Theory of weak crystallization

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A complete theory, based on the soft mode mechanism proposed by Landau [Zh. Eksp. Teor. Fiz. 7, 627 (1937)], is developed for a liquid-crystal transition with low latent heat. Thermodynamic fluctuations alter substantially the results and change the form of the phase diagram. Thus, besides the transition from a liquid to a body-centered cube, the only transition possible without allowance for fluctuations, direct transitions appear from the liquid into other cubic phases and a one-dimensional density wave. Transitions into quasi-crystalline states, particularly the icosahedral state, are discussed.

1. INTRODUCTION

Landau's theory of the cholesteric state and of the so-called blue phases was subsequently considered by a number of workers (see, e.g., the review by Alexander13 from the standpoint of the symmetry of phases that can result from weak crystallization.

Interest in weak crystallization was aroused anew by interest in weak crystallization was aroused anew by the theory of the cholesteric state and of the so-called blue phases. The first in this field was the work by Dmitriev and one of us.1 We wish to single out here specially two seminal investigations in this field, by Kleinert and Maki6 and by Grebel, Hornreich, and Strickman.15 It is interesting, as indicated by Kleinert and Maki, that an icosahedral quasiperiodic phase can be realized in a metastable state in cholesteric crystals. Finally, recent experimental discoveries stimulated a burgeoning interest in quasiperiodic phases, particularly planar pentagonal icosahedral ones. A number of studies in this field, within the framework of Landau's approach, followed right away.16,17

It became clear long ago, however, that even though all the transitions described by the energy (1) are jumpslike, thermodynamic fluctuations can influence weak crystallization substantially. The reason is that the order parameter of the theory has in fact an infinite number of component (k traces a whole sphere of radius k0), and this naturally enhances the role of the fluctuations (details will be given in Sec. 4). The first investigation in this direction was carried out by one of us back in 1975.17 A transition was considered into the state of a density wave (the analog of a cholesteric helix) defined by only one vector k. According to the Landau theory, such a transition should be continuous in view of the absence of third-order terms. Allowance for the fluctuations, however, transforms it into a first-order transition, the absence of cubic terms notwithstanding. A correct general conclusion reached in Ref. 12 is that the liquid-crystal transition is always of first order whether or not triangles are present in the reciprocal lattice (Fig. 1). Nothing like a complete investigation of the phase diagram, with allowance for fluctuations, was carried out at that time. The estimate of the energy of the non-one-dimensional phases contained errors which are corrected in the present paper.

The phase diagram with allowance for fluctuations was investigated later by Dyugaev18 for the case of a pion condensate. His result agrees in principle with ours in the strong-fluctuation limit, viz., there is one L→BCC transition.

\[ \delta \phi_p = \sum_k \lambda_k \phi_k \]

appears in the liquid. By virtue of the isotropy, this expansion contains in the leading approximation only vectors k of fixed length k0, for which the coefficient of the second-order term in the Landau expansion has a minimum. The corresponding Landau energy is

\[ \phi_k = \sum |k| + \sum \lambda_k \phi_k \phi_{k'} \]

(1)

To be able to discard the higher orders in a theory of this kind, it is necessary that the amplitudes \( \phi_k \) be small. This yields

\[ \max \{ \phi_k \} < \lambda. \]

Landau's analysis of Eq. (1) has shown immediately that the absolute minimum of the energy (1) is reached for a set of momenta k from which it is possible to construct a maximum number of closed triangles (Fig. 1). The transition to such a state will take place, regardless of the sign of \( \phi_k \), already at \( \tau > 0 \), i.e., will be a first-order transition.

The first to consider weak crystallization in greater detail were apparently Kirzhnits and Nepomnyashchii.6 They have pointed out that the phases described by sets of k with triangles are BCC. On the other hand, they failed to notice that, if \( \lambda \) depends strongly on the momenta and \( \tau \) is long enough, absolute stability can be possessed also by phases without triangles, such as FCC. A transition into an FCC phase can occur only via the chain of first-order transitions L→BCC→FCC.

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tion. Dyugaev's paper is in itself quite complicated. He used a microscopic approach and took into account simultaneously the contributions of the nucleons and pions. It is therefore difficult to compare his results with a phenomenological approach such as Eq. (1).

We present below, for the simplest case of an interaction \( \lambda \) that does not depend on the momenta, a complete analysis of the phase diagram, with allowance for the fluctuations, and follow it up with a description of metastable states (Sec. 2). Although the calculations seem trivial, we present them in reasonable detail, since many years of experience with studies of this type, for example of the blue phase,\(^3\) show that the calculations made by different workers are as a rule not in agreement.

Fluctuations produce two effects. The first is usual for any phase transition close to continuous, while the second is typical of the presence of a large number of order-parameter components. The calculations can be carried through to conclusion if the crystal has a large period (in atomic units), \( k_0 < 1 \), when the system does not come at all too close to a singular point and the fluctuations of the first type can be neglected. Let us carry out the corresponding estimates.

The Green's function in the liquid phase is obviously of the form

\[ G^{-1}(k) = -\varepsilon + \text{const} \left( |k| - k_0 \right)^3. \]  

A measure of the smallness of the usual fluctuation is the smallness of the diagram (Fig. 2a) at \( |k| > k_0 \) compared with \( \lambda \). This yields the known criterion \( \tau \gg \lambda^{1/3} \) which yields, combined with \( \tau < k_0 \),

\[ \lambda^{1/3} < \varepsilon < k_0. \]

This condition is, naturally, independent of the type of phase transition. If it is recognized, however, that \( k_0 \) is finite, i.e., that the order parameter has an infinite number of components, the diagram for the self energy (Fig. 2b) at \( \tau < k_0 \) turns out to be anomalously large. Its contribution \( k_0^2 \lambda \tau^{1/3} \) becomes comparable with \( \tau \) at the value \( \tau_\lambda \sim (\lambda k_0^3)^{1/3} \) that determines the fluctuational temperature of the transition. Substitution of \( \tau_\lambda \) in preceding inequality yields \( k_0^2 \ll \lambda \ll k_0 \).

For the reader not interested in the details of the calculations, we present their results.

As already mentioned, the fluctuation problem (1) is initially investigated in the simplest case \( \lambda(k_0^2 \lambda \ll k_0 \lambda) = \text{const} \). The theory can be made nondimensional in the variables

\[ \Phi \equiv \lambda \mu, \quad \frac{\lambda}{\mu}, \quad \frac{\lambda^2}{\mu^2}, \quad \frac{\lambda^3}{\mu^3}, \quad \frac{\lambda^4}{\mu^4}, \quad \frac{\lambda^5}{\mu^5}, \]

and the problem can be analytically solved completely. The natural variables for the phase diagram are \( \tau \) and \( k_0 \) (see Fig. 3 below). The quantity \( k_0 \) is a measure of the influence of the fluctuations: for small \( k_0 \) \((\mu/\lambda \ll 1)\) the transition is jumplike and without fluctuations. As \( k_0 \to \infty \) \((\mu/\lambda \gg 1)\) the temperature of a first-order transition is given, naturally by the already mentioned relation \( \tau_\lambda \sim (\lambda k_0^3)^{1/3} \).

In the absence of fluctuations \((k_0 = 0)\) there are in the three-dimensional case three absolutely stable phases BCC\(_1\), (the difference between BCC\(_1\) and the BCC\(_2\) phase that appears below is explained in Sec. 2), triangular phase \( \Delta \) (planar triangular lattice made up of liquid filaments), and a one-dimensional density wave \( 1 \). Lowering the temperature results in the transition cascade

\[ \text{L} \rightarrow \text{BCC}_1 \rightarrow \Delta \rightarrow 1. \]

This cascade was predicted by Kleinert and Maki,\(^5\) but no triangular phase was considered by Grebel et al.\(^7\) We note only that a direct comparison of the blue-phase theory\(^\dagger\) with our result is impossible, since an important role is played in the cholesteric phase by the order-parameter nematic component \( Q_{nm} \) with \( k = 0 \).

In the 2D case there is of course no BCC. The sequence of the transitions as the temperature is lowered is

\[ \text{L} \rightarrow \Delta \rightarrow 1. \]

Naturally, the equations that describe the \( \Delta \rightarrow 1 \) transition are independent of the dimensionality. The BCC\(_2\) and \( \Delta \) phases become narrower with enhancement of the fluctuations in the absolute-stability region. The BCC\(_1\) phase vanishes at a certain \( k_0 \) followed by the triangular phase \( \Delta \). This direct transition \( L \rightarrow 1 \) that survives in the case of large fluctuations can take place also if \( \mu/\lambda = 0 \) \((\mu/\lambda \gg 1)\) is essential for BCC\(_1\) and \( \Delta \). We have here a clear manifestation of the fact that the fluctuations themselves are capable of making the transition jumplike.

The phase diagrams plotted in the coordinates exactly defined by Eqs. (1), (4), and (19) are shown in Fig. 3.

\[ \tau^* \]

\[ r^* \]

\[ s^* \]

\[ t^* \]

\[ u^* \]

\[ v^* \]

\[ w^* \]

\[ x^* \]

\[ y^* \]

\[ z^* \]

\[ a \]

\[ b \]

\[ c \]

\[ d \]

\[ e \]

\[ f \]

\[ g \]

\[ h \]

\[ i \]

\[ j \]

\[ k \]

\[ l \]

\[ m \]

\[ n \]

\[ o \]

\[ p \]

\[ q \]

\[ r \]

\[ s \]

\[ t \]

\[ u \]

\[ v \]

\[ w \]

\[ x \]

\[ y \]

\[ z \]

\[ \text{FIG. 2} \]

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BCC region is too small to be drawn in the same scale as the $1 - L$ and $\Delta - L$ regions. The latter are shown on the principal part of Fig. 3. This part of the phase diagram is the same for 2D and 3D crystallizations, and in its scale the BCC and the end of the $1 - L$ line practically coincide with the origin in the two-dimensional case. The inset of Fig. 3 shows this vicinity. The dashed line is part of the $1 - L$ curve, which lands inside the BCC phase, in the 2D case. The external part of the $1 - L$ line is the same as in Fig. 3 and is independent of the dimensionality.

Besides the stable phases BCC, $\Delta$, and 1 there exist in the $\lambda = $ const model metastable crystalline phases. These are the orthorhombic phase, which includes in principle the FCC, hexagonal, and tetragonal systems and BCC. The triclinic system (and its particular cases—monoclinic, rhombohedral, and primitive cubic) is absolutely unstable. The model gives also a number of metastable quasiperiodic phases, primarily the icosahedral one.

The phase diagram (Fig. 3) which we have obtained in the theory with $\lambda (k, k', k, k') = $ const contradicts the simple crystallization concepts, from which it is expected that the order in the system increases with decrease of temperature. In this sense, the inverse sequence $L$, $1 - \Delta - \Delta - BCC$ would be natural. The cause is precisely the assumption that $\lambda$ is constant: as the temperature is lowered the amplitudes $\rho_{k}$ increase, the cubic terms that lead to energy gain for the crystals no longer play any role, and everything is determined by the value of $\lambda_{cr}$. Clearly, if $\lambda$ is independent of the interaction momenta its effective value is determined by a combinatorial factor which is minimal for a simple one-dimensional wave. It suffices at present to recall that in the case of weak crystallization we always have in general

$$\Phi \sim -c^{2}\lambda_{cr}.$$

Allowance for the dependence of $\lambda$ on the momenta, or more accurately on the angles between them, unearcs new possibilities. The analysis given in Sec. 3 shows that the phases that can be now absolutely stable (including also at low temperatures as $\tau \to -\infty$) are BCC, FCC, and curious-ly enough the simple cubic. As before, the rhombohedral phase is absolutely unstable. This is an immutable property of weak crystallization. The icosahedron 1 and other types of quasicrystals are in principle absolutely stable.

Of course, the dependence of $\lambda$ on the angles between $k$ actually introduces into the theory a large number of adjustment parameters. Therefore the construction of complete phase diagrams, which can now be in principle arbitrary, is hardly instructive although not too laborious. We recall finally that the one-dimensional structure 1 and the triangular $\Delta$, which are stable in the simple model, are realized in liquid crystals, viz., 1 is the smectic phase and $\Delta$ is the so-called disclastic phase. (The latter was first discussed as an abstract possibility by Landau$^{14}$.) It is simplest to include them in our theory as perturbations, by adding to (1) and arbitrarily weak interaction that is linear in the nematic tensor $Q_{\alpha\beta}$. This yields directly

$$Q_{\alpha\beta} = \frac{\partial \Phi}{\partial \rho_{k}} = \frac{1}{3} \delta_{\alpha\beta} \left( \frac{\partial \Phi}{\partial \rho_{k}} \right).$$

The interaction with $Q_{\alpha\beta}$ transforms thus the phase 1 into smectic $A$, and the phase $\Delta$ into disclastic. Finite fluctuations make possible direct transitions from a liquid into a smectic or disclastic. Of course, a realistic theory must allow for both the dependence of $\lambda$ on the angles and the finite character of the nematic tensor $Q_{\alpha\beta}$. It is readily conceivable that this leads to a variegated picture that describes real situations in liquid crystals.

2. SIMPLE MODEL $A(k, k', k, k') = $ const

We begin with the transformation of the fourth-order terms in (1). Since the density is real, the set of vectors $k$ consists of antiparallel pairs; each such pair, when necessary, will be labeled by Latin letters $n$ and $m$ ranging from 1 to the number $r$ of the independent vectors $k$. It is convenient to write the Fourier components of the density in the form

$$\rho_{n} = a_{n} \exp (i k_{n}).$$

We have three types of tetradrs $k, k, k, k'$:

$$kk-k-k-k-k-k-k,$$

and a nontrivial tetrad (Fig. 1) constituting a three-dimen-

sional closed quadrangle having no parallel sides.

With the foregoing taken into account, we can express the Landau energy in the form (cf. Refs 6 and 7)

$$\Phi_{n} = 2c^{2} \lambda + 12c^{4} - 65 \sum_{m} \rho_{m}^{2} + \sum_{m} \rho_{m}^{2} + 2 \sum_{n} \rho_{n}^{2} \rho_{m}^{2}, \quad (3)$$

where $A$ stands for the sum of the squares of the amplitudes

$$A = \sum_{n} a_{n}^{2},$$

and summation signs labeled n.t. denote sums over nontrivial (i.e., having no parallel sides) closed figures (Fig. 1). According to Ref. 12, to take the fluctuations into account it suffices to introduce self-energy corrections (Fig. 2b). This causes replacement of $\tau$ in the expression (2) for the liquid-phase Green's function by the reciprocal of the square of the correlation radius $x_{c}$ determined from the equation

$$x_{c} = 1 + 2 \lambda_{cr}^{2}, \quad \lambda_{cr} = -\lambda_{cr}^{2}.$$  \quad (4)

It is seen from (4) that $x_{c}$ is a positive quantity that increases monotonically with $\tau$. This means that the fluctuations stabilize the liquid phase all the way to $r \to -\infty$, when $x_{c}$ van-

ishes.

The correlation radius $r^{-1/2}$ in the crystalline phase is defined by a similar formula

$$x = r^{-1/2} \lambda_{cr} + 2 \lambda_{cr}^{2}.$$  \quad (5)

The expression for the energy, with allowance for the fluctuations, takes the form$^{12}$

$$\Phi = F(A) = 6c^{2} \sum_{m} a_{m}^{2} + \sum_{n} \rho_{n}^{2} \rho_{m}^{2} + \sum_{n} \rho_{n}^{2} \rho_{m}^{2}, \quad (6)$$

where $F(A)$ is determined by the relation (all the derivatives are taken, naturally, at a fixed temperature $r$ or, equivalent-

ly, at a fixed $x_{c}$):

$$dF/\lambda dr = 2c.$$  \quad (7)

It is more convenient to express $F$ in terms of $x$ with the aid of (5). Noting that

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we obtain directly
\[
\frac{dA}{dx} = \frac{1}{12\lambda} \left( \frac{a_k}{2\lambda} \right),
\]
(7)

we integrate with respect to \( A \) from zero to \( A \) corresponds to integration with respect to \( x \) from \( x_0 \) given by (4) to \( x \):
\[
F(A) = \int (x-\lambda)^2 + 3\lambda^2 (x-x_0). \tag{8}
\]

Expression (6) with \( F, x, \) and \( x_0 \) from (4), (5), and (8) yields the crystal energy reckoned from the liquid phase.

The relative stability of the phases is determined by that part of the energy (6) which depends on the specific configuration of momenta \( k, \) amplitudes \( a, \) and \( \theta \) for fixed \( A \).

We begin with the case when there are no nontrivial triangles or quadrangles. The structure-dependent part of the energy with 2\( \lambda \) momenta \((n + 1)A, (n + 1)A, (n + 1)A, (n + 1)A, \) is invariant to the phase of the triangle, the energy of such a state (which includes, for example, a hexagonal crystal) takes the form
\[
q = \sum a_i^2 + 12a_k a_k^2 \cos (\theta_i + \theta_j + \theta_k). \tag{9}
\]

Minimizing with respect to the amplitudes and phases, we get
\[
a_{ij} = a_{ij} = (A/3)^{1/2}, \quad q(\Delta) = -4/\mu (A/3)^{1/2} - 1/\lambda A. \tag{10}
\]

The simplest nontrivial lattice without triangles is a configuration of four momenta (Fig. 1b). It defines, as will become clear presently, an orthorhombic (OR) crystal. The energy depends now on the phases \( \theta \):
\[
q(\theta) = \sum a_i^2 + 4\lambda a_i a_j \cos (\theta_i + \theta_j + \theta_k). \tag{11}
\]

We get by minimizing with respect to the phases
\[
q = -\sum a_i^2 - 4\lambda a_i a_j \cos (\theta_i + \theta_j + \theta_k). \tag{12}
\]

The simplest is the \( \Delta \) lattice mentioned in the Introduction, made up of regularly arranged liquid filaments. There are three momenta \( k, \) and no rectangle can be formed from them:
\[
q = -\sum a_i^2 + 12a_k a_k \cos (\theta_i + \theta_j + \theta_k).
\]

One minimum of this expression coincides with (11) when \( a_4 = 0, \) and the other with (9) when \( a_1 = a_2 = a_3 = 0. \) The nontrivial extremum is a maximum.

The configuration next in complexity has two triangles and one quadrangle (see Fig. 1c). It is clear from the reasoning above that this is again an orthorhombic crystal OR. We write down directly the expression for the case of equal amplitudes \( a_i = (A/3)^{1/2} \) (it is a local minimum):
\[
q = \sum a_i^2 + 12a_k a_k \cos (\theta_i + \theta_j + \theta_k) - 12a_k a_k \cos (\theta_i + \theta_j + \theta_k). \tag{13}
\]

To minimize with respect to the angles, it makes sense to introduce the two variables
\[
\theta_i - \theta_j - \theta_k = \phi_i, \quad \phi_i = \theta_i - \theta_j - \theta_k.
\]

Clearly, the extremum corresponds to \( \phi_1 = \phi_2 = 0. \) We have
\[
\sin \Theta = \mu (\phi/2 + \lambda) \cos \Theta = 0.
\]

There exist thus two phases, one OR; with \( \Theta = 0 \) and \( \phi, \) and the other OR; with
\[
\cos \Theta = (A/3)^{1/2} \mu/8, \quad A > (A/3)^{1/2} \mu/8.
\]

Their energies are equal to
\[
q(\Theta) = \sum a_i^2 + 4\lambda a_i a_j + 12a_k a_k \cos (\theta_i + \theta_j + \theta_k),
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\[
q(\Theta) = -3a_k a_k \mu (\phi/2 + \lambda) \cos (\theta_i + \theta_j + \theta_k).
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Their energies are equal to
\[
q(\Theta) = \sum a_i^2 + 4\lambda a_i a_j + 12a_k a_k \cos (\theta_i + \theta_j + \theta_k),
\]
\[
q(\Theta) = -3a_k a_k \mu (\phi/2 + \lambda) \cos (\theta_i + \theta_j + \theta_k).
\]
six independent vectors $k_i$ that border the faces of a tetrahedron (Fig. 4). We have here four triangles and three rectangles. We define the three independent phases $\Theta_1$, $\Theta_2$ and $\Theta_3$ of the triangles by the equations

$$
\Theta_1 = \phi_1 + \phi_2 + \phi_3, \quad \Theta_2 = \phi_1 - \phi_2 + \phi_3, \quad \Theta_3 = \phi_1 + \phi_2 - \phi_3.
$$

The phase of the fourth triangle is, naturally, dependent:

$$
\phi_4 = \phi_1 + 2\phi_2 + \phi_3.
$$

Our choice of phases deliberately emphasizes the symmetry of the tetrahedron. On rotation about a threefold axis we have $1 \to 2 \to 3$, $4 \to 5 \to 6$ and $\Theta_1 \to \Theta_2$, $\Theta_2 \to \Theta_3$, $\Theta_3 \to \Theta_1$.

We write down directly the energy for equal amplitudes:

$$
\varphi(\lambda) = -8 \sin \pi \eta \left( |\lambda| A^4 + |\lambda_A| A^4 + |\lambda_B| A^4 \right) \sin \left( \frac{\pi}{2} \right).
$$

We confine ourselves to an extremum that has certainly the symmetry of a cube, when all the phases $\Theta_\alpha$ are equal. In this case $\Theta_i = 0$ and $\Theta_\alpha = 0$. Then

$$
6\pi \sin \left( \theta \sin \theta \right) + 8\lambda A^4 \sin 2\theta = 0.
$$

There are two obvious solutions with $\sin \theta = 0$, the phases $\text{BCC}_{1}$ and $\text{BCC}_{2}$. There exists, to be sure, one more extremum

$$
\cos \theta = -4 \lambda \left( \frac{A}{6} \right)^4 / \mu,
$$

but it is readily seen that it is not a minimum.

We write down the energies of the two BCC phases:

$$
\varphi(\text{BCC}_{1}) = -8 \lambda^4 \mu, \varphi(\text{BCC}_{2}) = -5 \lambda^4 \mu. \tag{12}
$$

Here, just as in the OR case, the BCC phase is preferred when the phases of the triangles are equal to $0$ or $\pi$, and those of the rectangles are zero. Preferred at large amplitudes is BCC_{2}, with the triangle phases equal to $\pi/2$ and those of the rectangles to $\pi$.

We consider, finally, one more (and actually the last) configuration of the momenta that make up a regular polyhedron—an icosahedron, i.e., a figure having 20 triangular faces (10 threefold axes), 30 edges (15 twofold axes) and 12 vertices (6 fivefold axes). The form of the icosahedron along a threefold axis is shown in Fig. 5. The faces and edges not shown are parallel to those shown.

The icosahedron has 15 phases $\Theta_\alpha$. Out of the 10 phases $\Theta_i$ of the triangles, only 9 are independent, since all 20 triangular phases are pairwise parallel and form a closed figure. We present by way of example two typical phases:

$$
\Theta_1 = \phi_1 + \phi_2 + \phi_3, \quad \Theta_2 = -\phi_1 - \phi_2 + \phi_3, \quad \Theta_3 = \phi_1 + \phi_2 - \phi_3.
$$

We have next 15 nontrivial quadrangles (equal to the number of edges). Each has the form shown in Fig. 1c. The phase of the quadrangle determined by the edge $n$ is the difference between the phases of the adjacent triangles, for example $\Theta_i \to \Theta_0$, for edge 2, etc. It is easy to verify that the contribution of the triangles is a maximum when all the phases $\Theta$ and $\Theta_\alpha$ are equal to zero or $\pi$. Clearly, this is an extremum. The energy of the corresponding quasicrystat I takes, for equal amplitudes, the form

$$
\varphi(\text{I}_{1}) = -8 \lambda^4 \mu. \tag{13}
$$

At large $A$ the preferred quasicrystal is again I, for which the contribution of the triangles is suppressed. We shall not write out the corresponding unwieldy equations, but present only an estimate, assuming the phases of the triangles to be $\pi/2$, and the phases of the rectangles to be $\pi$.

$$
\varphi(\text{I}_{1}) = -8 \lambda A^4. \tag{14}
$$

It can be seen that $\varphi(\text{I}_{1}) > \varphi(\Delta)$ and $\varphi(\text{I}_{1}) > \varphi(1)$, therefore the icosahedral phases are metastable.

A survey of Eqs. (9)-(12) shows that only the phases I, $\Delta$, and BCC, can be absolutely stable. The phases OR, BCC, and I are definitely metastable. Comparing (9), (11), and (12), we readily see that the phases BCC, $\Delta$, and I are absolutely stable respectively in the regions

$$
0 < A < \lambda \left( \frac{2(2-1)}{5-3} \right), \tag{15}
$$

To complete the theory we must calculate the energies of the phases I, $\Delta$, and BCC.

1. BCC. Using (6)-(8) and (12), we write down the conditions

$$
\varphi(\text{BCC}) = -8 \lambda^4 \mu, \tag{16}
$$

at constant $\lambda$ (or $\tau$) in the form

$$
\varphi(\lambda) = -8 \lambda^4 \mu. \tag{17}
$$

This yields

$$
\Delta = \frac{1}{16} \lambda \pm \left( \frac{1}{16} \lambda \right)^{1/2}. \tag{18}
$$
the dependence of \( \kappa \) and \( A \) on \( \tau \) or \( \kappa_2 \) is given by the intersection of the curves (16) and (5). From the equation given above for \( d\Phi / dx \) it follows that the minimum energy corresponds to the larger values of \( x \). Note that the amplitude corresponding to the maximum \( x \) lies in the metastable region.

The number of calculations needed is negligible. All can be carried out by using the dimensionless units indicated in the Introduction and by obtaining the energy as a function of the dimensionless temperature and fluctuation intensity. The character of the intersection of this curve with (5) is indicated in Fig. 6b. The minimum again corresponds to larger values of \( s \) and \( A \).

2. Triangular phase \( \Delta \). The condition \( d\Phi / dx = 0 \) takes the form

\[
d\Phi / dx = \frac{1}{\sqrt{3}}(1+\frac{3\kappa}{2\kappa^*})[1-(\frac{3\mu}{2\kappa^*})\mu-\Delta] = 0.
\]

The extremum takes place on the line

\[
A^* = -3\mu / \frac{2\kappa^*}{4}, (4\mu / (6\kappa^*+\pi / 2))^3
\]

The character of the intersection of this curve with (5) is indicated in Fig. 6b. The minimum again corresponds to larger values of \( s \) and \( A \).

3. Density wave 1.

\[
d\Phi / dx = \frac{1}{\sqrt{3}}(1+\frac{3\kappa}{2\kappa^*}) (\kappa-\Delta) = 0,
\]

or \( A = \kappa / 6\Delta \). We have again the situation of Fig. 6b.

The phase diagram is shown in Fig. 3 above. The transition temperatures in the Landau limit are

\[
\begin{align*}
\tau(L \rightarrow BCC) &= \frac{\mu_0}{3\mu} = 0.089\mu^3/\lambda^2, \\
\tau(BCC \rightarrow \Delta) &= -0.035\mu^3/\lambda^2, \\
\tau(\Delta \rightarrow 1) &= -2.152\mu^3/\lambda^2.
\end{align*}
\]

In the case of strong fluctuations, only the transition \( L \rightarrow 1 \) is left, at the temperature

\[
\tau(L \rightarrow 1) = -2.00(\mu^3)^{1/3}.
\]

The character of the phase diagram can be understood also qualitatively. At fixed fluctuations, the amplitude increases as the temperature is lowered, i.e., motion takes place over the region of the existence of the phases (15) from the left to right away from the liquid. On the contrary, with increase of the fluctuations at a fixed temperature, the amplitude decreases in accordance with Eq. (5), i.e., motion takes place along the chain (15) from right to left towards the liquid. This tendency is physically understandable, since enhancement of the fluctuations stabilizes the liquid phase. All this taken together leads to the following general conclusion: when the fluctuations increase the phases of intermediate amplitude vanish and the ultimately surviving phase is stable in the large-amplitude limit. We note an amusing situation described in Fig. 6a for BCC, and, according to (13), for I. On the upper metastable branch, the reciprocal correlation radius \( x^{1/3} \) in the crystalline phase decreases with decrease of the temperature \( \tau \) (and of \( \kappa_2 \)) and approaches zero, i.e., the point of absolute instability. In this case \( A \) is constant. Thus, we might be able in principle to observe a critical Ornstein-Zernike opalescence in cubic and icosahedral crystals. For \( x \) we have the equation

\[
\kappa = \kappa_2 / \xi^3, \quad \tau = -\kappa.
\]

As seen from (6a), the liquid state also loses stability in this place, although this last circumstance is undisputedly a property of the theory of weak melting.

The theory of two-dimensional crystallization in a model with constant \( \lambda \) is especially simple. There are naturally no nontrivial rectangles on a plane, and there is only one triangle. The fluctuations are given by the same equations (4)–(6) and (8). It is necessary only to replace in them the expression for \( A \) in (4) by another given by the diagram of Fig. 2b in the two-dimensional case:

\[
A = -\kappa_2 / 4.
\]

It follows from an analysis of the equations obtained above that only two phases, triangular \( \Delta \) and one-dimensional I, can be stable. All the remaining phases are saddles. The triangular phase is stable at small amplitudes, and the one-dimensional one at large ones; the inequality (15) is then transformed into

\[
0 < A < (\mu / 3)^{1/3} < A^*<\infty.
\]

The phase diagram (Fig. 3) is constructed with the aid of the expressions already obtained for the energy. It is necessary to add to (17) only the temperature of the \( L \rightarrow \Delta \) transition in the Landau limit:

\[
\tau(L \rightarrow \Delta) = -\mu^2/3^3 = 0.067\mu^3/\lambda^2.
\]

Strong fluctuations "eat up" the triangular phase. The equation for \( \tau(L \rightarrow I) \) remains (18) as before.

It is expedient to discuss the relation between the conclusions of the weak-melting theory, which requires a first-order transition for crystallization, with the picture developed by Halperin and Nelson (see Ref. 15) for the melting of a two-dimensional lattice. In this picture the lattice melts via two second-order transitions: from a crystal to a liquid crystal (LC) and from the liquid crystal to an isotropic liquid. We note first that, in contrast to three-dimensional liquid crystals, where the transition is always of first order, the \( L \rightarrow LC \) transition can in the two-dimensional case be also continuous, if the symmetry of the liquid crystal is not lower than fourfold. This remark reconciles in fact the two ap-
This is easily proved by differentiating (24) with respect to \( a_{n,m}^2 \):

\[
\frac{\partial \Phi}{\partial a_{n,m}^2} = 2 \alpha I + \alpha \sum_{i=1}^{4} \sum_{a} \left( \lambda(n,m) - \lambda_{i} \right) a_{n,m}^2 + a \sum_{\phi} \phi \partial \Phi / \partial \phi.
\]

We begin with the case when the nontrivial configurations of Fig. 1 are absent. The structure-dependent part of (26) for \( \phi \) vectors is given by:

\[
\Phi(\phi) = \sum_{n,m} I(n,m) a_{n,m}^2 + I = 2 \alpha I + \alpha \sum_{2} \left( \lambda(n,m) - \lambda \right) a_{n,m}^2 + a \sum_{\phi} \phi \partial \Phi / \partial \phi.
\]

With this normalization the energy \( \phi(1) \) of the one-dimensional wave is zero. If all the minima of \( \lambda(n,m) \) as functions of the angle are positive, then Eq. (27) has only one minimum for the one-dimensional wave, and all the remaining extrema are saddles. The situation is the same here as for \( \lambda = \text{const} \). Let now \( -\lambda_{c} \) be the smallest negative minimum \( \lambda \) corresponding to an angle \( \beta \) between the vector pairs. There is only one nonfrustrated configuration that yields (at least a nonlocal) minimum of (27). It is made up of four vectors with the same angle \( \beta \) between them (Fig. 7a). The end points of the vectors are then the vertices of a regular tetrahedron. The energy of this free quasicrystal (four free phases \( \Phi_{c} \) ) is:

\[
\Psi(\phi) = \sum_{n,m} I(n,m) a_{n,m}^2 + I = 2 \alpha I + \alpha \sum_{2} \left( \lambda(n,m) - \lambda \right) a_{n,m}^2 + a \sum_{\phi} \phi \partial \Phi / \partial \phi.
\]

States with smaller numbers of momenta will be saddles or maxima. Therefore the rhombohedral system, as stated in the Introduction, remains unstable.

Configurations with more than four momenta are frustrated. At large \( r \) a system with energy (27) for \( \lambda(n,m) \) can be typical glasslike properties, but a discussion of such questions is outside the scope of this article.

The fact that \( \lambda(n,m) \) depends only on \((v,v_{a})\) makes
it possible for states with $\beta = \pi/2$ to be minima, for it is precisely at $\beta = \pi/2$ that there are only three vectors with equal angles between them (Fig. 7a becomes degenerate). The corresponding state is a primitive cubic (PC) crystal. We present an expression for its energy in the simplest case (21). Note that in this case the nontrivial extrema $\beta \neq \pi/2$ do not exist at all. We have

$$\phi(\text{PC}) = -8\langle l_1, l_2, l_3, l_4, A \rangle^4, \quad A = l_3/l_1.$$  

We write down in the simplest variant also the energies of the FCC and BCC phases. The configuration $k$, that describes the FCC is an irreducible tetrad (Fig. 7b) with $k_i$ directed along the four body diagonals of a cube. All the angles $\theta$ between the vectors are equal, with $\cos \theta = -1/3$. After minimization with respect to the phases we have from (21), (22), and (26)

$$\phi(\text{FCC}) = -8\langle l_1, -l_2, l_2, -l_1, A \rangle^4 - 4\|l_1, l_2, l_3, A \rangle^4, \quad A = l_3/l_1.$$  

Finally,

$$\phi(\text{BCC}) = -4\langle l_1, -l_2, l_2, -l_1, A \rangle^4, \quad A = l_3/l_1.$$  

It must be taken into account in the calculations that in a tetrahedron (Fig. 4) the angles between the vectors are 60, 90, and 120°.

It is easily seen from Eqs. (28)–(30) that all the states, viz., of the one-dimensional wave $I$, PC, FCC, FEE and BCC, can be absolutely stable, depending on the relations between $\lambda_i$ and $\lambda_i$. The arguments in Sec. 2 show that in the case of strong fluctuations only the low-temperature phases of the Landau theory, in which the triangles are immaterial, survive. Therefore even in the rather simple model (21), (22) the fluctuations make possible, besides the direct transition $L \rightarrow I$, also the direct transitions $L \rightarrow \text{FCC}, \text{BCC,PC}$.

It was apparently the transition $L \rightarrow \text{BCC}$, for the strong fluctuation which was apparently obtained by Dyugaev,13 for in his problem the interaction was patently dependent on the angles.

In two-dimensional crystallization, allowance for the dependence of $\lambda$ on the angles makes rhombic, and particularly quadratic in the solutions stable. Let us compare the energies of $C_1$ and $A_2$:

$$\psi(\lambda) = -8\frac{1}{2}A_2[A_2^2 - 6\langle l_1, -l_2, l_2, -l_1, A \rangle^4, \quad A = l_3/l_1.$$  

$$\psi(C_1) = -8\langle l_1, -l_2, l_2, -l_1, A \rangle^4, \quad A = l_3/l_1.$$  

We see that at large $\lambda$ the quadratic lattice is preferred. At $\lambda > \pi/2$ a new transition cascade becomes possible $L \rightarrow \Delta \rightarrow \cdots$ or the direct transition $L \rightarrow \Delta$ for strong fluctuations.

4. SYMMETRY BREAKING AND FLUCTUATIONS

The concept of broken symmetry was formulated exactly by Pierre Curie back in the past century in the statement: "Only symmetry breaking produces a phenomenon." His meaning was that in view of the spherical symmetry of the main laws, the nature of the properties of all substances other than classical gases is connected in one way or another with symmetry breaking. However, it was Landau, in his 1937 papers,14 who made the concept of broken symmetry into a tool of theoretical physics, by distinguishing between symmetry losses in jumplike and continuous transitions, and by singling out two types of energy dependence on the order parameter.

The distinctive features of jumplike and continuous transitions are in Landau's theory singularities ("folds") of the general situations from the standpoint of catastrophe theory (a symmetrical "fold" in the continuous case). The situation changed radically when account was taken of fluctuations. The singularity at the point of a continuous transition turned out to be special and dependent on the details of the fluctuational functional, such as the number of components of the order parameter and the number of significant charges. It became clear gradually, however, that fluctuations can in principle also restore the universality, by turning a transition that is continuous according to Landau into a jumplike one. The first in this direction was the already mentioned paper by one of us,12 where it was shown in essence that even at the Landau critical points,15 where $\mu$ in Eq. (1) is zero, crystallization due to fluctuations is a first-order transition. A number of workers have shown next (see the citations in Refs. 17 and 18) that in a large number of transitions describable by a multicomponent order parameter and by a large number of charges, fluctuations transform a transition that is continuous according to Landau into a jumplike one. Finally, one of us has advanced the hypothesis that a general transition that is continuous according to Landau, i.e., with a large number of components of the order parameter and with more than two charges, has an overwhelming probability of becoming a first-order transition when fluctuations are taken into account. By the same token, exceptions are transitions of the simplest type, viz., one-component, quantum, ferromagnetic, and others. This hypothesis was subsequently proved by Michel.19

It is of interest to note that the statement that a general transition is of first order was formulated and proved by Dykhne and one of us20 even before the advent of the fluctuation theory of continuous processes. The general transition was regarded in Ref. 20 as a transition with a random Hamiltonian, and the corresponding free energy was determined, using the method of Yang and Lee,21 from the roots of a high-order random polynomial.

We note in conclusion that in the theory of weak crystallization the fluctuations act quite uniquely: they suppress the specific role of the triangles, by the same token erasing the difference between weak and normal crystallization. From the aforementioned general viewpoints this is, of course, not surprising.

Note: Following Eq. (2) is an erroneous statement that the theory is valid only if $k_3 < 1$ and $k_3 \leq \lambda < k_3$. Actually, however, the contribution of the fluctuations determined by Fig. 2a is always negligible, as shown by one of us in Ref. 12. This eliminates completely from the theory the constraint on the period of the crystal.

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1Here and elsewhere we use the quantities $\rho$, $k$, $\mu$, $I$, expressed in the appropriate atomic or thermal units.


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