

Isolated point on a first-order transition curve

P. B. Vigman, A. I. Larkin, and V. M. Filev

L. D. Landau Theoretical Physics Institute, USSR Academy of Sciences
Zh. Eksp. Teor. Fiz. 68, 1883–1893 (May 1975)

An isolated Landau point can exist on a first-order transition curve. Near this point the transition line and the thermodynamic quantities have power singularities. The form of these singularities is investigated in the case when the order parameter is a tensor; this corresponds to the transition of a nematic liquid crystal to an isotropic liquid. The critical exponents are calculated approximately.

PACS numbers: 64.70. -p, 61.30. +w

1. INTRODUCTION

According to Landau's theory^[1], isolated singular points can exist on first-order phase-transition curves. At these points the coefficient of the cubic term in the expansion of the free energy in the order parameter is equal to zero. This picture can also remain valid when fluctuations are taken into account. In this case, all the thermodynamic quantities, as functions of the temperature and pressure, have a singularity at the isolated point. In particular, the first-order phase-transition curve, the heat of the transition and the specific-volume change in the transition have a power singularity. All these dependences are characterized by three indices: two are the same as those in second-order phase transitions while the third describes the way in which the coefficient of the cubic term vanishes.

The transition of the isotropic phase of a liquid crystal to the nematic phase is investigated in detail in the paper. This transition is first-order. Appreciable pre-transition phenomena indicate that the transition is close to being second-order. Baskakov, Semenchko and Byankin^[2], by extrapolating the experimental dependence of the specific-volume discontinuity on the temperature and pressure, conclude that an isolated point exists.

There exists an appreciable region in which the fluctuations become important and the Landau theory is not applicable. Below we calculate the critical indices of the transition to the isotropic phase by the methods of expanding in $\epsilon = 4 - d$ ^[3] and in N^{-1} ^[4].

The order parameter in the nematic phase of liquid crystals is a tensor. It is shown that in a broad region of pressures the nematic phase should possess axial symmetry and be described by a uniaxial ellipsoid of revolution. Near the isolated point a narrow region without axial symmetry (a biaxial phase) can exist. Between these phases a second-order transition is possible.

2. GENERAL SCALING-THEORY RELATIONS

We shall consider a phase transition describable by a certain order parameter Q . The Hamiltonian responsible for the transition has the form

$$\mathcal{H} = A Q^2 + B Q^3 + C Q^4 + L k^2 Q^2. \quad (1)$$

Here $k^2 Q^2$ is the symbolic form of the invariant quadratic in Q and in the wave-vector \mathbf{k} , and Q^2 , Q^3 and Q^4 are the second-, third- and fourth-order invariants. The next higher powers of Q in the Hamiltonian induce asymmetry in the pattern of the transition and, possibly, a splitting of the more ordered phase into several new phases. The role of the high powers will be determined below for a specific structure of Q .

We assume the quantities A and B to be smooth functions of pressure and temperature. Expanding near the points of interest in the (P, T) -plane enables us to describe the phase transition in the coordinates of the (A, B) -plane. We shall assume that there exists only one third-order term in the Hamiltonian, so that, in the (P, T) -plane, the cubic term disappears on the line $B(P, T) = 0$.

On this line the dependence of the Green function on the modulus k has the form

$$G(k) \propto [A + k^2 + \Sigma(A, k)]^{-1}, \quad (2)$$

where Σ is the self-energy part.

At a certain point on the line $B = 0$ a second-order phase transition occurs. This point is determined by the condition

$$G^{-1}(0) = 0$$

or

$$A(T_0, P_0) + \Sigma(A(T_0, P_0), 0) = 0. \quad (3)$$

At the point itself, as in ordinary second-order transitions, the Green function has a power dependence on k :

$$G^{-1} \propto k^{2-\eta} \quad (\eta > 0), \quad (4)$$

and, near T_0 on the line $B(P, T) = 0$,

$$G^{-1}(0) \propto A^\nu, \quad (5)$$

i.e., near the transition point^[5],

$$G^{-1}(k, A) \propto k^{2-\eta} g(A^\nu k^{-2+\eta}). \quad (6)$$

Here and below, the letter A denotes the difference $A - A(P_0, T_0)$, which, near the transition point, depends linearly on $\tau = (T - T_0)/T_0$ and $\pi = (P - P_0)/P_0$.

On the line $B = 0$ all physical quantities are determined by the Green function, and the singularities of all the quantities are determined by the two indices η and γ . For example, the singular part of the thermodynamic potential Φ is proportional to $A^{\gamma d/(2-\eta)}$. The vertex parts Γ_{2n} have the form

$$\Gamma_{2n}(k) = A^{1/n(2-\eta) - d(n-1)/(2-\eta)} \Gamma_{2n}(k^{2-\eta} A^{-\gamma}). \quad (7)$$

In the vicinity of the line $B = 0$ there appears the new vertex Γ_3 , with its own index Δ_3 that cannot be expressed in terms of η and γ . In first order in B ,

$$\Gamma_3 \propto B k^{\Delta_3}. \quad (8)$$

The expansion of the potential Φ_0 in a series in B is depicted by the graphs shown in Fig. 1.

Estimating the diagrams with the aid of formulas (6) and (8), we can convince ourselves that the series can be collected into a sum of the form

$$\Phi_0 = A^{\gamma d/(2-\eta)} \varphi(z^2), \quad (9)$$



FIG. 1

where

$$z^2 = B^2 A^{[2\Delta_1 - 3(2-n) + d] \gamma / (2-n)} \quad (10)$$

The vertices Γ_n are expanded in the same parameter:

$$\Gamma_n(0) = A^{[n(2-n) - d(n-2)] \gamma / 2(2-n)} \gamma_n(z) \quad (11)$$

For even n the functions $\gamma_n(z)$ are even, while for odd n they are odd functions of z .

The vertices $\Gamma_n(0)$ determine the expansion of the potential Φ in powers of the mean order parameter:

$$\Phi - \Phi_0 = \sum_{n=2}^{\infty} \frac{1}{n!} \Gamma_n(0) \langle Q \rangle^n - \langle Q \rangle h, \quad (12)$$

where the external field h and $\langle Q \rangle$ are conjugate quantities. The relationship between the order parameter $\langle Q \rangle$ and the field h is determined by the minimizing condition $\partial \Phi / \partial \langle Q \rangle = 0$.

The solution of this equation has the form

$$\langle Q \rangle = A^{\Delta_0} q(z, A^{-(d+2-n)\gamma/2(2-n)} h), \quad \Delta_0 = \frac{\gamma(d-2+n)}{2(2-n)} \quad (13)$$

In particular, below the transition point, for $h = 0$, the spontaneous moment is

$$Q_s = A^{\Delta_0} q(z, 0), \quad (14)$$

and the thermodynamic potential Φ has the form (9), but with another function $\varphi_1(z)$. The transition line is determined from the condition that the thermodynamic potentials of the phases be equal, which is fulfilled for a certain $z^2 \sim 1$. Using (10), we obtain the transition line in the (A, B) coordinates:

$$B^2 \propto A^{[-2\Delta_1 + 3(2-n) - d] \gamma / (2-n)} = A^x \quad (15)$$

If $x < 2$, the transition line is tangential to the line $A = 0$, as in the Landau theory. If $x = 2$, the transition line has a sharp bend, while for $x > 2$ it has (at the point $A = B = 0$) a singularity in the form of a "beak".

Eq. (15) has a solution for small A and B only when $x > 0$. In the case $x < 0$ the cubic vertices are so small that they have no influence on the thermodynamics, i.e., the phase transition will be a second-order transition along the line $A = 0$.

It should also be noted that for $\Gamma_4 < 0$ there will be a first-order transition even at the point $A = B = 0$.

3. LANDAU THEORY FOR THE NEMATIC-ISOTROPIC TRANSITION

The phase transition of a nematic liquid crystal to an isotropic liquid is described by a tensor order parameter. The anisotropic part $Q_{\alpha\beta}$ of the dielectric tensor $\epsilon_{\alpha\beta}$ can serve as such a quantity^[6]:

$$Q_{\alpha\beta} = \epsilon_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \text{Sp } \epsilon.$$

In the isotropic phase $Q_{\alpha\beta} = 0$. From three-dimensional traceless tensors we can construct one second-order invariant: $I_2 = \text{Tr} Q^2$; one third-order: $I_3 = \text{Tr} Q^3$; one fourth-order: $\text{Tr} Q^4 = \frac{1}{2} I_2^2$; one fifth-order: $\text{Tr} Q^5 = \frac{5}{6} I_2 I_3$; and two irreducible six-order invariants: I_2^3 and $\text{Tr} Q^6 = \frac{1}{4} I_2^3 + \frac{1}{3} I_3^2$.

Consequently, the thermodynamic potential of the nematic phase in the Landau form will be^[7]

$$\Phi - \Phi_0 = A I_2 + B I_3 + \frac{1}{2} C I_2^2 + D I_2 I_3 + \frac{1}{2} E I_3^2 + \frac{1}{3} E' I_2^3. \quad (16)$$

A second-order phase transition is possible only at the point $A = B = 0$. The coefficients A and B determine the distance from this point and are linear functions of T and P near this point. The coefficients C, D, E and E' are assumed to be quantities independent of P and T . The last term in the expression (16) does not lead to any qualitative changes. It will not be taken into account below.

In the nematic crystal the following phases are possible: a biaxial phase, in which the eigenvalues of $Q_{\alpha\beta}$ are different, and a uniaxial phase with two equal eigenvalues. Depending on the sign of the eigenvalues, there can be two different uniaxial phases. In one of these the dielectric ellipsoid is a prolate ellipsoid of revolution, and in the other it is oblate. In these variables the potential has a minimum at

$$I_2 = \frac{DB - EA}{EC - D^2}, \quad I_3 = \frac{DA - BC}{EC - D^2}, \quad (17)$$

if $CE > D^2$. If $CE < D^2$ the biaxial phase is absent, and I_2 and I_3 are not independent variables. To determine the region of existence of the biaxial phase we shall make use of the inequality $I_2^3 \leq 6I_3^2$. The equals sign determines the boundary of the biaxial region. For small A we have

$$B = ADC^{-1} \pm 6^{-1/2} A^{3/2} C^{-3/2} (CE - D^2). \quad (18)$$

On these lines a second-order transition occurs from the uniaxial phases to the biaxial phase; in one uniaxial phase $I_3 = 6^{-1/2} I_2$, and in the other $I_3 = -6^{-1/2} I_2^{3/2}$. Substituting these values into (16) and minimizing with respect to I_2 , we find the thermodynamic potentials of both phases.

The nematic-isotropic phase transition line is defined by the equality of the thermodynamic potentials of the two phases. For small B we have

$$A = \frac{1}{2} 6^{-1} B^2 C^{-1} + 6^{-2} B^3 D C^{-3}. \quad (19)$$

If $CE < D^2$, the biaxial phase does not arise and a first-order transition between the two uniaxial phases occurs along the line

$$A = BCD^{-1} \pm 6^{-1/2} B^{3/2} D^{-3/2} \quad (20)$$

with liberation of the latent heat

$$q = -\frac{B}{D} T \frac{\partial A}{\partial T} + \left(-\frac{A}{D} + \frac{C}{D^2} B \right) T \frac{\partial B}{\partial T}. \quad (21)$$

The phase diagram for the case $CE > D^2$ is given in Fig. 2. I is the region of the isotropic liquid. Regions II and III are described by a uniaxial tensor, and IV is the region of the biaxial phase. If the biaxial phase exists

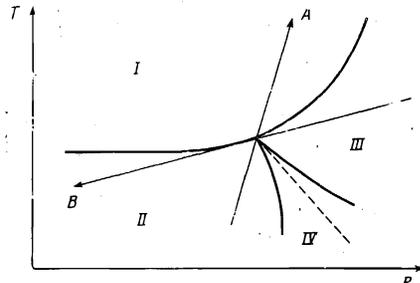


FIG. 2

at all, it is in a narrow region whose width is determined by the sixth-order term. The narrowness of this region is associated with the fact that for $B = 0$ the fourth-order term does not completely lift the degeneracy (for the same I_2 there can be different I_3), and therefore it is necessary to take the next higher terms into account.

The qualitative picture of the transition is also conserved when fluctuations are taken into account. However, the transition curves are described in the scaling region by power functions with fractional exponents, to the calculation of which we now turn.

4. CALCULATION OF THE CRITICAL INDICES IN THE APPROXIMATION OF SMALL ϵ AND LARGE $2j + 1$

The critical indices η , γ and Δ_3 depend essentially on the structure of the order parameter. The tensor structure of the variable $Q_{\alpha\beta}$ determines the structure of the Green function:

$$G_{ab}(k) = T^{-1} \langle Q_a(k) Q_b(0) \rangle, \quad a = (\alpha, \beta), \quad b = (\gamma, \delta).$$

For $k = 0$ the Green function has the form

$$G_{ab}(0) = G \Delta_{ab}, \quad (22)$$

where

$$\Delta_{ab} = \Delta_{\alpha\beta}, \quad \gamma_0 = 1/2 (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) - \delta_{\alpha\beta} \delta_{\gamma\delta} / n, \quad (23)$$

$$\Delta_{\alpha\alpha, \gamma\gamma} = \Delta_{\alpha\beta, \gamma\delta} = 0, \quad \Delta = \Delta_{\alpha\beta, \alpha\beta} = \frac{n^2 + n}{2} - 1,$$

n is the dimensionality of the tensor $Q_{\alpha\beta}$.

Below we shall see that as the isolated point is approached the anisotropic part (which depends on the vector k) of the Green function increases more slowly than the isotropic part, and the Green function retains the structure (22) for $k \neq 0$ too.

At the transition point itself,

$$G_{ab} = g k^{-2+n} \Delta_{ab} = G(k) \Delta_{ab}. \quad (24)$$

In this approximation the vertex parts also have an isotropic form:

$$\Gamma_{abc} = \Gamma_3(k) \Delta_{abc}, \quad (25)$$

$$\Gamma_{abcd} = 1/3 \Gamma_4(k) (\Delta_{ab} \Delta_{cd} + \Delta_{ac} \Delta_{bd} + \Delta_{bc} \Delta_{ad}).$$

The symbol Δ_{abc} has zero trace over each of the pairs a, b, c :

$$\Delta_{abc} = \frac{1}{8} \left\{ o_{abc} - \frac{n+4}{n} (o_{aobc} + o_{aboc} + o_{coba}) + \frac{2(n+2)(n+4)}{n^2} o_{aobc} \right\}.$$

Here $o_{\alpha\beta\gamma\dots\delta}$ is a quantity that is symmetric in all the indices and constructed from all possible Kronecker symbols. For example,

$$o_{ab} = \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\beta\gamma} \delta_{\alpha\delta}, \quad \Delta_{ab} = \frac{1}{2} \left(o_{ab} - \frac{n+2}{n} o_{aob} \right).$$

In an analogous way, all multi-index quantities in the theory are expressed in terms of the symbols $o_{\alpha\beta\dots\gamma}$.

To calculate the critical indices we shall assume the dimensionality of space to be close to four^[3]: $d = 4 - \epsilon$. In first order in ϵ the Green function remains free while the vertex $\Gamma_4(k^2)$ is determined from a parquet equation which differs from the equations of the scalar and vector models^[7] only by a numerical coefficient that is combinatorial in origin and is associated with the multiplicity of the quantity:

$$\Gamma_4(p) = 4! \frac{C}{2} - \frac{4}{3} \frac{\Delta+8}{2(2\pi)^4} \int_{p' < k} \Gamma_4^2(k) \frac{d^{4-\epsilon} k}{k^4}.$$

In the long-wavelength limit of interest, we have, in first order in ϵ ,

$$\Gamma_4 = \frac{3}{4} \frac{2\epsilon}{\Delta+8} (8\pi^2)^{\epsilon} p^{\epsilon}. \quad (26)$$

The index γ is most easily calculated using the Ward identity

$$\frac{\partial G_{ab}^{-1}(0)}{\partial A} = \mathcal{F}_{ab}(0) = \mathcal{F} \Delta_{ab}.$$

To first order in ϵ , for \mathcal{F} we have the equation

$$\mathcal{F}(k) = 2! - \frac{4}{3} \frac{\Delta+2}{2} \int_{p' > k} \Gamma_4 \mathcal{F} \frac{d^{4-\epsilon} p}{(p^2+A)^2 (2\pi)^4}. \quad (27)$$

Substituting Γ_4 from (26) and solving Eq. (27), we obtain

$$\mathcal{F} = 2! A^{\epsilon(\Delta+2)/2(\Delta+8)},$$

whence

$$\gamma = 1 + \frac{\Delta+2}{2(\Delta+8)} \epsilon.$$

Solving the analogous equation for the cubic vertex

$$\Gamma_3(k) = 3! B - \frac{4}{3} \frac{1}{2} 6 \int_{p' > k} \Gamma_4 \Gamma_3 \frac{d^{4-\epsilon} p}{(p^2+A)^2 (2\pi)^4},$$

we find

$$\Gamma_3 = 3! B \left(\frac{k}{\Lambda} \right)^{\epsilon\eta/(\Delta+8)}, \quad \Delta_3 = \frac{6}{\Delta+8} \epsilon. \quad (28)$$

The index η appears only in second order in ϵ . To second order in Γ_4 , the correction to the Green function is equal to

$$G^{-1} - k^2 = - \frac{\Delta+2}{3!3} \int_k^{\Lambda} \Gamma_4^2 G(k_1) G(k_2) G(k-k_1-k_2) \frac{d^{4-\epsilon} k_1 d^{4-\epsilon} k_2}{(2\pi)^8}. \quad (29)$$

Substituting the expression (26) for Γ_4 to first order in ϵ and omitting the terms that do not depend on k , which determine the shift in the transition point, we obtain

$$G^{-1}(k) = g^{-1} k^2 \left(1 - \frac{\Delta+2}{2(\Delta+8)^2} \epsilon^2 \ln \frac{k}{\Lambda} \right).$$

Comparing this expression with (24), we find

$$\eta = \frac{\Delta+2}{2(\Delta+8)^2} \epsilon^2. \quad (30)$$

In the isotropic case under consideration, the analytic continuation from four-dimensional space can be effected in two ways. In one case, the dimensionality of the tensor $Q_{\alpha\beta}$ is equal to the dimensionality of space, and in first order in ϵ we must put $n = 4$ in the formulas (23)–(30). In the other case the dimensionality of the tensor remains constant ($n = 3$).

Besides expanding in ϵ , there exists a way of calculating the indices that uses the large number of components of the field. In three-dimensional space the order parameter $Q_{\alpha\beta}$ has five independent components. It is possible to generalize the model in such a way that the number of independent components becomes a large number $2j + 1$, and calculate the indices η , γ and Δ_3 for large j .

The traceless tensor $Q_{\alpha\beta}$ is equivalent to a spinor Ψ_m^j with rank $j = 2$. In the new variables the Hamiltonian has the form

$$\mathcal{H} = (A+k^2) I_2 + B I_3 + 1/2 C I_2^2, \quad (31)$$

where

$$I_2 = \sum_{m=-j}^{m=j} |\Psi_m^j|^2, \quad I_3 = \sum_{m,k} \begin{pmatrix} j & j & j \\ m & -m+k & -k \end{pmatrix} \Psi_m^j \Psi_{-m+k}^j \Psi_{-k}^j.$$

In this form j can be regarded as any number. On the

line $B = 0$, (31) coincides with the Hamiltonian in the problem of a second-order phase transition with $N = 2j + 1$ fields. For this model the indices η and γ to first order in N^{-1} are equal to^[4]:

$$\eta = \frac{2}{3\pi^2} \frac{1}{2j+1}, \quad \gamma = 2 \left(1 - \frac{12}{\pi^2} \frac{1}{2j+1} \right). \quad (32)$$

To determine the index Δ_3 to terms of $O(N^{-2})$ it is sufficient to calculate the diagram represented in Fig. 3. The wavy line is the interaction in the "ladder" approximation. Calculation of the diagram gives

$$\Gamma_3 = B \left(1 - 6 \int \frac{d^3p}{(2\pi)^3} G^{(0)} \left(\mathbf{p} + \frac{\mathbf{k}}{2} \right) G^{(0)} \left(\mathbf{p} - \frac{\mathbf{k}}{2} \right) \frac{2C}{1 + 2C(2j+1)\Pi(p)} \right),$$

where

$$\Pi(p) = \int k^{-2} (\mathbf{p} + \mathbf{k})^{-2} \frac{d^3k}{(2\pi)^3}.$$

For small \mathbf{k} , the region of small \mathbf{p} is important in the integral, and we can neglect the 1 in the denominator of the integrand. As a result, we obtain $\Gamma_3 = B(1 + 12 \ln k / \pi^2 (2j + 1))$. Comparing this with the cubic vertex that follows from scaling arguments, we obtain the index $\Delta_3 = 12/\pi^2 (2j + 1)$.

The next terms in the expansion of the thermodynamic potential have the form

$$\Gamma_5 I_5 I_3 + \frac{1}{2} \Gamma_6 I_3^2 + \frac{1}{3} \Gamma_6' I_3^2 + \dots$$

The index of the vertex Γ_6' is determined by formula (7), and the vertices Γ_5 and Γ_6 should have independent indices Δ_5 and Δ_6 . The calculation of the indices Δ_5 and Δ_6 by means of the ϵ -expansion and the expansion for large $2j + 1$ is performed analogously to that of Δ_3 and leads to the following values:

$$\begin{aligned} \Delta_5 &= \frac{\Delta + 26}{\Delta + 8} \epsilon, & \Delta_5 &= 1 + \frac{176}{3\pi^2(2j+1)} \\ \Delta_6 &= \frac{30\epsilon}{\Delta + 8}, & \Delta_6 &= \frac{60}{\pi^2(2j+1)}. \end{aligned}$$

The different ways of calculating the critical indices give different values for γ , η and χ . It is of importance, however, that for any method x lies in the region $0 < x < 2$, so that the qualitative picture of the vicinity of the isolated point is the same as in the Landau theory.

5. EFFECT OF Γ_5 AND Γ_6

We shall consider now the change in the pattern of the transition when fifth and sixth powers of Q , with bare vertices D and E respectively, appear in the Hamiltonian. Their qualitative influence is the same as in the Landau approximation. The term with the fifth power leads to asymmetry of the pattern of the transition about the line $B = 0$, and the term with the sixth power leads to the possibility of the existence, in a narrow region, of a phase without axial symmetry. Quantitatively, these phenomena are described by the vertices Γ_5 and Γ_6 . There appears a correction

$$\int \Gamma_5 G^d k \infty DA^{(1+\eta+\Delta_5)\gamma/(2-\eta)} + \delta B, \quad (33)$$

to the cubic vertex Γ_3 , where δB is determined by the large-momentum region, does not depend on A and leads to a shift of the critical point in B . Below, B , like A , will be reckoned from the value at the critical point.

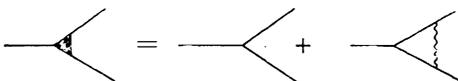


FIG. 3

The first term leads to the result that in the formulas of Sec. 2 the parameter $z = BA^{-\chi/2}$ must be replaced by

$$\tilde{z} = \{B + DA^{(1+\eta+\Delta_5)\gamma/(2-\eta)}\} A^{-\chi/2}. \quad (34)$$

In accordance with this, the curve of the transition to the isotropic phase and the transition lines between the two ordered phases become asymmetric with respect to the line $B = 0$. As in the Landau theory, a biaxial phase exists only for $\Gamma_6 > 0$. The width of the region in the (A, B) -plane is

$$\Delta B \infty \Gamma_6 S p Q^3 \infty A^{\gamma\Delta_6/(2-\eta)+3\Delta_6}. \quad (35)$$

6. THE VERTEX PARTS AND GREEN FUNCTIONS

We now investigate the question of the stability of the isotropic form of the Green function in the scaling region. For this we introduce into the Hamiltonian an anisotropic part $\lambda(\partial/\partial x_\alpha)(\partial/\partial x_\beta) Q_\alpha \gamma Q_\beta$, which leads to the free Green function

$$\begin{aligned} G_{ab}^{(0)-1} &= k^2 (\Delta_{ab} + \lambda \kappa_a \kappa_b - \lambda \kappa_{ab}), \\ G_{ab}^{(0)} &= k^{-2} \left(\Delta_{ab} - \frac{\lambda}{1+3\lambda/4} \kappa_a \kappa_b + \frac{\lambda}{1+\lambda/2} \kappa_{ab} \right), \end{aligned}$$

$$\kappa_a = k_a k_b / k^2 - \delta_{ab} / n,$$

$$\kappa_{ab} = k_a k_b k_\gamma k_\gamma / k^4 - (k_a k_\gamma \delta_{\beta\gamma} + k_a k_\beta \delta_{\gamma\beta} + k_\beta k_\gamma \delta_{\alpha\beta} + k_\beta k_\alpha \delta_{\gamma\alpha}) / 4k^2.$$

In the scaling region the exact Green function has the form

$$G_{ab}^{-1} = k^{-2} (\Delta_{ab} + \lambda_1(k) \kappa_a \kappa_b - \lambda_2(k) \kappa_{ab}), \quad (36)$$

where $\lambda_i(k) = \lambda k^{\eta_i}$.

To prove the stability of the isotropic form of the Green function it is necessary to show that the η_i are positive. Then, in the region of small \mathbf{k} , we can neglect the anisotropic parts of the Green functions. As in the calculation of η , to calculate the indices η_i we find the self-energy part in second order of perturbation theory from formula (29). Substituting into this formula the expression (26) for Γ_4 and the expression (35) for the Green functions G , we obtain

$$\lambda_i = \lambda (1 + \eta_i \ln k), \quad \eta_1 = \eta_2 = \frac{2}{3} \frac{\Delta}{\Delta + 2} \eta = \frac{\Delta}{3(\Delta + 8)} \epsilon^2.$$

In the approximation of large j , the indices η_i are calculated just like the index η in formula (32). As a result we obtain $\eta_i = 4\eta/5$. Thus, the indices η_i are positive, and the Green function becomes isotropic as the singular point is approached.

For numerical reasons, like η , the exponents of the anisotropic parts of the Green function have been found to be small. Therefore, the scaling region, in which the Green function is isotropic and the estimates obtained above for the indices are valid, is narrow. There exists a region

$$1 \ll \ln \frac{\Lambda^2}{A^2} \ll \eta_1^{-1},$$

in which the Green function can be anisotropic. In this region the vertices have a form corresponding to scaling theory, with indices depending on the anisotropy parameter λ . Being functions of $\eta \ln(\Lambda^2/A^2)$, these parameters depend slowly on T and P . Experiments^[8] on light scat-

	η	γ	Δ_3	Δ_5	Δ_6	χ
$(2i+1)^{-1}$	0.013	1.52	0.24	2.18	1.20	1.78
$\epsilon, n=3$	0.021	1.27	0.46	2.38	2.3	1.31
$\epsilon, n=4$	0.019	1.32	0.35	2.06	1.8	1.47

tering by liquid crystals give evidence of the smallness of the anisotropic part of the Green function in this region too. Therefore, the results obtained above are valid in a broad range of temperatures.

The treatment of the anisotropic region by means of the ϵ -expansion has certain difficulties of principle in addition to the great calculational difficulties. The point is that the relation $\text{Tr}Q^4 = \frac{1}{2}(\text{Tr}Q^2)^2$ is fulfilled only for two-row and three-row traceless matrices. For four-row matrices there are two fourth-degree terms in the expansion of the thermodynamic potential: $\Gamma_1(\text{Tr}Q^2)^2$ and $\Gamma_2\text{Tr}Q^4$.

For isotropic Green functions the parquet equations for these vertices have the form

$$8\pi^2 \frac{d\Gamma_1}{dy} = \frac{1}{3} \left(\frac{n^2+n}{2} + 7 \right) \Gamma_1^2 + \frac{2n^2+3n-6}{3n} \Gamma_1\Gamma_2 + 3\Gamma_2^2 \left(\frac{1}{6} + \frac{1}{n^2} \right),$$

$$8\pi^2 \frac{d\Gamma_2}{dy} = 4\Gamma_1\Gamma_2 + \frac{2n^2+9n-36}{6n} \Gamma_2^2, \quad y = \ln \frac{k}{\Lambda}.$$

These equations were obtained by Lubensky and Priest^[9], who also found the fixed points of the equations.

The values of the indices obtained above correspond to the solution $\Gamma_2 = 0$, while Γ_1 is determined by (26). It is easy to convince oneself that this solution is unstable. If there is a small bare vertex for Γ_2 , then, at a certain distance from the proposed second-order transition point, the vertex Γ_1 changes sign and a first-order transition occurs. Anisotropic terms in the Green function lead to the same effect. Thus, in the four-dimensional case, when the matrix $Q_{\alpha\beta}$ is also a four-row matrix, there exist two essentially different solutions. For one solution, $\Gamma_2(0) = 0$ is an isolated singular point, while for the other a first-order transition occurs even at $B = 0$. We do not know which of these solutions has the analytic continuation to which a state in the real, three-dimensional world corresponds.

7. CONCLUSION

In the scaling region the thermodynamic potential has the form

$$\Phi \propto T\xi^{-3}, \quad (37)$$

where ξ is the correlation length, which is measured by optical methods^[8]. The dependence of ξ on the temperature and pressure is described by a universal function of the form

$$\xi = (T - T_c)^{-\nu/(2-\eta)} f \left(\frac{T - T_k}{T_k - T_c} \right), \quad T_k - T_c \propto (P - P_0)^{2/\alpha}. \quad (38)$$

Here T_k is the temperature of the first-order transition, $T_c(P)$ is the boundary of the metastable region, and P_0 is the pressure at the isolated point. The latent heat of the transition is of the order of the singular part of the entropy and has the pressure dependence

For $T - T_c \gg T_k - T_c$ the dependence of ξ on the temperature has the form $\xi \propto (T - T_c)^{\gamma/(2-\eta)}$. At pressures close to P_0 in the nematic phase, there should be a transition between the two nematic phases. In one of these the dielectric permittivity is described by a prolate ellipsoid, and in the other by an oblate ellipsoid. Between these phases a narrow region is possible in which there exists a phase without axial symmetry. The phenomenological theory cannot predict in which substances and at what pressures an isolated singular point will exist. The possibility that the coefficient of the fourth power in the thermodynamic potential is negative is not ruled out. In this case, the phase transition to the isotropic liquid will be first-order even at the point at which the coefficient of the cubic term vanishes.

In the majority of liquid crystals the phase transitions are almost second-order: even at normal pressure, $T_k - T_c \sim 1^\circ$ ^[2,10]. In order to find the region of applicability of formulas (37)–(38), it is necessary to find the boundary between the scaling region and the Landau region. Estimating the region of applicability of the Landau theory by means of the Ginzburg criterion $CT/\xi^3 A^2 \ll 1$, we obtain that this boundary runs at a distance of the order of degrees from the phase-transition line. Therefore, at normal pressure, we are between the region of applicability of the Landau theory and the scaling region, and we cannot expect a universal temperature dependence of all the quantities.

¹L. D. Landau and E. M. Lifshitz, *Statisticheskaya fizika* (Statistical Physics) (Sec. 140), 2nd Edition, Nauka, 1965 [English translation published by Pergamon Press, Oxford, 1969].

²V. Ya. Baskakov, V. K. Semchenko and V. M. Byankin, *Zh. Eksp. Teor. Fiz.* **66**, 792 (1974) [*Sov. Phys.-JETP* **39**, 383 (1974)].

³K. G. Wilson and M. E. Fisher, *Phys. Rev. Lett.* **28**, 240 (1972).

⁴S.-K. Ma, *Phys. Rev. A* **7**, 2172 (1973).

⁵A. Z. Patashinskiĭ and V. L. Pokrovskii, *Zh. Eksp. Teor. Fiz.* **50**, 439 (1966) [*Sov. Phys.-JETP* **23**, 292 (1966)].

⁶P. G. de Gennes, *Phys. Lett.* **30A**, 454 (1969).

⁷R. Alben, *Phys. Rev. Lett.* **30**, 778 (1973).

⁸B. Chu, C. S. Bak and F. L. Lin, *Phys. Rev. Lett.* **28**, 1111 (1972).

⁹T. C. Lubensky and R. G. Priest, *Phys. Lett.* **48A**, 103 (1974).

¹⁰T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.* **25**, 503 (1970).

Translated by P. J. Shepherd
203