

New types of ordering in liquid crystals

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Possible types of liquid-crystalline order in systems consisting of rod-shaped or diskotic, as well as structurally more complicated, molecules are examined. Special attention is devoted to new liquid-crystalline phases. Their basic physical properties are analyzed. The phase diagrams and the peculiarities of the critical behavior are investigated in each case. Analogies to some well-known problems in the physics of the condensed state are discussed.

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1. INTRODUCTION

Research on the physics of liquid crystals progressed rapidly in the last two decades. Reviews, monographs, and numerous original scientific papers were published, and international conferences were held. In the early years of this “boom” reviews and conferences were dedicated primarily to general problems involving the physics and chemistry of liquid crystals (structural classification, phase diagrams, synthesis, etc.), but boundaries between separate areas of the science of liquid crystals gradually appeared. This general trend in the development of all sciences can be simply illustrated by bibliographic citations of reviews and monographs.

The first review in Russian by I. G. Chistyakov¹ appeared in *Uspekhi Fizicheskikh Nauk* in 1966 and was devoted to the general subject of liquid crystals. The well-known monograph by de Gennes entitled “The Physics of Liquid Crystals”² (1974, translation into Russian 1977), for example, is of the same nature. On the other hand, Pikin’s monograph³ published in 1981 examines primarily the theory of different types of instabilities in liquid crystals, and the book by Belyakov and Sonin⁴ (1982) concerns only the optics of cholesteric liquid crystals.

Such a separation into separate specialties already occurred a long time ago in, for example, solid-state physics. A review entitled “Solids” in *Uspekhi Fizicheskikh Nauk* would now appear very peculiar. This probably has to do with the fact that the general problems of solid-state physics have now been solved. For example, all possible symmetry groups of solid crystals have been classified.

An entirely different situation exists in the physics of liquid crystals. All possible types of intermediate (falling between solid crystals and an isotropic liquid) phases have not yet been discovered. Their properties have by no means been investigated completely, even theoretically. Five years

has already passed since the time that the “last” monograph of a general nature was published (1977, translation into Russian 1980).⁵ During the course of these years, new types of ordering have been discovered in liquid crystals (so-called diskotic and cubic phases, new types of smectics, etc.). Appreciable progress has also been made in understanding the nature of liquid-crystalline ordering, characteristic of phase transitions, relation between purely “liquid-crystalline” problems and general problems in the physics of the condensed state, theory of critical phenomena, etc. The entire scope of such problems is not reflected in the review literature, either in this country or abroad. On the other hand, there is a considerable literature on this subject (especially in the last two years) dispersed over different (often inaccessible) publications (papers on the physics of liquid crystals are occasionally published in mathematical, physical, chemical, biological, technical, and even medical journals).

These circumstances justify the publication of a review in *Uspekhi Fizicheskikh Nauk* on general progress in the physics of liquid crystals.

2. SYSTEMS OF ROD-SHAPED MOLECULES

a) Nematic–isotropic-liquid phase transitions

We shall examine a system of rod-shaped molecules. At sufficiently high temperature the molecules move freely and rotate relative to one another. We have actually an ordinary isotropic liquid (I) with full rotational and translational symmetry:

$$O(3) \times T(3).$$

The thermal motion partially “freezes” as the temperature decreases. The rod-shaped form of the molecules leads to the fact that in some temperature range the molecules can no

longer rotate freely relative to one another, but their centers of mass can move freely relative to one another. In this temperature range, full translational symmetry $T(3)$ remains (the centers of mass of the molecules are distributed uniformly, as in an isotropic liquid), but rotational $O(3)$ symmetry is broken. In the simplest form of rod-shaped molecules, the group $O(3)$ is replaced by one of the uniaxial symmetry groups D_∞ or $D_{\infty h}$ (depending on the presence of a center of symmetry). Thus, in this temperature range, the ordinary uniaxial nematic phase N with symmetry

$$D_{\infty h} \times T(3)$$

is stable. All presently known thermotropic nematic liquid crystals (i.e., liquid crystals in which a phase transition occurs with a change in temperature) have precisely such uniaxial symmetry. There are two examples⁶ of a more complicated biaxial breaking of rotational symmetry in lyotropic liquid crystals (i.e., liquid crystals in which the phase transition occurs with a change in concentration). This phase corresponds to the so-called biaxial nematic liquid crystals N_2 . In the case of biaxial nematics, different symmetry groups, which are subgroups of $O(3)$, are in principle admissible: orthorhombic, triclinic, hexagonal, or cubic. Groups, which are forbidden in solids by the presence of the crystal lattice, are also possible. Generally speaking, there are no grounds for excluding the subgroups of $O(3)$ with a fifth or seventh order, etc., axis. The symmetry of actually existing N_2 phases has not yet been established.

The physical order parameter that distinguishes N- or N_2 -phases from an isotropic liquid I is a symmetrical traceless tensor of rank two $Q_{\alpha\beta}$, related linearly to the anisotropic part of the dielectric or magnetic susceptibility. Within the framework of Landau's theory, the N (or N_2)-I phase transition is described by a corresponding expansion of the free energy density f ²:

$$\begin{aligned} f &= f_0 + f_1, \\ f_0 &= \frac{1}{2} A Q_{\alpha\beta}^2 - \frac{1}{3} B Q_{\alpha\beta}^3 + \frac{1}{4} C (Q_{\alpha\beta}^2)^2 + \dots, \\ f_1 &= \frac{1}{2} L_1 \left(\frac{\partial Q_{\alpha\beta}}{\partial x_\gamma} \right)^2 + \frac{1}{2} L_2 \left(\frac{\partial Q_{\alpha\beta}}{\partial x_\beta} \right)^2 + \dots \end{aligned} \quad (1)$$

The presence of a cubic invariant in (1) makes the I-N phase transition a first-order transition. The characteristic feature of practically all known thermotropic nematics (and several thousand of them are currently known) is that the I-N transition is very nearly a second-order phase transition. This closeness is characterized numerically by the parameter $\delta \equiv (T_c - T^*)/T_c \ll 1$ (T_c is the temperature of the true first-order phase transition and T^* is the temperature at which $A(T^*) = 0$, i.e., at which a second-order transition would occur). In most liquid crystals that have been studied, the parameter $\delta \sim 10^{-3}$.⁷ In any mean-field theory with an interaction described by a single coupling constant, we have $\delta \sim 1$.

Several possible explanations of this fact have been proposed, but none of them agrees with the experimental data as a whole. The problem is that on the one hand, scattering of light in the isotropic phase⁸ is described well by Curie's law (and, therefore, in agreement with the mean-field theory, we must have $\delta \sim 1$), while on the other, calorimetric data⁹ indi-

cate some transitional behavior (so-called cross-over) from critical and tricritical to "mean-field" behavior.

It could be that fluctuations of the smectic order parameter which interact with the orientational order parameter, are always present.

X-ray diffraction studies show^{1,2,5} that as a result of fluctuation, "virtual" smectic clusters (so-called cybotactic clusters) can form in the nematic phase. Other degrees of freedom, related with, for example, the conformation of molecular chains, etc., could be important. However, no model of this kind agrees quantitatively with the experimental data (and, in particular, such models do not explain the smallness of the parameter δ).

The question as to why the nematic-isotropic-liquid phase transition is always precisely a *weak* first-order transition can be approached somewhat differently.

It could be that fluctuations are not at all small, while in the isotropic phase, Curie's law involves an analysis of experimental data over a too-wide temperature interval. Strongly developed fluctuations could alter the character of the I-N transition and make it a very weak first-order phase transition. This was first pointed out by Nelson and Pelcovits.¹⁰ Indeed, the Hamiltonian corresponding to the free energy (1) can be rewritten in a simplified form. We shall take into account the fact that the order parameter in the N phase is uniaxial:

$$Q_{\alpha\beta} = s \left(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right), \quad (2)$$

where \mathbf{n} is the director and s is the modulus of the order parameter. We shall assume further that the coefficients of elasticity in (1) are equal $L_1 = L_2$, and we shall neglect fluctuations of the modulus. Then, instead of (1) we obtain

$$F = \frac{1}{2} L \int d\mathbf{r} |\nabla Q_{\alpha\beta}|^2 = \frac{1}{2} K \int d\mathbf{r} (\nabla \mathbf{n})^2, \quad (3)$$

where

$$K = 2Ls^2.$$

In this approximation, the nematic is equivalent to the model of interacting three-component spins with fixed length.

In the two-dimensional case $d = 2$, for model (3), there exists a continuous phase transition at zero temperature $T_c = 0$ (i.e., fluctuations with $d = 2$ are so strong that they completely suppress the phase transition into the isotropic liquid at finite temperature). In a space with $d = 2 + \varepsilon$, the transition temperature differs from zero and $T_c \sim (d - 2)$. The fluctuations are strong as before, and the transition remains a second-order phase transition. Of course, this is all valid if fluctuations of the modulus can be neglected. Fluctuations of the modulus can be included in model (3) using perturbation theory,¹⁰ and they are indeed insignificant. The second remark is related with the fact that the transition to $d = 3$ does not correspond to small values of ε . For this reason, with $d = 3$ the cubic invariant, which is absent in the three-component spin model could become important. The phase transition becomes a first-order transition. However, the reason noted above (strong fluctuations with $d = 2$, making $T_c = 0$ and leading to a continuous transition) indicates a

tendency for such a transition to be close to a second-order phase transition.

An analogous argument also works for biaxial nematics. In the simplest single-constant approximation with the same assumptions as above concerning the fluctuations of the modulus, the Hamiltonian (3) is equivalent to the model of five-component spins of fixed length. With an obvious relabelling of the components, we obtain

$$F = \frac{1}{2} \tilde{L} \int d\mathbf{r} |\nabla Q_{\alpha\beta}|^2 = \frac{1}{2} \tilde{L} \int d\mathbf{r} (\nabla_\gamma y_\mu)^2, \quad (4)$$

where $\mu = 1, 2, 3, 4, 5$; $\gamma = 1, 2, \dots, d$ (d is the dimensionality of the space);

$$Q_{12} = \frac{y_3}{\sqrt{2}}, \quad Q_{13} = \frac{y_2}{\sqrt{2}}, \quad Q_{23} = \frac{y_1}{\sqrt{2}},$$

$$Q_{11} = \frac{1}{\sqrt{2}} \left(\frac{y_4}{\sqrt{3}} + y_5 \right), \quad Q_{22} = \frac{1}{\sqrt{2}} \left(\frac{y_4}{\sqrt{3}} - y_5 \right),$$

$$Q_{33} = -\frac{2y_4}{\sqrt{6}}.$$

The uniform part of the free energy (not containing gradients) determines $\text{Sp } Q_{\alpha\beta}^2$ and, therefore, the "spin length," since

$$Q_{\alpha\beta}^2 = y_\mu^2.$$

Thus fluctuations with $d = 2$ make the biaxial-nematic-isotropic-liquid phase transition a second-order phase transition, and the temperature of the transition (T_c) equals zero in this case. With $d = 2 + \varepsilon$, as long as fluctuations of the modulus can be neglected, the transition remains a continuous one and the temperature of the transition is low. It therefore appears that the transition with $d = 3$ will be a second-order phase transition or close to it. Of course, the critical indices depend on the number n of spin components. For this reason, phase transitions from the uniaxial nematic into the isotropic liquid ($n = 3$) or from a biaxial nematic into an isotropic liquid ($n = 5$) belong to different universality classes (for a more detailed discussion see, for example, Ref. 11).

We have examined isolated N-I or N_2 -I transitions. A combined N_2 -I-N phase diagram can also be constructed. If higher (fifth and sixth) order terms are included in Landau's expansion (1), then the phase diagram in, for example, the P - T plane will look schematically like the diagram shown in Fig. 1.

There exists another factor, characteristic for phase transitions from a uniaxial or biaxial nematic into an isotropic liquid, which was pointed out by Pokrovskii *et al.*¹² As already mentioned, the order parameter for such transitions is a symmetrical tensor of rank two with vanishing trace.

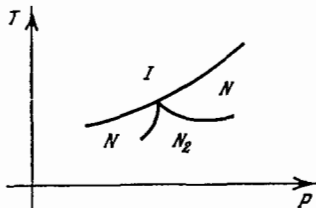


FIG. 1. Smectic form of the state diagram N_2 -I-N.

This tensor is characterized in three-dimensional space by two invariants (since $\text{Sp } Q_{\alpha\beta} = 0$). These invariants can be chosen, for example, as the diagonal elements of the tensor: λ_1, λ_2 , and λ_3 , which are interrelated by the condition $\lambda_1 + \lambda_2 + \lambda_3 = 0$. However, it is more convenient to choose a different system of invariants: $\text{Sp } Q_{\alpha\beta}^2$ and $\text{Sp } Q_{\alpha\beta}^3$. The point is that within Landau's theory, for example, the free energy is a complicated algebraic function of the invariants λ_1, λ_2 , and λ_3 and a simple power-law function of the invariants $X = \text{Sp } Q_{\alpha\beta}^2$ and $Y = \text{Sp } Q_{\alpha\beta}^3$.

These systems of invariants are interrelated in an obvious manner:

$$X = \lambda_1^2 - \lambda_2^2 + \lambda_3^2, \quad Y = \lambda_1^3 + \lambda_2^3 + \lambda_3^3 \quad (\lambda_1 + \lambda_2 + \lambda_3 = 0). \quad (5)$$

The thermodynamic potential of the system is in general some function of the variables X and Y : $\Phi(X, Y)$.

Let the function $\Phi(X, Y)$ have an absolute minimum at some point X_0, Y_0 . Then X_0, Y_0 determines the equilibrium value of the order of the nematic liquid crystal. Equations (5) also determine the characteristic values of the order parameter in this equilibrium state. In addition, in general, $\lambda_1 \neq \lambda_2 \neq \lambda_3$, which corresponds to a biaxial nematic liquid crystal. It is, of course, possible that at some special points two of the characteristic values will be equal, in which case a uniaxial nematic liquid crystal is obtained.

Exactly the opposite situation exists experimentally. Several thousand thermotropic nematic liquid crystals are now known (i.e., liquid crystals in which the phase transition occurs with a change in temperature), and they all are uniaxial. It is clear that this fact cannot be related with random circumstances. On a microscopic level, the uniaxial nature of nematic liquid crystals is a result of the plate-like elongated form of the molecules and their almost free rotation around the long axis. In the macroscopic language, the uniaxiality of liquid crystals imposes some restrictions on the form of the function $\Phi(X, Y)$. The point is that the function $\Phi(X, Y)$ does not necessarily have an absolute minimum. In addition, even when such a minimum does exist, it may be inaccessible among the permissible values of the parameters X and Y , which are interrelated by a Cauchy-Bunyakovskii type inequality following from (5):

$$|Y| \leq \frac{1}{\sqrt{6}} X^{3/2}. \quad (6)$$

In these two cases (i.e., when $\Phi(X, Y)$ does not have an absolute minimum or inequality (6) is not satisfied at the minimum), both partial derivatives $\partial\Phi/\partial X$ and $\partial\Phi/\partial Y$ differ from zero. It is easy to see (see Eqs. (7)-(9) below) that at the saddle point in which only one of the derivatives $\partial\Phi/\partial X$ or $\partial\Phi/\partial Y$ differs from zero, the eigenvalues of the tensor $Q_{\alpha\beta}$, which minimize the thermodynamic potential, equal zero or are complex, which does not correspond to real liquid crystals. To determine the equilibrium form of the order parameter $Q_{\alpha\beta}$, it is necessary to minimize the function $\Phi(X, Y)$:

$$\frac{\partial\Phi}{\partial Q_{\alpha\beta}} = 2 \frac{\partial\Phi}{\partial X} Q_{\alpha\beta} + 3 \frac{\partial\Phi}{\partial Y} \left(Q_{\alpha j} Q_{j\beta} - \frac{1}{3} \delta_{\alpha\beta} Q_{j m} \right)^2 = 0. \quad (7)$$

It is easy to verify with a simple substitution that the uniaxial tensor of the form $Q_{ij} = s(n_i n_j - \frac{1}{3} \delta_{ij})$, where \mathbf{n} is a unit vector, satisfied Eqs. (7). In addition, the modulus of the

order parameter s must obey the condition

$$2 \frac{\partial \Phi}{\partial X} + s \frac{\partial \Phi}{\partial Y} = 0. \quad (8)$$

It can be shown that Eqs. (7) do not have other solutions. To do so, we rewrite (7) in a system of coordinates in which the tensor $Q_{\alpha\beta}$ is diagonal. Since in this case $\lambda_3 = -(\lambda_1 + \lambda_2)$, we obtain from (7)

$$\begin{aligned} 2 \frac{\partial \Phi}{\partial X} \lambda_1 &= -3 \frac{\partial \Phi}{\partial Y} \left[\lambda_1^2 - \frac{2}{3} (\lambda_1^2 + \lambda_2^2 + \lambda_1 \lambda_2) \right], \\ 2 \frac{\partial \Phi}{\partial X} \lambda_2 &= -3 \frac{\partial \Phi}{\partial Y} \left[\lambda_2^2 - \frac{2}{3} (\lambda_1^2 + \lambda_2^2 + \lambda_1 \lambda_2) \right]. \end{aligned} \quad (9)$$

Dividing the first of these equations by the second (this can always be done since by definition $\partial \Phi / \partial X \neq 0$ and $\partial \Phi / \partial Y \neq 0$) and transforming to the variable $z = \lambda_1 / \lambda_2$, we arrive at a cubic equation for z , which does not depend on the derivatives $\partial \Phi / \partial X$ and $\partial \Phi / \partial Y$. Inasmuch as $z = 1$ is the root of this equation ($\lambda_1 = \lambda_2 = -s/3$), it is easy to find the remaining roots $z = -2$ and $z = -1/2$, which likewise correspond to the uniaxial tensor Q_{ij} ($\lambda_1 = 2s/3, \lambda_2 = -s/3$ or $\lambda_1 = -s/3, \lambda_2 = 2s/3$). Equation (7) has no other roots. Thus, in this situation ($\partial \Phi / \partial X \neq 0$ and $\partial \Phi / \partial Y \neq 0$), the order parameter can only be uniaxial.

As follows from Landau's expansion (1), the isotropic-liquid-nematic phase transition is a first-order phase transition:

$$f_0 = \frac{1}{2} A Q_{\alpha\beta}^2 - \frac{1}{3} B Q_{\alpha\beta}^3 + \frac{1}{4} C Q_{\alpha\beta}^4 + \dots$$

Such an expansion is admissible if the moduli of the eigenvalues $|\lambda_1|$ and $|\lambda_2|$ are sufficiently small. The coefficient A vanishes at some point T^* , close to the transition point T_c . It follows from the experimental data^{1,5,7} that the jump in the modulus of the order parameter at the transition point is $\bar{s} \sim 0.4$ and the ratio $(T_c - T^*)/T^* \sim 10^{-3}$, i.e., the coefficient B in the expansion (1) is relatively small, but remains finite in a comparatively narrow temperature interval of existence of the nematic phase. For this reason, we can conclude that in the entire region of existence of the nematic, the derivative $\partial \Phi / \partial Y = B \neq 0$ and, therefore, the order parameter Q_{ij} is uniaxial (according to Eq. (8) and $\partial \Phi / \partial X \neq 0$). Thus, in the microscopic language, the uniaxiality of all nematic liquid crystals is related with the smallness of the coefficient B in Landau's expansion (1). Experimental data¹³ likewise show that the coefficient B is virtually independent of pressure and, for this reason, it is unlikely that an isolated point where $B = 0$ will be observed.

Summarizing, we can say that the nature of the isotropic-liquid-nematic phase transitions is still not completely understood. In addition, even general fundamental questions (reason for the weak "first-order nature" of the transition, etc.), not to mention the detailed description of the temperature dependences of the heat capacity, scattering cross section, and other critical effects, are not understood. The construction of a theory of this transition is a task for the future. Systematic experiments on a homologous series of liquid crystals, which would permit establishing, for example, the dependence of the thermodynamic parameters, critical indices, etc., on the length and conformation of the flexi-



FIG. 2. Structure of a smectic-A liquid crystal.

ble chains or on the width of the temperature interval of existence of the nematic and smectic phases, are also required.

b) Nematic-smectic-A transition

Above, we examined the behavior as the temperature decreases of an isotropic liquid consisting of rod-shaped particles. A natural consequence of the shape of the molecules is that in such a system, first of all, the rotational group is broken, i.e., a transition into the nematic phase occurs.

Rod-shaped molecules which make up liquid crystals are usually constructed in such a way that they have a rigid central core to which one or two flexible terminal chains are connected. In addition, the interaction of molecules via the terminal groups is much stronger than via the "lateral surfaces," i.e., central cores. This circumstance leads to a series of important consequences. First of all, as the temperature decreases further, an entire range of parameters can exist in the nematic phase in which the interaction of the lateral surfaces is still too small to produce quasicrystalline ordering in a plane perpendicular to the long axes of the molecules, but the interaction of the terminal groups is now strong enough for one-dimensional crystalline ordering to appear along the long axes of the molecules. The situation described above corresponds to partial breakdown of translational invariance. The phase which is being formed here is called a smectic-A liquid crystal (or, more briefly smectic-A). The symmetry of smectic-A in the system of centrosymmetrical molecules (i.e., achiral) is

$$D_{\infty h} \times T(2).$$

Several models of the smectic-A phase exist (see, for example, Refs. 2, 3, 5, and 7). In any case, a smectic-A differs from a nematic by the presence of a density of mass centers of molecules modulated along the director.

$$\rho(\mathbf{r}) = \rho_0 \left\{ 1 + \frac{1}{\sqrt{2}} [\psi(\mathbf{r}) \exp(iq_0 \mathbf{n} \cdot \mathbf{r}) + \text{c.c.}] \right\};$$

Here $2\pi/q_0$ is the distance between smectic layers. The complex modulation amplitude $\psi(\mathbf{r})$ is the order parameter for the nematic-smectic-A transition in De Gennes' model,² in which higher order harmonics of the density are neglected.

In what follows, we shall examine precisely this model because, first, the experimental data⁵ indicate that higher order harmonics are not significant and, second, inclusion of higher order harmonics (and their interaction with the fundamental harmonic) reduces to a renormalization of the coefficients of the Hamiltonian in de Gennes' model. Landau's expansion of the free energy in powers of ψ and $\nabla \psi$ must also include the invariance of the system under a simultaneous rotation of the director \mathbf{n} and the direction of modulation of

the density (i.e., the system of smectic layers). We thus obtain²

$$H_s = \int dr \left[A^0 |\psi|^2 + \frac{1}{2} U^0 |\psi|^4 + C_{\parallel}^0 |\nabla_{\parallel} \psi|^2 + C_{\perp}^0 |(\nabla_{\perp} - iq_0 \delta \mathbf{n}) \psi|^2 \right].$$

Here $A^0 = a(T - T_{c0})/T_{c0}$ and T_{c0} is the temperature of the nematic-smectic-A transition in the mean-field approximation; U^0 , C_{\parallel}^0 , and C_{\perp}^0 are the coefficients in Landau's expansion and, in addition, the form of the last term takes into account the local, i.e., gauge, invariance mentioned above.

The complete Hamiltonian must also include the contribution from the energy of deformation of the director, the so-called Frank elastic energy:

$$H_N = \int dr \left[\frac{1}{2} \bar{K}_1 (\text{div } \mathbf{n})^2 + \frac{1}{2} \bar{K}_2 (\mathbf{n} \text{ rot } \mathbf{n})^2 + \frac{1}{2} \bar{K}_3 [\mathbf{n} \text{ rot } \mathbf{n}^2] \right],$$

where \bar{K}_i are the start-up values of Frank's moduli (i.e., neglecting fluctuations of the smectic order parameter ψ).

The complete Hamiltonian $H_s + H_N$ is similar to the Ginzburg-Landau Hamiltonian for the superconductor-normal-metal phase transition. The start-up anisotropy of the correlation lengths can be eliminated with the help of a scale transformation, after which we have

$$H = H_s + H_N = \int \left\{ a_0 |\psi|^2 + \frac{1}{2} u_0 |\psi|^4 + |(\nabla - iq_0 \delta \mathbf{n}) \psi|^2 \right\} dr + \int \left\{ \frac{1}{2} K_1^0 (\nabla \mathbf{n})^2 + \frac{1}{2} K_2^0 \sum_{i,j} (\nabla_i n_j - \nabla_j n_i)^2 + \frac{1}{2} K_3^0 \sum_j (\nabla_{\parallel} n_j)^2 \right\} dr; \quad (10)$$

where

$$a_0 = \frac{A^0}{C^0}, \quad u_0 = \frac{U^0}{(C^0)^2}, \quad K_{1,2}^0 = \bar{K}_{1,2} \left(\frac{C_{\parallel}^0}{C_{\perp}^0} \right)^{2/3}, \\ K_3^0 = \bar{K}_3 \left(\frac{C_{\parallel}^0}{C_{\perp}^0} \right)^{-1/3}, \quad (C^0)^3 = C_{\parallel}^0 (C_{\perp}^0)^2.$$

The Ginzburg-Landau Hamiltonian for the superconductor-normal-metal transition has the form

$$H_{GL} = H_s + \frac{1}{2} K \int \sum_{i>j} (\nabla_i A_j - \nabla_j A_i)^2 dr, \quad (11)$$

where we must make the substitution $q_0 = 2e$ (e is the electron charge) in H_s , and $K = \mu_0/4\pi$ (μ_0 is the Bohr magneton). The vector potential \mathbf{A} has two independent components, since changes of \mathbf{A} are restricted by the condition of gauge invariance. Analogous restrictions exist on the deviation of the director $\delta \mathbf{n}$, but they are related with the condition of orthogonality $\delta \mathbf{n} \cdot \mathbf{n}_0 = 0$.

The Hamiltonians (10) and (11) would coincide exactly if $K_1^0 = 0$ and $K_2^0 = K_3^0$. In general, for liquid crystals this is, of course, not the case. The term $K_1^0 (\text{div } \mathbf{n})^2$ destroys the gauge invariance of superconductors:

$$H_{GL} \{ \psi e^{iq_0 L(\mathbf{r})}, \mathbf{A}(\mathbf{r}) + \nabla L(\mathbf{r}) \} \equiv H_{GL} \{ \psi(\mathbf{r}), \mathbf{A}(\mathbf{r}) \}.$$

There is also another very important difference between

the Hamiltonians (10) and (11). The point is that according to the well-known assertion by Landau and Peierls (see Ref. (14)), true long-range order cannot in general exist in smectic liquid crystals, i.e., $\langle \psi \rangle = 0$, while in superconductors $\langle \psi \rangle \neq 0$. The absence of long-range order in smectics is related with the fact that in these crystals (as in any three-dimensional system with one-dimensional modulation of the density), fluctuations of the displacements (phases of the order parameter) diverge. These divergences lead to many difficulties (including fundamental difficulties) in calculations performed using the Hamiltonian (10). Dunn and Lubensky¹⁵ proposed an artificial technique involving the introduction of a continuous gauge, parameterized by the angle θ :

$$\Phi(\mathbf{r}) = \psi(\mathbf{r}) e^{iq_0 L_{\theta}(\mathbf{r})}, \\ \mathbf{A}_{\theta}(\mathbf{r}) = \delta \mathbf{n}(\mathbf{r}) + \nabla L_{\theta}(\mathbf{r}).$$

The real function $L_{\theta}(\mathbf{r})$ is determined by the choice of gauge:

$$\mathbf{v}(\theta, \mathbf{p}) \cdot \mathbf{A}_{\theta}(\mathbf{p}) = 0, \\ \mathbf{v}(\theta, \mathbf{p}) = \hat{\mathbf{e}}_1 \cos \theta + i \hat{\mathbf{p}} \sin \theta, \quad (12)$$

where $\mathbf{A}_{\theta}(\mathbf{p})$ are the Fourier components of $\mathbf{A}_{\theta}(\mathbf{r})$; $\hat{\mathbf{e}}_1$ is a unit vector along \mathbf{n}_0 ; and $\hat{\mathbf{p}} = \mathbf{p}/|\mathbf{p}|$.

For $\theta = 0$, the vector $\mathbf{A}_{\theta} \perp \mathbf{n}_0$ and the condition of orthogonality is satisfied. For $\theta = \pi/2$, $\mathbf{v} = i \hat{\mathbf{p}}$ and $\mathbf{A}_{\pi/2}(\mathbf{p})$ are transverse relative to $\hat{\mathbf{p}}$. True long-range order exists in this gauge and the divergences characteristic for smectic liquid crystals do not occur. All calculations in the gauge with $\theta = \pi/2$ are analogous to those for the superconductor-normal-metal transition. In this sense, this gauge can be called a superconducting gauge.

The problem lies in the fact that the gauge $\theta = \pi/2$ does not satisfy the orthogonality condition $\delta \mathbf{n} \cdot \mathbf{n}_0 = 0$, i.e., $\mathbf{A}_{\pi/2}$ does not have the significance of a director.

Thermodynamic characteristics such as, for example, the heat capacity do not depend on the gauge. For this reason, they can be calculated in any convenient gauge. On the other hand, some important quantities (the correlation function, for example) depend explicitly on the gauge. It is also interesting to note the distinguishing feature of the superconducting gauge. Long-range order is conserved only with $\theta = \pi/2$. Dunn and Lubensky¹⁵ showed that $\langle \psi_{\pi/2} \rangle \geq \langle \psi_{\theta} \rangle$ for all θ .

The most difficult problem is the transition from the gauge $\theta = \pi/2$, which is convenient for performing calculations, to the physical gauge $\theta = 0$. The difficulty lies in the fact that at $\theta = 0$ the conditions of applicability of the approximations usually used in calculations of the critical indices and other characteristics of the transition are no longer satisfied. In addition, even in the gauge $\theta = \pi/2$, the universality class depends on the start-up values of elastic moduli.¹⁵ In all cases, the relations between indices, known from the theory of similarity, are satisfied:

$$\gamma_{\theta=\pi/2} = \nu_{\parallel} (2 - \eta_{\parallel}) = \nu_{\perp} (2 - \eta_{\perp}),$$

where the symbols \parallel and \perp refer to the direction parallel or perpendicular to the director. The index of the heat capacity does not depend on the gauge and satisfies the general relation of the theory of similarity:

$$2 - \alpha = \nu_{\parallel} + (d - 1) \nu_{\Delta}.$$

The susceptibility $\chi_0(q, \tau)$ in an arbitrary gauge is related with the susceptibility in the superconducting gauge. There are, however, no reliable analytical results for $\theta = 0$. It is interesting¹⁶ that already in the nematic phase (i.e., for $\tau > 0$), the correlation lengths ξ_{\parallel}^* and ξ_{\perp}^* , measured from x-ray scattering, differ from ξ_{\parallel} and ξ_{\perp} found from the change in gauge-independent characteristics (for example, from Frank's moduli). As $\tau \rightarrow +0$ independently of the values of ν_{\parallel} and ν_{\perp} we have $\xi_{\parallel}^* \sim \xi_{\parallel}^{*2} / \ln \xi_{\perp}^*$. This unusual behavior is a precursor of the fact that there is no long-range translational order in the smectic phase (i.e., for $\tau < 0$). In addition, this fact could indicate that the critical point for the nematic-smectic-A transition is isotropic ($\nu_{\parallel} = \nu_{\perp}$), in spite of the fact that experimentally $\nu_{\perp}^* < \nu_{\parallel}^*$. At an isotropic critical point with $d = 3$ and $\theta = 0$, the correlation function $G_0(\mathbf{r}, \tau = 0)$ decreases as a function of distance more rapidly than any power of $|\mathbf{r}|$ (for large $|\mathbf{r}|$), so that the susceptibility $\chi_0(\tau = 0)$ is finite. The susceptibility diverges as $\tau = \tau_1 < 0$, while the heat capacity and elastic moduli have singularities at $\tau = 0 > -\tau_1$.

The situation, of course, changes if $\nu_{\parallel} \neq \nu_{\perp}$. If the smectic-A-nematic transition occurs due to the formation of dislocation loops (so-called topological melting), then, as Nelson and Toner¹⁷ showed, $\nu_{\parallel} = 2\nu_{\perp}$. In this case,¹⁸ for example, $\eta_{\parallel}(\tau = 0) \neq \eta_{\parallel}(\tau = -0)$ and $\eta_{\perp}(\tau = 0) \neq \eta_{\perp}(\tau = -0)$, i.e., the critical point does not coincide with the endpoint on the line of stationary points of the smectic-A phase (while for $\nu_{\parallel} = \nu_{\perp}$: $\eta_{\parallel}(\tau = -0) = \eta_{\parallel}(0)$ and $\eta_{\perp}(\tau = -0) = \eta_{\perp}(0)$). In the liquid-crystalline gauge K_1 is always a real variable. The renormalization group equation for K_1 has the following stationary points: $K_1^* = 0$, $K_1^* = \infty$ or $0 < K_1^* < \infty$, but $\nu_{\parallel} = (5 - d)\nu_{\perp}$ (d is the dimensionality of the space). In the first case, there is a superconducting analogy; in the second, there is an anisotropic scaling with the nonuniversal relation $\nu_{\parallel} > \nu_{\perp}$; and, in the third, we always have $\nu_{\parallel} = (5 - d)\nu_{\perp}$.

In general, from the point of view of the power-law falling off of the correlations and the absence of long-range translational order, smectic-A liquid crystals appear to be similar to two-dimensional systems. There is, however, a very important difference, related with the role of anharmonic terms.^{19,20} In a two-dimensional degenerate system (for example, an isotropic Heisenberg magnetic material), the Hamiltonian in the harmonic approximation has the following form:

$$H_0 = \frac{1}{2} J \int d^2r (\nabla \mathbf{m})^2.$$

Anharmonic terms are proportional to higher order powers of the gradient and are not dangerous in the long-wavelength limit. Indeed, the first anharmonic contribution to the correlation function $\sim \int d^2q/q^2 q^3 \rightarrow 0$ as $q \rightarrow 0$. The gradient part of the free energy of the smectic-A phase (i.e., the elastic energy of smectic-A), however, is anisotropic. For this reason, in this case, there are "dangerous" anharmonic terms, leading to significant corrections to the correlation function. We shall discuss this question in greater detail, following primarily Ref. 20.

Let us separate out in the Hamiltonian (10) of the smectic-A liquid crystal the modulus and phase of the order parameter,

and let us fix the modulus. For $\tau < 0$, the phase of the order parameter is related with the displacement of the smectic layers (4). Using this relation, we obtain from (10) in the harmonic approximation

$$H_0 = \int \left[\frac{1}{2} B \left(\frac{\partial u}{\partial z} \right)^2 + \frac{1}{2} K_1 \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 \right] d^3r,$$

where B is the modulus of elasticity, related with the compressibility of the system of smectic layers.

In terms of Fourier components

$$H_0 = \frac{1}{2} \int d^3q (Bq_{\parallel}^2 + K_1 q_{\perp}^4) |u(\mathbf{q})|^2.$$

The Hamiltonian H_0 describes the so-called Lifshitz critical point.²¹ It can be shown that the entire region of existence of the smectic-A phase is a Lifshitz point with parameters $m = 2$ and $n = 1$ (m is the number of the components of the soft mode, i.e., m shows how many coefficients in front of the components $(\nabla_{\perp} u)^2$ vanish, and n is the number of components of the order parameter).

At a true Lifshitz point the Gaussian approximation, for which the correlation function is given by

$$\langle u(\mathbf{q}) u(0) \rangle \equiv g(q_{\parallel}, \mathbf{q}_{\perp}) \sim \begin{cases} q_{\parallel}^{-2}, & \text{if } \mathbf{q}_{\perp} = 0, \\ q_{\perp}^{-4}, & \text{if } q_{\parallel} = 0, \end{cases}$$

is unstable. The interaction $\sim |u(\mathbf{q})|^4$ leads in three-dimensional space to a change in the indices of the correlation function $g(q_{\parallel}, \mathbf{q}_{\perp})$, i.e., to a different (non-Gaussian) stable stationary point.

In contrast to an ordinary Lifshitz point, an interaction of fluctuations of the displacement which does not vanish as $\mathbf{q} \rightarrow 0$ does not exist in a smectic liquid crystal. A dangerous interaction in this case is, for example,

$$H_{\text{int}} = \frac{\gamma_0}{4!} \int d^3r (\nabla_{\perp} u)^4.$$

There are also dangerous third-order anharmonic terms

$$\sim \int d^3r \frac{\partial u}{\partial z} (\nabla_{\perp} u)^2,$$

which always arise when the symmetry of the smectic relative to the simultaneous rotation of layers and of the director is taken into account. For example, the simplest diagrams for the self-energy part of the Green's function $g(q_{\parallel}, \mathbf{q}_{\perp})$ (Fig. 3) give

$$\Sigma(q) = -\gamma_0^2 \left(\frac{7}{3} - 8 \ln \frac{4}{3} \right) q_{\perp}^4 \frac{\ln a}{8\pi^2}.$$

Analogously, the vertex function $\Gamma(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \mathbf{p}_4)$, describing renormalization of the interaction (Fig. 4) is given by:

$$\Gamma = -4q_{\perp}^4 \gamma_0 \left(1 - 9\gamma_0 \frac{\ln a}{4\pi} \right).$$

Here a is a dimensionless cutoff parameter in the diverging integrals.

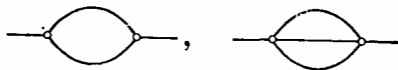


FIG. 3. Anharmonic corrections to the correlation function of displacements of layers in smectic-A.

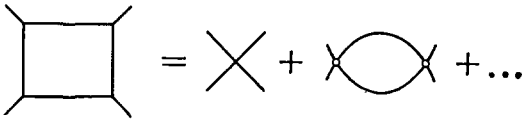


FIG. 4. Renormalization of interaction in the smectic-A phase.

The problem of summing all diagrams of this type for $\gamma_0 \ln a \gg 1$ is well known (the so-called parquet approximation). We present the final expressions for the correlation functions:

$$g^{-1}(q_{\perp}, q_{\parallel} = 0) \sim q_{\perp}^4 \left(1 + \gamma_0 \ln \frac{1}{aq_{\perp}}\right)^{2/5}, \quad (13)$$

$$g^{-1}(q_{\parallel}, q_{\perp} = 0) \sim q_{\parallel}^2 \left(1 + \gamma_0 \ln \frac{1}{aq_{\parallel}}\right)^{-4/5}. \quad (14)$$

In terms of the harmonic part of the elastic energy of the smectic-A phase, Eqs. (13) and (14) indicate a nonanalytic, with respect to the wave vector renormalization of the moduli B and K_1 :

$$B^* \rightarrow B(1 - \gamma_0 \ln q_{\parallel} a)^{-4/5},$$

$$K_1^* \rightarrow K_1(1 - \gamma_0 \ln q_{\perp} a)^{2/5}.$$

Thus the gradient expansion does not, strictly speaking, make any sense. For small wave vectors, the renormalized value of the modulus of elasticity $B^* \rightarrow 0$, while Frank's constant $K_1^* \rightarrow \infty$. Rough estimates¹⁹⁻²⁰ show that for realistic values of the parameters for A smectics, the logarithmic corrections to the moduli lie at the limits of accuracy of present optical methods.

It is more promising, in this sense, to measure the dependence on the magnetic field.²⁰ For calculations, it is convenient to introduce into the harmonic Hamiltonian H_0 , aside from the magnetic field, an additional contribution to the elastic energy:

$$\frac{\partial^2 u}{\partial z^2} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right).$$

These terms are usually not included because they are significant only for z -dependent displacements of the layers and are therefore small compared with the "solid-state" term $(\partial u / \partial z)^2$. However, such terms arise with renormalization of the start-up harmonic Hamiltonian and, in addition, are required in order to restore the symmetry of the system.

Thus the complete Hamiltonian of the smectic-A phase is

$$H = \frac{1}{2} \int d^3 q (B q_{\parallel}^2 + K_1 q_{\parallel}^2 q_{\perp}^2 + \chi_a h^2 q_{\perp}^2 + K_1 q_{\perp}^4) |u(\mathbf{q})|^2 + \frac{\chi_a}{4!} \int d^3 q_1 d^3 q_2 d^3 q_3 d^3 q_4 \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4) (q_{1\perp} q_{2\perp}) \times (q_{3\perp} q_{4\perp}) u(\mathbf{q}_1) u(\mathbf{q}_2) u(\mathbf{q}_3) u(\mathbf{q}_4).$$

It is convenient to introduce instead of the scalar field $u(\mathbf{q})$ a two-component vector field:

$$\xi = q_{\perp} u(\mathbf{q}).$$

With the help of this vector field, the start-up function is given by

$$\tilde{g}_0(\mathbf{q}) \equiv \langle \xi(\mathbf{q}) \xi(-\mathbf{q}) \rangle = \frac{1}{B[x^2/(1-x^2)] + \tilde{K}q^2 + \chi_a h^2}.$$

In a large range of angles $x \ll 1$ ($x = \cos \theta$, where θ is the polar angle), the problem has become equivalent to the problem of a phase transition in four dimensions. The role of "mass" (or proximity to the transition point) is played by the magnetic field $\chi_a h^2$. The logarithmic corrections (13) and (14) correspond to the well-known results for a phase transition with $d = 4$ and $n = 2$. Instead of the wave-vector dependences found above, we now have magnetic-field dependences (of the susceptibility, heat-capacity, structure factor, intensity of light scattering, effective elastic moduli, etc.), which can in principle be checked more simply experimentally.

Of course, the analogy to the problem of a phase transition cannot be complete because of the presence of triple vertices, which are small for $x \ll 1$.

Thus, we have described in this section the smectic-A phase and its transition into a nematic liquid crystal. It should be noted that here the situation is clearer from the theoretical point of view than for the nematic-isotropic-liquid transition. In particular, within the framework of the de Gennes' model, all possible stationary points describing the nematic-smectic-A transition have been established. The experimental situation is more confused. Data obtained by different groups often contradict one another. This could be related in part with the use of unsuccessful or inadequate methods of investigation (for example, differential scanning calorimetry). The reason could be more profound and it is necessary to take into account the narrowness of the region of existence of the smectic-A phase and, therefore, of the interaction of the smectic-A, nematic, and other order parameters. This work has not yet been performed. A somewhat more detailed discussion of this will be given in the next section.

c) C and B smectics

As the temperature decreases further, smectic-A liquid crystals transform into a modification with even lower symmetry. Now even the $D_{\infty h} \times T(2)$ group is broken. The breaking of uniaxial symmetry $D_{\infty h}$ corresponds physically to the appearance of tilting of molecules relative to the smectic layers. Such liquid crystals are called C smectics. Their symmetry is now biaxial. For example:

$$C_{2h} \times T(2).$$

Another possibility is related with breaking of two-dimensional translational symmetry $T(2)$. In the simplest case complete crystallization occurs. The symmetry of the molecular crystal formed is described by one of 230 Fedorov groups.

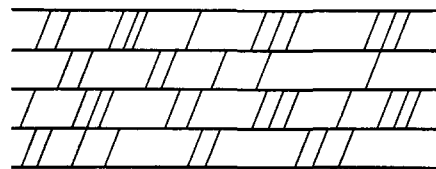


FIG. 5. Structure of smectic-C liquid crystal.

There is, however, in many cases a less trivial breaking of $T(2)$. Based on an analysis of experimental data, Birgenau and Litster²² proposed the possibility of a transition from the smectic-A phase into a liquid crystal, which is a three-dimensional analog of the hexatic phase, i.e., into a layered system such that in each layer there is long-range orientational order of bonds between nearest-neighbor particles.

We shall describe this situation in somewhat greater detail. Crystalline order, as is well known, is described by the Fourier components of the mass density $\rho_{\mathbf{g}}$, where \mathbf{g} is a reciprocal lattice vector. In the presence of true long-range order $\langle \rho_{\mathbf{g}} \rangle \neq 0$. In an ordinary liquid, $\langle \rho_{\mathbf{g}} \rangle = 0$, while the correlation function $\langle \rho_{\mathbf{g}}(\mathbf{r}) \rho_{\mathbf{g}}(0) \rangle$ decreases exponentially with distance:

$$\langle \rho_{\mathbf{g}}(\mathbf{r}) \rho_{\mathbf{g}}(0) \rangle \sim e^{-r/\xi}, \quad r \rightarrow \infty,$$

where ξ is of the order of several angstroms.

True long-range order does not exist in two-dimensional systems due to strong fluctuations. However, at sufficiently low temperatures the correlation function decreases in a power-law fashion and not exponentially:

$$\langle \rho_{\mathbf{g}}(\mathbf{r}) \rho_{\mathbf{g}}(0) \rangle \sim r^{-\eta_{\mathbf{g}}}, \quad (15)$$

where the index $\eta_{\mathbf{g}}$ depends on the temperature and on the elastic moduli. Together with the power-law falling off of correlations (quasi-long-range order), there is a real long-range order in the orientation of bonds. We introduce the angle θ between an arbitrary axis in the plane and the direction of the bond between neighboring particles. If we are talking about hexagonal symmetry (and we are discussing precisely this type of smectic-B), then it is convenient to choose $\psi = e^{6i\theta}$ as the orientational order parameter. Thus the following sequence of phases occurs in two-dimensional systems: 1) a solid crystalline phase with quasi-long-range translational order and long-range orientational order of bonds; 2) an intermediate phase with short-range translational order and quasi-long-range orientational order of bonds (this phase is called a hexatic liquid crystal; the solid-state shear moduli vanish in this phase, but anisotropy and the concomitant contribution to the elastic energy, similar to the Frank energy in nematics, are present); 3) a liquid phase with short-range translational and orientational order.

Order in a layer is very important in the formation of a smectic-B layered system. If the layers are solid, then due to the interaction between them, quasi-long-range translational order becomes true long-range order (since the susceptibility in the phase with a power-law falling-off of correla-

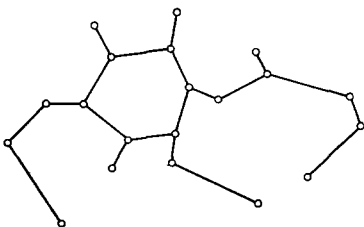


FIG. 6. Two-dimensional hexatic liquid crystal (system with short-range translational order and quasi-long-range orientational order of bonds).

tions is infinite). Crystalline B smectics are obtained in this manner. If the layers are hexatic liquid crystals, then a hexatic smectic-B is obtained with short-range translational order (the susceptibility of the phase with short-range order is finite) and long-range orientational order of the bonds. Finally, the packing of the liquid layers corresponds to a smectic-A.

Traditionally, systems which result from both types of breaking of the $T(2)$ group are called smectic liquid crystals of type B (smectic-B), although the first type of B crystals are true anisotropic three-dimensional crystals. The existence of both types of B smectics may be considered to be firmly established.^{23,24}

The smectic-A-smectic-C transition has been studied quite well theoretically and experimentally (see, for example, Pikin's monograph³). For this reason, we shall limit ourselves only to a brief description of existing models, drawing attention to only some new (not reflected in Ref. 3) questions.

We first note that the A-C transition must be examined more systematically, taking into account the presence of a nematic phase. Two models have been proposed, which describe in a unified manner the N-, A-, and C-phases. Chu and McMillan's model²⁵ works with different order parameters for smectic modulation of the density and of the tilt angle. The form of the phase diagram is determined by the nature of the interaction of the order parameters. In the simplest case of a quadratic interaction, such that the tilt angle necessarily equals zero in the absence of a smectic order parameter, the phase diagram contains a triple point at which the N-A-C phases coexist. The N-C transition is a second-order phase transition. In this transition, all three Frank's moduli diverge: $\delta K_i \sim \xi$ (ξ is the correlation length, while in de Gennes' simplified model,² which examines this transition as an isolated transition, $\delta K_i \sim \xi^{2/3}$).

Another type of model was proposed by Chen and Lubensky.²⁶ In this case, a single order parameter describing the modulation of the density is used. However, for the N-A transition, the free energy minimum corresponds to a density modulation with wave vector $\pm q_0 \mathbf{n}$ (\mathbf{n} is the director, $q_0 = 2\pi/l$, l is the distance between the smectic layers), and additional modulation in a direction perpendicular to the director appears for the C phase. This additional modulation is mathematically related with the change in the sign of the coefficient in front of ∇_{\perp}^2 (the index \perp indicates directions orthogonal to the director). For this reason, the point of coexistence of all three phases is a Lifshitz critical point, since this coefficient vanishes at this point. All three Frank moduli diverge on the line of the N-C transition $\delta K_i \sim \xi^2$, and at the Lifshitz point $\delta K_{1,2} \sim \ln \xi$, $\delta K_3 \sim \xi$.

Recent experimental data²⁷ on the topology of the phase diagram in the neighborhood of a N-A-C point and on the critical indices do not agree with any of the models described above. In any case, for the substances investigated in Ref. 27 it may be viewed as firmly established that the triple N-A-C point is not a Lifshitz point.

It is possible that in order to give an adequate description of the situation, it is necessary to use a tensor order parameter of the following form²⁸:

$$P_{ij} = \rho_0 (1 + \psi) (\alpha_0 \delta_{ij} + \alpha_a Q_{ij}); \quad (16)$$

where ρ_0 is the average molecular density, ψ is the smectic modulation of the density, α_0 and α_a are the isotropic and anisotropic parts of the polarizability, and Q_{ij} is a symmetrical tensor with zero trace. It is very important that the tensor Q_{ij} can be biaxial even for cylindrical molecules, if the normal to the smectic layers is not parallel to the director. This is the degree of biaxiality η and describes the transition into the C phase, while the amplitude of the density modulation ψ_0 is the order parameter of the A phase. The expansion of the free energy, taking into account this circumstance and the form of the tensor (16), has the following form:

$$F = A\psi_0^2 + \frac{1}{2} B\psi_0^4 + \frac{1}{3} D\psi_0^6 + a\eta^2 + \frac{1}{2} b\eta^4 - c\eta^2\psi_0^2, \quad (17)$$

where $A = A_0(T - T^*)$, $A_0, B, D, a, b, c > 0$. Expansion (17), in accordance with the experimental data,¹⁷ gives a tricritical point on the A-C line near the N-A-C point and correctly describes the phase diagram found experimentally.

It is also impossible to exclude the possibility that different types of N-A-C phases, described by the different models discussed above, exist. Another characteristic of A and C phases, which was pointed out by Anisimov,²⁹ should also be taken into account in the interpretation of experimental data. The point is that the N-A and A-C transitions are very weak in the sense that the order parameter in them is small. Indeed, the amplitude of modulation of the density in the A phase is small compared to the average density. Analogously, the tilt angle of molecules in the C phase is also small. This weakness of the transition most likely indicates the smallness of the coefficient in front of the square of the order parameter in Landau's expansion. For this reason, for weak transitions the singularities of thermodynamic quantities such as the heat capacity should be weakly manifested, and often they are not observed at all.

We shall now consider B smectics. As already noted above, the existence of at least two types of B smectics has been clearly established: real three-dimensional crystals and systems formed by a stack of hexatic liquid crystals.

Smectic-B liquid crystals of the first type are distinguished from "ordinary" molecular crystals by the presence of a strong anisotropy of elastic moduli with and between layers. If the elastic energy of this type of smectic-B is written in the usual manner, then we obtain, for example for hexagonal symmetry

$$H_{el} = \frac{1}{2} \int [(\lambda + \mu) \left(\frac{\partial u_\alpha}{\partial x_\alpha} \right)^2 + \mu \left(\frac{\partial u_\alpha}{\partial x_\beta} \right)^2 + \nu \left(\frac{\partial v}{\partial z} \right)^2 + \gamma \left(\frac{\partial v}{\partial x_\alpha} \right)^2 + \gamma \left(\frac{\partial u_\alpha}{\partial z} \right)^2 + \varepsilon \frac{\partial u_\alpha}{\partial x_\alpha} \frac{\partial v}{\partial z}] d^3r,$$

where u_α is the displacement vector within a layer, x_α is the coordinate within a layer, and v is the displacement and z is the coordinate perpendicular to a layer. The elastic moduli γ and ε are small compared with the remaining moduli λ, μ , and ν .

The anisotropy of the elastic moduli leads to the very unique character of the diffraction of x-rays by films consisting of this type of smectic-B liquid crystals³⁰: for sufficiently

thin films with N layers, roughly speaking less than the anisotropy of the elastic moduli, the scattering has a "two-dimensional" character. In particular, the Debye-Waller factor drops off in a power-law fashion. For a larger number of layers the scattering is "three-dimensional." We note the reasons for this behavior without presenting the detailed calculations. The point is that for films of finite thickness, the integrals over the wave vector entering into the expression for the structure factor are replaced by a sum over the wave numbers corresponding to the finite size:

$$\kappa d = \pm \frac{2\pi n}{N}$$

($n = 1, 2, \dots, [N/2]$ and d is the thickness of the film). Separation of the two-dimensional contribution to the structure factor corresponds to the possibility of the existence of synchronous oscillations of all layers (i.e., $n = 0$).

The situation with the second type of smectic-B is more confused. As already mentioned above, according to current concepts, such mesophases are formed by a system of layers, each of which is a hexatic liquid crystal (i.e., translational order is absent, but there is an orientational order of the bonds between particles). Usually, one is dealing with hexagonal orientational order, this is the origin of the term hexatic. Disappearance of hexatic order in layers, i.e., a transition to liquid layers, corresponds to a phase transition in a smectic-A liquid crystal. When the tilting of molecules relative to the layer is included, a smectic-C liquid crystal also appears in the phase diagram.

It is convenient to introduce the following parameters, which characterize the symmetry breaking leading to the second type of B and C smectics³¹:

$$P_g = P_0 e^{6i\theta_0}, \quad \phi_t = \phi_0 e^{i\varphi_0}; \quad (18)$$

where P_g fixes the orientational (hexagonal) order of the bonds and φ_t fixes the tilting of the molecules.

In terms of these order parameters, $P_g = 0$ and $\varphi_t = 0$ in a smectic-A and $P_g \neq 0$ and $\varphi_t = 0$ in a smectic-B of the second kind. In the simplest model proposed by Bruinsma and Nelson,³¹ the hexatic-liquid-crystal-isotropic-liquid phase transition is described by a classical X - Y model:

$$H_g = J_g \sum_{i,j} \cos[\delta(\theta_i - \theta_j)], \quad (19)$$

where the modulus of the angle θ_i is $\pi/3$, and the summation extends over the nearest neighbors. The angle θ_i is the angle between the bond connecting the nearest neighbors and some fixed axis. Analogously, the transition between smectic-A and -C liquid crystals is likewise described by the X - Y model:

$$H_t = J_t \sum_{i,j} \cos(\phi_i - \phi_j). \quad (20)$$

The principal assumption of the model³¹ is related with the form of the interaction:

$$H_{int} = -h \sum_i \cos(6\theta_i - 6\phi_i). \quad (21)$$

In the mean-field approximation, the solution found in Ref. 31 gives the phase diagram illustrated in Fig. 7.

It is important to note that although formally the "usual" smectic-C phase (i.e., $P_g = 0$, $\varphi_t \neq 0$) does not occur in this model, hexatic order rapidly decreases with distance to

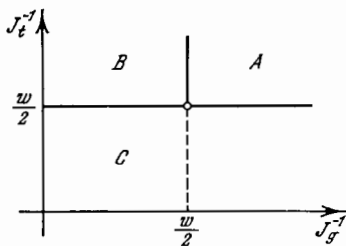


FIG. 7. State diagram with smectic-A, -B, and -C liquid crystals.

the right of the dashed line and is actually extremely small in the entire region $J_g^{-1} > w/2$. It is still not known where real C smectics fall with respect to P_g . It is for this reason that in Fig. 7 we designated as C the entire region $J_t^{-1} < w/2$.

The second type of B smectics can be identified experimentally by the hexagonal modulation of the structure factor or by the unusual features of melting, i.e., transition into the A phase. These unusual features are related with the fact that with a B-A transition it is the hexagonal order within a layer, and not the three-dimensional translational order, that melts. The results obtained by Calder *et al.*³² and by Stishov *et al.*³³ are an indication of this unusual melting of B smectics.

It is also important to note that the identification of B smectics of the second kind by the hexagonal modulation of the structure factor requires perfect liquid-crystal specimens. The problem is that diffuse scattering by different types of defects can imitate modulation of scattering with angular scanning. As is well known, the structure factor of diffuse scattering by defects does not become infinite at nodes of the reciprocal lattice; it usually has the bell shape as a function of the momentum, and it is in general anisotropic, which is what makes this contribution similar to the structure factor of hexatic liquid crystals.

3. SYSTEMS OF DISKOTIC MOLECULES

a) Phase diagram

Liquid crystals, formed by diskotic molecules, the so-called diskotics recently discovered by Chandrasekhar *et al.*,³⁴ are increasingly attracting the attention of researchers. This is due, on the one hand, to the potential importance of such systems in applications and, on the other, to the very interesting physics of the mesophases themselves. A unique situation, predicted by Landau and Peierls (see Ref. 14), occurs in diskotics. In one dimension the system has the properties of a liquid, and in the other two it is a solid. Of course, the analogy to a liquid should not be understood literally as the possibility of free one-dimensional flow. For example, in attempts to realize Poiseuille flow in a capillary, due to the ordering effect of the surface, a boundary layer arises with a rigid two-dimensional lattice, preventing flow and leading to anomalously high viscosities. This is completely analogous to the well-known permeation phenomenon in smectics.² The fact that the system is a one-dimensional liquid indicates only the absence of correlations in the arrangement of the centers of mass of the molecules along a straight line. From the point of view of the hydrodynamic manifestations of

such a liquid, the crystal is similar (although, of course, not identical (see Refs. 35-37)) to an anisotropic solid.

On the other hand, for purposes of structural classification as well as for investigations of phase transformations in such liquid crystals, the absence or presence of correlations in the arrangement and orientation of diskotic particles is very important.

Let us examine the condensed system formed by diskotic molecules. At sufficiently high temperatures the centers of mass of the molecules as well as their orientation under the action of thermal motion vary chaotically in time and space. This state is reminiscent of an ordinary isotropic liquid, which has full translational and rotational symmetry:

$$T(3) \times O(3).$$

As the temperature decreases, the thermal motion slows down and full symmetry is partially destroyed. Due to the anisotropic diskotic shape of the molecules, a situation can arise in which the translational symmetry is conserved while the rotational group is broken going over into one of the uniaxial groups, for example $D_{\infty h}$. Figuratively, we can say that as the temperature decreases, diskotic molecules slip freely relative to one another, but can no longer rotate freely.

Such a phase, having the symmetry, for example,

$$D_{\infty h} \times T(3),$$

is the analog of the ordinary nematic phase. It is distinguished from nematic liquid crystals (nematics) formed by rod-shaped molecules only by other indications of the anisotropy of the dielectric permittivity and other tensor characteristics. However, although the global symmetry of nematic phases consisting of diskotic and rod-shaped molecules is identical, their local symmetry relative to hydrodynamic transformation $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{u}$ is different. The point is³⁸ that in ordinary nematics the role of the director is played by the average orientation of the long axes of molecules, i.e., a contravariant vector, while in nematics consisting of diskotic molecules the director is the normal to the plane of the predominant orientation of molecules, i.e., a covariant vector.

As the temperature decreases still further, translational symmetry is also broken. Diskotic molecules are usually constructed in such a way that they contain a rigid central core and flexible hydrocarbon chains, lying primarily in a plane determined by the rigid core. This structure of the molecules leads to the possibility of a partial breakdown of translational invariance: the interaction of molecular tails in the plane of the disks is much stronger than between different disks. Such an interaction can therefore, in principle, lead to the formation of one of the two-dimensional crystal lattices, while one-dimensional translational invariance is conserved in the orthogonal direction. We shall call such a phase a strictly diskotic phase. Its symmetry group is represented in the form

$$T(1) \times L \times \hat{R}, \quad (22)$$

where L is the symmetry group of one of the admissible two-dimensional lattices, and \hat{R} is a subgroup of the $O(3)$ group: the symmetry group of the director \mathbf{n} . The group \hat{R} includes

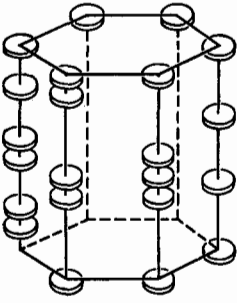


FIG. 8. Structure of a diskotic liquid crystal.

transformations belonging to the group $Z_2 \cdot \mathbf{n} \rightarrow -\mathbf{n}$, relative to which the physical characteristics of diskotic and nematic phases are invariant. For example, if we have a hexagonal lattice, then \hat{R} forms the group D_{6h} (in contrast to the nematic phase, for which the corresponding group is $D_{\infty h}$).

We can say pictorially that a diskotic liquid crystal has a two-dimensional lattice consisting of liquid columns (while A smectics, for example, have a one-dimensional lattice consisting of liquid layers).

The above discussion concerned the orthogonal diskotic phase, when the director \mathbf{n} , oriented along the liquid columns, is simultaneously perpendicular to the planes of the two-dimensional lattice. In the case of tilted structures, when the director forms some fixed angle θ with the normal, the symmetry of the system is lowered. For tilted diskotic phases

$$\hat{R} = C_{2h}.$$

We introduce the following notation for phases arising in systems of diskotic molecules: Cr refers to the crystalline phase, D_t to the tilted diskotic phase; D_0 to the orthogonal diskotic phase; N_D to the nematic phase; and I to the isotropic phase.

If pretransitional fluctuations are neglected, then Cr is an ordinary molecular crystal and I is an ordinary isotropic liquid. As noted, N_D is a nematic liquid crystal, differing from the usual nematic crystal by the signs of the anisotropy coefficients. In particular, in the N_D phase we have the usual Frank expansion of the elastic energy, related with the deformations of the director field. However, in the ordinary nematics the Frank moduli are $K_1 \approx K_3 > K_2$. In the N_D phase the relations $K_1 \approx K_2 > K_3$ are expected since only a longitudinal bending deformation $\sim (1/2)K_3[\mathbf{n} \text{ curl } \mathbf{n}]^2$ is permissible in D_0 and D_t phases.

The energy of distortion of the D_0 phase is given by the elastic deformation of a two-dimensional lattice and, in addition, the longitudinal bending deformation of the director field $(1/2)K_3[\mathbf{n} \text{ curl } \mathbf{n}]^2$ (the remaining deformations $(1/2)K_1(\text{div } \mathbf{n})^2$ and $(1/2)K_2[\mathbf{n} \text{ curl } \mathbf{n}]^2$ are "forbidden" by the rigid two-dimensional lattice of liquid columns).

In the D_t phase, intermolecular forces determine only the polar angle of inclination of the liquid columns (or of the director) relative to the plane of the lattice. However, this does not lead to corrections to the elastic energy of the D_t phase. The point is that the presence of a lattice of liquid columns, just as in the D_0 phase, forbids twisting ($\sim K_2$) and

transverse bending ($\sim K_1$) deformations, related with the "free" components δn_x and δn_y . The component δn_z , on the other hand, is determined by the tilt angle. This is what distinguishes the situation in the D_t phase from the case of C smectics, where all three contributions to the Frank energy are present from the components δn_z and δn_y , which do not determine the tilt angle.

b) Phase transitions

It is convenient to combine the phases occurring in a system of diskotic molecules into groups, which can be examined together using a single order parameter. The Cr, D_t , and D_0 phases form the first group. The D_t and D_0 phases differ from the molecular crystal Cr primarily by translational invariance $T(1)$ along the liquid columns. In the Cr phase crystalline order arises in this direction, in connection with which the density becomes a periodic function:

$$\delta \rho_1 = \frac{1}{2} \left(\sum_{\mathbf{x}} \psi_{\mathbf{x}} e^{i\mathbf{x}r} + \text{c.c.} \right), \quad (23)$$

where $\psi_{\mathbf{x}}$ is the complex amplitude of modulation of the density, while \mathbf{x} is a vector in the reciprocal lattice oriented in a direction perpendicular to the plane of the lattice (z axis). The amplitude is a slowly varying function of the coordinates: $|\nabla \psi| \ll |\psi|$. It is natural to choose the quantity $\delta \rho_1$ as the order parameter for the group of phases being studied.

The D_0 , D_t , and N_D phases form the other group. In contrast to the N_D phases, the D_0 and D_t phases have a two-dimensional lattice of liquid columns. For this reason, the density is a two-dimensional periodic function:

$$\delta \rho_2 = \frac{1}{2} \left(\sum_{\mathbf{p}} \chi_{\mathbf{p}} e^{i\mathbf{p}r} + \text{c.c.} \right). \quad (24)$$

Here the vectors \mathbf{p} lie in the plane of the two-dimensional lattice (for the D_0 phase, $\mathbf{p} \cdot \mathbf{n} = 0$ and for the D_t phase, $\mathbf{p} \cdot \mathbf{n} \neq 0$). The quantity $\delta \rho_2$ plays the role of the order parameter.

The group formed by the Cr, D_0 , and D_t phases is easiest to examine. On crystallization, the tilt of the liquid columns relative to the lattice does not change at all in the first approximation. In addition, the transition is related with the fundamental period κ , while the larger reciprocal lattice vectors 2κ , 3κ , etc., can be viewed as a perturbation. Terms proportional to $\psi_{2\kappa}^2$, $\psi_{2\kappa}^4$ as well as an interaction of the type $\psi_{2\kappa}^2 \psi_{\kappa}^* \psi_{\kappa}$ arise in the free energy. After $\psi_{2\kappa}$ is eliminated, the coefficient in front of ψ_{κ}^4 is effectively decreased. If the sign of this coefficient changes, then a first-order phase transition will occur. In the opposite case, the interaction of the amplitudes of the density with different vectors of the reciprocal lattice can be neglected (taking it into account simply as a renormalization of the coefficients in Landau's expansion). In this case, we have the following expansion of the free energy in powers of $\delta \rho_1$ or, which is the same thing, ψ_{κ} :

$$F = F_0 + \frac{1}{2} a |\psi_{\kappa}|^2 + \frac{1}{4} c |\psi_{\kappa}|^4 + \gamma_{\parallel} \left| \frac{\partial \psi_{\kappa}}{\partial z} \right|^2 + \gamma_{\perp} |(\nabla_{\perp} - i\kappa \delta \mathbf{n}) \psi_{\kappa}|^2 + F_{e1}; \quad (25)$$

where F_0 is the elastic energy of the D_0 or D_t phase; a , c , γ_{\parallel} ,

and γ_1 are the coefficients in Landau's expansion; and F_{el} is the Frank energy related with the admissible deformations of the director in the D_0 and D_t phases. The gradient terms in (25) originate from the two possible quadratic invariants:

$$|(\mathbf{n}\nabla)\rho_1|^2, \quad |[\mathbf{n}\nabla]\rho_1|^2.$$

We shall examine the phase D_t making the assumption that the tilting of the columns is small $\theta \ll 1$. In this case, the entire effect of tilting reduces to an angle-dependent renormalization of the coefficient

$$a = a_0 + \gamma_{\parallel}(1 - \theta^2)\kappa^2 + \gamma_{\perp}\theta^2\kappa^2, \quad (26)$$

where $a_0 = \alpha_0(T - T^*)$ is the start-up expansion coefficient and, as usual, $a = \alpha(T - T_c)$, where T_c is the transition temperature.

Expansion (25) is formally analogous to the free energy functional for the nematic-smectic phase transition or the Ginzberg-Landau functional for the superconductor-normal metal transition. Just as in these cases, the transition is described by a two-component order parameter (complex amplitude ψ_x). For this reason, the free energy does not contain terms that are cubic in the order parameter, and from the point of view of Landau's theory, such a transition could be a second-order transition. (This is determined by the ratio between the coefficients in the expansion in front of ψ_x and ψ_{2x} .) Striction effects, i.e., interaction with the gauge field $\delta\mathbf{n}$, do not change this result. As first noted by Pikin,³ exclusion of fluctuations $\delta\mathbf{n}$ from (25) leads to a term $\sim \psi_x^2$ (and not ψ_x^3 , as for A smectics and superconductors) and, for this reason, does not change the character of the transition. Actually, the $Cr-D_0$ or $Cr-D_t$ transitions are first-order phase transitions. However, although the corresponding jumps are not very small, they are still an order of magnitude smaller^{34,39} than with complete melting of ordinary molecular crystals. The reasons for this are not completely understood. The effect of fluctuations in this case cannot be too large. The point is that the degeneracy along the directions of the vector κ is absent for the D_0 and D_t phases since a two-dimensional lattice is already present (in contrast to the case of a transition from the isotropic phase, where only the modulus of the vector κ is fixed and its orientation can be arbitrary, which is what leads to the large phase volume for fluctuations, which in their turn can change the character of the transition). The first type of phase transition is apparently related with the interaction of the order parameter ψ_x and noncritical modulations of the density ψ_{2x} , etc.

The angle θ is an independent order parameter. A separate Landau expansion of the free energy must be written for it. Minimization determines the temperature dependence of θ and, for example, the dependence of θ on the concentration or pressure P . The temperature of the D_0-Cr or D_t-Cr transitions, on the other hand, is determined from (16) with the condition $\theta = 0$ or $\theta \neq 0$, respectively. In this case, depending on the ratios between the coefficients in Landau's expansion, diverse types of phase diagrams are possible. As an illustration, Fig. 9 shows the simplest example of D_0 , D_t , and Cr phase diagrams.

We shall now proceed to the group of phases N_D , D_0 , D_t . We shall examine a hexagonal lattice and, just as above,

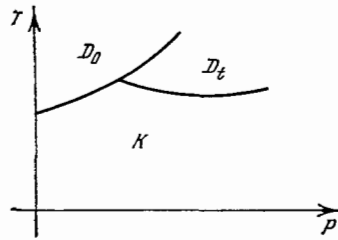


FIG. 9. Schematic illustration of the possible form of a D_0 - D_t - Cr phase diagram.

we shall retain only the amplitudes of the fundamental period p_0 . Then, instead of (24), we have

$$\delta\rho_2 = \frac{1}{2}(\chi_{p_1}e^{ip_1r} + \chi_{p_2}e^{ip_2r} + \chi_{p_3}e^{ip_3r} + \text{c.c.}),$$

where

$$p_1 + p_2 + p_3 = 0, \quad p_1^2 = p_2^2 = p_3^2 = p_0^2,$$

$$p_1p_2 = p_1p_3 = p_2p_3 = -\frac{1}{2}p_0^2.$$

With a N_D-D_0 or N_D-D_t transition, in the N_D phase the fluctuation lattice of liquid columns can be oriented arbitrarily in a plane perpendicular to \mathbf{n} . The corresponding degeneracy indicates the arbitrariness of the angle β , formed, for example, by the vector \mathbf{p}_1 and one of the axes of the coordinate system.

We shall include the degeneracy explicitly:

$$\delta\rho_2 = \frac{1}{2} \left[\int_0^{\pi/3} \chi_{p_1}(\beta) \exp(ip_1(\beta)r) \frac{d\beta}{\pi} + \int_0^{\pi/3} \chi_{p_2}(\beta) \exp(ip_2(\beta)r) \frac{d\beta}{\pi} + \int_0^{\pi/3} \chi_{p_3}(\beta) \exp(ip_3(\beta)r) \frac{d\beta}{\pi} + \text{c.c.} \right]. \quad (27)$$

The Landau expansion of the free energy in powers of $\delta\rho_2$ or χ_{p_i} can be easily written down with the help of symmetry considerations. In this case, we have an invariant of third order

$$I_3 = \int_0^{\pi/3} \chi_{p_1}(\beta) \chi_{p_2}(\beta) \chi_{p_3}(\beta) \frac{d\beta}{\pi} \quad (28)$$

and two independent fourth-order invariants

$$I'_4 = I_2^2 = \left[\sum_{i=1}^3 \int_0^{\pi/3} |\chi_{p_i}(\beta)|^2 \frac{d\beta}{\pi} \right]^2, \quad (29)$$

$$I_4 = \sum_{i=1}^3 \int_0^{\pi/3} |\chi_{p_i}(\beta)|^4 \frac{d\beta}{\pi}.$$

The gradient terms must include two types of symmetry: gauge symmetry, related with simultaneous rotation of the director and the plane of the lattice, and an invariance originating from the degeneracy with respect to the angle β . We thus obtain

$$I_{\parallel} = \sum_{i=1}^3 \int_0^{\pi/3} \frac{d\beta}{\pi} \left| \left(\frac{\partial}{\partial z} + i \mathbf{p}_i(\beta) \delta \mathbf{n} + i (\mathbf{n} \Omega) (\mathbf{n} \times \mathbf{p}_i)_z \right) \chi_{p_i}(\beta) \right|^2, \quad (30)$$

$$I_{\perp} = \sum_{i=1}^3 \int_0^{\pi/3} \frac{d\beta}{\pi} \left| [\nabla_{\perp} - i (\Omega \mathbf{n}) (\mathbf{n} \times \mathbf{p}_i(\beta)) + i \delta \mathbf{n}_{\perp} (\mathbf{n} \mathbf{p}_i)] \chi_{p_i}(\beta) \right|^2,$$

where the parameter Ω reflects the rotational freedom of clusters in the lattice of liquid columns relative to the director in the N_D phase, while the term $\mathbf{p}_i(\beta) \delta \mathbf{n}$ is related with the gauge invariance. We shall present the derivation of Eq. (30). The invariant gradient terms for the symmetry of the N_D phase $D_{\infty h} \times T(3)$ evidently have the following form⁴⁰:

$$I'_{\parallel} = \sum_{i=1}^3 \int_0^{\pi/3} \left| \frac{\partial}{\partial z} \chi_{p_i}(\beta) \right|^2 \frac{d\beta}{\pi},$$

$$I'_{\perp} = \sum_{i=1}^3 \int_0^{\pi/3} |\nabla_{\perp} \chi_{p_i}(\beta)|^2 \frac{d\beta}{\pi}.$$

The z axis is determined by the equilibrium value of the director \mathbf{n}_0 . However, we also have local invariance, mentioned above. For example, when all vectors \mathbf{p}_i are rotated by some angle Ω , the displacements $\mathbf{u}(\mathbf{r})$ transform according to the law $\mathbf{u} = [\Omega \mathbf{r}]$. In the ordered phase (for $T < T_c$), the displacements $\mathbf{u}(\mathbf{r})$ are related with the phase of the order parameter:

$$\varphi_i = -\mathbf{p}_i [\Omega \mathbf{r}] = \mathbf{r} [\Omega \mathbf{p}_i].$$

Therefore,

$$\nabla \varphi_i = [\Omega \mathbf{p}_i],$$

from where we obtain

$$\nabla \chi_{p_i} = i [\Omega \mathbf{p}_i] \chi_{p_i}.$$

Here, the rotation of the director changes by

$$\delta \mathbf{n} = -[\mathbf{n}_0 \Omega].$$

From here we can write the expansion

$$\Omega = (\Omega \mathbf{n}_0) \mathbf{n}_0 + [\mathbf{n}_0 \delta \mathbf{n}].$$

Analogously,

$$\Omega \times \mathbf{p}_i = (\Omega \mathbf{n}_0) [\mathbf{n}_0 \mathbf{p}_i] - (\mathbf{p}_i \delta \mathbf{n}) \mathbf{n}_0,$$

i.e.,

$$\frac{\partial}{\partial z} \chi_{p_i} = -i (\mathbf{p}_i \delta \mathbf{n}) \chi_{p_i} + i (\mathbf{n}_0 \Omega) [\mathbf{n}_0 \mathbf{p}_i],$$

$$\nabla_{\perp} \chi_{p_i} = i (\Omega \mathbf{n}_0) [\mathbf{n}_0 \mathbf{p}_i] \chi_{p_i} + i \delta \mathbf{n}_{\perp} (\mathbf{n} \mathbf{p}_i).$$

Expressions (30) follow from here.

The lattice is already fixed below the transition point T_c . In this case we must set $(\mathbf{n} \Omega) = 0$ in Eqs. (27)–(30) and, in addition, we have

$$\chi_{p_i}(\beta) \sim \delta(\beta - \beta_0).$$

In order to describe the complete phase diagram of N_D – D_0 – D_t systems, it is also necessary to include an expansion with respect to the tilt angle. The simplest assumption is that the

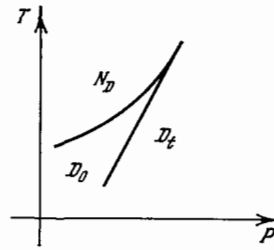


FIG. 10. N_D – D_0 – D_t phase diagram.

tilt angle θ is independent of the order parameter. The phase diagram of the system changes depending on the powers of θ and χ_{p_i} included in the Landau expansion. The situation where the interaction of the order parameters is $\sim \chi_{p_i}^2$ is illustrated in Fig. 10.

The other possibility does not require the introductions of an additional order parameter. If, while varying the pressure (or some other external parameter), the sign of the coefficient in front of I_{\parallel} from (30) changes, then configurations with $\mathbf{n} \mathbf{p} \neq 0$ will correspond to a minimum of the energy. In this case, higher-order gradient terms of the type

$$[(\mathbf{n} \nabla)^2 \delta \rho_2]^2 \text{ and } [(\mathbf{n} \times \nabla)^2 \delta \rho_2]^2$$

must, of course, also be included. The point of coexistence of N_D , D_0 , and D_t phases, in which the coefficient in front of I_{\parallel} vanishes, will be a Lifshitz critical point. The corresponding phase diagram is schematically illustrated in Fig. 11.

Finally, the N_D – I phase transition is analogous to the transition from an ordinary nematic liquid crystal into an isotropic liquid.

If the transitions examined above are close to second-order phase transitions, then they are accompanied by fluctuation phenomena, which can be observed, for example, in the scattering of light. The critical growth of the elastic moduli is a more specific result for liquid crystals with orientational degrees of freedom. Thus, with a D – Cr phase transition, the only Frank modulus admissible in the diskotic phase K_3 increases:

$$K_3 \sim \xi_{\perp},$$

where ξ_{\perp} is the correlation length in a direction perpendicular to the lattice for the D – Cr transition. The situation is less trivial for a N_D – D phase transition. The formation of clusters of the diskotic phase in the nematic phase, which do not transfer the torsional and transverse bending deformations, leads to an effective critical growth of the corresponding Frank moduli K_1 and K_2 . The real dependence of K_1 and K_2

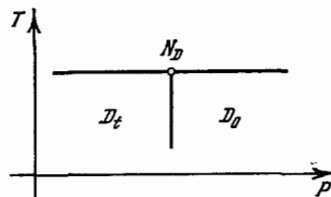


FIG. 11. N_D – D_0 – D_t phase diagram with a Lifshitz critical point.

on the correlation lengths (or, which is the same thing, on the proximity to the transition point) is determined by the model of the transition used. If the degeneracy in a plane perpendicular to the director is unimportant due to the interaction with tensor fluctuations of the orientational order parameter,^{36,40} then the growth of K_1 and K_2 is proportional to the correlation length:

$$K_1 \sim K_2 \sim \xi_{\parallel}.$$

In the opposite limiting case, when orientational fluctuations are insignificant, the rotational degeneracy of the two-dimensional lattice must be included.⁴¹ The corresponding part of the Hamiltonian now depends only on the modulus of the wave vector in the plane of the lattice $\sim (q_{\perp}^2 - p_0^2)^2$. Such an increase of the phase volume of fluctuations leads to stronger dependences

$$K_1 \sim K_2 \sim \xi_{\parallel} \xi_{\perp}.$$

Analogous results can also be obtained for the fluctuation growth of the coefficients of viscosity.⁴¹

We note finally that in the terminology used in Sec. 1, a diskotic is a Lifshitz point with $m = 1$ and $n = 2$. However, in this case, dangerous anharmonicities do not exist in three-dimensional space. Nevertheless, near a transition into the nematic phase, the situation is close to a Lifshitz point with $m = 3$ and $n = 2$. Near this point, the indices of the correlation function change (see Ref. 20 for a more detailed discussion).

c) Dimensionality effects⁴²

As is well known, the most important parameter of condensed systems is the static structure factor $S(\mathbf{q})$. The dependence $S(\mathbf{q})$ determines the integral scattering characteristics of, for example, neutron or x-ray scattering. In ordinary three-dimensional crystals, $S(\mathbf{q})$ represents a collection of Bragg peaks, whose position is determined by the reciprocal lattice vectors, and a diffuse background. This separation of the scattered radiation into regular reflections and a diffuse background is strictly speaking possible only in infinite crystals. In this case, the terms proportional to δ functions in expressions for the scattering intensity describe regular reflections and terms that do not contain a δ -function factor describe the smooth distribution of diffuse scattering. Thermal vibrations in three-dimensional systems attenuate the intensity of regular reflections due to the Debye-Waller factor, but they do not give rise to line broadening. In crystals with finite sizes $\sim R$, the δ -functions are replaced by some peaks with finite width $\sim R^{-1}$ and, in this case, are indistinguishable from a diffuse background. Actually, however, the characteristic widths of the diffuse background for wave vectors near Bragg peaks greatly exceed the width of δ -function peaks, related with the dimensions of the specimen. Indeed, in an isotropic three-dimensional system, the characteristic nonuniformity of the diffuse background is of the order of $E/\tau^2 T$ (where E is the elastic modulus, τ is the reciprocal lattice constant, and T is the temperature). For typical values of the parameters ($E \sim 10^{11}$ erg/cm³, $\tau \sim 10^8$ cm⁻¹, $T \sim 10^{-14}$ erg), this quantity $\sim 10^9$ cm⁻¹, which

greatly exceeds the R^{-1} width of Bragg peaks for all admissible sizes of specimens.

A different situation occurs in systems with partial translational ordering, whose great diversity gives us different types of liquid crystals. For example, if we are concerned with one-dimensional translational order (smectic liquid crystal), then in an infinite specimen δ -function Bragg peaks are completely absent because the Debye-Waller factor diverges. However, near reciprocal lattice sites the structure factor is singular, which reflects the slow (power-law) falling-off of correlations in such systems. For a finite system with smectic order, the anomalous part of the diffuse background dominates the quasi-Bragg scattering as well (since the Debye-Waller factor does not diverge in finite-dimensional systems). And, depending on the parameters of the system, a finite specimen of a smectic liquid crystal behaves, in the sense of x-ray and neutron scattering, either analogously to an ordinary crystal (i.e., it has relatively narrow Bragg peaks) or analogously to an infinite smectic (i.e., the singular diffuse background dominates).

The principal method for determining the structure of diskotics is x-ray scattering. In addition, it is most convenient to use a geometry in which scattering occurs in the plane of the two-dimensional lattice of the diskotic phase. In this case, the most important question from the experimental point of view is the method for distinguishing Bragg peaks of the two-dimensional lattice formed by liquid columns of the diskotic phase from the corresponding Bragg peaks of the ordinary three-dimensional crystalline structure. By definition of the structure factor S , we have

$$S(\mathbf{q}, \kappa) = \left| \sum_{\mathbf{a}} \exp(i\mathbf{q}\mathbf{a}) \right|^2 \langle e^{i\mathbf{q}\mathbf{u} + i\kappa v} \rangle + \sum_{\mathbf{a}, \mathbf{a}'} e^{i\mathbf{q}(\mathbf{a}-\mathbf{a}')} \langle \exp[ii\mathbf{q}(\mathbf{u}_{\mathbf{a}} - \mathbf{u}_{\mathbf{a}'} + i\kappa(v - v'))] \rangle$$

(\mathbf{a} is a vector in the two-dimensional lattice of liquid columns). The first term corresponds to coherent Bragg scattering and the second describes the diffuse background (non-coherent scattering). We begin with the coherent scattering

$$S_c(\mathbf{q}, \kappa) = \left| \sum_{\mathbf{a}} e^{i\mathbf{q}\mathbf{a}} \right|^2 \langle e^{i\mathbf{q}\mathbf{u} + i\kappa v} \rangle.$$

The first sum in an infinite crystal gives, in the usual manner, δ -function Bragg peaks, and the second factor is the Debye-Waller factor:

$$\left| \sum_{\mathbf{a}} \exp(i\mathbf{q}\mathbf{a}) \right|^2 = N \frac{(2\pi)^2}{v_0} \sum_{\boldsymbol{\tau}} \delta(\mathbf{q} - \boldsymbol{\tau}),$$

$$\langle e^{i\mathbf{q}\mathbf{u} + i\kappa v} \rangle = e^{-2W};$$

where v_0 is the area of an elementary cell in the two-dimensional lattice; N is the number of cells; and, $\boldsymbol{\tau}$ is a reciprocal lattice vector. In a finite crystal, the δ -functions are replaced by some (depending on the shape of the specimen) δ -like functions with width R^{-1} .

Less trivial dimensionality effects can appear in the Debye-Waller factor. In the harmonic approximation we have

$$2W = \langle (i\mathbf{q}\mathbf{u} + \kappa v)^2 \rangle.$$

Substituting here the expression for the correlation functions, we obtain

$$2W = \frac{q^2}{(2\pi)^3} \int d^2p dt \left(\frac{T}{E p^2 + K_3 t^4} \right) + \frac{\kappa^2}{(2\pi)^3} \int d^2p dt \frac{T}{E t^2}. \quad (31)$$

Different types of dimensionality effects are, in principle, possible. In the simplest case, it may be assumed that the properties of the finite system are the same as those of an infinite system. In other words, we can examine an infinite system, but the scattering is realized in some small part of it. In this case, all dimensionality effects are related simply with restrictions on the range of integration. We shall examine a system with dimensions $L' \times L = \times L$ (L is the direction along the liquid columns).

The problem contains a characteristic parameter with the dimensions of length:

$$\Lambda = \sqrt{\frac{K_3}{E}}.$$

Far from a transition into the nematic phase, Λ is of the order of the molecular size d , but near the transition point $E \rightarrow 0$ and $\Lambda \rightarrow \infty$. The second term in (31), which occurs if $\kappa \neq 0$, describes scattering by liquid columns. The dimensionality dependences of the corresponding contribution to the Debye-Waller factor are trivial:

$$2W_f = \frac{\pi T \kappa^2}{E a^2} L \left(1 - \frac{a^2}{L'^2} \right)$$

(a is the period of the lattice of liquid columns).

We note, however, that the "liquid" contribution $2W_f$ is practically independent of the dimension L .

We shall now examine the case $\kappa = 0$. The scattering is determined by the lattice of liquid columns. Let $L' \rightarrow 0$ (actually, it is required that $\Lambda L' \gg L^2$). We then have

$$2W = \frac{T q^2}{(2\pi)^3 E L} \int \frac{d^2p}{p^2} + \frac{T q^2}{E (2\pi)^3} \int \frac{d^2p dt}{p^2 + \Lambda^2 t^4}.$$

The first term describes the contribution of a single lattice layer and the second describes the contribution of the three-dimensional system. We thus obtain

$$2W = \frac{T q^2}{2\pi E L} \ln \frac{L'}{d} + \frac{T q^2}{2\pi^2 E \sqrt{\Lambda a}} \left[\varphi \left(\frac{\sqrt{a\Lambda}}{d} \right) - \varphi \left(\frac{\sqrt{a\Lambda}}{L} \right) \right], \quad (32)$$

where

$$\varphi(x) = -4x \ln x + x \ln(1+x^4) + \frac{1}{2^{5/2}} \ln \frac{1+\sqrt{2}x+x^2}{1-\sqrt{2}x+x^2} + \frac{1}{2^{3/2}} \operatorname{arctg} \frac{\sqrt{2}x}{1-x^2}.$$

The asymptotic behavior of this function is given by

$$\begin{aligned} \varphi(x) &= -4x \ln x & \text{as } x \rightarrow 0, \\ \varphi(x) &= 2^{-3/2} \pi & \text{as } x \rightarrow \infty. \end{aligned}$$

To observe dimensionality effects in this case, the following inequality must be satisfied:

$$L \ll \frac{\pi (\Lambda a)^{1/2} \ln(L'/d)}{\varphi((\Lambda a)^{1/2}/d)} \equiv L_{c2}.$$

The separation of the Debye-Waller factor into two- and three-dimensional contributions has the following significance. In reality, we have a sum over integer-valued vectors $t = 2\pi n/L$. Equation (32) corresponds to singling out the

term $n = 0$ and replacing the remaining terms in the sum by an integral over t . Such a replacement is justified because in our system there is a mode with $T = 0$, in which the crystal-line layers move as a whole. Such a mode is admissible only at the free boundaries of the diskotic liquid crystal layer. On the other hand, since the dependences are quite weak (logarithmic), it is possible to single out accurately only the term with $n = 0$. As $L^2 \sim L' \Lambda \rightarrow \infty$, the two-dimensional contribution to the Debye-Waller factor approaches zero and a transition into the "three-dimensional" case thus occurs.

The other situation occurs when $L^2 \gg L' \Lambda$. Here, we must replace the sum by an integral over the transverse momenta:

$$2W = \frac{2\pi T q^2}{E L'^2} \sum_{m, n} \int \frac{dt}{\Lambda^2 t^4 + (m^2 + n^2) 4\pi^2 / L'^2}.$$

The terms $m = n = 0$, however, cannot be singled out. The point is that such a mode would correspond to synchronous bending of all liquid chains, and therefore, simply to bending of the entire specimen as a whole. A cylindrical specimen of a diskotic liquid crystal is in itself unstable relative to such bending; bending of the entire specimen as a whole is, however, forbidden by the boundary conditions (simply speaking, by the presence of rigid lateral walls of the vessel bounding the liquid crystal). A simple but cumbersome calculation gives

$$2W = \frac{T q^2 \sqrt{\pi}}{8E \sqrt{\Lambda a}} \left(1 - \sqrt{\frac{a}{L'}} \right).$$

We note that in the given geometry, dimensionality effects are much more significant in diskotic liquid crystals than in ordinary three-dimensional crystals because $\sqrt{a}/L' \gg a/L'$.

In three-dimensional crystals with chain-like anisotropy dimensionality effects also have a different character. The point is that we now can single out a one-dimensional mode related with synchronous compression of all chains. This mode includes displacement of ν atoms:

$$2W = \frac{T \kappa^2}{2\pi E L'^2} \int \frac{dt}{t^2} + \frac{T \kappa^2}{(2\pi)^3 E} \int \frac{dt d^2p}{t^2 + \delta p^2}.$$

Such a separation is justified analogously to the one presented above. The three-dimensional integral is proportional to $\sim (T \kappa^2)/(E a)$, and the one-dimensional integral to $(T \kappa^2 L)/(E L'^2)$. Dimensionality effects are appreciable for $L' < \sqrt{\Lambda a}$. A chain-type anisotropy only improves this inequality. Thus, in diskotic liquid crystals with a geometry $\Lambda L' < L^2$, the largest dimensionality effects occur when $\kappa = 0$ and $q \neq 0$, while in three-dimensional chain-like crystals, they are more strongly manifested when $\kappa \neq 0$ and $q = 0$.

Diffuse scattering can be examined in an analogous manner.

Comparing the expressions for the "two-" and "three-dimensional" contributions to diffuse scattering, we find that dimensionality effects are manifested in diffuse scattering when $L^2 < \Lambda L'$ with thicknesses L much less than some critical value L_{d2} :

$$L_{d2} = \frac{8 \sqrt{\Lambda r}}{\ln(z^2/\Lambda r)} \ln \frac{r}{L'}.$$

(r and z are the coordinates of the scattering region).

We shall not present the expressions for the structure factor of diffuse scattering because they are very cumbersome. We shall only describe the results qualitatively. If the dimensions of the scattering region satisfy the condition $\Lambda L' > L^2$, then we have two characteristic lengths L_{c2} and l_{d2} . The quantity L_{c2} is determined only by the structural parameters of the diskotic liquid crystal, temperature, elastic moduli, and dimensions. The parameter L_{d2} depends also on the region of scattering being examined, i.e., on the wave vectors p . It is easy to see that when the following inequalities are satisfied.

$$\sqrt{\frac{\Lambda}{p}} \gg d, \quad \frac{\Lambda x^2}{p} \gg 1$$

we always obtain

$$L_{d2} > L_{c2}.$$

We thus have in this case:

1) For $L < L_{c2} < L_{d2}$, diffuse and coherent scattering are determined by two-dimensional fluctuations. The structure factor has the form

$$S(p, 0) \sim \Lambda^{-x} \frac{1}{p^{2-x}} + \delta(p) L^{1(2-2x)},$$

where the index $x = Tq^2/4\pi E$.

2) In the region $L_{c2} < L < L_{d2}$, coherent scattering is now three-dimensional, while the diffuse scattering still has a singular two-dimensional character.

3) Finally, for $L > L_{d2}$, both types of scattering are determined by three-dimensional fluctuations.

In a geometry $\Lambda L' < L^2$, such a separation of scattering into one-dimensional (chain-like) and three-dimensional contributions is impossible for reasons already discussed above. The one-dimensional contribution to the structure factor occurs only for diffuse scattering and is related with displacements v of particles along the liquid columns. For $x \neq 0$, this contribution competes with the three-dimensional scattering by displacements of the two-dimensional lattice of these columns.

Let us summarize. The structure factor of diskotic systems has an entire series of singularities. We should first indicate that diffuse scattering plays a much more important role in diskotic liquid crystals than in three-dimensional systems. The point is that in diskotic liquid crystals the Debye-Waller factor is large and coherent scattering is correspondingly weakened. The ratio of the intensities of both types of scattering is larger in diskotic liquid crystals than in ordinary three-dimensional crystals by the following factor:

$$\frac{B^{3/4} K_3^{1/4} \varphi((\Lambda a)^{1/2}/d)}{E a^{1/2} \delta f(a\delta/d)} \sim 10^2,$$

where $f(x) = x \ln(1+x^2) + 2 \operatorname{arctg} x - 2x \ln x$, δ is the anisotropy parameter of the three-dimensional system, $B \sim 10^9$ erg/cm³ is the modulus of elasticity of the diskotic liquid crystal, and $E \sim 10^{11}$ erg/cm³ is Young's modulus of the three-dimensional crystal.

The second distinguishing feature of diskotic systems is manifested in the presence of strong dimensionality effects

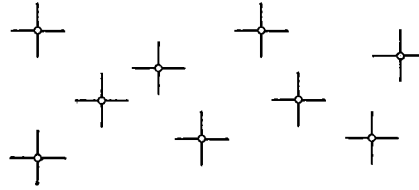


FIG. 12. Hypothetical structure of cubic liquid crystals (the centers of mass of the "molecules" are distributed randomly, but there is a cubic orientational symmetry).

for thicknesses for which there are no dimensionality effects in the corresponding three-dimensional system. Indeed, in an isotropic three-dimensional system dimensionality effects are manifested for sizes $R \sim a$. In an anisotropic system, dimensionality effects extend up to large sizes $L \sim d/\delta$ or $L' \sim a/\delta$. Dimensionality effects are even stronger in diskotic liquid crystals, and they extend up even larger thicknesses due to the factor $\ln L/\sqrt{a\Lambda}$ or $\ln \sqrt{L'\Lambda}/d$.

4. CUBIC LIQUID CRYSTALS

Up to now we have been examining liquid crystals corresponding primarily to uniaxial breaking of complete rotational symmetry $O(3)$. This is related primarily with the shape of the molecule and the symmetry of intramolecular interaction. Molecular shapes even more complicated than rod-shaped or diskotic are, in principle, possible. Patashinskiĭ and Mitus⁴³ and, independently, Nelson and Toner¹⁷ examined breaking of $O(3)$ symmetry corresponding to cubic symmetry. The molecules forming such a liquid crystal can be represented pictorially in the form of "jacks" with a number of arms (Fig. 12). At sufficiently high temperatures the jacks move freely and rotate relative to one another. We have the isotropic phase

$$O(3) \times T(3). \quad (32)$$

However, as the temperature decreases, a situation can in principle arise when these jacks, continuing to move freely, no longer can rotate relative to one another because such rotation is prohibited by the interaction of the long arms. In this case, $O(3)$ symmetry is broken, and in particular, cubic symmetry of such a liquid crystal is possible. For example,

$$O_h \times T(3).$$

It is convenient to describe these "jacks" by a distribution of bonds-arms, emanating from a given point r :

$$f(r, \Omega),$$

where Ω is the solid angle.

This function $f(r, \Omega)$ can be expanded in spherical harmonics

$$f(r, \Omega) = \sum_{l=0}^{\infty} \sum_{m=-l}^l Q_{lm}(r) Y_{lm}(\Omega), \quad (33)$$

where $Y_{lm}(\Omega)$ are the spherical harmonics. In an isotropic liquid $f(r, \Omega)$ averaged over a physically infinitely small volume is a constant

$$f_0 \equiv \langle f(r, \Omega) \rangle = \frac{\langle Q_{00} \rangle}{\sqrt{4\pi}} = \text{const.}$$

In uniaxial liquid-crystals, only the second harmonic in (33) need be retained. Finally, in the cubic liquid crystals discussed here, the first nonvanishing term of the expansion in (33) corresponds to $l = 4$:

$$\langle \delta f(r, \Omega) \rangle \equiv \langle f(r, \Omega) \rangle - f_0 = \sum_{m=-4}^4 \langle Q_{4m}(r) Y_{4m} \rangle.$$

In real cubic crystals $\langle Q_{4m}(r) \rangle \neq 0$. However, they also have the group of finite translations of a three-dimensional crystal.

Actually, not all nine components of the order parameter Q_{4m} of a cubic liquid crystal are independent. It is always possible to transform to a system of coordinates in which only the components $\langle Q_{40} \rangle$, $\langle Q_{44} \rangle = \langle Q_{4,-4} \rangle$ differ from zero. Another characteristic of the cubic symmetry is the equality

$$\left(\frac{\langle Q_{4,\pm 4} \rangle}{\langle Q_{40} \rangle} \right) = \sqrt{\frac{5}{14}}.$$

Instead of the order parameter Q_{4m} , it is possible to use a tensor of rank four of a special form, called a nonor, to describe cubic liquid crystals:

$$\langle \delta f(r, \Omega) \rangle = \langle Q_{ijkl}(r) \rangle e_i e_j e_k e_l,$$

where \mathbf{e} is a unit vector related with the solid angle Ω . A tensor Q_{ijkl} of this type can be expressed in terms of the components of a triplet of orthogonal vectors l, m , and n :

$$\langle Q_{ijkl} \rangle = Q_0 \left[l_i l_j l_k l_l + m_i m_j m_k m_l + n_i n_j n_k n_l - \frac{1}{5} (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \right],$$

where Q_0 is the modulus of the order parameter.

In cubic liquid crystals, all tensors of rank two reduce to scalars δ_{ij} . However, their optical properties differ from the properties of an isotropic liquid. For example, in an isotropic liquid birefringence in an electric field is proportional to $\sim E_i E_j$, and in a cubic liquid crystal invariant combinations with a more complicated structure: $Q_{ijkl} E_k E_l$. The order parameter of a cubic liquid crystal is manifested directly in the characteristics determined by tensors of rank four, for example, in the viscosity tensor. There are experimental indications of the existence of such liquid crystals.⁴⁴ Possible candidates are the so-called smectic D, which give isotropic textures.

In conclusion, we shall describe phase transitions from a cubic liquid crystal into a true solid crystal and into the isotropic liquid. Just as we did for the diskotic liquid crystals, we shall choose as the order parameter for the cubic-liquid-crystal-solid transition the Fourier harmonics of the density, corresponding to reciprocal lattice vectors of the solid crystal,

$$\psi_{\mathbf{x}}(\mathbf{r}) = |\psi_{\mathbf{x}}(\mathbf{r})| e^{i\mathbf{x}\cdot\mathbf{u}(\mathbf{r})},$$

where $\mathbf{u}(\mathbf{r})$ are the displacement vectors. The elasticity of the cubic liquid crystal is determined by the gradients of the vector triplet l, m , and n , or, which is the same thing, the set of three rotational angles θ . An obvious symmetry exists:

$$\begin{aligned} \theta(\mathbf{r}) &\rightarrow \theta(\mathbf{r}) + \theta_0, \\ \psi_{\mathbf{x}}(\mathbf{r}) &\rightarrow \psi_{\mathbf{x}}(\mathbf{r}) \exp(i\mathbf{x} \cdot [\theta_0 \mathbf{r}]). \end{aligned}$$

Taking this symmetry into account, the expansion of the free energy for the cubic-liquid-crystal-solid-crystal transition has the following form:

$$\begin{aligned} F &= \frac{1}{2} A \sum_{\mathbf{x}} |\mathbf{x}(\nabla - i[\mathbf{x}\theta])\psi_{\mathbf{x}}|^2 \\ &+ \frac{1}{2} B \sum_{\mathbf{x}} |[\mathbf{x}(\nabla - i[\mathbf{x}\theta])\psi_{\mathbf{x}}]|^2 \\ &+ \frac{1}{2} a \sum_{\mathbf{x}} |\psi_{\mathbf{x}}|^2 + b \sum_{\mathbf{x}_1+\mathbf{x}_2+\mathbf{x}_3} \psi_{\mathbf{x}_1} \psi_{\mathbf{x}_2} \psi_{\mathbf{x}_3} + \dots \\ &+ \frac{1}{2} K_1 |[\nabla\theta]|^2 + \frac{1}{2} K_2 (\nabla\theta)^2, \end{aligned}$$

where a depends linearly on the temperature, b is a constant. A and B correspond to the elastic moduli of the solid body that forms below the transition point, and K_1 and K_2 are the elastic moduli of the cubic liquid crystal (analogous to Frank's coefficients in nematics).

Within the framework of Landau theory, the transition being discussed is a phase transition of the first kind (a nonvanishing third-order invariant exists). There are no grounds for expecting large fluctuations and changes in the type of transition due to them.

The transition from the cubic crystal into the isotropic liquid is described by the expansion of the free energy

$$F = \frac{1}{2} K' (\nabla Q_{ijmn})^2 + a (Q_{ijmn})^2 + b (Q_{ijmn})^3 + \dots$$

From the point of view of Landau theory, this transition must also be a first-order phase transition. However, in this case, there is justification for expecting that the fluctuations will be strong enough to make this transition a second-order phase transition or close to it.

Indeed, if the fluctuations of the modulus are neglected (the analysis by Nelson and Toner¹⁷ shows that this approximation is justified), then we have the following form of the free energy:

$$F = \frac{1}{2} K \int d^d r [|\nabla \mathbf{l}|^2 + |\nabla \mathbf{m}|^2 + |\nabla \mathbf{n}|^2],$$

where $K = 4Q_0^2 K'$, and d is the dimensionality of the space.

Each orthogonal triplet of vectors \mathbf{l}, \mathbf{m} , and \mathbf{n} can be put into correspondence with three complex 2×2 matrices. In this case

$$F = \frac{1}{2} (4K) \int d^d r \text{Sp}(\nabla U^+ \nabla U).$$

This equality is actually related with a homomorphism between the rotational group and $SU(2)$. Each $SU(2)$ matrix can be expanded as follows:

$$U(\mathbf{r}) = x_0(\mathbf{r}) + i\boldsymbol{\sigma}\mathbf{x}(\mathbf{r}),$$

where $\boldsymbol{\sigma}$ are the Pauli matrices and, in addition, $x_0^2 + \mathbf{x}^2 = 1$. We can now write down the free energy of a cubic liquid crystal in terms of the unit four-vector:

$$F = \frac{1}{2} (8K) \int d^d r (\nabla x_\alpha)^2.$$

All results on the critical behavior of four-spins are well known.¹¹ With $d = 2$, the fluctuations are so strong that they make a phase transition at a finite temperature impossible.

However, for $d = 2 + \varepsilon$, a continuous phase transition occurs at the temperature

$$T_c = 8\pi K (d - 2).$$

For this reason, it appears that in three-dimensional space (i.e., $\varepsilon = 1$) the cubic-liquid-crystal-isotropic-liquid phase transition will also be a second-order transition or close to it.

5. CONCLUSIONS

Thus, above we examined some new types of ordering in liquid crystals. In most case, there are no reliable (and, sometimes, none at all) experimental data on these new systems. For this reason, the experimental aspects have practically not been discussed in this review. In view of the limited scope of the review, a whole set of problems related with dipole ordering in liquid crystals, as well as with chiral systems, was deliberately not considered here. In recent years, ferro- or antiferroelectric liquid crystals have been studied actively. There are reasons for assuming that the characteristics of some of the new smectic phases (I, F, etc.) are related precisely with some form of dipole ordering. According to the purely structural classification used in this review, however, all these mesophases must be placed among the different types of B smectics. The interaction of the ferroelectric, smectic, and nematic order parameters leads to a large variety of phases and phase transitions between them. In particular, commensurate or incommensurate smectics, smectics with modulation of layers, etc., are possible in such systems. However, the analysis of these very specific problems can be a subject for a separate review. The same applies to chiral systems as well, which include cholesteric liquid crystals which have been studied for a long time, the relatively recently discovered chiral C* smectics, and the blue phase of cholesterics, which is being studied once again. The absence of a center of inversion is characteristic for all these systems. For this reason, in these systems, there is usually a nonvanishing so-called Lifshitz invariant, which leads to the inhomogeneity of the ground state. For example, a cholesteric is a helically twisted nematic, the C* phase is a helically twisted smectic-C, and the blue phase has a cubic lattice in a field of orientations (i.e., according to the terminology of this section, it is a chiral cubic liquid crystal). This, as a rule, small (on a molecular level) right/left asymmetry ($\sim 10^{-3}$) leads to a radical difference in almost all properties of chiral and achiral systems. The monograph by Belyakov and Sonin⁴ examines these problems in detail. Finally, we have not discussed at all the new aspects of the dynamics of liquid crystals, which also could be a subject of a separate review.

In conclusion, it is my pleasant duty to thank V. L. Ginzburg for stimulating my interest in the subject of this review and for discussing its content during my participation at a seminar at FIAN SSSR, as well as D. I. Khomskii for many useful remarks.

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