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Abstract

The phenomenological theory of crystal ordering is formulated in terms of local crystal-order parameter. This parameter is a set of rank-4 tensors. Phase transition from liquid to crystal phase is studied for a cubic crystal. The temperature interval ΔT of an overheated crystal is small: $\Delta T / T_c^* \leqslant 0.02$. The pre-melting anomalies are shown to exist.

Dense liquid exhibits, in small volumes, a crystallike structure. The main difference between the crystal and the liquid is the existence of long-range ordering of the local structure.

To obtain the complete picture of thermodynamics and structure properties both in the crystal and dense liquid one needs a microscopic theory, based on the actual hamiltonian of the system.

The experimental data show that the change both of density and energy at crystallization is small (a few percents). These small changes are strongly related to the settlement of the long-range order. A theory treating these small changes is expected to be less complicated.

The long-range effects can be treated by means of the fields $\Lambda(x)$ of local crystal-order parameters. The "physical point" x denotes here a small volume V of the system, a cluster containing n_0 atoms. Its local structure (local order) is imposed by strong interactions between the nearest atoms. The cluster's characteristic length $r_0 = V^{1/3}$ is large in comparison to the crystal-lattice size ; consequently, the macroscopic description doesn't account for the translational-invariance effects. Nevertheless, the other symmetry elements (rotation axes, reflection planes etc) can be easily treated. In other words, the settlement of the long-range correlations of the local anisotropy characteristics and not of the translational invariance plays the central role in our theory.

The aim of this work is to introduce the local crystal-order parameter and to study the simplest models of crystal lattices.

The physical picture of the state of a dense matter we use is that of a system of relatively rigid clusters[1]. Consider such a cluster in an effective potential imitating the interaction with other particles. For the cluster big enough its ground state corresponds to a crystal. The low energy excitations are the phonon-like ones. The softest modes, corresponding to the cluster's characteristic length r_0 describe its deformation and rotation. In this work it is assumed that for temperatures $T \leqslant T_c$, T_c being the melting temperatures, the fluctuations of the corresponding degrees of freedom determine the degree of "imperfectness of long-range crystalline order.

In general, a few types of local crystal order with nearly the same energy may represent the arrangement of atoms in a cluster; the boundary conditions select the lowest energy one. For $T \leqslant T_c$, the boundary conditions for the cluster are close to that in an ideal lattice, in opposite to the liquid case ($T > T_L^*$). At T_c the quantitative change of boundary conditions takes place and the local structure may change. In this work such an effect is not taken into consideration.

Note, that when the short-range interactions are not strong enough to form a relatively stable cluster our theory can't be applied. Such a system remains liquid at any T (e.g., liquid He).

The location of atoms in a cluster is uniquely characterized by the set of multipole moments of each independent density component (corresponding to different sorts of atoms, electron density etc). The multipole moments are tensors of appropriate ranks. The zeroth moment (scalar) and the first moment (vector) describe the fields of the averaged (over the cluster) density and of mass center displacement of a cluster, respectively. The quadrupole moment (irreducible rank-2 tensor) characterizes the liquid-crystal-type anisotropy of atoms' locations [1].

The anisotropy, intimately connected with the crystal ordering is reflected in the higher multipole moments (tensors of rank $l \geqslant 4$). In the simplest case of the cubic lattice, the cubic tensors of rank $l < 4$ are isotropic. The lowest-rank symmetrical cubic tensor corresponding to the non-trivial (i.e. nonunit) representation of the rotation group O(3) is the rank-4 irreducible tensor. Such a tensor characterizes the directions of cubic crystal axes. In the case of the hexagonal symmetry the orientation of the crystal axes is fixed by rank-6 tensor. The multipole moments corresponding to

rank-4 (rank-6 in the hexagonal case) tensors are necessary and sufficient to reflect the existence of the crystal ordering (anisotropy). In this paper they are referred to as local crystal-order parameters $\Lambda(x)$. For a given $\Lambda(x)$, the fluctuations of short-range degrees of freedom are described by high rank tensors ($l \gg 1$). The short-range degrees of freedom have no straightforward relation to local crystal ordering. The characteristic time of their fluctuations is small in comparison with that of rank-4 (rank-6) tensors.

There is an analogy with the nematic-liquid crystal theory, in which the anisotropy of molecules' orientations can be described by geometric or material order parameter. The former is the field of the quadrupole moment of the density, the latter - the irreducible part of local dielectric (magnetic) susceptibility, that reflects the anisotropy of atoms' locations. The geometric order parameter of a crystal is the field of irreducible rank-4 tensor (the hexagonal crystal is the only exception), and the material one is the irreducible part of the elastic constants tensor. Note, that by fixing the fourth (sixth) multipole moment one fixes only a small number of all $3n_0$ degrees of freedom of cluster particles.

The description of the system is given in terms of macroscopic tensor fields $\Lambda(x)$ of rank 6 and lower. The probability dW of a given configuration $\{\Lambda(x)\}$ is

$$dW \sim \exp\{-H\{\Lambda\}/T\}\, D\Lambda(x), \tag{1}$$

where $D\Lambda(x)$ is the measure in the space of configurations $\{\Lambda(x)\}$. The effective hamiltonian $H\{\Lambda\}$ is the average of Gibbs distribution over all microscopic configurations with fixed $\Lambda(x)$. $H\{\Lambda\}$ depends functionally on $\Lambda(x)$ and is a function of thermodynamic variables. Unlike the fluctuation theory of second order phase transitions [2], in this theory there is no universal expansion for $H\{\Lambda\}$ and one has to introduce the model effective hamiltonian. The fluctuations of the tensor field $\Lambda(x)$ at point x are rotation $\hat{g}(x)$ and deformation $\delta\Lambda(x)$:

$$\Lambda(x)=\hat{g}(x)\left[\Lambda_0+\delta\Lambda(x)\right], \qquad (2)$$

where Λ_0 is a fixed set of tensors and $\delta\Lambda(x)$ is due to the change of invariants of field $\Lambda(x)$. The assumption that clusters are rigid implies that form-fluctuations $\delta\Lambda(x)$ are small, i.e. $\delta\Lambda(x)/\Lambda_0 \ll 1$. When r_0 increases, the anisotropic part of Λ_0 vanishes and the form-fluctuations become dominant. The "best" r_0 is obtained from minimal value of $\delta\Lambda(x)/\Lambda_0$.

Let's examine the simplest case, i.e. the one-component density problem with cubic symmetry of local structure (order). Consider the no form-fluctuation case first. Then

$$\Lambda(x)=\hat{g}(x)\Lambda_0 , \qquad (3)$$

where $\Lambda_0, \Lambda(x)$ are rank-4 cubic tensors. In the simplest case Λ_0, the geometric characteristics of local structure, describe 3 mutually perpendicular axes $n_\alpha^{(i)}$ (i = 1,2,3) of a cubic crystal, so

$$\Lambda_{\alpha\beta\gamma\delta}(x)=\sum_{i=1}^{3} n_\alpha^{(i)}(x)\, n_\beta^{(i)}(x)\, n_\gamma^{(i)}(x)\, n_\delta^{(i)}(x). \qquad (4)$$

Tensors Λ_0 and $\Lambda(x)$ are reducible ; their irreduable parts can be obtained by substraction of an isotropic tensor. The simplest hamiltonian $H\{\Lambda\}$ of local order interactions is

$$H\{\Lambda\}=\int dx\,dx'\,J(x-x')\,\Lambda_{\alpha\beta\gamma\delta}(x)\,\Lambda_{\alpha\beta\gamma\delta}(x'). \qquad (5)$$

$H\{\Lambda\}$ will be treated via the mean field approximation (MFA). Denote

$$h_{\alpha\beta\gamma\delta}=\nu\langle\Lambda_{\alpha\beta\gamma\delta}\rangle\ ; \quad \nu=\int dx\,J(x). \qquad (6)$$

One has

$$\langle\Lambda_{\alpha\beta\gamma\delta}\rangle=Z^{-1}\int\Lambda_{\alpha\beta\gamma\delta}(\hat{g})\,e^{-\frac{1}{T}H_{MFA}(\hat{g})}\,d\hat{g}, \qquad (7)$$

where $H_{MFA}=-h_{\alpha\beta\gamma\delta}\Lambda_{\alpha\beta\gamma\delta}(\hat{g})$ and $Z=\int\exp[-H_{MFA}/T]\,d\hat{g}$. The MFA eqs. (6)-(7) give the extremal values of $\langle\Lambda_{\alpha\beta\gamma\delta}\rangle$

for thermodynamic potential $\phi(\langle\Lambda_{\alpha\beta\gamma\delta}\rangle)$,

$$\phi=-T\ln Z+h_{\alpha\beta\gamma\delta}\langle\Lambda_{\alpha\beta\gamma\delta}\rangle, \qquad (8)$$

where $h(\langle\Lambda\rangle)$ is given by eq. (6).

The solutions of eqs. (6)-(7) have the cubic symmetry. For the non-zero components of averaged local order parameter $\langle D_{\alpha\beta\gamma\delta}\rangle$, where $D_{\alpha\beta\gamma\delta}$ is the irreducible part of $\Lambda_{\alpha\beta\gamma\delta}$, one has

$$D_{\alpha\alpha\beta\beta}=3A(T)\left(\delta_{\alpha\beta}-1/3\right). \qquad (9)$$

Eqs. (6)-(7) for A(T) were solved numerically. The plot of A versus T is given in Fig. 1. The solution $A(T)=0$ corresponds to the macroscopically isotropic phase (liquid). It minimizes $\phi(A)$ for temperatures $T_L^*<T<\infty$, with T_L^* being the solution of equation $\partial^2\phi/\partial A^2\big|_{A=0,T=T_L^*}=0$. T_L^* is the temperature of absolute instability of the liquid phase. The macroscopically anisotropic phase (crystal) with $\langle D_{\alpha\beta\gamma\delta}\rangle\neq 0, (A\neq 0)$, minimizes $\phi(A)$ for $0\leq T<T_c^*$, with T_c^* denoting the temperature of absolute instability of the crystal (see Fig. 1). The melting temperature T_c, at which $\phi(A)=\phi(0)$, is close to T_c^*:

$$\left(T_c^*-T_c\right)/T_c^* \sim 0.02 \qquad (10)$$

ν in eq. (6) fixes the temperature scale only.

Let's examine the small form-fluctuations (strains). The "strain" contribution to $H\{\Lambda\}$ is, in harmonic approximation with respect to the strain tensor $u_{\alpha\beta}$ (see [3])

$$H_{el}\{\tilde{\Lambda},u\}=\frac{1}{2}\int\tilde{\Lambda}_{\alpha\beta\gamma\delta}(x)\,u_{\alpha\beta}(x)\,u_{\gamma\delta}(x)\,dx. \qquad (11)$$

Formula (11) generalizes the well-known one of the theory of elasticity [3]. $\tilde{\Lambda}_{\alpha\beta\gamma\delta}(x)$ is the elastic contacts tensor of the cluster located at x. In the case of local cubic symmetry

$$\tilde{\Lambda}(x)=\hat{g}(x)\tilde{\Lambda}_0 \qquad (12)$$

where $\tilde{\Lambda}_0$ - fixed cubic tensor of rank 4. Thermodynamics of the system can be obtained from the the thermodynamic potential $\phi(T,\sigma_{\alpha\beta})$:

$$\phi(T,\sigma_{\alpha\beta}) = -T\ln Z \; ; \; Z = \int \mathcal{D}\hat{g}(x)\,\mathcal{D}u_{\alpha\beta}(x)\, e^{-\frac{1}{T}H} ,$$

$$H = H\{\Lambda\} + H_{el} - \sigma_{\alpha\beta}\int u_{\alpha\beta}(x)\,dx , \qquad (13)$$

where $\sigma_{\alpha\beta}$ is stress tensor.

Note that the answer to the question whether stress $\sigma_{\alpha\beta}$ can be created by surface forces depends on the dynamics of the relaxation process of parameters. This problem is beyond the scope of this letter.

In the case of an isotropic $\tilde{\Lambda}_0$ the elastic term H_{el} is $\hat{g}$ - independent. When $\tilde{\Lambda}_0$ contains an anisotropic part, the contributions to mean elastic constants tensor can be calculated in a way proposed by Lifshitz and Rozenzweig [4]. The contributions to the heat capacity (ΔC_p) and to the coefficient of linear expansion ($\Delta\alpha_T$) due to anisotropic character of atoms' arrangement (crystalline order) are

$$\Delta C_p \sim \Delta\alpha_T \sim -\frac{dA(T)}{dT} \sim \left(T_c^* - T\right)^{-1/2} . \qquad (14)$$

The smallness of the temperature interval $\Delta T/T_c^*$ of metastable crystal, eq. (10), results in the existence of pre-melting phenomena near T_c. The more detailed analysis is given in [5] for a different model hamiltonian.

The most characteristic features of the theory - the numerical value of $\Delta T/T_c^*$ and the pre-melting phenomena - are common for the continuous - rotation model and the discrete one (i.e., where only a few relative orientations are allowed). The later one, equivalent to the 4-state Potts model is studied in [5].

In the case of lower symmetry of the local order parameter Λ_0 a set of phase transitions between the crystalline phases with different point symmetry occurs; the liquid - crystal mesophase may exist. The details will be published elsewhere.

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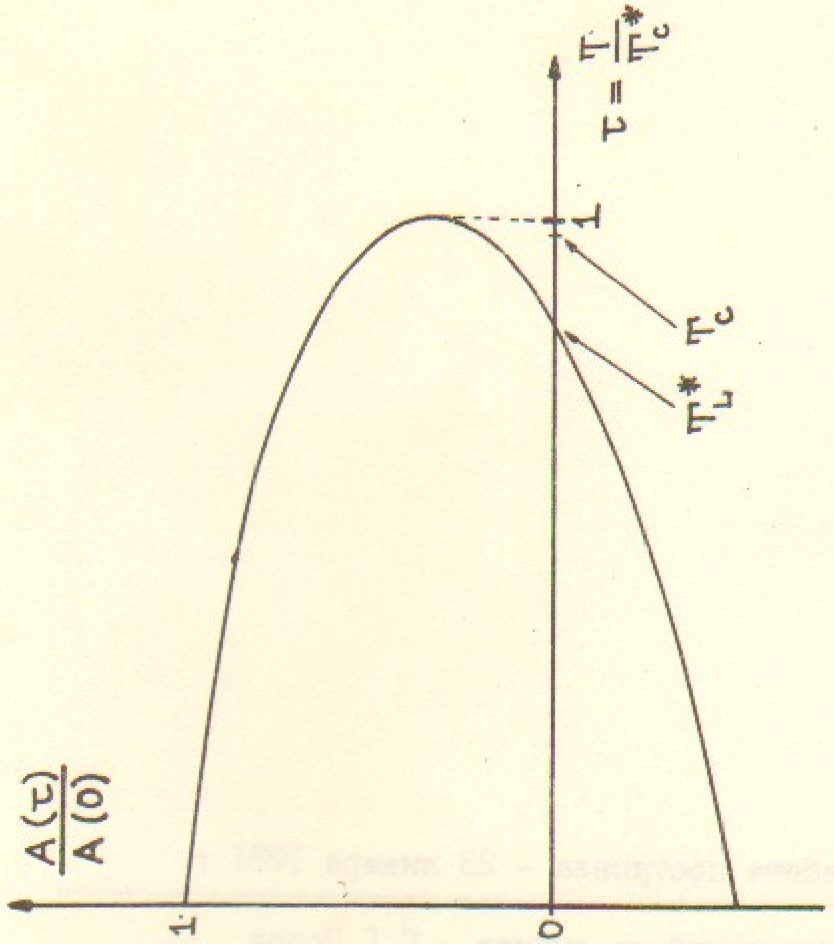

Fig. 1. Temperature dependence of amplitude A.