The theory of mesoscopic fluctuations is applied to inhomogeneous solids consisting of chaotically distributed regions with different crystalline structure. This approach makes it possible to describe statistical properties of such mixture by constructing a renormalized Hamiltonian. The relative volumes occupied by each of the coexisting structures define the corresponding geometric probabilities. In the case of a frozen heterophase system these probabilities should be given a priori. And in the case of a thermal heterophase mixture the structural probabilities are to be defined self-consistently by minimizing a thermodynamical potential. This permits to find the temperature behavior of the probabilities which is especially important near the points of structural phase transitions. The presence of these structural fluctuations yields a softening of a crystal and a decrease of the effective Debye temperature. These effects can be directly seen by nuclear gamma resonance since the occurrence of structural fluctuations is accompanied by a noticeable sagging of the Mössbauer factor at the point of structural phase transition. The structural fluctuations also lead to the attenuation of sound and increase of isothermic compressibility.

I. INTRODUCTION

There are many examples of matter consisting of regions, chaotically distributed in space, with different structural properties. For instance, such are some polymorphic materials. Another example is a crystal subject to strong mechanical stress after which the cracks and branches of dislocation are formed in it. These defects have a tendency to group inside compact regions. The latter, from the point of view of statistical physics, can be treated as nuclei of the amorphised phase inside a crystalline matrix [1]. A similar picture develops in crystals under the action of irradiation by fast neutrons when the pores and regions of disorder arise. Under strong irradiation cracks also appear. These defects form groups and clusters randomly distributed in space, e.g. as is shown in Figs. 1 and 2. For a statistical description of an irradiated crystal the defected regions can be treated as embryos of disordered, usually rarefied, phase inside an ordered, more dense, crystalline structure [2,3]. The relative volume occupied by the disordered phase can be measured, with a good accuracy, by investigating the nuclear gamma resonance spectra and the behavior of the Mössbauer factor [4,5].

In the considered examples the germs of a disordered structure are randomly distributed in space inside an ordered structure. This is why these germs can be called the spatial structural fluctuations. With respect to time, they are frozen, which means that their average lifetime, $\tau_f$, is much longer than the characteristic time of an experiment, or the observation time, $\tau_{obs}$, that is: $\tau_f \gg \tau_{obs}$. In the opposite case, when $\tau_f \ll \tau_{obs}$, we have thermal structural fluctuations. The example of the latter are even more numerous than those of the frozen structural fluctuations.

Water, the most widespread matter on Earth, gives us a cogent example of a system consisting of at least two coexisting structures, which is supported by numerous experiments studying its thermodynamic and dielectric properties and analysing the Raman spectroscopy data [6 - 8]. A very convincing is the molecular - dynamic investigation [9] showing that fluctuations in water can be decomposed into two components: a fast component ($10^{-14} - 10^{-13}$ s) associated with the libration motion in one of the water inherent structures and a slow component ($10^{-12} - 10^{-11}$ s) associated with the water structure changes. These thermal structural fluctuations in water are related to large local energy fluctuations involving about 10–100 molecules.

Thermal structural fluctuations often appear in the vicinity of structural phase transitions. In principle, these fluctuations are possible near both types of structural transitions, near displacive as well as near order–disorder type. The distinction between the two types of structural phase transitions can be traced, for example, by their different isotope effects [10], although in the presence of strong fluctuations this distinction becomes less pronounced [11 - 13]. The existence of structural fluctuations around the point of a phase transition reveals itself in the so-called pretransitional phenomena [14,15].

The freezing - melting phase transition is also a kind of structural transitions. Below the melting point, the fluctuational lattice dissociation can arise breaking the local crystalline symmetry, while above the freezing point the structural fluctuations are represented by quasicrystalline clusters inside a fluid phase with no crystalline structure. Only taking into account the existence of these structural fluctuations it is possible to develop a realistic theory of
melting and crystallization [16,17]. Such fluctuations should be especially important during the melting of small clusters [18] and solid–fluid phase transition of quantum systems [19].

Quantum crystals exhibit near phase transition points the well observed fluctuational coexistence of competing structures. This takes place, for example, in solid $^4$He along the line of the structural transition between h.c.p. and b.c.c. phases and also in the solid mixture of $^4$He with $^3$He along the stratification line [20]. These local fluctuational effects involve usually about 100 particles.

Fluctuations of one phase inside another can be called [21] the heterophase fluctuations. The structural fluctuations are just a sort of the latter. An extensive description of a great number of systems exhibiting these fluctuations has been done in the recent review [22]. Therefore, we now shall limit ourselves by the examples considered above, mentioning only that the structural fluctuations can play a crucial role in high - temperature superconductors [23].

The heterophase fluctuations are mesoscopic since the characteristic size of such a fluctuation, $l_f$, satisfies the inequality

$$a \ll l_f \ll L,$$

in which $a$ is the average distance between particles of the system and $L$ is the linear size of the latter. This drastically distinguishes the mesoscopic structural fluctuations from the microscopic fluctuations of particles inside the same structure. Thus, the oscillations of particles in a crystal in the vicinity of the corresponding lattice sites are the most known microscopic fluctuations, the root - mean - square deviation of a particle from its lattice position being $r_0 \ll a$.

Another characteristic feature of the heterophase fluctuations is that the typical energy of each of them is much larger than the average single - particle energy [24]. This seems to be quite understandable since a heterophase fluctuation, being mesoscopic by its nature, involves many particles whose number is $N_f \gg 1$.

The system with structural fluctuations are difficult to describe. This is because such systems are nonuniform with the nonuniformity occurring on mesoscopic scale [22]. Each structural nucleus can have a complicated ramified form and can exhibit nontrivial motion [24]. Some thermodynamic features of such systems can be seized by simple phenomenological models (see discussion in Ref.[22] and also [25,26]). However, in phenomenological treatment one usually has to invoke one or several fitting functions designed to satisfy particular experiments. Of course, this is not satisfactory from the point of view of statistical mechanics. These and other difficulties have been discussed and illustrated by a mechanical model in Ref.[27].

Recently, a consistent statistical approach has been developed for treating the systems with mesoscopic heterophase fluctuations [22]. In the present paper we apply this approach to the systems with structural fluctuations. In Sec.II the main steps of constructing a renormalized Hamiltonian for such systems are explained, the general equations for the structural probabilities and stability conditions are analysed. In Sec.III we concretize the problem for the coexisting crystalline structures. The behavior of structure probabilities in the vicinity of a temperature of a structural phase transition is studied in Sec.IV, using the Debye approximation. A very effective tool for examining the properties of structural fluctuations is the Mössbauer effect. Therefore, in Sec.V we scrutinize the peculiar behavior of the Mössbauer factor near the temperature of structural phase transition and show how the presence of structural fluctuations yields characteristic saggings of the Mössbauer factor. These fluctuations also lead to the attenuation of the sound velocity and to the enhancement of the isothermal compressibility, as is discussed in Sec.VI. Résumé is given in Sec.VII. Everywhere below the system of units is used where $\hbar = k_B = 1$.

**II. RENORMALIZED HAMILTONIAN**

Consider a system in which two structures can coexist. We enumerate the structures by the index $\nu = 1, 2$. In the case when both structures are crystalline, each of them is characterized by a set

$$A_\nu = \{ \vec{a}_i^{\nu} | i = 1, 2, \ldots N \} \quad (\nu = 1, 2)$$

of lattice vectors $\vec{a}_i^{\nu}$. As is discussed above, the distribution of structures in the space is random. Therefore, it is necessary to define the procedure of averaging over structure configurations. Each configuration can be given by specifying which regions $V_\nu$ ($\nu = 1, 2$) of the total system volume $V$ are occupied by this or that structure, so that

$$V = \cup_\nu V_\nu = V_1 \cup V_2.$$ 

Such a specification can be defined [22] by fixing a set

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

(1)
of functions

\[ \xi_\nu(\xi) \equiv \begin{cases} 1, & \vec{r} \in V_\nu \\ 0, & \vec{r} \notin V_\nu \end{cases} \] (2)

that are called the manifold characteristic functions, or the manifold indicator functions, or simply, the manifold indicators. In this way, a distribution of structures in space, that is a structure configuration, is uniquely defined by a covering \( \{V_\nu | \nu = 1, 2\} \) of \( V \), or, equivalently, by the indicator set (1) of manifold indicators (2). The many of all possible collections of \( \xi \) form the topological space \( T(\xi) \). In order to define the averaging over structure configurations, we need to introduce a functional measure on \( T(\xi) \). This procedure with all mathematical details has been thoroughly described in a series of papers [17,28 - 30] and expounded in a recent review [22]. Therefore, there is no need to repeat it here. But for the logical self-consistency of the present exposition we will delineate the main steps of this procedure.

Each fixed structure configuration depicts a nonuniform system which can be characterized by the quasiequilibrium Gibbs ensemble with a distribution proportional to \( e^{-\Gamma(\xi)} \), where \( \Gamma(\xi) \) is a quasi-Hamiltonian defined for a given set (1). Specifying a functional measure \( \int D\xi \) on the topological space of structure configurations, we can write the partition function as

\[ Z = Tr \int e^{-\Gamma(\xi)} D\xi, \] (3)

where \( Tr \) means the trace over all quantum-mechanical degrees of freedom, or over the phase space in the classical case. The renormalized Hamiltonian \( \tilde{H} \) is defined by the relation

\[ \int e^{-\Gamma(\xi)} D\xi = e^{-\tilde{H}/T}, \]

which yields

\[ \tilde{H} = -T \ln \int e^{-\Gamma(\xi)} D\xi. \] (4)

Then the partition function (3) becomes

\[ Z = T r e^{-\tilde{H}/T}. \]

For each particular structure a space \( \mathcal{H}_\nu \) of microscopic states is to be defined, consisting of wave functions enjoying the property of the corresponding structural symmetry. The latter, in the case of a crystalline structure, is the symmetry of a given crystalline lattice. The renormalized Hamiltonian (4) acts on the fiber space

\[ \mathcal{Y} = \otimes_\nu \mathcal{H}_\nu = \mathcal{H}_1 \otimes \mathcal{H}_2. \] (5)

From definition (4) it is clear that the renormalized Hamiltonian should depend on the probability weights of coexisting structures. These structure probabilities \( w_\nu \) have the meaning of the geometric probabilities, that is, each \( w_\nu \) determines the ratio of the effective volume occupied by the phase \( \nu \) to the total volume of the system. According to this definition, the standard probability properties

\[ 0 \leq w_\nu \leq 1, \quad \sum_\nu w_\nu = w_1 + w_2 = 1 \] (6)

hold. In the case of a frozen structure distribution the structure probabilities \( w_\nu \) are to be given a priori. For thermal structural fluctuations the values of \( w_\nu \) are to be found from the minimization of a thermodynamic potential

\[ f = -\frac{T}{N} \ln Tr e^{-\tilde{H}/T} \] (7)

under condition (6). Taking into account the normalization condition for \( w_\nu \) explicitly, we may write

\[ w_1 \equiv w, \quad w_2 \equiv 1 - w. \] (8)
Thence, the extremum of (7) with respect to \( w \) is given by the equation

\[
\frac{\partial f}{\partial w} = \frac{1}{N} < \frac{\partial \tilde{H}}{\partial w} > = 0,
\]

where \( < \ldots > \) implies the statistical average which for an operator \( \hat{A} \) is written as

\[
< \hat{A} > \equiv \text{Tr} \hat{\rho} \hat{A}, \quad \hat{\rho} \equiv \frac{1}{Z} e^{-\tilde{H}/T}.
\]

Remind that according to (4) the renormalized Hamiltonian \( \tilde{H} = \tilde{H} (\{ w_\nu \}) \) depends on structure probabilities. In addition to Eq.(9) defining \( w_\nu \), we have the inequality

\[
\frac{\partial^2 f}{\partial w^2} > 0 \quad (0 \leq w \leq 1)
\]

showing that the found \( w_\nu \) provide us with the minimum of (7). Eq.(10) is the stability condition with respect to variations of structure probabilities. From (7) and (10) we have

\[
\frac{1}{N} \left\{ < \frac{\partial^2 \tilde{H}}{\partial w^2} > - \frac{1}{T} \left( \frac{\partial \tilde{H}}{\partial w} \right)^2 \right\} > 0.
\]

As far as the second term in (11) is always non-negative, the necessary stability condition is

\[
\left\{ < \frac{\partial^2 \tilde{H}}{\partial w^2} > \right\} > 0.
\]

To proceed further, we have to concretize the situation. Denote by \( \vec{R}_{i\nu} \) the position of a particle \( i \) in a structure \( \nu \) and by \( \vec{p}_{i\nu} \) the momentum of this particle in the same structure; here \( i = 1, 2, \ldots, N \) and \( \nu = 1, 2 \). Let \( \Phi(\vec{R}_{ij\nu}) \) be the potential of interaction between the particles \( i \) and \( j \) for which

\[
\vec{R}_{ij\nu} = \vec{R}_{i\nu} - \vec{R}_{j\nu}.
\]

Realizing the procedure described above, after the averaging over structure configurations we obtain [22] the renormalized Hamiltonian

\[
\tilde{H} = \oplus_\nu H_\nu = H_1 \oplus H_2,
\]

which is a direct sum of terms

\[
H_\nu = w_\nu \sum_{i=1}^{N} \frac{\vec{p}_{i\nu}^2}{2m} + \frac{w_\nu^2}{2} \sum_{i \neq j}^{N} \Phi(\vec{R}_{ij\nu}),
\]

where \( m \) is a particle mass.

With the renormalized Hamiltonian given by (14) and (15), Eq.(9) yields

\[
w = \frac{2\Phi_2 + K_2 - K_1}{2(\Phi_1 + \Phi_2)},
\]

where

\[
K_\nu = < \frac{1}{N} \sum_{i=1}^{N} \frac{\vec{p}_{i\nu}^2}{2m} >
\]

is the mean kinetic energy per particle in the structure \( \nu \) and
\[ \Phi_\nu \equiv < \frac{1}{2N} \sum_{i \neq j}^N \Phi(\vec{R}_{ij\nu}) > \]  

(18)

is the mean potential energy per particle in the same structure. The necessary condition (12) gives

\[ \Phi_1 + \Phi_2 > 0. \]  

(19)

Additional stability conditions follows from the requirement that \( 0 \leq w_\nu \leq 1 \), which leads to the inequalities

\[ -2\Phi_1 \leq K_1 - K_2 \leq 2\Phi_2. \]  

(20)

Condition (20) has to be true always since it secures the correct definition (6) of the structure probabilities. If (20) does not hold, this means that the considered structures cannot coexist, even in a metastable mixed state, and the system is to be in a pure state corresponding to the structure that provides the minimum of the thermodynamic potential (7). While when conditions (11),(12) or (19) are not valid but (20) holds, the system with structural fluctuations can exist in a metastable state.

The described approach has been applied to different systems (see [22]). It has made it possible to construct a consistent theory of melting and crystalization [16,17] by considering the coexisting solid and liquid structures. It is possible to note that when applying this approach to one - and two - dimensional crystals we immediately come to the conclusion that in these crystals the infinite long - range order is impossible. Really, suppose that the index \( \nu = 1 \) corresponds to a crystalline periodic structure, and \( \nu = 2 \), to a uniform liquid structure. As is known after Peierls [31], the phonon potential energy of one - and two - dimensional crystals diverges. In our case this means that \( \Phi_1 \to \infty \). Then from (16) it follows that \( w \equiv w_1 \to 0 \), and, respectively, \( w_2 \to 1 \). This shows that one - and two - dimensional periodic structures have zero probability to exist.

The stability condition (19) has a simple physical interpretation permitting to understand which structures can, in principle, coexist. All structures can be roughly divided into two sorts, rigid and soft, according to the sign of \( \Phi_\nu \). The structure can be called rigid if \( \Phi_\nu < 0 \) since this implies that the particles are strongly bound. And we can say that the structure is soft if \( \Phi_\nu > 0 \) since the particles forming it are weakly bound or unbound. The stability condition (19) tells us that two structures can thermally coexist only when at least one of them is soft. Two rigid structures cannot thermally coexist in a stable system. For example, liquid has a soft structure. Therefore, a periodic crystalline structure and uniform liquid structure can, in principle, coexist near the solid - liquid phase transition point [16,17]. Several examples of possible thermal coexistence of different phases have been considered for lattice - gas models (see review [22]). Thus, for a lattice - gas model containing two phases with different densities it has been shown that such a system is unstable when the effective interaction between particles is attractive [2] but the system becomes stable if the effective interaction is repulsive [3]. Of course, lattice - gas models can give only a rough parody on real systems with more complicated structures, although these models often describe well chemical processes [32]. Low dimensionality (less than three) also makes it more difficult the appearance of thermal structural fluctuations. For instance, the latter, as has been rigorously shown [29,33 - 35], do not arise in the two - dimensional Ising - type models, though can exist in three - dimensional ones. Nevertheless, a frozen metastable coexistence of two different structures seems to be always possible. The condition for the appearance of thermal structural fluctuations changes to be more favorable in the vicinity of a structural phase transition where at least one of, or even both, coexisting structures become unstable and soft.

### III. CRYSTALLINE STRUCTURES

Consider the case when two coexisting structures are both crystalline being characterized by different lattice vectors. Lattice sites of each structure are given by a vector set \( \{ \vec{a}_{i\nu} | i = 1, 2, \ldots, N \} \). As usual [36], we can expand \( \Phi(\vec{R}_{ij\nu}) \) in Hamiltonian (15) in powers of the deviations

\[ \vec{a}_{i\nu} \equiv \vec{R}_{ij\nu} - \vec{a}_{i\nu} \]  

(21)

from the lattice sites, limiting ourselves by the second order of this expansion. We are interested here in qualitative understanding of the behavior of a heterostructural system, therefore we will not discuss such questions that do not change principally this behavior although can be important in quantitative calculations for particular substances. These questions include the account of interparticle correlations [17,37 - 40] of anharmonicities [41,42], and of vacancies [43]. Instead, we can think of \( \Phi(\vec{R}_{ij\nu}) \) as of an effective potential adjust to take into account these effects, at least partially.
After expanding Hamiltonian (15) in powers of deviations (21), we get

$$H_\nu = E_{\nu}^{st} + H_{\nu}^{ph},$$

where the first term

$$E_{\nu}^{st} = Nu_{\nu}^2U_\nu$$

is a static potential energy with

$$U_\nu = \frac{1}{2N} \sum_{i \neq j}^{N} \Phi(\vec{a}_{ij\nu}) \left( \vec{a}_{ij\nu} \equiv \vec{a}_{i\nu} - \vec{a}_{j\nu} \right),$$

and the second term

$$H_{\nu}^{ph} = w_{\nu} \sum_{i=1}^{N} \frac{p_{i\nu}^2}{2m} + \frac{w_{\nu}^2}{2} \sum_{i,j}^{N} D_{ij\nu} u_{i\nu}^\alpha u_{j\nu}^\beta$$

is the phonon Hamiltonian with the dynamical matrix

$$D_{ij\nu} = \frac{\partial^2 \Phi(\vec{a}_{ij\nu})}{\partial a_{i\nu}^\alpha \partial a_{j\nu}^\beta}, \quad (i \neq j)$$

$$D_{ii\nu} = N \sum_{j (\neq i)} \frac{\partial^2 \Phi(\vec{a}_{ij\nu})}{\partial (\vec{a}_{i\nu}^\alpha)^2}. $$

The mean potential energy (18) becomes

$$\Phi_\nu = U_\nu + \frac{1}{2N} \sum_{i,j}^{N} \sum_{\alpha,\beta}^{3} D_{ij\nu}^{\alpha\beta} < u_{i\nu}^\alpha u_{j\nu}^\beta >. $$

The Hamiltonian (25) can be diagonalized in a standard way by introducing the transformations

$$\vec{u}_{i\nu} = \sum_{k,s} \vec{e}_{ks\nu} \left( \frac{2mN}{\omega_{ks\nu}} \right)^{1/2} \left( b_{ks\nu} + b_{-ks\nu}^+ \right) e^{i\vec{k} \cdot \vec{a}_{i\nu}},$$

$$\vec{p}_{i\nu} = -i \sum_{k,s} \left( \frac{m\omega_{ks\nu}}{2N} \right)^{1/2} \vec{e}_{ks\nu} \left( b_{ks\nu} - b_{-ks\nu}^+ \right) e^{i\vec{k} \cdot \vec{a}_{i\nu}},$$

using the orthogonality condition

$$\frac{1}{N} \sum_{i=1}^{N} \vec{e}_{k\nu} \cdot \vec{e}_{k'\nu} e^{i(k-k') \cdot \vec{a}_{\nu}} = \delta_{kk'} \delta_{ss'},$$

and defining the frequencies $\omega_{ks\nu}$ by the eigenvalue problem

$$w_{\nu} = \sum_{j=1}^{N} \sum_{\beta=1}^{3} D_{ij\nu}^{\alpha\beta} e^{i(k-k') \cdot \vec{a}_{j\nu}} = \omega_{ks\nu}^2 e_{ks\nu}^\alpha,$$

whose eigenfunctions are the polarization vectors $\vec{e}_{ks\nu}$. As a result, we have the phonon Hamiltonian

$$H_{\nu}^{ph} = w_{\nu} \sum_{k,s} \omega_{ks\nu} \left( b_{ks\nu}^+ b_{ks\nu} + \frac{1}{2} \right).$$
Although the way of obtaining (30) is standard, following it we have to be very cautious paying much attention to the nontrivial dependence of the Hamiltonian on the structure probability factors \( w_\nu \). Because of this, the phonon frequencies defined by (29) become dependent on \( w_\nu \) as well. The structure probability \( w_\nu \) enters also in all main averages such as the phonon distribution

\[
n_{ks\nu} \equiv \langle b_{ks\nu}^+ b_{ks\nu} \rangle = \left[ \exp \left( \frac{w_\nu \omega_{ks\nu}}{T} \right) - 1 \right]^{-1},
\]

the momentum squared

\[
\langle \vec{p}_{\nu}^2 \rangle = \frac{m}{2N} \sum_{k,s} \omega_{ks\nu} \coth \frac{w_\nu \omega_{ks\nu}}{2T},
\]

and the correlation function

\[
\langle u_{\alpha i\nu}^\alpha u_{\beta j\nu}^\beta \rangle = \frac{\delta_{ij}}{2N} \sum_{k,s} e_{\alpha ks\nu} e_{\beta ks\nu} \coth \frac{w_\nu \omega_{ks\nu}}{2T}. \tag{33}
\]

In its turn, Eq.(16) for the structure probability involves the mean kinetic energies (17),

\[
K_\nu = \frac{1}{4N} \sum_{k,s} \omega_{ks\nu} \coth \frac{w_\nu \omega_{ks\nu}}{2T}, \tag{34}
\]

and the mean potential energies (18),

\[
\Phi_\nu = U_\nu + D_\nu,
\]

\[
D_\nu = \frac{1}{4N} \sum_{j=1}^N \sum_{k,s} \sum_{\alpha,\beta} e_{\alpha ks\nu} e_{\beta ks\nu} D_{ij\nu} \coth \frac{w_\nu \omega_{ks\nu}}{2T}. \tag{35}
\]

The internal energy of the heterostructural system is

\[
E = \langle -H \rangle = E_1 + E_2,
\]

\[
E_\nu = \langle H_\nu \rangle = E_\nu^{st} + E_\nu^{ph}, \tag{36}
\]

where the static energy is given by (23) and the phonon energy is

\[
E_\nu^{ph} = \langle H_\nu^{ph} \rangle = \frac{w_\nu}{2} \sum_{k,s} \omega_{ks\nu} \coth \frac{w_\nu \omega_{ks\nu}}{2T}. \tag{37}
\]

The latter, using the relations

\[
K_\nu = w_\nu D_\nu, \quad w_\nu \Phi_\nu = w_\nu U_\nu + K_\nu, \tag{38}
\]

can be written as

\[
E_\nu^{ph} = N(w_\nu K_\nu + w_\nu^2 D_\nu) = 2Nw_\nu K_\nu. \tag{39}
\]

Thus, we see that the internal energy (36) depends on temperature directly and also through the structure probabilities \( w_\nu \). Consequently, the specific heat of a heterophase system,

\[
C_\nu = \frac{\partial E}{\partial T} = \left( \frac{\partial E}{\partial T} \right)_w + \left( \frac{\partial E}{\partial w} \right)_T,
\]

contains an additional term, as compared to the specific heat of a pure single - structure system. This excessive term makes it possible to explain the so - called specific - heat anomalies observed in heterophase systems [24,44].

The free energy (7) takes the form

\[
f = f_1 + f_2, \quad f_\nu = \frac{1}{N} E_\nu^{st} + \frac{T}{N} \sum_{k,s} \ln \left( 2 \sinh \frac{w_\nu \omega_{ks\nu}}{2T} \right), \tag{40}
\]

which demonstrates the nonlinear dependence on the structure probabilities \( w_\nu \).
IV. STRUCTURE PROBABILITIES

The equation defining the structure probabilities can be written either as Eq.(16) with substituted there mean kinetic energies (34) and potential energies (35) or can be obtained by the direct minimization of (40) with respect to $w \equiv w_1$ and taking into account (6). Both ways, as can be checked, yield the same answer. To analyse this equation, we have first of all to remember that phonon frequencies, given by the eigenvalue problem (29), depend on structure probabilities. To make this dependence explicit, we introduce the notation

$$\omega_{k\alpha \nu} \equiv w_{\nu}^{1/2} \varepsilon_{k\alpha \nu},$$

$$\varepsilon_{k\alpha \nu}^2 \equiv \frac{1}{m} \sum_{j=1}^{N} \sum_{\alpha,\beta} D_{\alpha \beta}^j \varepsilon_{k\alpha \nu} \varepsilon_{k\beta \nu} e^{i \vec{k} \cdot \vec{a}_{\alpha \nu}},$$

in which $\varepsilon_{k\alpha \nu}$ does not contain $w_{\nu}$. Emphasizing the dependence on $w_{\nu}$ explicitly, we have for the kinetic energy (34)

$$K_{\nu} = \frac{w_{\nu}^{1/2}}{2N} \sum_{k,s} \varepsilon_{k\alpha \nu} \coth \left( \frac{w_{\nu}^{3/2} \varepsilon_{k\alpha \nu}}{2T} \right).$$

For the internal energy (36) we get

$$E = E_1 + E_2, \quad E_{\nu} = N w_{\nu}^2 U_{\nu} + 2N w_{\nu} K_{\nu}.$$

The free energy (40) becomes

$$f = f_1 + f_2,$$

$$f_{\nu} = w_{\nu}^2 U_{\nu} + \frac{T}{N} \sum_{k,s} \ln \left( 2 \sinh \frac{w_{\nu}^{3/2} \varepsilon_{k\alpha \nu}}{2T} \right).$$

Minimizing (43) with respect to $w$, with the use of notation (8) and relations

$$\frac{\partial f}{\partial w} = \frac{\partial f}{\partial w_1} - \frac{\partial f}{\partial w_2}, \quad \frac{\partial f}{\partial w_{\nu}} = 2w_{\nu} U_{\nu} + 3K_{\nu},$$

we obtain

$$w = \frac{2U_2 + 3(K_2 - K_1)}{2(U_1 + U_2)}.$$

From the inequalities $0 \leq w \leq 1$, assuming that

$$U_1 + U_2 < 0,$$

we have a necessary condition

$$U_2 \leq \frac{3}{2} (K_1 - K_2) \leq -U_1$$

for $w$ to be considered as a probability.

To further simplify the analyses, let us resort to the Debye approximation. For this, we pass to the thermodynamic limit by using the change

$$\frac{1}{N} \sum_{k,s} \rightarrow \frac{1}{\rho} \sum_{s=1}^{3} \int_{D} \frac{d \vec{k}}{(2\pi)^3},$$

where

$$D \equiv \{ \vec{k} \mid k \equiv | \vec{k} | \leq k_D \}.$$
is the Debye sphere, and the Debye momentum $k_D$ being defined by the normalization $\frac{1}{N} \sum_{k,s} 1 = 1$ giving

$$k_D = (6\pi^2 \rho)^{1/3}, \quad \rho \equiv \frac{N}{V}.$$ 

The phonon spectrum in the Debye approximation acquires the linear form, for which one has to make the substitution

$$\varepsilon_{ks\nu} \to \varepsilon_{k\nu} = c_{\nu} k,$$

$$c_{\nu}^2 \equiv \lim_{k \to 0} \frac{1}{3} \sum_{s=1}^{3} \left( \frac{\varepsilon_{ks\nu}}{k} \right)^2.$$

The quantity $c_{\nu}$ plays the role of the sound velocity in a pure $\nu$-structure. From (41), using the orthogonality property

$$\sum_{s=1}^{3} e_{ks\nu}^\alpha e_{ks\nu}^\beta = \delta_{\alpha\beta},$$

one gets

$$c_{\nu}^2 = - \lim_{k \to 0} \sum_{j=1}^{N} \sum_{\alpha=1}^{3} D_{ij\nu} \left( \frac{k a_{ij\nu}}{6mk^2} \right)^2.$$

In this way, for the kinetic energy (42) we have

$$K_{\nu} = \frac{36T^4}{\Theta_{\nu}^3 w_{\nu}} \int_0^{\Theta_{\nu}/2T} x^3 \coth x dx \quad (48)$$

and for the free energy $f_{\nu}$ we get

$$f_{\nu} = w_{\nu}^2 U_{\nu} + \frac{72T^4}{\Theta_{\nu}^3} \int_0^{\Theta_{\nu}/2T} x \ln(2 \sinh x) dx,$$

where we have introduced the notation

$$\Theta_{\nu} \equiv w_{\nu}^{3/2} T_{\nu D} \quad (T_{\nu D} \equiv c_{\nu} k_D). \quad (50)$$

Here, $T_{\nu D}$ is the Debye temperature of a pure $\nu$-structure, while $\Theta_{\nu}$ can be called an effective Debye temperature of a structure inside a mixed heterostructural system.

Formulas (48) - (50) show that the low and high temperature limits for a heterostructural system are to be defined not with respect to $T_{\nu D}$ but with respect to the effective temperature $\Theta_{\nu}$ given by (50). The latter is renormalized by the factor $w_{\nu}^{3/2}$ itself depending on temperature. To analyse the behavior of the structural probability (44) we need to write accurately the corresponding temperature limits for the kinetic energy (48).

In the case, when

$$T \ll \frac{\Theta_{\nu}}{2\pi} = \frac{w_{\nu}^{3/2}}{2\pi} T_{\nu D},$$

we can use the integrals

$$\int_0^\infty \frac{x^{2n-1}}{e^x - 1} dx = (-1)^{n-1} (2\pi)^{2n} B_{2n},$$

in which $B_n$ are the Bernoulli numbers,

$$B_0 = 1, \quad B_1 = -\frac{1}{2}, \quad B_2 = \frac{1}{6}, \quad B_3 = 0, \quad B_4 = -\frac{1}{30}, \ldots$$
In particular,
\[
\int_0^\infty \frac{x^3}{e^x - 1} \, dx = \frac{\pi^4}{15}, \quad \int_0^\infty \frac{x}{e^x - 1} \, dx = \frac{\pi^2}{6}.
\]
This yields for the kinetic energy (48)
\[
K_\nu \simeq \frac{9}{16} T_{\nu D} w_{\nu}^{1/2} + \frac{3\pi^4 T^4}{10T_{\nu D}^3 w_{\nu}^{1/2}}.
\]
(51)

In the opposite limit, when
\[
T \gg \frac{\Theta_\nu}{2\pi} = \frac{w_\nu^{3/2}}{2\pi T_{\nu D}},
\]
using the expansion
\[
\coth x \simeq \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} \quad (x < \pi),
\]
we find
\[
K_\nu \simeq \frac{3T}{2w_\nu} + \frac{3T_{\nu D}^2}{40T} w_\nu^2.
\]
(52)

To make the following expressions less cumbersome, it is convenient to introduce the dimensionless static energies
\[
u_1 = \frac{U_1}{T_{1D}}, \quad \nu_2 = \frac{U_2}{T_{1D}},
\]
\[
u = \frac{-U_1 + U_2}{T_{1D}} = -(\nu_1 + \nu_2).
\]
(53)

In the case of (45), the latter value is positive, \( \nu > 0 \). Also, we shall use the notation
\[
t = \frac{T}{T_{1D}}, \quad \tau = \frac{T_{2D}}{T_{1D}}.
\]
(54)

For definiteness, we assume that the structure corresponding to \( \nu = 1 \) has a higher Debye temperature, that is, \( T_{1D} > T_{2D} \). Hence, the parameter \( \tau \) from (54) lies in the region \( 0 < \tau < 1 \).

Now, let us understand the behavior of the structural probability (44) in the vicinity of the temperature \( T_s \) of a structural phase transition. This can be a phase transition either between two different crystalline structures or between a regular crystalline structure and an irregular glassy structure. The latter consideration is possible owing to many similarities between crystalline and glassy states \([45,46]\) and because the Debye approximation is applicable to both of them. The qualitative behavior of the structural probabilities near the structural transition temperature \( T_s \) is mainly influenced by the relation between \( T_s \) and the effective temperatures (50). It is possible to distinguish three cases that can be conditionally called the low - temperature, mid - temperature and high - temperature cases.

Begin with the low - temperature situation when the structural transition temperature satisfies the inequality
\[
T_s < \frac{w_{\nu}^{3/2}}{2\pi T_{\nu D}} \quad (\nu = 1, 2).
\]
(55)
Then, for the kinetic energies of both structures we can use the approximation (51) which is to be substituted into (44). To simplify the resulting expression, we notice that as \( w_{\nu} \leq 1 \) and \( T \approx T_s \), hence the variable \( t \) defined in (54) can be considered, according to (55), as small parameter, since \( t < 1/2\pi = 0.159 \). This yields
\[
w \simeq \alpha_0 - \alpha_0 t^4,
\]
(56)
where \( \alpha_0 \) is a solution of the equation
\[
u_1\alpha_0 + \frac{27}{32} \sqrt{\alpha_0} = u_2(1 - \alpha_0) + \frac{27}{32} \tau \sqrt{1 - \alpha_0},
\]
and

\[ \alpha_4 = \frac{144\pi^4(\sqrt{\alpha_0} - \tau^3\sqrt{1-\alpha_0})}{5\tau^3[64u\sqrt{\alpha_0(1-\alpha_0)} - 27(\sqrt{1-\alpha_0} + \tau\sqrt{\alpha_0})]} \]

Remind that \( w = w_1 \) corresponds to a more rigid structure for which \( T_{1D} > T_{2D} \). Eq.(56) shows that the probability of the more rigid structure quickly decreases as temperature increases in the vicinity of the structural - transition temperature \( T_s \).

Consider now the case when the transition temperature \( T_s \) is, in some sense, intermediate satisfying the condition

\[ \frac{w_{3/2}^3}{2\pi} T_{2D} < T_s < \frac{w_{3/2}^3}{2\pi} T_{1D}. \]  \( \text{(57)} \)

Then, the kinetic energy of the more rigid structure can be approximated by Eq.(51) while that of the more soft is to be approximated by (52), which gives

\[ K_1 \simeq \frac{9}{16} T_{1D}\sqrt{w} + \frac{3\pi^4T^4}{10T_{1D}^4\sqrt{w}}, \]
\[ K_2 \simeq \frac{3T^2}{2(1-w)} + \frac{3T_{2D}^2}{40T}(1-w)^2. \]

Substituting this into (44), we find

\[ w \simeq 1 - \alpha_1 t, \]  \( \text{(58)} \)

where

\[ \alpha_1 = \frac{72}{32u_1 + 27}. \]

Now again the probability of the more rigid structure decreases with increasing temperature, although not so quickly as in (56). The solution (58) exists only if \( \alpha_1 > 0 \). If \( \alpha_1 \leq 0 \), we have to put \( w = 1 \), which means that there are no structural fluctuations.

Finally, pass to the high - temperature case, when

\[ T_s > \frac{w_{3/2}^3}{2\pi} T_{\nu D} \quad (\nu = 1, 2). \]  \( \text{(59)} \)

For the kinetic energies of both structures we can use the approximation (52). Then, (44) yields

\[ w \simeq \frac{1}{2} + \frac{\beta_1}{t} \]  \( \text{(60)} \)

for \( t \gg 1 \) and

\[ \beta_1 = \frac{1}{36}(u_1 - u_2). \]

In the vicinity of the structural phase transition the structure probabilities are close to each other, \( w \approx 1/2 \). The latter equation becomes asymptotically exact if \( u_1 \rightarrow u_2 \). This is analogous to the case (55) for which (56) also gives \( w \approx 1/2 \) if the properties of both coexisting structures are similar to each other, that is if \( \tau \approx 1 \) and \( u_1 \approx u_2 \).

The above analysis shows that the appearance of thermal structural fluctuations near the point of a structural phase transition is facilitated when both coexisting structures have close characteristics.

V. MÖSSBAUER FACTOR

The occurrence of structural fluctuations around the point of a structural transition can lead to the emergence of various anomalies of observable quantities [22], such as the strong enhancement of specific heat and of diffusion
coefficient [22,24,47]. A detailed analysis of experimental data [48 - 51] confirms that, probably, the most common feature of structural transitions is an anomalous sagging of the Mössbauer factor near the transition point. Such a sagging, as has been proved [52,53], cannot be explained by the existence of a soft phonon mode, which can lead solely to a fracture of the Mössbauer factor but by no means to a sagging. However, the general softening of a crystal due to the arising structural fluctuations can provoke these saggings, as we demonstrate below.

The Mössbauer factor of a heterostructural system consisting of two thermally coexisting structures is written in the form

$$f_M = |w_1\varphi_1 + w_2\varphi_2|^2 = f_M(T, w),$$

(61)

where $w = w(T)$ is the structure probability given by (44), and

$$\varphi_\nu = e^{-W_\nu} = \varphi_\nu(T, w_\nu),$$

$$W_\nu = \frac{q^2}{2} r_\nu^2 = E_q m r_\nu^2 \quad (E_q \equiv \frac{q^2}{2m}),$$

(62)

here $E_q$ is the recoil energy; $q$, the absolute value of a gamma - quantum momenta; and

$$r_\nu^2 = \frac{1}{3} \sum_{\alpha=1}^{3} <u_\alpha^a u_\alpha^a>$$

(63)

is the mean - square oscillation amplitude of a particle in a $\nu$ - structure. The correlation function (33) in the Debye approximation is

$$<u_\alpha^a u_\beta^a> = \frac{6T^2 w_\nu}{m \Theta_\nu^2} \int_0^{\Theta_\nu/2T} x \coth x dx.$$  

(64)

Whence, the mean - square amplitude (63) becomes

$$r_\nu^2 = \frac{6T^2 w_\nu}{m \Theta_\nu^3} \int_0^{\Theta_\nu/2T} x \coth x dx.$$  

(65)

The low - and high - temperature asymptotes for (65) are

$$r_\nu^2 \approx \frac{w_\nu}{m \Theta_\nu} \left(\frac{3}{4} + \frac{\pi^2 T^2}{2 \Theta_\nu^2}\right) \quad (T \ll \frac{\Theta_\nu}{2\pi}),$$

$$r_\nu^2 \approx \frac{w_\nu}{m \Theta_\nu} \left(\frac{3T}{\Theta_\nu} + \frac{\Theta_\nu}{12T}\right) \quad (T \gg \frac{\Theta_\nu}{2\pi}).$$  

(66)

Using (66), and remembering formula (50), for the function $\varphi_\nu$ defined in (62) we have

$$\varphi_\nu \approx \exp \left(\frac{-3E_q}{4T_{2D} w_\nu^{1/2}}\right) \quad (T < \frac{\Theta_\nu}{2\pi}),$$

$$\varphi_\nu \approx \exp \left(\frac{-3T E_q}{T_{2D} w_\nu^2}\right) \quad (T > \frac{\Theta_\nu}{2\pi}).$$  

(67)

In order to elucidate the influence of structural fluctuations appearing near the temperature $T_s$ of a structural transition, we will compare the Mössbauer factor (61) of a heterostructural system with the Mössbauer factor

$$f_M(T, 0) \equiv \exp \left\{ -12E_q T_{2D}^2 \int_0^{T_{2D}/2T} x \coth x dx \right\}$$

(68)

of a pure high - temperature structure corresponding to $\nu = 2$. The asymptotic values of the reference factor (68) are

$$f_M(T, 0) \approx \exp \left(\frac{-3E_q}{2T_{2D}}\right) \quad (T < \frac{T_{2D}}{2\pi}).$$  

12
\[ f_M(T, 0) \simeq \exp \left( -\frac{6TE_0}{2T^2_{2D}} \right) \quad (T > \frac{T_{2D}}{2\pi}). \]  

(69)

The change of the Mössbauer factor influenced by the presence of structural fluctuations is convenient to characterize by the relative deviation

\[ \delta f_M(T, w) = \frac{f_M(T, w)}{f_M(T, 0)} - 1. \]  

(70)

Consider first the case when the temperature of a structural transition is such that

\[ T_s < \frac{\Theta_{\nu}}{2\pi} \quad (\nu = 1, 2). \]  

(71)

For \( T \approx T_s \) we have

\[ \varphi_1(T, w) \simeq \left[ f_M(T, 0) \right]^\frac{1}{2\sqrt{\pi}} \quad \tau / \sqrt{w}, \]

\[ \varphi_2(T, w) \simeq \left[ f_M(T, 0) \right]^\frac{1}{2\sqrt{\pi}} \frac{1}{1 - w}. \]

Therefore, for the relative change (70) we get

\[ \delta f_M(T_s, w) \simeq \frac{1}{f_0} \left[ \left| w f_0^{\tau/2\sqrt{\pi}} + (1 - w) f_0^{1/2\sqrt{\pi}} \right| - 1, \right] \]  

(72)

where

\[ f_0 \equiv f_M(T_s, 0), \quad w = w(T_s). \]

If we assume that \( w \approx 1/2 \), then (72) transforms to

\[ \delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4f_0} \left( f_0^{\tau/\sqrt{2}} + f_0^{1/\sqrt{2}} \right)^2 - 1. \]

When the two coexisting structures are drastically different, so that \( T_{1D} \gg T_{2D} \), that is \( \tau \ll 1 \), then

\[ \delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4f_0} (1 + f_0^{0.707})^2 - 1 \quad (\tau \ll 1), \]

and when they are similar, so that \( \tau \approx 1 \), then

\[ \delta f_M \left( T_s, \frac{1}{2} \right) \simeq f_0^{0.414} - 1 \quad (\tau \approx 1). \]

To estimate these quantities, let us take the reference Mössbauer factor \( f_0 \) from the region

\[ 0.7 \leq f_0 \leq 0.9. \]  

(73)

Then, we obtain

\[ 0.033 \leq \delta f_M \left( T_s, \frac{1}{2} \right) \leq 0.128 \quad (\tau \ll 1), \]

\[ -0.137 \leq \delta f_M \left( T_s, \frac{1}{2} \right) \leq -0.043 \quad (\tau \approx 1). \]  

(74)

As we see, a sagging at \( T_s \) can be directed upward as well as downward, depending on the parameter \( \tau \equiv T_{2D}/T_{1D} \) characterizing the difference between the structures. When \( \tau \approx 0.5 \), there is no sagging at all.

Turn now to the case when the temperature of a structural transition is in the interval

\[ \frac{\Theta_2}{2\pi} < T_s < \frac{\Theta_1}{2\pi}. \]  

(75)
Hence, at \( T \approx T_s \) one gets
\[
\varphi_1(T, w) \simeq [f_M(T, 0)]^{\tau^2/8\sqrt{w}},
\]
\[
\varphi_2(T, 1 - w) \simeq [f_M(T, 0)]^{1/2(1-w)^2}.
\]
For the relative change (70) we find
\[
\delta f_M(T_s, w) = \frac{1}{f_0} \left| \frac{w f_0^{-\tau^2/8\sqrt{w}}}{f_0^{1/2(1-w)^2}} + (1 - w) f_0^{-1/2(1-w)^2} \right|^2 - 1
\]
When \( T_s \) is in the middle of the interval (75), we can use the approximation
\[
t_s \equiv \frac{T_s}{T_{1D}} \simeq \frac{1}{2} (1 + \tau).
\]
Taking \( w \approx 1/2 \), we reduce (76) to
\[
\delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4 f_0} \left( f_0^{0.177} + f_0^2 \right)^2 - 1.
\]
Considering again two limiting situations of very different and similar structures, we have
\[
\delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4 f_0} (1 + f_0^2)^2 - 1 \quad (\tau \ll 1),
\]
\[
\delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4 f_0} \left( f_0^{0.177} + f_0^2 \right)^2 - 1 \quad (\tau \approx 1).
\]
Taking the values of \( f_0 \) from (73), we come to the result
\[
-0.207 \leq \delta f_M \left( T_s, \frac{1}{2} \right) \leq -0.090 \quad (\tau \ll 1),
\]
\[
-0.271 \leq \delta f_M \left( T_s, \frac{1}{2} \right) \leq -0.108 \quad (\tau \approx 1).
\]
Here the sagging are always directed downward.
If the structural transition occurs at high temperature, when
\[
T_s > \frac{\Theta_\nu}{2\pi} \quad (\nu = 1, 2),
\]
then
\[
\varphi_1(T, w) \simeq [f_M(T, 0)]^{\tau^2/2w^2},
\]
\[
\varphi_2(T, w) \simeq [f_M(T, 0)]^{1/2(1-w)^2}
\]
at \( T \approx T_s \). The relative change (70) becomes
\[
\delta f_M(T_s, w) \simeq \frac{1}{f_0^2} \left| \frac{w f_0^{\tau^2/2w^2}}{f_0^{1/2(1-w)^2}} + (1 - w) f_0^{-1/2(1-w)^2} \right|^2 - 1.
\]
For \( w \approx 1/2 \) Eq.(79) gives
\[
\delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4 f_0} \left( f_0^{2\tau^2} + f_0^2 \right)^2 - 1.
\]
from where
\[ \delta f_M \left( T_s, \frac{1}{2} \right) \simeq \frac{1}{4f_0} \left( 1 + f_0^2 \right)^2 - 1 \quad (\tau \ll 1), \]
\[ \delta f_M \left( T_s, \frac{1}{2} \right) \simeq f_0^3 - 1 \quad (\tau \approx 1). \]

Thence, invoking (73), we obtain
\[ -0.207 \leq \delta f_M \left( T_s, \frac{1}{2} \right) \leq -0.090 \quad (\tau \ll 1), \]
\[ -0.657 \leq \delta f_M \left( T_s, \frac{1}{2} \right) \leq -0.271 \quad (\tau \approx 1). \]

All saggings are again directed downward.

Thus, we see that the appearance of structural fluctuations near the temperature of a structural phase transition can yield a noticeable sagging of the Mössbauer factor as a function of temperature. In the majority of cases this sagging is directed downwards. The sagging can be easily observed if \( w \approx 1/2 \), and immediately disappears when any of the structure probabilities tends to zero. For example, suppose that the probability of the structure fluctuations of a high-temperature more soft phase inside a low-temperature more rigid structure is very small, so that \( w_2 \equiv x \ll 1 \).

Expanding (61) in powers of \( x \), we have
\[ f_M(T, 1-x) \simeq f_M(T, 1) \left[ 1 - \left( 2 + \frac{3E_q}{2T_{1D}} \right) x \right]. \]

In the standard Mössbauer experiments the recoil energy is negligibly small as compared to the Debye temperature, \( E_q \ll T_{1D} \), usually \( E_q/T_{1D} \sim 10^{-7} \). Therefore, the change of the Mössbauer factor
\[ f_M(T, 1-x) \simeq f_M(T, 1)(1-2x) \quad (x \ll 1) \]
is also quite small and disappears as soon as \( x \to 0 \).

To illustrate that the values of saggings at \( T_s \) are in agreement with experiment, let us consider the structural transition between the low-temperature cubic phase and the high-temperature rhombic phase in the compounds Sn\(_{1-x}\)Ge\(_x\)Te. The characteristic temperatures of the latter are \( T_s \approx 190K \) and \( T_{1D} \approx T_{2D} \approx 150K \). Mössbauer investigation [54] display the existence at \( T_s \) of a pronounced sagging of the Mössbauer factor, \( \delta f_M^{exp}(T_s) \approx -0.4 \).

The considered characteristic temperatures correspond to inequality (78) and to \( \tau \approx 1 \). The measured Mössbauer sagging is in agreement with the second line of estimate (80).

### VI. SOUND VELOCITY

The existence of structural fluctuations near a phase transition point can also lead to a distinct attenuation of the velocity of sound
\[ v_s = \lim_{k \to 0} \frac{1}{k} \sum_{\nu} \frac{\delta}{\delta \nu k \nu} \langle H_{\nu}^{ph} \rangle. \]

To trace out the dependence of the sound velocity (81) on the structure probabilities, let us introduce the notation
\[ c_{\nu} \equiv \lim_{k \to 0} \frac{\varepsilon_{\nu k \nu}}{k} \]
for the sound velocity with polarization \( s \) inside a pure structure \( \nu \). According to (30) and (31), the sound velocity (81) in a heterostructural substance takes the form
\[ v_s = w_1^{3/2} c_{s1} + w_2^{3/2} c_{s2}. \]
Defining the average, with respect to polarizations, velocities of sound for a heterostructural system,

\[ v \equiv \frac{1}{3} \sum_{s=1}^{3} v_s, \quad (84) \]

and for a pure \( \nu \)-structure,

\[ c_{\nu} \equiv \frac{1}{3} \sum_{s=1}^{3} c_{s\nu}, \]

we get

\[ v = w_1^{3/2} c_1 + w_2^{3/2} c_2, \quad (85) \]

where each of \( c_{\nu} \) is given by (47).

The relative decrease of the sound velocity, due to arising structural fluctuations, can be characterized by

\[ \delta v(w) \equiv \frac{v}{c_2} - 1. \quad (86) \]

In the Debye approximation we have

\[ \frac{c_2}{c_1} = \frac{T_{2D}}{T_{1D}} \equiv \tau. \]

Therefore, (86) gives

\[ \delta v(w) = \frac{1}{\tau} w^{3/2} + (1 - w)^{3/2} - 1. \quad (87) \]

Assuming that at the temperature \( T_s \) of a structural transition one has \( w \approx 1/2 \) and \( \tau \approx 1 \), we obtain

\[ \delta v \left( \frac{1}{2} \right) \approx -0.293 \quad (T = T_s). \]

This decrease of the sound velocity is completely due to the onset of mesoscopic structural fluctuations and can happen even at first-order phase transitions when there are no microscopic critical fluctuations [55] related to second-order phase transitions. For example, a similar decrease of the sound velocity occurs at freezing point of water [56].

As far as the average sound velocity (84) can be expressed through the derivative

\[ \frac{\partial P}{\partial \rho} = mv^2 \]

of pressure with respect to density, and the same derivative is involved into the definition of the isothermal compressibility

\[ \kappa_T \equiv -V \left( \frac{\partial P}{\partial V} \right)^{-1} = \left( \frac{\partial P}{\partial \rho} \right)^{-1}, \]

we can easily find the influence of structural fluctuations on the latter. Thus, introducing the isothermal compressibility of pure structures,

\[ \kappa_{\nu} \equiv \frac{1}{m \rho_{c_\nu}^2}, \]

for a heterostructural system we find

\[ \kappa_T = \left[ \left( \frac{w_1^3}{\kappa_1} \right)^{1/2} + \left( \frac{w_2^3}{\kappa_2} \right)^{1/2} \right]^{-2}. \quad (88) \]
Defining the relative change of compressibility by

\[ \delta\kappa_T(w) \equiv \frac{\kappa_T}{\kappa_2} - 1, \]

and using the previous notation, we come to

\[ \delta\kappa_T(w) = \frac{\tau^2}{\frac{w^{3/2} + \tau(1 - w)^{3/2}}{2}} - 1. \]

If at the point of a structural phase transition we have \( w \approx 1/2 \) and \( \tau \approx 1 \), then

\[ \delta\kappa_T\left(\frac{1}{2}\right) \approx 1 \quad (T = T_s). \]

This means a strong increase of compressibility.

VII. CONCLUSION

The main aim of this paper has been to present a general approach for describing statistical properties of heterostructural systems. This approach can be used for treating heterogeneous system with frozen structural fluctuations induced e.g. by shock waves or irradiation. Then, the relative volumes occupied by each structure, or the structure probabilities, are additional thermodynamic variables which can be defined experimentally by different means, for example by nuclear gamma resonance [4,5]. Probably, the most promising application of this approach is to considering substances with thermal structural fluctuations. This is of great importance for describing systems with structural phase transitions. The appearance of structural fluctuations around the phase transition point leads to various pretransitional, or precursor, phenomena that are often manifested in pronounced anomalies of thermodynamic and dynamic characteristics. The liquid - solid phase transition can be regarded as a kind of such structural transitions [16,17]. There are other numerous examples of structural transitions accompanied by the occurrence of structural fluctuations whose existence can be observed by different experiments. Some of the examples have been discussed in this paper.

A number of other examples has been reviewed recently [22]. As is well known, structural fluctuations play a decisive role in high - temperature superconductors [23], in solids with martensitic transformations [57,58], and in crystals with perovskite structure whose structural transitions are accompanied by experimentally well observed pretransitional structural fluctuations [59,60]. A more detailed theoretical consideration of these particular substances is supposed to be done in separate publications, basing on the approach developed in the present paper.

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[1] D.Curran, L.Seaman, and D.Shockey, Phys. Rep. 147, 253 (1987).
[2] V.I.Yukalov, Int. J. Mod. Phys. B 3, 311 (1989).
[3] E.P.Kadantseva and V.I.Yukalov, Int. J. Mod. Phys. B 3, 465 (1989).
[4] S.V.Sinitsin, A.N.Spirin, and M.N.Uspensky, Hyperfine Interact. 29, 1217 (1986).
[5] V.I.Yukalov, Hyperfine Interact. 56, 1657 (1990).
[6] R.J.Speedy and C.A.Angell, J. Chem. Phys. 65, 851 (1976).
[7] J.Rousset, E.Duval, and A.Boukenter, J. Chem. Phys. 92, 2150 (1990).
[8] S. Mashimo and N.Miura, J. Chem. Phys. 99, 9874 (1993).
[9] I.Ohmine, H.Tanaka, and P.Wolynes, J. Chem. Phys. 89, 5852 (1988).
[10] T.Hidaka, Ferroelectrics 137, 291 (1992).
[11] S.Stamenkovic, N.Pakida, V.Aksenov, and T.Siklos, Ferroelectrics 14, 655 (1976).
[12] A.Bruce, T.Schneider, and E.Stoll, Phys. Rev. Lett. 43, 1284 (1979).
References:

[13] I.Ohnari, J. Phys. C 15, 4781 (1982).
[14] A.R.Ubbelohde, *Molten State of Matter* (Wiley, New York, 1978).
[15] A.D.Bruce and R.A.Cowley, *Structural Phase Transitions* (Taylor and Francis, London, 1981).
[16] V.I.Yukalov, Phys. Lett. A 81, 433, (1981).
[17] V.I.Yukalov, Phys. Rev. B 32, 436 (1985).
[18] T.L.Beck and R.S.Berry, J. Chem. Phys. 88, 3910 (1988).
[19] K.J.Runge and G.V.Chester, Phys. Rev. B 38, 135 (1988).
[20] D.I.Pushkarov, *Quasiparticle Theory of Defects in Solids* (World Scientific, Singapore, 1991).
[21] J.Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946).
[22] V.I.Yukalov, Phys. Rep. 208, 395 (1991).
[23] V.I.Yukalov, Int. J. Mod. Phys. B 6, 91 (1992).
[24] Y.L.Khait, Phys. Rep. 99, 237 (1983).
[25] Y.Koga, Chem. Phys. Lett. 31, 571 (1975).
[26] Y.Koga, Coll. Phenomena 3, 1 (1978).
[27] V.I.Yukalov, Pretransitional Phenomena and Fluctuations of Crystalline Structure (Commun. JINR E17 - 89 - 677, Dubna, 1989).
[28] V.I.Yukalov, Physica A 144, 352 (1987).
[29] V.I.Yukalov, Physica A 144, 369 (1987).
[30] V.I.Yukalov, Phys. Lett. A 125, 95 (1987).
[31] R.Peierls, *Surprises in Theoretical Physics* (Princeton Univ., Princeton, 1979).
[32] V.I.Yukalov, Phys. Lett. A 109, 254 (1985).
[33] V.I.Yukalov, Ferroelectrics 82, 11 (1988).
[34] V.I.Zubov, Phys. Rev. A 42, 3324 (1990).
[35] V.I.Yukalov, in *Abstracts of Meeting on Applied Mössbauer Spectroscopy* (Moscow, 1988), p.115.
[36] V.I.Yukalov, in *Abstracts of Conference on Application of Mössbauer Spectroscopy in Material Science* (Izhevsk, 1989), p.97.
[37] V.I.Yukalov, Solid State Commun. 69, 393 (1989).
[38] V.I.Yukalov, Hyperfine Interact. 55, 1165 (1990).
[39] G.Meissner and K.Binder, Phys. Rev. B 12, 3948 (1975).
[40] K.Binder, G.Meissner, and H.Mais, Phys. Rev. B 13, 4890 (1976).
[41] I.A.Dobryakov, Izv. Vuz. Fiz. N1, 103 (1989).
[42] V.I.Yukalov and A.S.Shumovsky, Lectures on Phase Transitions (World Scientific, Singapore, 1990).
[43] F.Sciortino and S.Sastry, J. Chem. Phys. 100, 3881 (1994).
[44] P.C.Clapp, Physica D 66, 26 (1993).
[45] A.Saxena and G.Barsch, Physica D 66, 195 (1993).
[46] B.Rechav, Y.Yacoby, E.Stern, J.Rehr, and M.Newville, Phys. Rev. Lett. 72, 1352 (1994).

**Figure Captions**

**Fig.1.** The typical distribution of defect clusters inside a metal irradiated by fast neutrons.

**Fig.2.** Pores and cracks in a metal irradiated by fast neutrons: darker regions correspond to the amorphised phase with disordered structure.