lattice. The order parameter in the transition $D \leftrightarrow K$ is the multicomponent vector ψ , which specifies the two-dimensional lattice; finally, the order parameter for the transition $N_D \leftrightarrow I$ is chosen to be a uniaxial, second-rank tensor Q_{ik} (symmetric, with a zero trace).

The total thermodynamic potential, characterizing the entire phase diagram of the diskotic liquid crystals, can be written as follows:

$$\Phi = \Phi_1(Q_{ik}) + \Phi_2(\psi) + \Phi_3(Q_{ik}, \psi) + \Phi_4(\chi) + \Phi_5(Q_{ik}, \chi). \quad (1)$$

The potential $\Phi_1(Q_{ik})$ for the transition $N_D \leftrightarrow I$ is well known.² The potential $\Phi_2(\psi)$ describes the formation of the two-dimensional lattice:

$$\begin{aligned} \Phi_2(\psi) = & \frac{1}{2} a_2 \sum_{\mathbf{p}} \psi(\mathbf{p}) \psi(-\mathbf{p}) - \frac{1}{3} b_2 \sum_{\mathbf{p}_1 \mathbf{p}_2 \mathbf{p}_3} \psi(\mathbf{p}_1) \psi(\mathbf{p}_2) \psi(\mathbf{p}_3) \\ & \times \delta(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3) + \frac{1}{4} c_2 \sum_{\mathbf{p}_1 \mathbf{p}_2 \mathbf{p}_3 \mathbf{p}_4} \psi(\mathbf{p}_1) \psi(\mathbf{p}_2) \psi(\mathbf{p}_3) \psi(\mathbf{p}_4) \\ & \times \delta(\mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 + \mathbf{p}_4) + D_{\parallel} \sum_{\mathbf{p}} \left| \left(\frac{\partial}{\partial z} + i \delta \mathbf{n} \mathbf{p} \right) \psi(\mathbf{p}) \right|^2 \\ & + D_{\perp} \sum_{\mathbf{p}} \left| Q_{\perp} \psi(\mathbf{p}) \right|^2 + \Phi_{el}; \end{aligned} \quad (2)$$

$$\Phi_{el} = \frac{1}{2} K_{33} [\mathbf{n}_0 \cdot \text{rot } \delta \mathbf{n}]^2 + \frac{1}{2} K_{22} (\mathbf{n}_0 \cdot \text{rot } \delta \mathbf{n})^2 + \frac{1}{2} K_{11} (\text{div } \delta \mathbf{n})^2.$$

Here $a_2, b_2, c_2, D_{\parallel}, D_{\perp}$ are the coefficients in the Landau expansion, and the K_{ii} are the Franck moduli.

The gradient terms in (2) reflect the invariance of the D phase under a simultaneous rotation of the director and of the plane of the two-dimensional lattice; Φ_{el} is the Franck distortion energy in the N_D phase. The moduli K_{22} and K_{11} are very large in the D phase, because of the rigidity of the two-dimensional lattice,³ so that deformations corresponding to these moduli are forbidden.

At the transition $N_D \leftrightarrow D$ there should be a fluctuational increase in the moduli K_{22} and K_{11} (with a correlation length $\sim \xi$), since regions of size $\sim \xi$ which do not transmit the twisting and transverse bending of the \mathbf{n} field arise in the N_D phase in a fluctuational manner near the transition. The simplest form of the "mixed" part of the thermodynamic potential is

$$\Phi_3 = - \sum_{\mathbf{p}} | \psi(\mathbf{p}) |^2 f \{ Q_{ij} \}, \quad (3)$$

where $f(Q_{ij}) > 0$, and f contains all possible invariants of the types $p_i p_j Q_{ij}$, Q_{ij}^2 , etc.

The assumption $f(Q_{ij}) > 0$ follows from the basic physics of the problem, in which the dipole orientational ordering caused by the formation of the two-dimensional lattice intensifies the attractive forces between molecules, i.e., reduces the energy of the

system (see Ref. 4 for a corresponding discussion of the smectic phases).

In expansion (2) we have $a_2 > 0$ and $c_2 > 0$, since all the D phases have orientational ordering, and no orientationally disordered D phases are known. We do not need to minimize the complete functional in (2) in order to find just the qualitative behavior. To simplify the problem slightly, we will characterize the order parameter $\psi(\mathbf{p})$ by the modulus $m(\mathbf{p})$ and the phase $\phi(\mathbf{p})$. We assume that the basic state depends exclusively on the modulus of $m(\mathbf{p})$, which is in turn determined by the modulus of the wave vector, p .

The basic state corresponds to a fixed period $p_0 = 2\pi/a$, where a is the period of the two-dimensional hexagonal lattice. In this approximation, (2) reduces to

$$\Phi_2 = \frac{1}{2} \tilde{a}_2 m^2(p_0) - \frac{1}{3} \tilde{b}_2 m^3(p_0) + \frac{1}{4} \tilde{c}_2 m^4(p_0) \quad (4)$$

$$\Phi_3 = -m^2(p_0) \tilde{f}(Q_{ij})$$

$[\tilde{a}_2, \tilde{b}_2, \tilde{c}_2, \tilde{f}]$ are the renormalized parameters from (2).

A minimization of $\Phi_2 + \Phi_3$ from (4) yields

$$\left\{ \begin{array}{l} m = b_2 + [\tilde{b}_2^2 - 4 \tilde{c}_2 (\tilde{a}_2 - 2\tilde{f})]^{1/2} / 2 \tilde{c}_2 \\ m = 0 \text{ in the } N_D \text{ phase.} \end{array} \right. \quad (5)$$

A transition to the D phase can occur only if the parameters (the temperature, for example) satisfy the condition

$$\tilde{a}_2 - 2\tilde{f} < \frac{2}{9} \frac{\tilde{b}_2^2}{\tilde{c}_2} \quad (6)$$

A diskotic phase is thus possible only if the orientational ordering, Q_{ik} , is sufficiently high.

If

$$\tilde{f} = \frac{1}{2} \tilde{a}_2 - \frac{1}{9} \tilde{b}_2^2 / \tilde{c}_2, \quad (7)$$

then the $I \leftrightarrow N_D$ and $N_D \leftrightarrow D$ transition lines intersect. At $\tilde{f} > \frac{1}{2} \tilde{a}_2 - \frac{1}{9} \tilde{b}_2^2 / \tilde{c}_2$, the D phase arises directly from the isotropic phase. Finally, the $D \leftrightarrow K$ transition is analogous to the phase transition from a smectic A liquid crystal to a nematic liquid crystal. The implications of this analogy have been studied elsewhere.³ From the standpoint of the Landau theory, the $D \leftrightarrow K$ transition (i.e., the transition to the phase of complete solidification) may be a second-order transition (since the order parameter χ is a two-component parameter, and there are no invariants of third order in χ). The interaction with the orientational degrees of freedom [Φ_3 in Eq. (1)] does not alter the nature of the phase transition. The corresponding contributions to the free energy are⁴

$$T (D_{\perp} / K_{33})^{3/2} | p_0 \chi |^5.$$

This property represents a fundamental distinction between the $D \leftrightarrow K$ transition and the (smectic A)—nematic transition [and the superconductor—(normal metal) transition], in which the interaction with the gauge degrees of freedom (the orientational order in liquid crystals) leads to terms proportional to the cube of the order parameter (and thereby alters the nature of the phase transition, from second-order to first-order).

The longitudinal bending modulus K_{33} increases in a fluctuational manner at the transition $D \leftrightarrow K$. The reasons for this increase were discussed earlier for the case of the $D \leftrightarrow N_D$ transition.

In summary we wish to emphasize that the thermodynamic potential in (1) draws a consistent qualitative picture of the phase transitions and of the accompanying symmetry properties of diskotic liquid crystals.

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¹J. Billard, *Liq. Cryst. One and Two Dimens. Order* Berlin e.a., 1980, p. 383.

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³E. I. Kats, *Zh. Eksp. Teor. Fiz.* **75**, 1819 (1978) [*Sov. Phys.—JETP* **48**, 916 (1978)].

⁴S. A. Pikin, *Strukturnye prevrashcheniya v zhidkikh kristallakh* (Structural Conversions in Liquid Crystals), Nauka, Moscow, 1981.

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