Theory of condensed matter based on the hypothesis of a local crystalline order

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A new statistical theory of condensed matter is proposed. It is based on the assumption that the matter has a local crystalline order. The structure of an element of the matter is determined by the correspondence between the atoms and the sites of a regular "tangent" lattice. The concept of a dislocation is generalized to the case of a varying orientation of the tangent lattice. The probable configurations of the system, which generally do not have long-range order, are described in terms of strain, rotation, and dislocation-density fields. The Hamiltonian of the system is found as a functional of these fields in the approximation of small elastic stresses and small defect concentrations. The relations among the fields which parametrize the physical configuration (a compatibility condition) are determined. A method is proposed for summing over the distribution of dislocations in the Gibbs ensemble by transforming to an integration over the configurations of auxiliary fields, i.e., disorder parameters. The phase states of the system and phase transitions between these states are found.

1. INTRODUCTION

In the various states of condensed matter—crystalline, amorphous solid, and liquid (melt)—the energy of a volume element of the system is a strong function of the relative arrangement of the atoms. At a given density, the difference between the energies of different local configurations of atoms is large in comparison with the characteristic thermal energy; i.e., the relative positions of the atoms are correlated in a small element of the system. In condensed matter, only certain configurations of particles occur with an appreciable probability, implying that a definite local structure exists. In a crystal at a sufficiently low temperature the relative positions of atoms are determined to within small fluctuations by the elementary translation vectors of the ideal lattice. The local structure satisfies the conditions of the Fedorov theorem.[1] At higher temperatures, where the displacement amplitudes of atoms from their local-equilibrium positions become significant, the concept of local structure must be defined. The actual question is whether we can treat the instantaneous arrangements of atoms in an element of the condensed matter as a result of displacements from certain ideal positions.

Ideas regarding local ordering of condensed matter, not only in the crystalline state but also in the amorphous solid and the liquid state, are not new. They are discussed by Ubbelohde[2] and Ziman.[3] Various suggestions have been offered regarding the nature of the ordering. It has been postulated[4–6] that in phases other than crystalline phases the atoms group together in arbitrary clusters, which cannot be treated as part of a regular lattice. It has been suggested[7–9] that the local structure of liquids and gases is not a Fedorov structure, i.e., that the relative positions of the particles correspond to some regular packing in a space with a constant curvature. If these structures are to be embedded in a plane space, there would have to be a rather high density of topological structural defects. Condensed systems (in particular, $2D$ systems) have been described in several papers[10–14] under the assumption of a local crystalline order. Mitus' and one of the present authors[13,14] have offered a description of the melting of a crystal to form a liquid with a local Fedorov order on the basis of a simple phenomenological model.

The existence of states with a local Fedorov structure has been solidly established for $2D$ condensed systems.[15,16] In the liquid phase an ordered cluster contains 20 to 50 atoms.[16] For $3D$ systems there is apparently still no experimental evidence which directly demonstrates the existence of a local order in an amorphous solid or liquid state. There is indirect evidence[16,17] for a local crystalline order in melts of simple materials; the number of atoms whose relative positions are correlated is of order 10^2. In amorphous phases of substances with nonbinary interactions (directed bonds) the structure may be more complicated. Near the melting point, we recall, the amplitude of the probable displacements of atoms from their equilibrium positions is approximately a quarter of the interatomic distance. At such average thermal displacements, the positions of the atoms in a small element of the system may be regarded as fluctuations of an ideal configuration with either a Fedorov or non-Fedorov structure. We believe that a parametrization of configurations of condensed matter by means of ideal local lattices is to be preferred to approaches which assume non-Fedorov structures.

We will be discussing a condensed system whose local structure is approximately that of a regular lattice. For definiteness we assume that the local lattice is a simple cubic lattice. Most of the calculations below will be independent of the type of local lattice, and there will be no difficulty in repeating the arguments for more complicated lattices. Our purpose in this paper is to parametrize that class of configurations of a condensed system for which there is a local crystalline order and in which long-range order is generally absent. If matter with a local crystalline order is to be isotropic at the macroscopic scale, the orientations of elements of the system which are far from each other must be independent. We assume that this independence is realized because of a finite density of line structural defects, i.e., dislocations.

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Accordingly, in order to study a class of states of condensed matter which is broader than the state of a crystal with isolated defects, we need to describe both the local order and the disorder in the system. The specification of all the components of the order in a solid (the local structure and the defect distribution) makes it possible to parametrize the set of configurations which are statistically probable in the condensed state and to reduce the problem to a study of a system with an effective Hamiltonian of fields describing the local order and disorder. In this paper we propose a solution for this problem. Our description is self-consistent if the disorder in the system can be treated as a deviation from some completely definite crystalline order. This hypothesis of a local crystalline order of condensed matter is the basic suggestion of this paper.

2. TANGENT LATTICE AND BURGERS VECTOR IN A MEDIUM WITH A FINITE DISLOCATION DENSITY

As in the theory of real crystals, the problem of describing a local order consists of establishing the correspondence between atoms, which we treat as points, and the sites of an ideal lattice. Following this procedure, we can determine the local structure and its defects. As will be shown below, the concept of a dislocation in a locally ordered medium with a finite defect density is not the same as the well-known concept[18] of an isolated dislocation in a crystal. The most important distinction is that the Burgers vector does not remain constant along the dislocation; it undergoes a rotation determined in a self-consistent way by the entire set of defects.

We consider a configuration of condensed matter with a defect density low enough that the characteristic distance between dislocations is large in comparison with the interatomic distance. The assertion that the relative arrangement of atoms in a given element is approximately the same as the arrangement of lattice sites means that there can be a mutually one-to-one mapping of the atoms onto the lattice sites which conserves the neighborhood relation. The nearest neighbors of an atom correspond to those sites which are closest to its image on the lattice. Let us assume that this correspondence has been established in the vicinity of an atom with the coordinates $\mathbf{r}$. We impose a lattice on the system, and we choose image coordinates $\mathbf{r}'$ and a rotation $[\hat{g}(\mathbf{r})]$ with respect to the fixed basis so that the following quantity is minimized:

$$\Delta(\mathbf{r})=\sum_{n}(\mathbf{r}_n-\mathbf{r}_n')^2. \tag{1}$$

Here the $\mathbf{r}_n$ are the coordinates of the atoms which belong to the element under consideration, and $\mathbf{r}_n'$ are the coordinates of the corresponding sites. The radius of the region for which sum (1) is calculated must be smaller than the distance between dislocations. We call the regular lattice which minimizes (1) the "local lattice" or the lattice which is "tangent" to the system at point $\mathbf{r}$.

Let us construct a tangent lattice, choosing a neighboring atom as the center of region $\mathbf{r}_1$. In the neighborhood of the point r_1 there are atoms which do not belong to the neighborhood of the point r. Let us find the corresponding lattice sites for these atoms. Constructing the quantity $\Delta(\mathbf{r}_1)$ as in (1) for the new element, and minimizing it, we find the tangent lattice at the point $\mathbf{r}_1$ and the rotation $\hat{g}(\mathbf{r}_1)$. Moving atom by atom along some path in the system, we construct along this path a mapping of the atoms onto the sites of the local lattice, and we find its rotation field $\hat{g}(\mathbf{r})$. By definition, the only new work which is done on the mapping in a given step is for those atoms for which the mapping was not determined in the preceding step. The type of lattice and its parameters are assumed to be identical for all elements of the system. If the region of local order is large, there is no difficulty in establishing the values of the lattice parameters, since they fluctuate only slightly from element to element. If the fluctuations of the parameters are significant, we can find average values of the parameters over the system by (for example) minimizing the energy of the elastic strain with respect to the ideal positions. The construction described in this manner is correct if the number N of atoms whose relative positions are correlated is large in comparison with unity.

While the procedure for establishing the correspondence of the lattice is single-valued in each step, it is generally not single-valued for the overall path. As we move along a closed contour an ambiguity of the mapping may arise, a discrepancy of the corresponding contour on the lattice, which shows that the contour encloses a line defect. If the tangent lattice does not undergo a rotation, the construction is the same as that which is used in the theory of dislocations in a crystal to determine the Burgers vector of the defect. In this case the Burgers vector $\mathbf{b}$ is

$$\mathbf{b}=\sum_{i=1}^{3} n_i\mathbf{b}_i^0, \tag{2}$$

where the n_i are integers, and the $\mathbf{b}_i^0$ are the elementary translation vectors of the fixed lattice. In the case under consideration in the present paper, the orientation of the tangent lattice differs from point to point along the path, and for an arbitrary path there is no invariant concept of a discrepancy of the contour on the tangent lattice. If the defect density is low, we can ignore the rotation of the tangent lattice in a region small in comparison with the dislocation core. Shrinking the closed path to this size, we can determine the dislocation Burgers vector $\mathbf{b}(\mathbf{r})$ at the point r (within small corrections on the order of the defect density):

$$\mathbf{b}(\mathbf{r})=\sum_{i=1}^{3} n_i\mathbf{b}_i(\mathbf{r}). \tag{3}$$

Here, as in (2), the n_i are integers. The elementary translation vectors of the tangent lattice, $\mathbf{b}_i(\mathbf{r})$, are related to the corresponding vectors of the fixed lattice by

$$\mathbf{b}_i(\mathbf{r})=\hat{g}_{ik}(\mathbf{r})\mathbf{b}_k^0. \tag{4}$$

For a small relative rotation of the tangent lattice over a distance on the order of the interatomic distance $a(a\hat{g}^{-1}\nabla g\ll 1)$, the Burgers vector varies slowly along the defect line. Relations (3) and (4) replace the condition that the Burgers vector remains constant along an isolated dislocation in a crystal, and they show that this vector rotates along with the tangent (local) lattice. This is an important point for dislocations which are long in comparison with the distance λ_g over which the relative rotation of the local lattices becomes substantial. These are the dislocations which disrupt the orientational order in a crystal. Gilman[19] has attempted to extend the concept of a Burgers vector to configurations of an amorphous system. However, this quantity can be defined systematically only with respect to a tangent lattice, as we are proposing in the present paper.

When the atomic configuration of condensed matter is mapped onto a tangent lattice, the distribution of point defects is also established. An atom which has no image on the lattice is an interstitial atom; a lattice site which has no corresponding atom is a vacancy. Point defects can be regarded as the limit of a dislocation loop as its size is reduced.

3. HAMILTONIAN OF CONDENSED MATTER AND COMPATIBILITY CONDITION

According to the hypothesis of local crystalline order, those configurations whose size λ_g is large in comparison with the interatomic distance a appear in the statistical ensemble of the condensed matter with a predominant weight. In a first approximation in the small parameter $p = a/\lambda_g$, we ignore the rotation of the tangent lattice in a description of the properties of an element of the system of size $\lambda < \lambda_g$, and we use the relations from the theory of crystals. The energy of an element of condensed matter can be described as a functional of the configuration of atoms as a series in the magnitudes of the elastic stresses. The energy of the cores of dislocations—small regions near defect lines for which the approximation of the theory of elasticity is unsatisfactory—will be taken into account separately.

In the approximation of Hooke's law,[18] the elastic energy of the material, H_{el}, is the sum of local contributions which depend quadratically on the stress tensor σ_{ij}. For a cubic lattice the energy of an element centered at the point **r** is

$$h_{el}(\mathbf{r})=\frac{1}{4\mu}(\sigma_{\alpha\beta}{}^2+P\sigma_{\alpha\alpha}{}^2)+\lambda\sum_{\alpha=1}^{3}\sigma_{\alpha\alpha}\sigma_{\alpha\alpha};\quad P=\frac{-\nu}{1+\nu}. \tag{5}$$

The Greek indices specify the components of the tensors with respect to local coordinate systems which coincide in direction with the anisotropy axes of the tangent lattice. We use the standard notation[18] for the elastic moduli: μ is the shear modulus, ν is the Poisson ratio, and λ is the modulus of the cubic anisotropy. We find the value of H_{el} for a given configuration by transforming expression (5) to a global coordinate system (common to the entire object) and integrating over the volume of the system:

$$H_{el}=\int dV\left\{\frac{1}{4\mu}(\sigma_{ij}{}^2+P\sigma_{ii}{}^2)+\lambda T^{ijkl}\sigma_{ij}\sigma_{kl}\right\}, \tag{6}$$

where T^{ijkl} is the completelt symmetric tensor

$$T^{ijkl}(\mathbf{r})=\sum_{\alpha=1}^{3}U^{i\alpha}(\mathbf{r})U^{j\alpha}(\mathbf{r})U^{k\alpha}(\mathbf{r})U^{l\alpha}(\mathbf{r}). \tag{7}$$

The matrix $U^{ij}(\mathbf{r})$, which represents the rotation operator $\hat{g}(\mathbf{r})$, sends the local coordinate axes into the basis vectors of the global coordinate system. Writing the function H_{el} in continuum form implies a smoothing of the fields over scale lengths on the order of the interatomic distance. The functional (6) is a generalization of the familiar expression from the theory of elasticity to the case in which the directions of the local-anisotropy axes vary. It is convenient to identify the irreducible part of tensor (7):

$$\tilde{T}^{ijkl}=T^{ijkl}-{}^1/_5(\delta^{ij}\delta^{kl}+\delta^{ik}\delta^{jl}+\delta^{il}\delta^{jk}). \tag{8}$$

The parameters of functional (6) are then redefined:

$$\mu\to\tilde{\mu}=\frac{\mu}{1+{}^8/_5\mu\lambda},\quad P\to\tilde{P}=\frac{P+{}^4/_5\mu\lambda}{1+{}^8/_5\mu\lambda}. \tag{9}$$

At this point we drop the tilde. Tensor (8) may be thought of as a parameter of the orientational order.[12,13]

Expression (6) incorporates the elastic energy of the material due to both the compatible and the incompatible strains of the lattice. We single out corresponding components of H_{el}, for which we introduce a vector potential φ_i and a tensor potential A_{ij} of the stress field:

$$\sigma_{ij}=\mu(\partial_i\varphi_j+\partial_j\varphi_i)-\frac{2\mu P}{1+3P}\delta_{ij}\partial_k\varphi_k-\varepsilon_{ikl}\partial_kA_{lj}. \tag{10}$$

This representation of the field σ_{ij} is single-valued if the gauge of the potential A_{ij} is fixed. We specify this gauge by means of the condition

$$\partial_iA_{ij}=0. \tag{11}$$

For physical configurations the stress tensor is symmetric with respect to an interchange of its indices. We meet this requirement by imposing a relationship on the components of the field A_{ij}:

$$\varepsilon_{ikl}\partial_kA_{lj}=\varepsilon_{jkl}\partial_kA_{li}. \tag{12}$$

The energy (6) of the elastic deformation of the material, written in terms of the potentials, transforms to the sum of the following terms:

$$H_{ph}\{\varphi\}=\int dV\frac{\mu}{2}\left[(\partial_i\varphi_j)^2+\frac{1+P}{1+3P}(\partial_i\varphi_i)^2\right], \tag{13}$$

$$H_d\{A\}=\int dV\left[\frac{1}{4\mu}(\delta_{ik}\delta_{jl}+P\delta_{ij}\delta_{kl})\varepsilon_{imn}\varepsilon_{kpq}\partial_mA_{nj}\partial_pA_{ql}\right.$$
$$\left.+\frac{1}{4\beta}(\varepsilon_{ikl}\partial_kA_{lj}-\varepsilon_{jkl}\partial_kA_{li})^2+\frac{1}{2\alpha}(\partial_iA_{ij})^2\right], \tag{14}$$

$$H_{int}\{\varphi,A,U\}=\int dV\lambda T^{ijkl}\sigma_{ij}\sigma_{kl}. \tag{15}$$

Functional (13) is the energy of the compatible elastic strain of the substance. The field $\varphi(\mathbf{r})$ obviously describes the displacements of atoms with respect to the positions which correspond to the minimum energy for the given distribution of dislocations and which are phonon degrees of freedom of the system. Functional (14) is the energy of the elastic strain caused by the dislocation distribution. The last two terms in (14) satisfy conditions (11) and (12) in the limit $\alpha,\beta\to 0$ for configurations with a finite energy. Expression (14) agrees with the expression[20] for the energy of a system of dislocations in an elastically isotropic solid,

$$H_d\{\alpha\} = \int dV\, dV' \frac{1}{2} \alpha_{li}(\mathbf{r}) D_{ij}{}^{ln}(\mathbf{r}-\mathbf{r}') \alpha_{nj}(\mathbf{r}'), \qquad (16)$$

if we require

$$M_{ij}{}^{ln} A_{nj}(\mathbf{r}) = \alpha_{li}(\mathbf{r}), \qquad (17)$$

where the operator M is the kernel of quadratic form (14). The field $\alpha_{ij}(\mathbf{r})$ is the dislocation density tensor:

$$\alpha_{ij} = \sum_D \tau_i(\mathbf{r}) b_j(\mathbf{r}), \qquad \tau_i(\mathbf{r}) = \oint \delta(\mathbf{r}-\mathbf{r}') dr_i', \qquad (18)$$

where $\mathbf{b}$ is the Burgers vector of the dislocation. The vector field $\boldsymbol{\tau}(\mathbf{r})$ is determined by integrating the δ-function along the dislocation loop. The summation in (18) is over all the dislocation configurations. The symbol $D(\mathbf{r})$ in (16) represents the operator which is the inverse of the kernel of quadratic form (14). In the limit $\alpha, \beta = 0$, the Fourier transform of this operator is

$$D_{ij}{}^{ln}(\mathbf{q}) = \frac{2\mu}{q^2} \left\{ \frac{1+P}{1+2P} S_{ij} S_{ln} - \frac{1}{2} S_{il} S_{jn} + \frac{P}{1+2P} S_{in} S_{jl} \right\},$$
$$S_{ij} = \delta_{ij} - n_i n_j, \qquad n_i = q_i / |\mathbf{q}|. \qquad (19)$$

In the first approximation in the parameter p, Eqs. (14) and (17) extend the relations of the theory of crystals to the class of configurations with a local crystalline order. The primary distinction is that the Burgers vectors are not assumed to be constant in the expression (18) for the dislocation density tensor. The term (15) describes the explicit interaction of the phonon, dislocation, and orientational degrees of freedom of the system. For most substances this term of the Hamiltonian can be treated as a perturbation.

The Hamiltonian H, of the system contains, in addition to H_{el}, the energy H_c of the dislocation core. If the dislocation density is not too high, the expression for H_c is the same as that in the theory of crystals. We assign an energy ε to a unit length of the defect core; in the simplest approximation, this energy depends only on the modulus of the dislocation Burgers vector. The energy of the defect core is

$$\oint \varepsilon n_i dr_i, \qquad dr_i = n_i dl.$$

The integral is over the dislocation loop; $\mathbf{n}$ is a unit vector tangent to the dislocation at each point of the dislocation. We can now write

$$H_c = \sum_D \oint \varepsilon n_i dr_i. \qquad (20)$$

The sum of expressions (13)–(15) and (20), along with (17), gives us the energy of an arbitrary configuration of an elastically strained condensed substance with a dislocation network.

The description of the configurations of a condensed substance by elastic-stress and dislocation-density fields requires some explanation. According to the Lindemann criterion, and under the assumption of a Gaussian probability distribution for the displacements of the atoms, we find that the probability for the displacement of an atom by more than half an interatomic distance is a few percent. Actually, large displacements of atoms result from collective motions during the excitation of the softest modes of the system. Fluctuations along these generalized coordinates lead to displacements comparable to the interatomic distance, and an ambiguity arises in the representation of the configuration as a set of defects and some elastic strain. We assume that a relative displacement is inelastic if it does not exceed half an interatomic distance. A larger displacement is regarded as a defect and described by a dislocation loop. In this manner, the interatomic interaction is extrapolated in accordance with a behavior which is regular in the limits of small and large displacements. In this description, even in the crystalline phase near the melting temperature, a few percent of the atoms belong to virtual defects with a formation energy comparable to the temperature.

Specifying an effective Hamiltonian does not exhaust the description of a condensed system. The fields which parametrize the configurations of the substance satisfy a local relation, the compatibility condition. For an element of the system of size $\lambda < \lambda_g$ this condition is the same, to first order in the parameter p, as the familiar expression from the theory of crystals.[21] One way to write this condition in the local coordinate system is

$$\partial_\beta \omega_\alpha = \alpha_{\alpha\beta} - {}^1/{}_2 \delta_{\alpha\beta} \alpha_{\gamma\gamma} - \varepsilon_{\alpha\gamma\delta} \partial_\gamma u_{\delta\beta}. \qquad (21)$$

Here the field $u_{\alpha\beta}(\mathbf{r})$ is the strain field, which can be written in terms of the stress tensor in accordance with Hooke's law; and $\omega_\alpha(\mathbf{r})$ is the field of infinitesimal rotations, which is related to the finite-rotation matrix by the familiar expression[1]

$$U_{ij} = (\exp[-\omega_k \hat{T}_k])_{ij}. \qquad (22)$$

The matrices T_k ($k = 1, 2, 3$) in (22) are the generators of the rotation group of the $3D$ Euclidean space, written in a vector representation. The field $\alpha_{\alpha\beta}(\mathbf{r})$ is the dislocation density tensor, determined by (18).

For a small relative rotation, the quantity $\partial_\beta \omega_\alpha$ can easily be expressed in terms of matrix (22); then relation (21) can be transformed to a basis which is common to the entire object. Making use of the invariance of the tangent lattice under transformations of the cubic group, we find

$${}^1/{}_2 \varepsilon_{ikl} T^{kmnp}(\mathbf{r}) \partial_j T^{lmnp}(\mathbf{r}) = \alpha_{ij} - {}^1/{}_2 \delta_{ij} \alpha_{kk} - \varepsilon_{ikl} \partial_k u_{lj}. \qquad (23)$$

Expression (23) generalizes the compatibility condition to the case in which the axes of the local cubic anisotropy do not have a constant orientation, and it holds to within small corrections on the order of the parameter p. According to (23), a rotation of the tangent lattice is determined by the dislocation distribution and the strain of the substance. In turn, the rotation field determines the rotation of the dislocation Burgers vectors [see (4)] and thus the local value of the dislocation density tensor. To specify the configurations of the system we need to specify the dislocation lines and the magnitudes of the Burgers vectors of the dislocations in the tangent coordinate system. The Burgers vectors in the global system are determined in a self-consistent manner along with the rotation field.

4. STATISTICAL THEORY OF CONDENSED MATTER

Configurations of atoms which satisfy the hypothesis of local crystalline order form a class of packings which maximize the density for a given local structure, generally in the absence of a long-range order. These configurations are characterized by the correlation lengths for the parameters of the translational and orientational order. The ideal packing is a limiting packing of this class, which corresponds to a minimum randomness. Another limiting case is a very dense gas, for which these correlation lengths are comparable to the interatomic distance. The properties of configurations with a local crystalline order correspond to the slightly indefinite concept of a "random dense packing" which can be found in the literature. This concept thus acquires a definite meaning. We believe that in a melt there is an overwhelming probability for configurations of this class; the size of the region of local order is large enough that we can restrict the discussion to the first approximation of the theory in the parameter $p = a/\lambda_g$. In this case, the statistical description of the condensed matter reduces to a study of the properties of a Gibbs ensemble with the Hamiltonian of the stress, rotation, and dislocation-density fields derived in the preceding section.

Certain properties of this model are obvious. At low temperatures ($T \ll \varepsilon$) the dislocation density is approximately zero, while the parameter of the orientational order averaged over the system, $\langle T^{ijkl} \rangle$, is nonzero. This anisotropic state is a crystal. At sufficiently low temperatures a minimum of the free energy should correspond to globally anisotropic configurations with a large, finite dislocation density. Differences in the symmetry of states imply the occurrence of a phase transition. The idea that the disruption of the long-range crystalline order in a substance is associated with the appearance of a dislocation network is well known.[16] Kleinert[22,23] and Obukhov[24] have recently described the melting of an elastically isotropic medium as a phase transition in a system of dislocation (or disclination) loops. They did not take up the orientational order in the substance; that approach is justified only for the crystalline state at temperatures which are not too high. Near the melting point and, in particular, in amorphous and liquid states, the interaction of the local structure and defects determines the physical properties of the system.

The probability density of configurations of condensed matter in thermal equilibrium at the temperature T is

$$w \propto \exp\left(-\frac{H_{el}+H_c}{T}\right)\delta\left(\lambda_{ij}^{(1)}(\mathbf{r})\right)\delta\left(\lambda_{ij}^{(2)}(\mathbf{r})\right), \tag{24}$$

$$\lambda_{ij}^{(1)}(\mathbf{r}) = M_{jn}{}^{il}A_{ln}-\alpha_{ij}, \tag{25}$$

$$\lambda_{ij}^{(2)}(\mathbf{r}) = \alpha_{ij}-{}^1/_2\delta_{ij}\alpha_{kk}-X_{ij}-\varepsilon_{ikl}\partial_k u_{lj},$$

where

$$X_{ij} = {}^1/_2\varepsilon_{ikl}T^{kmnp}(\mathbf{r})\,\partial_j T^{lmnp}(\mathbf{r}). \tag{26}$$

The operator M_{ij}^{ln}, the kernel of quadratic form (14), is given in the Appendix. The functional δ-functions in (24) ensure that conditions (17) and (23) are satisfied at all points of the system. In the first approximation in the modulus of the cubic anisotropy, the strain tensor is

$$u_{ij} = \frac{1}{2\mu}\sigma_{ij}+\frac{P}{2\mu}\delta_{ij}\sigma_{kk}. \tag{27}$$

We find the partition function of the condensed matter by summing probability density (24) over all possible spatial configurations of dislocations and the distribution of their Burgers vectors and by integrating over the configurations of the stress fields (i.e., the potentials) and the rotation fields:

$$Z = N\sum_{\{\alpha\}}\int D\varphi_i DA_{ij}DU_{ij}\exp(-H/T)\,\delta(\lambda^{(1)})\,\delta(\lambda^{(2)}). \tag{28}$$

The normalization factor N is chosen for convenience.

The partition function (28) is a complicated mathematical expression whose detailed analysis goes beyond the scope of the present paper. Our purpose here is to determine the possible phase states of the system and the nature of the transitions between them. For this purpose we seek the effective Hamiltonian of the orientational-order parameter, integrating over the other degrees of freedom. The calculations below are set forth in more detail in Ref. 25.

We write the δ-functions as the functional integrals

$$\prod_{\mathbf{r}}\delta(\lambda_{ij}(\mathbf{r})) = \int D\eta_{ij}\exp\left(-i\int dV\eta_{ij}\lambda_{ij}\right) \tag{29}$$

and in the partition function (28) we single out the expression Z_D, determined by the distribution of dislocations:

$$Z_D = \sum_{\{\alpha\}}\exp\left(-H_c/T+i\int dV\Phi_{ij}\alpha_{ij}\right), \tag{30}$$

where

$$\Phi_{ij} = \eta_{ij}^{(1)}(r)+({}^1/_2\delta_{ij}\delta_{ln}-\delta_{il}\delta_{jn})\,\eta_{ln}^{(2)}(r). \tag{31}$$

We use (18) and (20), and we write sum (30) as

$$Z_D = \sum_{\{\alpha\}}\exp\left\{-\sum_D\oint\left(\frac{\varepsilon}{T}n_i-i\Phi_{ij}b_j\right)dr_i\right\}. \tag{32}$$

The sum (32), whose terms are found by integrating the functions over spatial loops, can be written as a functional integral over configurations of the field variables. The concept of such a transformation is well known. This approach was used in Ref. 24 to sum over configurations of dislocations. However, the particular way in which the functional integral was written there cannot be used here (at any rate, before we take the continuum limit), since the quadratic form in the argument of the exponential function is not positive definite. It is written in the correct form below.

We introduce an auxiliary cubic lattice whose sites are separated by a distance which is the same as the average interatomic distance in the system. The dislocation loop is represented on the lattice by a broken line, formed by its links. At each site n we find a triad of scalar complex fields $\psi^{(\nu)}(\mathbf{r}_n)$ ($\nu = 1, 2, 3$). It can be shown[25] that the integral

$$Z_D = N_D\int\prod_n\Big[\Big(\prod_\nu d\psi^{(\nu)}(\mathbf{r}_n)\,d\psi^{*(\nu)}(\mathbf{r}_n)\quad\Big)$$

$$\times\Bigl(1+\sum_{\nu,d}\psi^{(\nu)}(\mathbf{r}_n)\psi^{*(\nu)}(\mathbf{r}_n+d)$$

$$\times G^{(\nu)}(\mathbf{r}_n,\mathbf{r}_n+d)\Bigr)\Bigr]$$

$$\times\exp\Bigl\{-\sum_{n,\nu}[|\psi^{(\nu)}(\mathbf{r}_n)|^2+g(|\psi^{(\nu)}(\mathbf{r}_n)|^2)^2]\Bigr\}, \tag{33}$$

where

$$G^{(\nu)}(\mathbf{r}_n,\mathbf{r}_n+d)=J\exp\Bigl[i\int_{r_n}^{r_n+d}\Phi_{ij}(r')b_j^{(\nu)}(\mathbf{r}')dr_i'\Bigr],$$

$$J=c\exp(-\varepsilon/T), \tag{34}$$

$$c=\int_0^\infty\exp(-x-gx^2)dx\Bigl[\int_0^\infty x\exp(-x-gx^2)dx\Bigr]^{-1},$$

agrees with sum (32) if we retain in it only those configurations which have no intersections of dislocations. The integral in (33) is normalized by the condition $Z_D = 1$ for $J = 0$. In each of the coefficients of the exponential functions we introduce a summation over the neighbors **d** of the given site and over the type of field, ν. The vectors $\mathbf{b}^{(\nu)}$ ($\nu = 1, 2, 3$) constitute a triad of vectors of elementary translations of the local lattice. In the sum we take into account dislocations with minimum Burgers vectors $\mathbf{b} = \pm\mathbf{b}^{(\nu)}$. The substitution

$$1+\varphi(\mathbf{r}_n)\to\exp\varphi(\mathbf{r}_n),$$

$$\varphi(\mathbf{r}_n)=\sum_{\nu,d}\psi^{(\nu)}(\mathbf{r}_n)\psi^{*(\nu)}(\mathbf{r}_n+d)G^{(\nu)}(\mathbf{r}_n,\mathbf{r}_n+d) \tag{35}$$

in integral (33) makes it possible to carry out the summation over a broader class of dislocation configurations. It is not difficult to see that in a generalization of this type the dislocations with minimum Burgers vectors enter the sum with their previous weight; furthermore, intersections of these vectors are allowed, as are dislocations with other than the minimum Burgers vectors. The interaction of defects with the field $\Phi_{ij}(\mathbf{r})$ is taken into account correctly for all dislocations, and the energy of their intersection can be taken into account by adjusting the parameter g, which is not fixed in integral (33). If g is nonzero and positive, the contribution of dislocations with large Burgers vectors is suppressed. Refining the function $G^{(\nu)}(\mathbf{r},\mathbf{r}')$ and the expressions of the argument of the exponential function in (33), we find representations which correspond progressively more accurately to sum (32). We restrict the discussion to the expression found after the replacement of (35). At nonzero temperatures the partition function is dominated by the dislocations with minimum Burgers vectors which are taken into account in it. The sum in (32) can thus be written as the functional integral

$$Z_D=N_D\int\prod_\nu D\psi^{(\nu)}D\psi^{*(\nu)}\exp(-H_d\{\psi^{(\nu)},\Phi_{ij}\}), \tag{36}$$

$$H_d=\sum_\nu\int dV\Bigl[|\psi^{(\nu)}|^2+g(|\psi^{(\nu)}|^2)^2$$

$$-\int dV'\Lambda(\mathbf{r}-\mathbf{r}')\psi^{(\nu)}_{(\mathbf{r})}\psi^{*(\nu)}_{(\mathbf{r}')}G^{\nu}(\mathbf{r},\mathbf{r}')\Bigr];$$

$$\Lambda(\mathbf{r}-\mathbf{r}')=\sum_{\mathbf{d}}\delta(\mathbf{r}'-\mathbf{r}-\mathbf{d}). \tag{37}$$

The fields $\psi^{(\nu)}$ should be regarded as smoothed over a distance on the order of the interatomic distance, since a precise localization of the core of dislocations is meaningless. These fields, which describes the defect distribution in the system, will be called "disorder parameters."

We write the partition function (28) as

$$Z=N\int DU_{ij}F\{U_{ij}\}. \tag{38}$$

Here the functional $F\{U_{ij}\}$ is an integral over configurations of the fields φ_i, A_{ij}, $\eta_{ij}^{(\eta)}$ and $\psi^{(\nu)}$. The integrand in $F\{U_{ij}\}$ is quite complicated; it can be reconstructed by means of (28)–(32), (34), (36), and (37). It can be seen[25] that if the anisotropic part of (15) is ignored in the elastic-strain energy some of these integrals turn out to be Gaussian and can be evaluated easily. As a result we find

$$F\{U_{ij}\}=\tilde{N}\int D\Phi_{ij}\prod_\nu D\psi^{(\nu)}D\psi^{*(\nu)}$$

$$\exp[-\tilde{H}\{\Phi_{ij}X_{ij}\}-H_d\{\psi^{(\nu)},\Phi_{ij}\}],$$

$$\tilde{H}\{\Phi_{ij},X_{ij}\}=\int\frac{d^3q}{(2\pi)^3}\Bigl[\frac{T}{2}\Phi_{li}O_1{}^{ln}_{ij}\Phi_{nj}+i\Phi_{li}O_2{}^{ln}_{ij}X_{nj}$$

$$+\frac{1}{2T}X_{li}O_3{}^{ln}_{ij}X_{nj}\Bigr]. \tag{39}$$

The operators $\hat{O}_n$ are given in the Appendix. At a temperature T the amplitude of the fluctuations of the field Φ_{ij} of scale size $\lambda\ll\mu/T$ is small in comparison with unity, and the functional H_d can be expanded in a series in large-scale harmonics. At a sufficiently high temperature, this expansion is valid for an arbitrary configuration of the field Φ_{ij}. To within terms quadratic in the field Φ_{ij} we find

$$\tilde{H}_d=\sum_\nu\int dV[JD|D_i^{(\nu)}\psi^{(\nu)}|^2+(1-nJ)|\psi^{(\nu)}|^2+g(|\psi^{(\nu)}|^2)^2], \tag{40}$$

where we are using the operator

$$D_i^{(\nu)}=\partial_i+i\Phi_{ij}b_j^{(\nu)},$$

and n is the number of nearest neighbors in the local lattice.

We consider a model system which differs from the original system in that functional (37) is replaced by its expansion in (40). This model correctly describes condensed matter in the high-temperature limit. Assuming that the fluctuations of the fields $\psi^{(\nu)}$ are weak (i.e., that the parameters J and $1 - nJ$ are not too small), we can identify in (40) a term which is quadratic in the field Φ_{ij}:

$$J\sum_\nu\int dV\langle|\psi^{(\nu)}|^2\rangle(\Phi_{ij}b_j^{(\nu)})^2. \tag{41}$$

If dislocations with different minimum Burgers vectors are equally probable in the phase state under consideration, the self-consistent average $\langle|\psi^{(\nu)}|^2\rangle$ does not depend on the index ν. Carrying out the summation in (41), we find

$$\int dV(m^2/2)\Phi_{ij}{}^2;\quad m^2=2J\langle|\psi|^2\rangle. \tag{42}$$

Using correction (42), we can carry out the integration in (39) over the configurations of the field Φ_{ij} in the Gaussian approximation. As a result we find the following effective Hamiltonian for the field of the orientational-order parameter:

$$H\{T^{ijkl}\}=\int dV\,{}^1/_2 X_{li}\Gamma_{ij}{}^{ln}X_{nj}. \tag{43}$$

The field X_{ij} is determined by (26). The operator Γ_{ij}^{ln} is given in the Appendix.

Hamiltonian (43) simplifies considerably if we restrict it to the first-order terms in the spatial derivatives of the rotation field. For a sufficiently small element of the system we can use the approximation

$$X_{ij}=\partial_j\omega_i+\ldots$$

It is not difficult to see that in the expression for the field energy density T^{ijkl} all the terms containing the transverse operators S_{jn} vanish. In this approximation the kernel of the effective Hamiltonian (43) can be written

$$\Gamma_{ij}^{ln}(\mathbf{q})=\frac{4\mu}{T(q^2+4\mu m^2/T)}\delta_{ij}S_{ln}. \tag{44}$$

We find the spherically symmetric part of the operator (44), replacing the operator S_{ln} by its average over angles. We find

$$H\{T^{ijkl}\}$$
$$=\int dV\,dV'\,T^{ilmn}(\mathbf{r})\,\partial_k T^{jlmn}(\mathbf{r})\,J(\mathbf{r}-\mathbf{r}')\,T^{ipqr}(\mathbf{r}')\,\partial_k T^{jpqr}(\mathbf{r}'). \tag{45}$$

The function $J(\mathbf{r})$ is the Fourier transform of the function

$$J(\mathbf{q})=\frac{2\mu}{3T(q^2+4\mu m^2/T)}. \tag{46}$$

The exchange integral $J(r)$ falls off exponentially at distance $\lambda>(T/4\mu m^2)^{1/2}$, so that for slowly varying fields T^{ijkl} the interaction can be assumed to be a local. To simplify the model further we use a lattice description, replacing the derivative of the field T^{ijkl} by a finite difference:

$$\partial_k T^{ijkl}(\mathbf{r})\to\frac{1}{|\mathbf{d}|}[T^{ijkl}(\mathbf{r}+\mathbf{d}_k)-T^{ijkl}(\mathbf{r})].$$

At the accuracy of these calculations we find

$$H\{T^{ijkl}\}=-\bar{J}\int dV\sum_d T^{ijkl}(\mathbf{r}+\mathbf{d})\,T^{ijkl}(\mathbf{r})+\text{const}, \tag{47}$$

where

$$\bar{J}=\frac{1}{d^2}\int dV J(\mathbf{r}).$$

The absolutely symmetric tensor T^{ijkl} in (47) may be regarded as irreducible. Transforming from reducible to irreducible tensors changes an unimportant constant.

We have reduced the effective Hamiltonian of the orientational-order parameter to the very simple form in (47). The statistical properties of a system with this Hamiltonian were studied in Refs. 13 and 14, where it was shown that the system undergoes a first-order phase transition. The average value of the orientational-order parameter, normalized (to unity) in the limit $T\to 0$, changes abruptly at the transition from a value of approximately 1/2 to 0. This transition is naturally interpreted as melting. The low-temperature anisotropic phase of the model system corresponds to the crystalline state, and the high-temperature, globally isotropic phase is a melt.

If we assume that the Burgers vectors have constant directions in the Hamiltonian of the disorder fields of model system (40), then this Hamiltonian is of the same form as the expression derived by Obukhov,[24] who studied the statistics of dislocations in a structureless medium. In the approximation of an effective field he showed that the system of fields $\psi^{(\nu)}$ ($\mathbf{b}^{(\nu)}=\text{const}$) undergoes a first-order phase transition which is of approximately second order at the temperature determined by the condition $nJ\approx 1$. At the phase transition, a condensate of the fields $\psi^{(\nu)}$ forms; this event was interpreted by Obukhov[24] as a transition to a liquid phase accompanied by the formation of a network of dislocations of infinite length. Melting, i.e., the disruption of the long-range orientational order, cannot occur without the formation of a finite dislocation density in the system. There is, however, the possibility of states with a condensate of fields $\psi^{(\nu)}$ and with a slow decrease in the correlation of the orientational-order field. A similar phase (hexatic) is observed in numerical simulations of 2*D* condensed systems.[26] A phase transition associated with a change in dislocation structure is obviously not a melting of the substance, in general. In certain substances the formation of a network of defects (i.e., the condensation of disorder fields) may occur at temperatures below the melting point. Such substances have an anisotropic intermediate phase which is not crystalline. The phase transition discussed in Ref. 24 corresponds in our theory to a transition between a crystal and an intermediate phase.

This analysis shows that the partition function in (28) describes the known phase states of condensed matter. We can classify them on the basis of the existence of nonzero average values (more precisely, Bogolyubov quasi-average values) of the parameter of the orientational order, T^{ijkl}, and of the fields $\psi^{(\nu)}$.

At low temperatures, in the crystalline phase, we have

$$\langle T^{ijkl}\rangle\neq 0,\quad \langle|\psi^{(\nu)}|\rangle=0.$$

At sufficiently high temperatures, in the molten phase, we have

$$\langle T^{ijkl}\rangle=0,\quad \langle|\psi^{(\nu)}|\rangle\neq 0.$$

The phase transition between these two phases is of first order. In certain substances there may be an intermediate phase (at least a metastable one):

$$\langle T^{ijkl}\rangle\neq 0,\quad \langle|\psi^{(\nu)}|\rangle\neq 0.$$

A state with $\langle T^{ijkl}\rangle=0$, $\langle|\psi^{(\nu)}|\rangle=0$ is obviously impossible.

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APPENDIX

The operators O_{ij}^{ln} which appear in this paper can be written in general as follows in the momentum representation:

$$O_{ij}^{ln}=(q^2)^s\{c_1S_{ij}S_{ln}+c_2S_{ij}n_ln_n+c_3S_{ln}n_in_j+c_4S_{il}S_{jn}+c_5S_{il}n_jn_n+c_6S_{jn}n_in_l+c_7S_{in}S_{jl}+c_8S_{in}n_jn_l+c_9S_{jl}n_in_n+c_{10}n_in_jn_ln_n\},$$

where the index s is an integer, and

$$S_{ij}=\delta_{ij}-n_in_j,\quad n_i=q_i/|q|.$$

We adopt the notation

$$a=\frac{1}{4\mu}+\frac{1}{\beta},\quad b=\frac{1}{4\mu}-\frac{1}{\beta},\quad c=\frac{P}{2\mu},\quad d=\frac{1}{\alpha}.$$

Here is a list, in this notation, of the operators, the nonvanishing coefficients, and the values of the index s:

$$M_{ij}^{ln}\ :\ c_1=a+b+c,\ c_2=d,\ c_3=a,\ c_4=-b,\ c_7=-c,\ c_{10}=d,\ s=1.$$

$$D_{ij}^{ln}:\quad c_1=\frac{a+b+c}{(a+b)(a+b+2c)},\quad c_2=\frac{1}{d},\quad c_3=\frac{1}{a},$$

$$c_4=\frac{b}{a^2-b^2},$$

$$c_7=\frac{c}{(a+b)(a+b+2c)},\quad c_{10}=\frac{1}{d},\quad s=-1.$$

$$O_{1\,ij}^{\ \ ln}=M_{ij}^{\ ln}-S_{ik}^{\ lm}Q_{kq}^{\ mp}S_{qj}^{\ pn},$$

$$O_{2\,ij}^{\ \ ln}=S_{ik}^{\ lm}Q_{kj}^{\ mn},\qquad O_{3\,ij}^{\ \ ln}=Q_{ij}^{\ ln}.$$

$$S_{ij}^{ln}:\quad c_1=2(a+b+c),\quad c_2=d,\quad c_3=2a+b,$$

$$c_4=-(a+b)/2,$$

$$c_5=-(a-b)/2,\quad c_6=-d/2,\quad c_7=-2c,\quad c_{10}=d/2,\quad s=1.$$

$$Q_{ij}^{ln}:\quad c_1=\frac{a+b+c}{4(a+b)(a+b+2c)},\quad c_2=\frac{1}{d},$$

$$c_3=\frac{2a}{2a^2+(6a+b)(a+b)},$$

$$c_4=\frac{(a-b)\left(a+b+\frac{d}{2}\right)}{8db(a+b)}-\frac{(3b-2a)\left(a-b+\frac{d}{2}\right)}{8db^2},$$

$$c_5=c_6=\frac{(a-b)\left(a+b+\frac{d}{2}\right)}{2db^2},\qquad c_7=\frac{-c}{4(a+b)(a+b+2c)},$$

$$c_{10}=\frac{a-b}{2b^2}+\frac{(a+b)^2}{db^2},\qquad s=-1.$$

$$\Gamma_{ij}^{ln}\big|_{\alpha,\beta=0}:\quad c_1=\frac{q^2}{4m^2}+\frac{\mu}{2T}\frac{1+P}{1+2P},\qquad c_2=\frac{q^2}{m^2},$$

$$c_3=\frac{4\mu q^2}{T\left(q^2+\frac{4\mu m^2}{T}\right)},\qquad c_4=-\frac{q^2}{8m^2}-\frac{\mu}{4T},$$

$$c_7=\frac{\mu}{2T}\frac{P}{1+2P},\qquad s=-1.$$

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