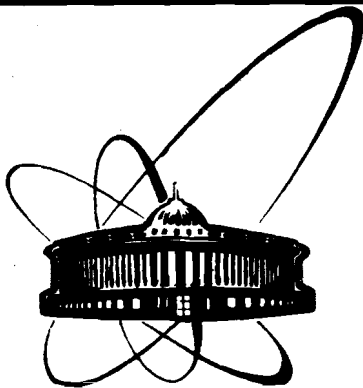


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ОБЪЕДИНЕННОГО
ИНСТИТУТА
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PRETRANSITIONAL PHENOMENA
AND FLUCTUATIONS
OF CRYSTALLINE STRUCTURE

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1. INTRODUCTION

In the crystals near first-order phase transitions there exist the so-called pretransitional phenomena^{/1/} when local fluctuations arise breaking the symmetry of the crystalline lattice. For example, under melting these fluctuations are connected with the local dissociation of the lattice and are the nuclei of liquid phase having no regular structure inside a solid with a fixed crystalline structure. Under structural phase transitions these fluctuations are metastable clusters with one crystallographic structure inside a matrix with another structure. Near the stratification point of a binary compound the stratification fluctuations can appear. Fluctuational coexistence of an ordered lattice and amorphous matter is also a kind of structural fluctuations.

The appearance of structural fluctuations near the phase-transition point leads to a number of pretransitional phenomena^{/1/} that are manifested in anomalies of thermodynamic and dynamic characteristics. Thus, the specific heat strongly increases near the transition point; in metastable matters the specific heat even can have a maximum below the transition point. The diffusion coefficient also displays an anomalous increase in the vicinity of the phase-transition point. The Mössbauer-effect probability has there a sharp sagging.

Fluctuations of one thermodynamic phase inside another have been called by Frenkel^{/2/} the heterophase fluctuations. Structural fluctuations are just a sort of the latter.

Matters in which the heterophase fluctuations occur are nonuniform and nonequilibrium, more correctly, they are quasi-equilibrium; all this strongly complicates their consistent statistical description without involving phenomenological considerations. However, it is possible to overcome the mentioned difficulties using the approach^{/3-7/} based on the averaging over heterophase configurations when calculating observables. As a result, one is able to define a renormalized Hamiltonian and equations for the probabilities of the corresponding phases. All observables depend only on microscopic parameters of a system and on thermodynamic variables, thus do not requiring the use of phenomenological functions. The

behaviour of the phase probabilities allows us to describe the phase transition itself and to explain the anomalies of thermodynamic and dynamic characteristics caused by the existence of pretransitional fluctuations of the crystalline structure.

This communication contains the results reported at the Twelfth European Crystallographic Meeting in Moscow, 1989.

2. AVERAGING OVER HETEROPHASE CONFIGURATIONS

In this Section we shall explain the main idea of obtaining the renormalized Hamiltonian after averaging over heterophase configurations. The mathematical details have been published earlier^{/5-7/}.

Let any heterophase configuration be described by separation of the real space V into two submanifolds V_ν ($\nu = 1, 2$) corresponding to two different thermodynamic phases. Such a separation is always possible with the help of the Gibbs method of separating surfaces^{/8/}. In the real space this separation can be fixed^{/5-7/} by the set

$$\xi = \{ \xi_\nu(\vec{r}) \mid \nu = 1, 2; \vec{r} \in V \}$$

of the two characteristic functions

$$\xi_\nu(\vec{r}) = \begin{cases} 1, & \vec{r} \in V_\nu, \\ 0, & \vec{r} \notin V_\nu, \end{cases}$$

assuming that

$$V_1 \cup V_2 = V.$$

The partition function for a fixed set of characteristic functions, that is, for a fixed phase configuration is given by

$$Z(\xi) = \text{Tr} e^{-\Gamma(\xi)},$$

here the trace is taken over inner degrees of freedom of the quasi-Hamiltonian $\Gamma(\xi)$ describing the quasi-equilibrium system. The total partition function is to be defined as an average of $Z(\xi)$ over all possible configurations of phases. The latter average in our case should be defined as a functional integral

over characteristic functions,

$$Z = \int Z(\xi) \mathcal{D}\xi.$$

The renormalized Hamiltonian \bar{H} is defined by the equation

$$\int e^{-\Gamma(\xi)} \mathcal{D}\xi = e^{-\bar{H}/\Theta},$$

Θ being the temperature, $k_B \equiv 1$. If we are able to find out the renormalized Hamiltonian, then we have for the partition function

$$Z = \text{Tr} e^{-\bar{H}/\Theta}.$$

The renormalization factors entering into the Hamiltonian \bar{H} are the geometric probabilities w_ν ($\nu = 1, 2$) of the corresponding phases.

The phase probabilities are to be found by minimizing the thermodynamic potential

$$y = -\frac{1}{N} \ln \text{Tr} e^{-\bar{H}/\Theta},$$

in which N is the number of particles in the system.

3. FLUCTUATIONS OF CRYSTALLINE STRUCTURE

Let the phase numbered ν have a structure described by the set $\{ \vec{a}_{i\nu} \}$ of crystalline vectors $\vec{a}_{i\nu}$ ($i = 1, 2, \dots, N$). The renormalized Hamiltonian is written^{/3-7/} as

$$\bar{H} = \bigoplus_\nu H_\nu = H_1 \oplus H_2, \quad (1)$$

where

$$H_\nu = w_\nu \sum_i \frac{p_{i\nu}^2}{2m} + \frac{w_\nu}{2} \sum_{ij} v(\vec{R}_{ij\nu}), \quad (2)$$

$\vec{p}_{i\nu}$ is the momentum of a particle of the number i in the phase ν , m is the mass, $v(\vec{R}_{ij\nu})$ is the interparticle interaction,

$$\vec{R}_{ij\nu} \equiv \vec{R}_{i\nu} - \vec{R}_{j\nu} \quad (3)$$

and $\vec{R}_{i\nu}$ is the corresponding space vector. For a particular

crystalline structure $v(\vec{R}_{ij\nu})$ can be expanded near the lattice sites given by $\{a_{ij\nu}\}$ and the phonon variables can be introduced either in the standard way or defining the relative displacement^{/9/}

$$\vec{u}_{ij\nu} = \vec{R}_{ij\nu} - \vec{a}_{ij\nu}, \quad (\vec{a}_{ij\nu} \equiv \vec{a}_{i\nu} - \vec{a}_{j\nu}). \quad (4)$$

According to their definition, the phase probabilities have the property

$$\sum_{\nu} w_{\nu} = 1, \quad 0 \leq w_{\nu} \leq 1. \quad (5)$$

Minimizing the thermodynamic potential

$$y = y(\vec{w}), \quad \vec{w} \equiv \{w_{\nu} | \nu = 1, 2\},$$

it is convenient to introduce the notation

$$w \equiv w_1, \quad 1 - w \equiv w_2. \quad (6)$$

Then, the equation for the phase probability takes the form

$$\frac{\partial y}{\partial w} = \frac{1}{N\Theta} \langle \frac{\partial \bar{H}}{\partial w} \rangle = 0. \quad (7)$$

Simplifying equation (7) we may neglect the dependence of displacement (4) on the probability w_{ν} , which is admissible at low temperatures. Then, with the use of the notation

$$K_{\nu} \equiv \langle \frac{1}{N} \sum_i \frac{p_{i\nu}^2}{2m} \rangle \quad (8)$$

and

$$\Phi_{\nu} \equiv \langle \frac{1}{2N} \sum_{ij} v(\vec{R}_{ij\nu}) \rangle, \quad (9)$$

equation (7) yields

$$w = \frac{2\Phi_2 + K_2 - K_1}{2(\Phi_1 + \Phi_2)}, \quad w_2 = \frac{2\Phi_1 + K_1 - K_2}{2(\Phi_1 + \Phi_2)}. \quad (10)$$

In the case when w is the probability of the basic phase, w_2 is the probability of structure fluctuations.

Formula (10) shows, for instance, that one-dimensional and two-dimensional crystals are impossible. This follows from the fact that, as is known, for these situations $\Phi_1 \rightarrow \infty$; thus $w \rightarrow 0$ if Φ_2 is finite. The latter is true when the second structure ($\nu = 2$) corresponds to the liquid.

4. SOME MODELS AND RESULTS

Begin first with a very simple mechanical model qualitatively illustrating some features of system with structural fluctuations. The following mechanical experiment has been accomplished^{/10/}.

The two-dimensional system was considered. The role of particles was played by solid triangles placed on a plane surface. In our case, the surface was made of fabric. The vibration of the surface modelled temperature fluctuations. By varying the intensity of vibrations, it was possible to regulate "the temperature". Changing the number of triangles we could vary the "particle" density. At high densities, the system presented a rigid crystalline structure pictured in Fig.1. At more moderate densities, the "temperature" fluctuation of triangles occurred; however all of them fluctuated in the vicinity of fixed points forming the same crystalline structure as in Fig.1. More correctly, the triangle centers of masses vibrated near the corresponding lattice sites, see Fig.2. At lower densities, the behaviour was as follows. For a period of time τ_{loc} each of the triangles was localized vibrating near its lattice site, thus preserving in the average the crystalline structure. Then, for a time τ_{del} the local breaking of the average cry-

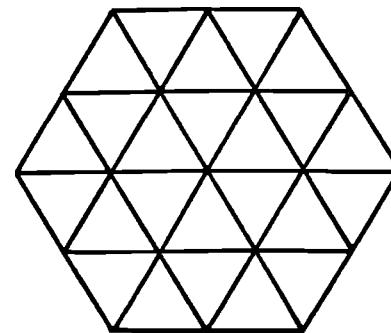


Fig.1. The close packed crystalline structure of the mechanical model.

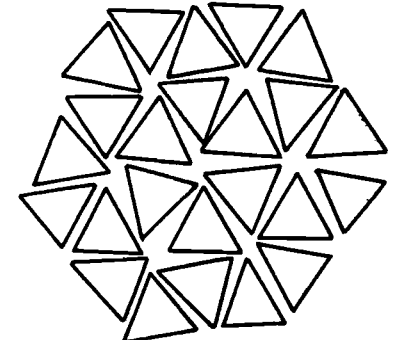


Fig.2. The mechanical model at intermediate densities displaying the pure crystalline order.

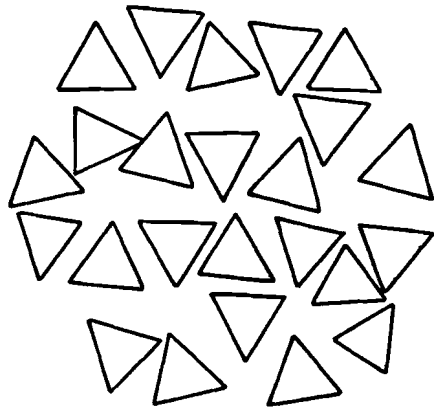


Fig.3. The mechanical model forming in the average a crystalline state but with structural fluctuations present.

stalline symmetry occurred, when some group of triangles moved chaotically interchanging their places. These chaotic movements of delocalized "particles" modelled the structural fluctuations corresponding to the fluctuational dissociation of the lattice of real crystals. The

low-density case is shown in Fig.3. The probability of the structural fluctuations could be defined as the ratio

$$w_2 = \tau_{del} / \tau_{loc} .$$

At very low densities there was no crystalline structure even in the average, this state corresponded to the pure liquid state.

The calculations of the phase probabilities (10) for the case of the crystal-liquid phase transition have been given by the author^{/5/} with the help of the correlated Hartree approximation. The results of the calculations for the inert-group crystals are presented in Figs.4 and 5, where θ_1 and θ_2 are the temperatures of the stability boundaries and θ_m is the temperature of melting.

The specific heat of a heterophase system has been calculated^{/10/} for a pseudospin model in the mean-field approximation. In metastable systems the specific heat can have a maximum below the critical temperature (see Fig. 6), and in stable systems it has a jump at the nucleation temperature θ_n , where the probability of heterophase fluctuations becomes non-zero (see Fig. 7).

The Mössbauer effect probability has also been calculated^{/9/} and its experimentally observed anomalous saggins have found an explanation as due to the presence of heterophase fluctuations near the transition point.

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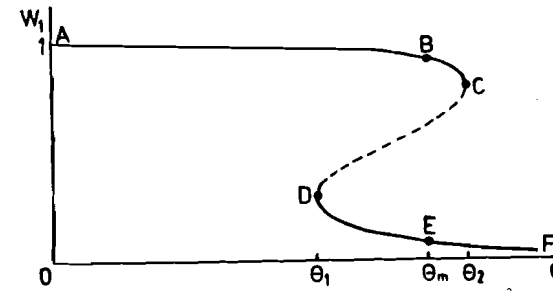


Fig.4. The probability of the crystalline state as a function of temperature.

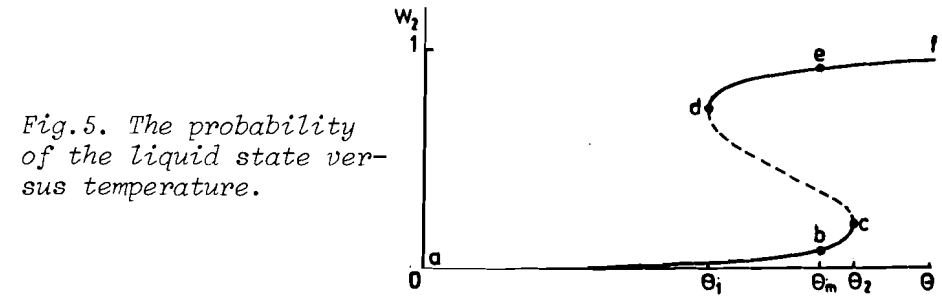


Fig.5. The probability of the liquid state versus temperature.

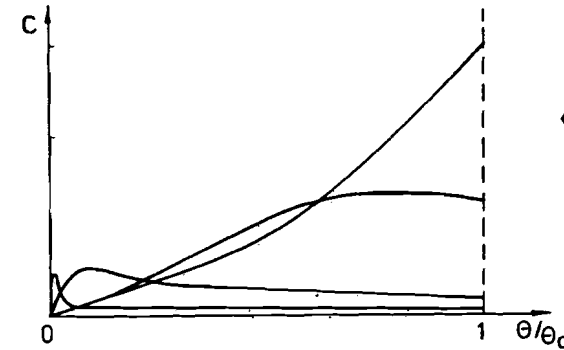


Fig.6. The specific heat of a metastable system for different interaction constants.

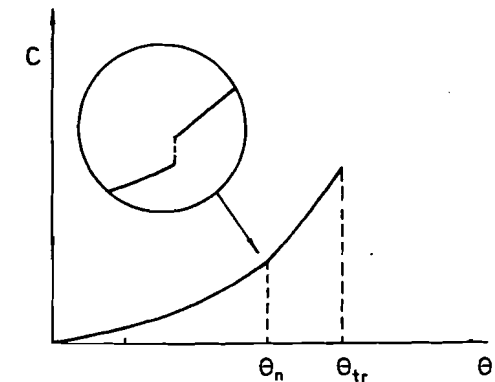


Fig.7. The jump of the specific heat at the nucleation point.

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Предпереходные явления и флуктуации
кристаллической структуры

Представлен метод для описания макроскопических флуктуаций одной кристаллической структуры внутри другой. Примерами таких флуктуаций служат: жидкостная локальная диссоциация решетки внутри кристалла, кристаллоподобные кластеры в жидкости, зародыши конкурирующих кристаллографических структур, флуктуации расслоения в бинарных смесях. Метод проиллюстрирован несколькими моделями.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1989

Yukalov V. I.

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Pretransitional Phenomena and Fluctuations
of Crystalline Structure

A method is presented for describing macroscopic fluctuations of one crystalline structure inside another. The examples of these fluctuations are: the liquidlike local dissociation of a lattice inside a crystal, crystalline clusters in the liquid, nuclei of competing crystallographic structures, stratification fluctuations in binary mixtures. The method is illustrated by several models.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1989