Landau theory of continuous liquid-crystal transitions

V. I. Marchenko

Institute of Solid-State Physics, Academy of Sciences of the USSR, Chernogolovka, Moscow Province

(Submitted 21 May 1991)
Zh. Eksp. Teor. Fiz. **100**, 1370–1377 (October 1991)

It is shown that continuous transitions from the liquid to the crystalline state are possible in the Landau theory of second-order phase transitions. Modulation of the density as a result of such transitions is a quadratic function of the order parameter represented by the correlation function of the density fluctuations. Different types of structures—smectics, crystals, incommensurate crystals, and quasicrystals—may occur, depending on the nature of the continuum of invariants in the Landau expansion.

It is usually assumed that crystalline ordering can appear only as a result of a first-order phase transition. This is based on an analysis of the feasibility of a second-order phase transition in an isotropic liquid[1] when the order parameter is the spatial modulation of the density

$$\rho(\mathbf{r})-\rho_0=\sum \rho_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}. \tag{1}$$

Since the quantities $\rho_{\mathbf{k}}$ remain invariant under transformations of the elements of the proper symmetry group of the vector **k** (see §134 in Ref. 2), the Landau expansion includes third-order invariants. However, this case does not allow for all the possibilities in the continuous transition of a liquid to a crystal.

Consider the correlation functions of the density fluctuations $\langle\Delta\rho_1\Delta\rho_2\rangle$, $\langle\Delta\rho_1\Delta\rho_2\Delta\rho_3\rangle$, and generally $G_n=\langle\Delta\rho_1\Delta\rho_2...\Delta\rho_n\rangle$, where $\Delta\rho_1=\rho(\mathbf{r}_1)-\rho_0$. We select the arguments of the function G_n in the form of $n-1$ linearly independent combinations of the coordinates $\mathbf{r}_1$, which are not affected by arbitrary translations, and of the coordinate $\mathbf{r}=(\mathbf{r}_1+\mathbf{r}_2+...+\mathbf{r}_n)/n$. In the homogeneous case the correlation functions are independent of r. In the inhomogeneous case we can expand their Fourier series

$$G_n(\mathbf{r})=\sum_{\mathbf{k}} G_{n\mathbf{k}}e^{i\mathbf{k}\mathbf{r}}. \tag{2}$$

The quantities $G_{n\mathbf{k}}$, which are functions of the $(n-1)$th coordinate, generally not remain invariant under the transformations of the elements of the proper symmetry group of the vector **k**.

The proper symmetry group of the vector $\mathbf{k}=0$ of a two-dimensional liquid is the group $C_{\infty v}$ (representing arbitrary rotations and reflections). This group has two one-dimensional representations, the identity and the pseudoscalar, and the functions transforming in accordance with these representations remain invariant under rotation but exhibit sign reversal as a result of reflection. All the other representations are two-dimensional and split into two classes: the functions belonging to the first class $(m,\ +)$ transform as a pair of functions $(\sin m\varphi,\ \cos m\varphi)$, where m are natural numbers and φ is angle; the functions belonging to the second class $(m,\ -)$ transform as products of a pseudoscalar and of a function with the moment m belonging to the first

sequently, has two one-dimensional representations, the identity and the pseudoscalar.

In the case of a three-dimensional liquid the proper symmetry group of the vector $\mathbf{k}=0$ is $SO(3)\times I$ (arbitrary rotation and inversion). Its irreducible $(2L+1)$-dimensional representations $(L,\ \pm)$, where L are integers, can be described as follows: 1) $(L,\ +)$ correspond to the usual spherical functions with angular momentum L; 2) $(L,\ -)$ correspond to products of the spherical functions and a pseudoscalar. The proper symmetry group of a nonzero wave vector is $C_{\infty v}$, representing rotation about the direction **k** and reflection by planes parallel to the wave vector **k**; its representations are given above.

The star of the wave vector **k** (see §134 in Ref. 2) consists of all arbitrarily oriented vectors with the same magnitude, so that representations with nonzero wave vectors are infinite-dimensional.

We expand the functions $G_{n\mathbf{k}}$ in terms of irreducible representations of the proper symmetry group of the wave vector. The pair correlation function may contain only the even moments with the "normal" behavior on reflection because of the transposition symmetry of the coordinates $G_2(\mathbf{r}_1,\mathbf{r}_2)=G_2(\mathbf{r}_2,\mathbf{r}_1)$: in the two-dimensional case if $\mathbf{k}=0$, the representations are $(m,\ +)$, whereas for a finite value of **k** there is only identical representation; in the three-dimensional case if $\mathbf{k}=0$, the representations are $(L,\ +)$ and for a finite **k**, they are $(m,\ +)$. In the expansion of the triple correlation function G_3 there are no limitations in the two-dimensional case. In the three-dimensional case any representation is obtained only in the quadruple correlation function G_4. In the case of the triple correlation function there is no anomalous behavior with respect to reflections: these representations are either pseudoscalar or $(L,\ -)$, $(m,\ -)$, since four points must be distributed in the three-dimensional space in order to specify a figure in which inversion is violated.

These ideas on the correlation functions are put forward above only to demonstrate the generally trivial circumstance that all the irreducible representations correspond to quite simple physical parameters and when they are introduced into the theory there is no need to invoke any models, such as those for the structure of molecules composing a liquid crystal (any symmetry breaking is permissible even in the case of a monatomic liquid).

correlation functions which include an anomalous contribution representing a change in the symmetry. It is natural to select the order parameter to be that part of the correlation function which minimizes n. The modulation of the density in a transition must then be a quadratic function of the order parameter, since expansion of the square of any representation always includes the identity representation of the symmetry group of the doubled wave vector.

Let us assume that the representation active in a transition is pseudoscalar with a finite wave vector. The quadratic (in components of the order parameter $\eta_{\mathbf{k}}$) term in the expression for the energy is

$$E_2=\sum_{\mathbf{k}} A(T,|\mathbf{k}|)|\eta_{\mathbf{k}}|^2, \tag{3}$$

where $\eta_{\mathbf{k}}=\eta^*_{-\mathbf{k}}$ because the order parameter (correlation function) is real. Near the phase transition the function A has the following form in the vicinity of its minimum:

$$A(T,|\mathbf{k}|)=\alpha(T-T_c)+g(k-f)^2. \tag{4}$$

There are no cubic invariants for the pseudoscalar representation. In the two-dimensional case symmetry considerations lead to the following fourth-order invariants for vectors with the same magnitude (the corresponding graph is shown in Fig. 1a):

$$E_4=\sum_{\mathbf{k},\mathbf{p}} b(\theta)|\eta_{\mathbf{k}}|^2|\eta_{\mathbf{p}}|^2. \tag{5}$$

Here, $b(\theta)$ is a function of the angle θ between the vectors $\mathbf{k}$ and $\mathbf{p}$ ($|\mathbf{k}|=|\mathbf{p}|=f$), which satisfies the obvious conditions

$$b(\theta)=b(-\theta),\quad b(\theta)=b(\pi-\theta). \tag{6}$$

In the future we shall represent the pairs of vectors $\mathbf{k}$ and $-\mathbf{k}$ by a single line segment. For example, the graphs in Figs. 1a and 1b are fully equivalent.

At first sight it is surprising that the function $b(\theta)$ is essentially nonanalytic at the point $\theta=0$. In fact, Eq. (5) should be regarded as the result of going over to a Fourier series in the following functional:

$$E_4=\iiiint D(1,2,3,4)\eta(1)\eta(2)\eta(3)\eta(4)\,d^2\mathbf{r}_1\,d^2\mathbf{r}_2\,d^2\mathbf{r}_3\,d^2\mathbf{r}_4, \tag{7}$$

where the kernel D is symmetric under transpositions of the arguments and falls rapidly at distances between the points $\mathbf{r}_i$ and $\mathbf{r}_j$, which are large compared with the interatomic distance (short-range action). These simple calculations yield

$$E_4=\sum_{\mathbf{k},\mathbf{p}} \beta(\theta)|\eta_{\mathbf{k}}|^2|\eta_{\mathbf{p}}|^2-\beta_0\sum_{\mathbf{k}}|\eta_{\mathbf{k}}|^4, \tag{8}$$

where $\beta_0=\beta(0)$ and the function $\beta(\theta)$ is

$$\iiiint D(1,2,3,4)\exp i[\mathbf{k}(\mathbf{r}_1-\mathbf{r}_2)+\mathbf{p}(\mathbf{r}_3-\mathbf{r}_4)]\,d^2\mathbf{r}_1 d^2\mathbf{r}_2 d^2\mathbf{r}_3 d^2\mathbf{r}_4, \tag{9}$$

which is obviously analytic. Comparing Eqs. (5) and (8), we can demonstrate that

$$b(\theta)=\beta(\theta)$$

if $\theta\neq 0$ and

$$2b(0)=\beta(0)$$

if $\theta=0$. The following point is of importance. In the first sum in the energy of Eq. (8) there are terms ($\mathbf{k}$, $-\mathbf{k}$, $\mathbf{p}$, $-\mathbf{p}$) for $\mathbf{p}=\mathbf{k}$ and $\mathbf{p}=-\mathbf{k}$, and these terms correspond to the same energy contribution. The second sum serves to remove the extraneous terms. This nonanalyticity ensures that a finite number of wave vectors appears at a phase transition.

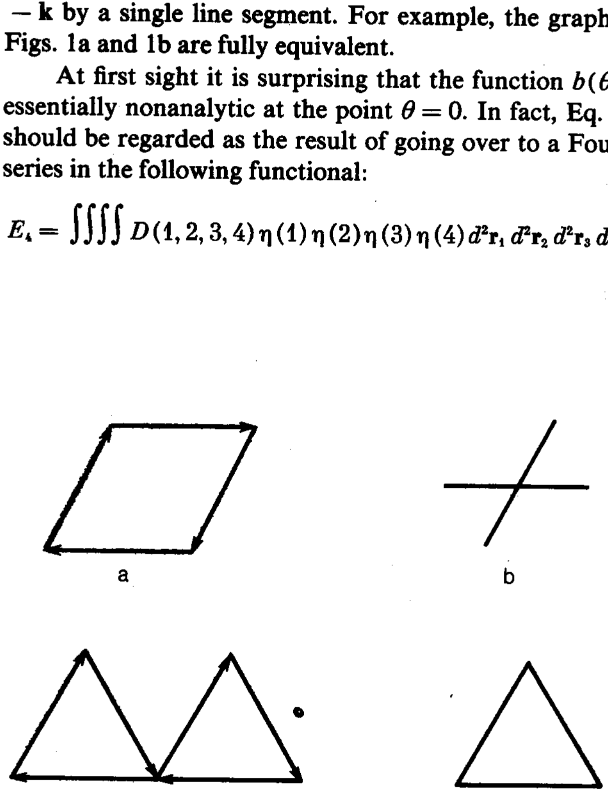
Varying the total energy E, i.e., the sum of Eqs. (3) and (8), we find the equilibrium equation for $\delta\eta^*_{\mathbf{k}}$:

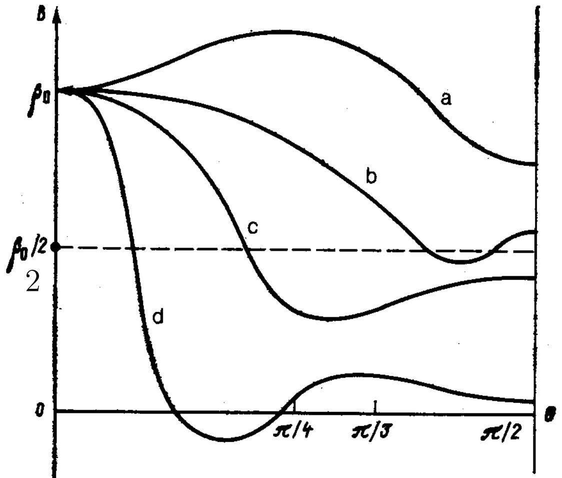
$$\eta_{\mathbf{k}}\Big\{\alpha(T-T_c)-2\beta_0|\eta_{\mathbf{k}}|^2+2\sum_{\mathbf{p}}\beta(\theta)|\eta_{\mathbf{p}}|^2\Big\}=0. \tag{10}$$

It follows from the condition (6) that the function $\beta(\theta)$ has extrema (such as a minimum or a maximum) at $\theta=0$ and $\theta=\pi/2$. The absolute minimum may be attained at some arbitrary value $\theta_{\min}$. Let us assume that the function $\beta(\theta)$ has the form of the representations in Fig. 2a, when only two harmonics η_f and η_{-f} (Fig. 3a) appear at a phase transition and we have

$$\eta_2{}^2=2|\eta_f|^2=\alpha(T_c-T)/\beta_0=\tau. \tag{11}$$

The symmetry of this smectic is due to the following ele-





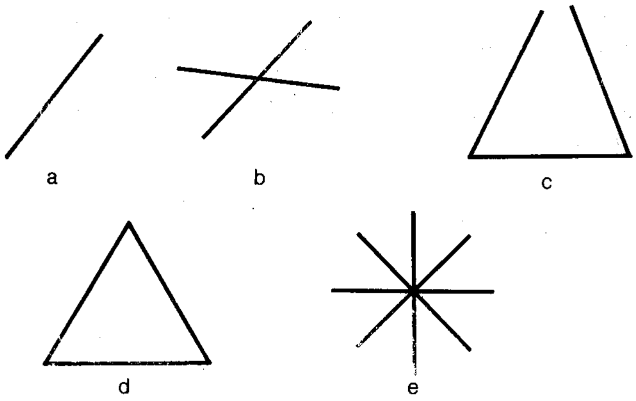


FIG. 3.

ments: the glide line representing the product of reflection and translation by π/f along the reflection line; reflection about a normal to the glide line; and arbitrary translations along this line. The condition for stability of the smectic phase against small perturbations reduces to the inequality

$$2\beta(\theta)-\beta_0>0. \tag{12}$$

If the function $\beta(\theta)$ varies, for example, in moving along a phase transition line in the p–T diagram, its minimum may drop to the critical value $\beta_0/2$. We shall show that up to this moment all the other solutions are characterized by a higher energy. With the exception of the angle $\theta=0$, we replace the function $\beta(\theta)$ with a constant $\beta_{\min}$ and then we can obviously reduce the energy of any solution. Next, summing the expressions in the braces for all $N>2$ vectors corresponding to a given solution, we obtain

$$\eta_N^2=\frac{N\beta_0\tau}{2(N-2)\beta_{min}+2\beta_0}, \tag{13}$$

which is less than the magnitude of the quantity given by Eq. (11) as long as the condition (12) is satisfied. However, the lowest energy in the Landau theory is the property of a state with the maximum absolute value of the order parameter.

If $\beta_{\min}=\beta_0/2$, then the energy minimum corresponds to structures with the wave vectors $\mathbf{f}_1$ and $\mathbf{f}_2$ inclined at an angle $\theta_{\min}$ to one another and with the arbitrary ratio $|\eta_{f1}/\eta_{f2}|$. The degeneracy is lifted if we allow for terms of the eighth order. Consequently, we either have a first-order transition to the crystalline state (Fig. 3b) with identical values of $|\eta_{f1}|=|\eta_{f2}|$, when the magnitude of the order parameter is

$$\eta_4^2=2\beta_0\tau/(2\beta_{min}+\beta_0), \tag{14}$$

or an intermediate phase and its ratio $|\eta_{f1}/\eta_{f2}|$ varies from zero to unity. In the latter case the crystal symmetry reduces to a twofold axis and translations. The crystal symmetry corresponding to Eq. (14) for $\theta_{\min}\neq\pi/2$ is governed by mutually perpendicular glide lines along the directions of the vectors $\mathbf{f}_1\pm\mathbf{f}_2$ with translations $\pi/f\cos(\theta_{\min}/2)$ and $\pi/f\sin(\theta_{\min}/2)$. If $\theta_{\min}=\pi/2$, the C_4 axis should be added to the symmetry elements.

any definite conclusions about the states with the minimum energy. Therefore, we assume first that the condition (12) is satisfied almost everywhere with the exception of a small interval near the angle $\theta_{\min}$. Moreover, we assume that $\beta_{\min}$ is only slightly less than $\beta_0/2$ (Fig. 2b).

If the angle $\theta_{\min}$ is not equal to $\pi/2$, we find that moving along the phase transition line changes the angle, which may become $\pi/2$ or $\pi/3$. When $\theta_{\min}$ becomes $\pi/2$, a second-order phase transition to a crystal with a higher symmetry then takes place. In this state the approach to the angle $\pi/3$ is impossible. A transition to a state which differs fundamentally from that of the crystal symmetry takes place first.

Expanding near the minimum function $\beta(\theta)$,

$$\beta(\theta)=\beta_{min}+{}^1/_2\beta''(\theta-\theta_{min})^2, \tag{15}$$

we can readily analyze the phase diagram as $\theta_{\min}$ approaches $\pi/3$. Critically close to the angle $\pi/3$ when

$$\delta_c^2=(\theta_{min}-\pi/3)^2=(\beta_0-2\beta_{min})/\beta'' \tag{16}$$

we find that an incommensurate density wave appears in a continuous manner in the crystal and this wave is directed at an angle $\theta_3=(2/3)\pi-(1/2)\delta_c$ to one of the lattice vectors (Fig. 3c). Therefore, the orientational and translational symmetries are lost completely. A closer approach to the angle $\pi/3$ rapidly increases the amplitude of the new wave and for $\delta_c/2$ a continuous transition to a crystal with the hexagonal symmetry takes place (Fig. 3d).

It is worth noting the following circumstance: these structures are described by an order parameter of the type

$$G^*=\sum_{\mathbf{f}}(\eta_{\mathbf{f}}\Phi_{\mathbf{f}}e^{i\mathbf{f}\mathbf{r}}+\eta_{\mathbf{f}}^*\Phi_{\mathbf{f}}^*e^{-i\mathbf{f}\mathbf{r}}), \tag{17}$$

where $\Phi_{\mathbf{f}}$ are pseudoscalar functions of the arguments given above and these functions are generally complex, i.e., they can be represented in the form

$$\Phi_{\mathbf{f}}=(\Phi_{\mathbf{f}}'+i\Phi_{\mathbf{f}}'')e^{i\varphi_{\mathbf{f}}}, \tag{18}$$

where the functions $\Phi_{\mathbf{f}}'$ and $\Phi_{\mathbf{f}}''$ are real and linearly independent, whereas the phase $\varphi_{\mathbf{f}}$ is simply an arbitrary number. The functions $\Phi_{\mathbf{f}}'$ and $\Phi_{\mathbf{f}}''$ corresponding to different vectors $\mathbf{f}$ differ only by substitution of the variables corresponding to rotation. It must be stressed that any relationship between the functions is determined not only by the symmetry considerations. In general, the expansion (17) may contain different functions Φ corresponding to different wave vectors. However, in the case of a phase transition we are interested in an instability corresponding to a definite change in state for a given wave vector. The change described by the functions $\Phi_{\mathbf{f}}'$ and $\Phi_{\mathbf{f}}''$ should, for reasons of symmetry, be the same for different wave vectors, apart from substitution of the variables. There is no reason to expect a relationship between the phases $\varphi_{\mathbf{f}}$, because the addition of some number to a phase represents a wave shift along the wave vector.

In the case of a smectic the freedom of the phase means that the structure may exhibit a translation relative to the liquid at rest. A crystal with four vectors has two phases, corresponding to the feasibility of lattice translation along two directions. A hexagonal structure with six vectors has three phases, and their sum becomes fixed when we allow for of the reflection symmetry of this crystal; reflection results in a transition from one possible state to another). In an incommensurate crystal all the phases are free. Structures of this kind are characterized by a specific phase symmetry: the state does not change when 2π is added to any of the phases.

We can easily show that quasicrystalline states may appear and they exhibit not only the phase symmetry, but noncrystalline rotation elements. We assume, for example, that the function $\beta(\theta)$ has the form shown in Fig. 2c, that its absolute minimum is located somewhere in the vicinity of the angle $\pi/4$, and there is no function $\beta(\theta)$ with special symmetry. The magnitude of the order parameter of the structure with the C_8 symmetry (Fig. 3e) is

$$\eta_8{}^2=\frac{4\beta_0\tau}{\beta_0+4\beta(\pi/4)+2\beta(\pi/2)}\,. \qquad (19)$$

Comparing the state with possible competitors, such as the conventional crystals with four vectors and the angles $\theta_{\min}$ and $\pi/2$, we find that when the relatively weak condition

$$4\{\beta(\pi/4)-B_{\min}\}<B_0-2\beta(\pi/2) \qquad (20)$$

is satisfied, the proposed structure has a lower energy. We can easily show that, as in the above case of a structure with six wave vectors, we can expect multicritical behavior with incommensurate and quasicrystalline phases.

If the function $\beta(\theta)$ has the form shown in Fig. 2d, i.e., when beginning from a certain small angle θ_0, it is small compared with β_0, then—as θ_0 decreases—a series of quasicrystalline states should be observed and should have symmetric N-ray stars with the number N increasing in proportion to θ_0^{-1}. A more refined study of the behavior of the function β may reveal the appearance of several wave vectors with random mutual orientation (incommensurate crystals).

In the three-dimensional case the fourth-order invariants are parametrized by two angles θ_1 and θ_2 (see Fig. 4) and the energy E_4 is

$$E_4=\sum\beta(\theta_1,\theta_2)\eta_{k1}\eta_{k2}\eta_{k3}\eta_{k4}-\beta_0\sum|\eta_k|^4, \qquad (21)$$

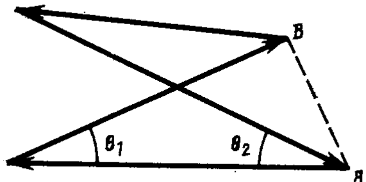
where the function β is real, since it is not affected by spatial reflection and the product of the parameters η_k transforms into a complex conjugate, because on reflection the vectors are transposed in such a way that the effect is equivalent to the reversal of their direction. Following the changes in the figure shown in Fig. 4, we can easily see that variation of their angles and plotting of figures consisting of exactly the same vectors but with a different closure demonstrates that the function $\beta(\theta_1,\theta_2)$ need be known only in the interval $[\theta_1,\theta_2]$ governed by the following condition: for a constant value of θ_1, the angle θ_2 varies from zero to its maximum $\theta_{\max}$ when the angle in the figure at the edge AB becomes $\pi/2$, i.e.,

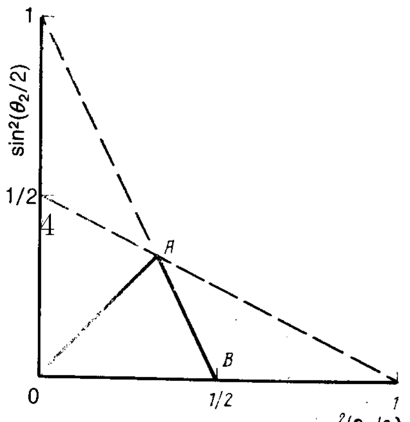
$$\sin\frac{\theta_{max}}{2}=2^{-1/2}\cos\frac{\theta_1}{2} \qquad (22)$$

and, since the function β is obviously symmetric under transposition of the arguments, the required region represents the triangle ABO shown in Fig. 5 and located in the $\sin^2(\theta_1/2)$, $\sin^2(\theta_2/2)$ plane. The symmetry of the function β means that the corners of the triangle correspond to local minima or maxima, whereas along the sides the derivative with respect to one of the angles (or with respect to a certain combination of the angles) vanishes.

Investigation of the possible situations is basically the same as in the two-dimensional case. However, we have to study a large number of competing structures. Let us assume that, for example, the function has a local minimum somewhere in the vicinity of the points $(0,\pi/3)$. Then, in addition to the two-dimensional structures in Figs. 3b, 3c, and 3d discussed above (in the three-dimensional case they are smectics), we have to allow for crystals: a) with three pairs (±) of the wave vectors (representing edges of a tetrahedron meeting at the same vertex); b) with the same number of vectors, but with a mutual orientation slightly differing from symmetric and with very different values of $|\eta_k|$; c) with six (corresponding to all the edges of a tetrahedron) pairs of vectors; d) with four pairs of vectors oriented along the edges of an octahedron meeting at one symmetric vertex; e) a crystal which is in the same relationship to the preceding case as case b to case a; f) a crystal with six pairs of vectors oriented along the edges of an octahedron; g) a quasicrystal with vectors oriented along the edges and diagonals of an icosahedron. Depending on the ratio of the parameters, we have all the structures except the smectic in Fig. 3b. The energy E_4 is the same for the smectic in Fig. 3d and for the crystal a; this degeneracy can be lifted if we allow for terms of sixth order (Figs. 1c and 1d).

These transitions do not exhibit a Lifshitz instability. This instability reduces to loss of the order parameter from the wave vector representation characterized by a certain proper symmetry to a representation of a different vector with a lower symmetry. In the case of a liquid the only vector special in respect of the symmetry is $\mathbf{k}=0$. We can also say that the selection of the representation with $|\mathbf{k}|=f$ [see Eq.





(4)] corresponds precisely to the absence of the Lifshitz invariant, but for any other value of **k** there is such an invariant: it is proportional to the derivative $\partial_{\mathbf{k}} A$. In the case of crystals the situation is similar. When the Lifshitz invariant exists in accordance with the symmetry considerations and changes the symmetry to a different one, but with the same proper symmetry of the wave vector (in the class of vectors of the general position on the axis, on a plane, or simply a general position without any proper symmetry), the transition is possible for that value of **k** for which the coefficient is minimal in quadratic terms of the Landau expansion.

It should be pointed out also that in the case of phase transitions described by two-dimensional representations of the wave vector group there are several functions representing the structure of the continuum of fourth-order invariants.

We shall elucidate the Ginzburg–Levanyuk criterion for these transitions. The "roton-like" behavior of the function $A(\mathbf{k})$ of Eq. (4) has the effect that the fluctuation correction to the specific heat (see §147 in Ref. 2) depends weakly on the dimensionality d of space:

$$\Delta C=\lambda_d T_c^2(\alpha/g)^{1/2}|T-T_c|^{-3/2}, \tag{23}$$

where the constant λ_d is equal to f for $d=2$ and to f^2/π for $d=3$. Comparing Eq. (23) with the characteristic jump in the specific heat α^2/β_0, we can find the condition of validity of the Landau theory:

$$\alpha|T-T_c|\gg(\lambda_d\beta_0)^{2/3}g^{-1/3}T_c^{4/3},$$

i.e., we must have

$$(\lambda_d\beta_0)^{2/3}g^{-1/3}T_c^{1/3}\ll 1.$$

[1] L. D. Landau, Zh. Eksp. Teor. Fiz. 7, 627 (1937).

[2] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Vol. 1*, 3rd ed., Pergamon Press, Oxford (1980).

Translated by A. Tybulewicz