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THE STATISTICAL DESCRIPTION OF LOCAL STRUCTURE OF CONDENSED MATTER

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The Statistical Description of Local Structure of Condensed Matter. I. General Theory

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ABSTRACT

The mathematical formalism for statistical description of local structure of condensed matter, based on the concept of the feature space of structural invariants is presented. The qualitative analysis of the fluctuations in this space is given; the probabilistic characteristics of the type of local structure are introduced and the problem of the effectiveness of the recognition is studied.

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1. INTRODUCTION

The qualitative concepts of local order in the spatial arrangement of atoms not only in crystals but also in other condensed phases of matter (melt, glass, amorphous solids) is well-known, see e. g. in [1, 2]. The quantitative theoretical study of local structure of condensed matter both on microscopic and phenomenological levels is possible provided that this concept has clear mathematical formulation. In general, various types of local structures of liquids can be discussed. In recent papers (Patashinskii and Shumilo [3], Mitus and Patashinskii [4], Hess [5], Nelson and Toner [6] and others) it was assumed that the local structure of the melt resembles that of the crystal. Sachdev and Nelson [7] and Steinhardt, Nelson and Ronchetti [8] use the icosahedron as the main structural unit of local order in metallic glasses and melts. Among other models, the most popular ones are Bernal's model of chaotic close-packing of atoms [9] and Zachariasen's model of chaotic lattice [9]. Different models may, in principle, correspond to different types of the matter.

The mathematical formulation of the concepts of local structure given in the above papers made it possible to study many of the phenomena related to the melting and the melts. In this way some new effects were predicted — the anomalous temperature dependence of the crystal's heat capacity near its melting point [4, 11], the logarithmic dependence of the width of the film of the fluid on the surface of the semi-infinite crystal near its melting point on the reduced temperature [12, 13], the structural phase transition in the melt, accompanied by the change of the type of local structure [14] and others.

No matter what the local order in melts is, it manifests itself in the presence of thermal fluctuations of atoms' positions. These fluctuations are characterized by the parameter $\xi = \xi'/a$, where ξ' denotes the mean-root-square thermal displacement of atoms from their supposed ideal positions and a denotes the mean interatomic distance. At the melting point $\xi = \xi_m = 0.07 \div 0.17$ for most of the elements [15].

In such the case the intuitive concepts of the resemblance of structures are insufficient for the quantitative analysis. It is necessary to work out the mathematical formalism destinated for the comparison and recognition of the type of local structure. The aim of this paper is to present such the formalism. As an example, in the second part of this paper, we apply our method to study the conditions of mutual distinction of some local structure patterns in the presence of thermal fluctuations and some other related topics. These patterns are the most popular candidates for the structural units of simple liquids.

The general concepts used throughout this paper were formulated earlier in [16] and are related to the ideas of the phenomenological theory of local crystal-order of condensed matter [4].

2. THE PARAMETERS OF LOCAL ORDER AND STRUCTURAL INVARIANTS

To study the space arrangement of atoms one has to know the positions of their centers. In what follows we restrict ourselves to the study of the discrete set G of points with coordinates $\vec{r}^{(a)}$ representing the centers of atoms. The atoms surround the central one located in the origin of the coordinate frame of the 3-D Euclidean space. Structural characteristics of a continuum were studied by Kuz'min and Patashinskii [17].

By definition, the geometrical structure of a set G of points can be determined by comparing G with each of the figures (sets of points) Γ_i, $i=0, 1, \ldots$ The figures Γ_i form the collection of ideal patterns of structure. This collection is to be chosen on the basis of physical concepts concerning local structure of condensed matter. The mathematical construction that realizes the rather intuitive idea of resemblance of figures is the one-to-one mapping of these figures. For the case of lattice-like structures, the «best» mapping of atoms' positions onto the lattice sites defines the type of the tangent lattice [3].

Once the set of ideal figures Γ_i, $i=0, 1, \ldots$, is chosen the problem of recognition of structures reduces to the problem of finding the ideal figure Γ_k, a deformed state of which is the «physical» structure. The concept of the geometrical structure of any of Γ_i coincides with the concept of Γ_i as the geometrical figure, i. e. is independent on the orientation of Γ_i in the space.

In what follows, it is assumed that each fluctuating structure can be thought of as a deformed («excited») state of one of the patterns Γ_i. In order to recognize and classify the fluctuating structures one has to study numerical characteristics of these structures. Subsequently, the phase space of these characteristics should be divided into domains representing the deformed states of patterns Γ_i. This division has probabilistic character (see below). In general, the domains can overlap with each other.

In order to study the resemblance of the figures let's introduce the local order-parameters — the irreducible multipole moments of the density [4, 5, 18]

$$T_{\alpha_1 \ldots \alpha_l} = \sum_{(a)} w(\vec{r}^{(a)})\, t^{(a)}_{\alpha_1 \ldots \alpha_l}\,, \tag{1}$$

where

$$t^{(a)}_{\alpha_1 \ldots \alpha_l} \equiv \overline{r^{(a)}_{\alpha_1} \ldots r^{(a)}_{\alpha_l}} \tag{2}$$

denotes the irreducible part of the Cartesian tensor $r^{(a)}_{\alpha_1} \ldots r^{(a)}_{\alpha_l}$. The summation in (1) extends over all the points $\vec{r}^{(a)}$. Function $w(\vec{r})$ defines the weight of the contributions to $T_{\alpha_1 \ldots \alpha_l}$ from different coordination shells. For example, for an infinite system one can *a priori* fix the size of the domain (cluster) in which the order is supposed to be local and then treat each of the atoms as the center of one of such the domains. The resulting description of the system in terms of parameter (1) is equivalent to the one used in the local order-parameter formalism [4, 18], provided that the weight function $w(\vec{r})$ is properly chosen. For different values of l the functions $w(\vec{r})$ can be different ones. For example, when $w(\vec{r}) \sim |\vec{r}|^{-l}$ then the expressions in (1) are nonnormalized spherical harmonics. The quantities $T_{\alpha_1 \ldots \alpha_l}$ form the basis of the irreducible representation of rank l of the 3-D rotation group O_3. The characteristics of the structure of a cluster have to be both rotationally and translationally invariant. They can be obtained via the contractions of indices of products of parameters $T_{\alpha_1 \ldots \alpha_l}$, $l=0, 1, \ldots$, i. e. they are all the scalars that can be constructed from the set $\{T_{\alpha_1 \ldots \alpha_l}\}$, $l=0, 1, \ldots$

The equivalent set of local order-parameters can be constructed with the help of another basis of the irreducible representation of the O_3 group, namely that of spherical harmonics Y_{lm}, see e. g. in Ref. [19]

$$T_{lm} = \sum_{(a)} w(\vec{r}^{(a)})\, t^{(a)}_{lm}\,, \tag{3}$$

where

$$t_{lm}^{(a)} = Y_{lm}(\Omega^{(a)}), \tag{4}$$

$\Omega^{(a)} = \{\varphi^{(a)};\ \theta^{(a)}\}$ denotes the polar and azimutal angles that fix the direction $\vec{r}^{a}/|\vec{r}^{(a)}|$, and $w(\vec{r})$ is a new weight function. $T_{\alpha_1 \ldots \alpha_l}$ and $t_{\alpha_1 \ldots \alpha_l}^{(a)}$ are the linear combinations of T_{lm} and $t_{lm}^{(a)}$, respectively. The invariants of T_{lm} can be constructed via the use of the standard formalism of angular momentum in quantum mechanics, see e. g. in Ref. [19].

The order-parameters (1), (3) have $2l+1$ independent components from which $2(l-1)$ independent invariants can be constructed. In what follows these invariants $\Psi_l^{(k)}$ $(l=0, 1 \ldots;\ k=1, \ldots, 2(l-1))$ will be referred to as structural invariants and the phase space $\{\Psi_l^{(k)}\}$ spanned by invariants $\Psi_l^{(k)}$ will be referred to, as usually in the problems of recognition, as the feature space. For the sake of simplicity the upper index in $\Psi_l^{(k)}$ will not be written out explicitely, i. e. Ψ_l will be use instead of $\Psi_l^{(k)}$. The structural invariants characterize the relative positions of all the atoms of the structure, independently on its orientation in space.

In what follows we'll study the structure of a cluster consisting of a finite (and not too big) number of atoms. The structure of the finite cluster is uniquely determined by the coordinates of its constituent atoms or by the finite set of algebraically independent invariants. For our main purpose, which is the description and the classification of local structures, it's sufficient to restrict oneself to the investigation of the small number of low-rank invariants, i. e. the ones constructed from the parameters (1), (3) with a few smallest values of l. The reason for such the simplification is that the high-rank invariants are sensitive to the small-scale fluctuations of the atoms positions. The relative fluctuations of invariants Ψ_l, resulting from thermal movements of atoms become stronger when l increases because the higher powers of $|\vec{r}^{(a)}|$ and the higher spherical harmonics are accounted for. As the result, the two distributions of the probability of fluctuations (see the next section) of invariants Ψ_l with $l \gg 1$, corresponding to two clusters with the same number of atoms overlap one another much stronger than distributions characterizing the fluctuations of Ψ_l with $l \sim 1$. It implies that the high-rank invariants are less effective for our purposes then the low-rank ones. For each value of l there exists the characteristic scale ξ_l of atom's displacement corresponding to the marked relative change of the invariant Ψ_l. The value of ξ_l decreases when l increases. When the values of ξ and ξ_l become of the same order of magnitude the invariant Ψ_l fluctuates strongly and is useless for the classification purposes.

The semi-quantitative physical picture of fluctuations of structural invariants presented here will be verified on some specific examples in the second part of this paper.

3. THE COMPARISON OF STRUCTURES: PROBABILISTIC ANALYSIS IN THE SPACE OF STRUCTURAL INVARIANTS

To each geometrical structure (i. e. finite or infinite set of points) there corresponds a point $\vec{\Psi} = \{\Psi_0, \ldots\}$ in the feature space $\{\Psi_l\}$. A slightly deformed state of the initial pattern is represented by a point $\vec{\Psi}'$ which is close to $\vec{\Psi}$. When the deformation is sufficiently small, i. e. the displacements of atoms are small enough, the structure of the deformed figure is similar to the initial one. The fluctuating structure is represented in the feature space by the distribution of probability of fluctuations of invariants Ψ_l and can be described in terms of the probability density $\rho(\vec{\Psi})$. Let's study a finite collection $\{\Gamma_i\}$ of initial ideal patterns. The general concepts of condensed-matter physics limit the possible arrangements of atoms in space to these described by the space-groups or some noncrystallographic groups. Each distribution $\rho(\vec{\Psi})$ has at some distance in the feature space «neighbours» $\rho_n(\vec{\Psi})$ that represent the deformed states of ideal patterns Γ_n. By the definition, the quantity

$$dw = \rho_n(\vec{\Psi}^{(0)};\ \xi) d\vec{\Psi}^{(0)} \tag{5}$$

is the probability of finding the values of invariants Ψ_l $(l=0, 1 \ldots)$ representing the fluctuations of the ideal pattern Γ_n in the vincinity $d\vec{\Psi}^{(0)} = \prod_l d\Psi_l^{(0)}$ of the point $\vec{\Psi}^{(0)}$. The solutions of the set of inequalities $\rho_n(\vec{\Psi}) < \text{const}$ $(n=1, \ldots)$ are the domains in the feature space that represent deformed states of ideal patterns Γ_n. Consider first the case when the fluctuations of the positions of atoms have an upper bound. For small values of ξ the distributions don't overlap one another; each point $\vec{\Psi}$ representing the deformed state of some pattern Γ_i can't simultaneously correspond to some other pattern $\Gamma_j (i \neq j)$, see Fig. 1,*a*. In this sense, the division of the feature space

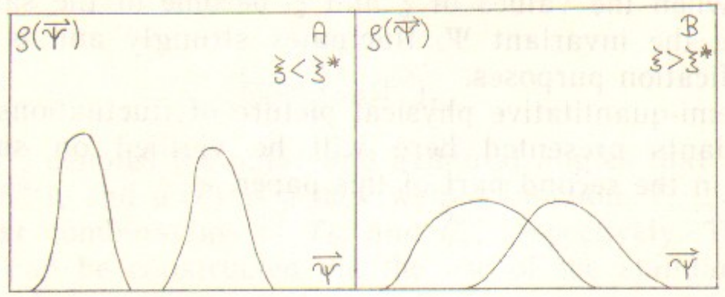

Fig. 1. The overlapping of the distributions of the fluctuations of invariants $\vec{\Psi}$.

into domains has deterministic character. When ξ increases the widths of distributions increase, too; for $\xi > \xi^*$ the two neighbouring distributions overlap one another, see Fig. 1,*b*. In such the case the division of the feature space has probabilistic character—some point $\vec{\Psi}$ can correspond to deformed states of two different patterns. This is the case of real physical systems, where at any $\xi \neq 0$ thermal displacements of atoms have no upper bounds. The plots of functions $\rho(\vec{\Psi})$ shown in Fig. 1 correspond to thermal fluctuations of atoms provided that one neglects the fluctuations of invariants with the probability density smaller than some fixed value. In order to study the resemblance of the fluctuating structures it's necessary to introduce the quantitative characteristics of the degree of the overlap of the distributions. In what follows we'll deal with this problem.

It's natural to study the problem of the classification of local structure types on the grounds of the theory of verification of statistical hypotheses, see e. g. in Ref. [20]. Let $\vec{\Psi}$ denote a point in the feature space and let the densities $\rho_i(\vec{\Psi})$, $i=1,2$, characterize the fluctuations of patterns Γ_1, Γ_2, see Fig. 2. The correspondence of the structure represented by $\vec{\Psi}$ to Γ_1 or Γ_2 is settled on using the critical domain S in space $\{\Psi_i\}$. Namely, when $\vec{\Psi}$ belongs to S then the hypothesis of the similarity of the fluctuating structure to Γ_1 is rejected. The effectiveness of the test depends on two parameters: the probability $E_1=\alpha$ (α is the significance level of the test) of erroneous rejection of the hypothesis (error of first kind) and probability $E_2=\beta$ ($1-\beta$ is the strength of the test) of the erroneous acceptance of the hypothesis (error of second kind). The choice of the test, i. e. of the critical domain S is, *a priori*, arbitrary. We study the two following cases.

In the first case the minimization of the total error $E=E_1+E_2$

is required. To this end one determines the type of the fluctuating structure represented by point $\vec{\Psi}$ via the maximal-probability decision rule. It states that the fluctuating structure is the deformed state of this of two patterns Γ_1, Γ_2 for which the value of $\rho(\vec{\Psi})$ is the bigger one. The total error E of recognition is

$$E=\int \min\{\rho_1(\vec{\Psi}); \rho_2(\vec{\Psi})\}\, d\vec{\Psi}\,. \tag{6}$$

The integration in (6) is carried over all the phase space of invariants. The boundary ∂S of the critical domain S coincides with the determinant surface that divides the feature space into two parts and consists of points $\vec{\Psi}_d$ such that $\rho_1(\vec{\Psi}_d)=\rho_2(\Psi_d)$. In general, $E_1 \neq E_2$.

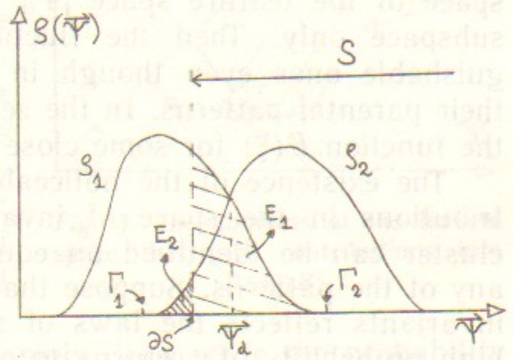

Fig. 2. The statistical recognition of the fluctuating structure (see text).

In the alternative approach one restores the «symmetry» between the fluctuating structures by imposing the condition $E_1=E_2$. In general, the total error E isn't minimal. Consider, for example, the important case of 1-D Gaussian distributions $\rho_i(\Psi)$. The boundary ∂S reduces to a single point Ψ_s, where $\Psi_s=\langle\Psi\rangle_1+t\sigma_1$, and the value of t is the solution of the equation $\langle\Psi\rangle_1+t\sigma_1=\langle\Psi\rangle_2-t\sigma_2$ ($\langle\Psi\rangle_2>\langle\Psi\rangle_1$). Here $\langle\ldots\rangle_i$, $i=1,2$, stands for «mean with the weight $\rho_i(\Psi)$» and σ_i denotes the mean-root-square deviation of fluctuations of invariant Ψ. In general, the boundary ∂S doesn't coincide with the determinant surface.

The two criterions of the recognition of the structures may lead to considerable discrepancies only when the shapes of the probability densities $\rho_i(\vec{\Psi})$ are remarkably different ones. These shapes can be characterized, e. g. by the central moments of $\rho_i(\vec{\Psi})$. When the differences are small both the criterions give practically the same results.

The functions $E(\xi)$, $E_1(\xi)$ and $E_2(\xi)$ are the simplest probabilistic characteristics of the type of the local structure of condensed matter and play the important role in the analysis of this structure. In particular they characterize the concentration of clusters with the structure of the Γ_1-type which will be identified as deformed states of the competitive pattern Γ_2 due to thermal fluctuations of atoms.

At small values of ξ this concentration is small and the fluctuating structure represents with the overwhelming probability a deformed state of pattern Γ_1.

When the overlapping of distributions is large, i. e. for values of $E \sim 0.5$, the concept of the type of local structure is useless. This is so because the necessary condition on which the classification scheme can be introduced, namely the existence of the one-to-one correspondence (e. g. the mapping described in Ref. [3]), between the deformed structure and the parental pattern Γ_i, is no more satisfied. The noticeable overlap can, in principle, take place only in a subspace of the feature space $\{\Psi_i\}$, if the analysis is restricted to this subspace only. Then the fluctuating structures become undistinguishable ones even though in fact they continue to «remember» their parental patterns. In the second part of this paper we evaluate the function $E(\xi)$ for some close packed-structures.

The existence of the noticeable fluctuational overlapping of distributions in the space of invariants implies that the fluctuating cluster can be identified on equal terms as the deformed state of any of the patterns. Suppose that the statistics of fluctuations of the invariants reflects the laws of motion of atoms. Then there is the high probability of «return» to nonparental pattern at, e. g., instantaneous cooling of the system by lowering the kinetic energy of atoms. In particular, these factors may be responsible for the formation of icosahedral clusters reported in Refs [7, 8]. We don't study here the kinetics of such the «transition». In fact, the «time of life» of a given structure may turn out to be macroscopic even if thermal fluctuations are sufficient for the «merging» of this and some other structures. In particular, the phase volume of the part of the feature space where the «structural diffusion» takes place may be small. The analogous phenomena are well-known in the theory of nucleation (see, e. g. in Ref. [21]).

In general, all the distributions $\rho_n(\bar{\Psi})$, $n=2,\ldots$, give contributions to the total probability $\mathscr{E}(\xi)$ of erroneous recognition of a given fluctuating structure represented by the density $\rho_1(\bar{\Psi})$. For $n>2$ the probability $\mathscr{E}(\xi)$ can be evaluated with the help of the formula for the probability of the sum of the events: $P(A \cup B) = P(A)+P(B)-P(A \cap B)$. Here A, B, $A \cup B$ and $A \cap B$ denote, respectively, the events of the recognition of the structure of interest as A-structure, B-structure, «A or B»-structure and «A and B»-structure. The probabilities P are evaluated by integrating $\rho_1(\bar{\Psi})$ over the domains of the space $\{\Psi_i\}$ corresponding to the events A, B and

$A \cap B$ (see Fig. 3 where $\bar{\Psi}=\{\Psi_1, \Psi_2\}$). For this reason we limit ourselves to the study of the case $n=2$ when $\mathscr{E}(\xi) \equiv E_1(\xi)$.

The functions $E(\xi)$, $E_1(\xi)$ and $E_2(\xi)$ can be evaluated numerically. On the other hand, the following concepts make it possible to obtain the closed analytical expressions.

Any 3-D structure consisting of a finite number $N>1$ of atoms is fully characterized by the set of $3N-6$ algebraically independent invariants. At the same time there may exist some specific inequalities between the values of invariants. Such the effect is well-known in the theory of nematic liquid-crystals [22]. Hovever, the algebraic independence of invariants Ψ_i doesn't imply the statistical independence of their fluctuations. The statistics of fluctuations of invariants is governed by the effective hamiltonian. Namely, let's write the probability density of fluctuations in the form

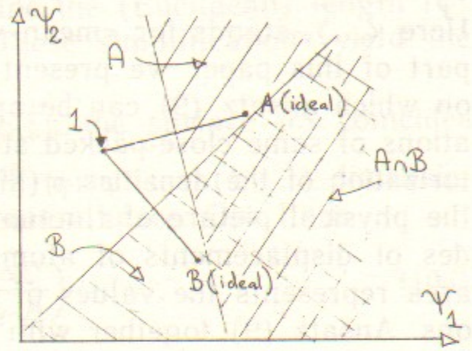

Fig. 3. The domains of the feature space that give contributions into $P(A \cup B)$.

$$\rho(\bar{\Psi}) = C \exp\{-F(\bar{\Psi})\}. \qquad (7)$$

Following the standard concepts of the theory of thermodynamic fluctuations, see e. g. in Ref. [23], we expand the function $F(\bar{\Psi})$ into the Taylor series up to the quadratic terms in the vicinity of point $\bar{\Psi}^{(0)}$ corresponding to the most probable value of fluctuations:

$$F(\bar{\Psi}) = F(\bar{\Psi}^{(0)}) + \frac{1}{2} \sum_{k,l} \beta_{kl} \Psi'_k \Psi'_l, \qquad (8)$$

where $\bar{\Psi}' = \bar{\Psi} - \bar{\Psi}^{(0)}$. The substitution of (8) into (7) yields the many-dimensional Gaussian distribution of fluctuations, for which $\bar{\Psi}^{(0)} = \langle \bar{\Psi} \rangle$. Here $\langle \ldots \rangle$ stands for «mean with the weight $\rho(\bar{\Psi})$», formula (7). The matrix $\|\beta_{kl}\|$ corresponding to the experimental data is positively defined. The standard procedure of diagonalization of matrix $\|\beta_{kl}\|$ yields the statistically independent linear combinations of invariants. The quantities β_{kl} are related to the elements of the covariance matrix $\|\mu_{kl}\|$: $\mu_{kl} \equiv \langle \Psi'_k \Psi'_l \rangle = \beta_{kl}^{-1}$, where β_{kl}^{-1} denotes the element of the matrix $\|\beta_{kl}^{-1}\|$ inverse to matrix $\|\beta_{kl}\|$, see [23].

Thus, for the fluctuations of statistically independent invariants corresponding to two chosen structures one has

$$\rho_i(\bar{\Psi}) = \prod_l \rho_i^{(l)}(\Psi_l), \quad i = 1, 2, \tag{9a}$$

where

$$\rho_i^{(l)}(\Psi_l) = \frac{1}{\sqrt{2\pi}\ \sigma_i^{(l)}} \exp\left\{ - \frac{(\Psi_l - \langle \Psi_l \rangle_i)^2}{2(\sigma_i^{(l)})^2} \right\}. \tag{9b}$$

Here $\langle \ldots \rangle_i$ stands for «mean with the weight $\rho_i(\bar{\Psi})$». In the second part of this paper we present the numerical analysis of conditions on which ansatz (9) can be applied to the description of the fluctuations of some close-packed structures. Let's discuss briefly the factorization of the densities $\rho_i(\bar{\Psi})$, formula (9a). In Fig. 4 we present the physical picture of fluctuations of invariants when the amplitudes of displacements of atoms have an upper bound. The shaded area represents the values of invariants accessible to the fluctuations. Ansatz (9) together with the requirement $\Psi_l \in \Omega_l$ where Ω_l denotes a compact subset on the axis Ψ_l holds within any rectangle lying inside the shaded area.

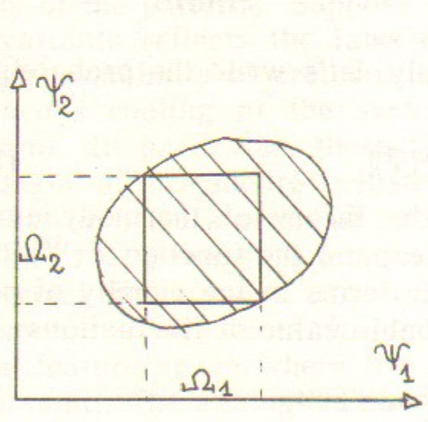

Fig. 4. The quantitative picture of the fluctuations in the feature space $\bar{\Psi} = \{\Psi_1, \Psi_2\}$ (see text).

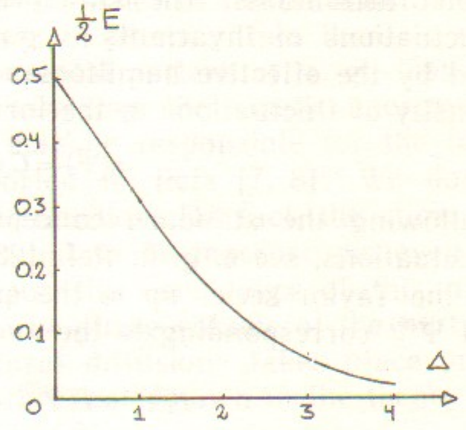

Fig. 5. The dependence of $\frac{1}{2}E$ on Δ, formula (10a).

The study of the fluctuations of the close-packed structures presented in the second part of this paper leads to the conclusion that the mean-root-square deviations $\sigma_i^{(l)}$ depend weakly on i. In what follows we neglect the differences between the values of $\sigma_i^{(l)}$ for different structures and take $\sigma_i^{(l)} \equiv \sigma_l$, where σ_l is structure-independent. To evaluate the integral (6) we translate and rotate the coordinate system in the phase space of invariants so that the centers $\langle \bar{\Psi} \rangle_i = \{\langle \Psi_0 \rangle_i, \ldots\}$ of the distributions lie on one of the new axes. It is also convenient to use the quantities σ_l as the units of the length on axes Ψ_l. Such the choice is the natural one for the problem of classification of structures. Namely, the values of dimensionless invariants $\varphi_l = \Psi_l / \sigma_l$ don't depend on the choice of the unit of length in real space. In the space $\{\varphi_l\}$ we define the (Euclidean) length $|\vec{\varphi}|$ of vector $\vec{\varphi} = \{\varphi_0, \ldots\}$ as $|\vec{\varphi}|^2 = \sum_l \varphi_l^2$. These simplifications yield the following identities $E_1(\xi) \equiv E_2(\xi) \equiv \frac{1}{2}E(\xi)$; the surface ∂S coincides with the determinant surface which, in turn, is a $(k-1)$-dimensional hyperplane in the k-dimensional feature space. One finds

$$E(\xi) = 1 - \Phi\left(\frac{\Delta(\xi)}{2\sqrt{2}}\right), \tag{10a}$$

where

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \tag{10b}$$

is the error function [24] and $\Delta(\xi)$ denotes the distance between the centers of the Gaussian distributions: $\Delta(\xi) = |\langle \vec{\varphi} \rangle_1(\xi) - \langle \vec{\varphi} \rangle_2(\xi)|$. The dependence of Δ on ξ is the consequence of the dependence of the parameters of $\rho_i(\bar{\Psi})$, formula (9), on ξ. The plot of the function $\frac{1}{2}E(\Delta)$ is shown in Fig. 5.

4. CONCLUSIONS

We have presented the mathematical formalism intended for the description (recognition and classification) of the local structure of condensed matter in the presence of thermal displacements of constituent atoms. This description turns out to be probabilistic in nature. Thus, the appropriate language for the study of the structure of matter is this of mathematical statistics. In particular, the treatment of the computer modelling results along the lines presented above would contribute to understanding of local structure of matter.

In the second part of this paper we apply the above formalism to the description of local structures of some close-packed clusters.

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II. CLOSE-PACKED STRUCTURES

The Statistical Description of Local Structure of Condensed Matter. II. Close-Packed Structures

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ABSTRACT

Conditions of the recognition of structures of the 13-atom clusters (fcc, hcp, icosahedron) in the presence of thermal fluctuations of their constituent atoms are studied in the framework of the mathematical formalism of structural invariants presented in the first part of this paper. The problem of the choice of small number of relevant invariants at various temperatures is investigated. The upper bound on the temperature of the existence of the close-packed «structural» liquid—the close-packed melt—is estimated. The order-parameter for the description of the structural phase transition melt-melt accompanied by the change of the local structure is discussed. The hierarchic picture of local structure of condensed matter is proposed.

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1. INTRODUCTION

In the first part of this paper [1] henceforth referred to as I, we have presented the mathematical formalism for the statistical description of local structure of condensed matter in the presence of thermal fluctuations of its constituent atoms. The aim of this paper is to study, at various temperatures, the mutual distinction of the structures that are the candidates for the structural units of simple liquids and to discuss some other topics related to local structure of condensed matter.

2. COMPUTER SIMULATION OF FLUCTUATIONS OF STRUCTURES OF 13-ATOM CLOSE-PACKED CLUSTERS

Let's discuss briefly the concept of local structure of liquid near its freezing line. As a rule, it's assumed that the small volumes of dense liquids containing 10^2-10^3 atoms, see e. g. Ref. [2], display some type of structure. In what follows we assume that strong correlations of atoms' positions exist at least in the volumes equivalent to the first coordination shells of the 3-D close-packed structures. The results presented below maintain valid when the domain of local order is larger.

The crystal structure of most of the elements near their melting lines is close-packed one. The *X*-ray, electron and neutron structural experiments show that, as a rule, the local structure of liquids near the freezing line resembles that of the parental crystal, see e. g. in hand-book [3]. The relative change of the density of simple liquids at freezing temperature constitutes a few percent. For that reason we have studied three 13-atom clusters, namely the «crystallographic» ones corresponding to nuclei of fcc and hcp crystals and the icosahedron, see also [4], as the candidates for the structural units of dense liquids. Each cluster has $N=12$ «outer» atoms, equidistant from the central one located in the origin of the coordinate frame of

the 3-D space. The distance from any of the atoms to the center is taken as unit of length. The computer simulation of fluctuations of the structures was performed as follows. Each of 12 atoms of the cluster was randomly displaced onto the surface of the sphere with radius ξ and with the center located in the atom's position in the ideal (i. e. nonfluctuating) cluster. No correlations of displacements of atoms were accounted for. Two weight functions $w(\vec{r})$ were used to evaluate the values of the order-parameter (I.3). Here (I.m) stands for formula (m) in I. In the first case one obtains the bond-order parameter [5]

$$Q_{lm}=\frac{1}{N}\sum_{(a)}Y_{lm}(\Omega^{(a)}). \tag{1}$$

The summation in (1) extends over all the points $\vec{r}^{(a)}$ — the centers of the atoms around the central one; Y_{lm} are spherical harmonics and $\Omega^{(a)}=\{\varphi^{(a)};\theta^{(a)}\}$ denotes the polar and azimuthal angles that fix the direction $\vec{r}^{(a)}/|\vec{r}^{(a)}|$. Parameter Q_{lm} characterizes angular correlations and is independent on radial fluctuations of the atoms. Such the fluctuations can be accounted for by the space order-parameter, defined as the sum of harmonic polynomials

$$R_{lm}=\frac{1}{N}\sum_{(a)}Y_{lm}(\Omega^{(a)})\,|\vec{r}^{(a)}|^{l}. \tag{2}$$

We have studied the invariants

$$Q_l^2=\frac{4\pi}{2l+1}\sum_{m/-l}^{l}|Q_{lm}|^2, \tag{3a}$$

$$R_l^2=\frac{4\pi}{2l+1}\sum_{m/-l}^{l}|R_{lm}|^2, \tag{3b}$$

for $l\leqslant 10$.

In addition to invariants Ψ_l ($\Psi_l=Q_l$, R_l) the dimensionless invariants $\varphi_l=\Psi_l/\sigma_l(\xi)$ are used, where

$$\sigma_l(\xi)=\frac{1}{3}\sum_{i/\Gamma}^{3}\sigma_i^{(l)}(\xi)$$

denotes the averaged over the close-packed structures value of the standard deviation $\sigma_i^{(l)}$ of the fluctuations of the invariants, see Sect. 3.1. The length $|\vec{\varphi}|$ of the vector $\vec{\varphi}=\{\varphi_0,\ldots\}$ was defined in I.

The statistics of independent fluctuations of atoms used here to find the density of probability of fluctuations of the invariants is different from the statistics of thermal fluctuations of the cluster's atoms in a large system where correlations are present due to the interaction. We assume that such the characteristics as the half-width of the distribution of fluctuations of invariants don't depend strongly on details of the statistics of fluctuations of atoms when the value ξ of the standard deviation of atoms' fluctuations is fixed.

The values of the invariants Q_l ($R_l=Q_l$) for the non-fluctuating clusters are given in Table, see also Fig. 2 in Ref. [4]. Unlike the cubic and icosahedral clusters the hexagonal cluster isn't central-symmetric one which results in the non-zero values of odd-rank tensors.

	Q_1	Q_2	Q_3	Q_4	Q_5	Q_6	Q_7	Q_8	Q_9	Q_{10}
fcc	0	0	0	.1909	0	.5745	0	.4039	0	.0129
hcp	0	0	.0761	.0972	.2516	.4848	.3108	.3170	.1379	.0102
ics	0	0	0	0	0	.6633	0	0	0	.3629

The results presented below were obtained on the basis of $n_0=400$ configurations (for each value of ξ) in the phase spaces $\{Q_l\}$, $\{R_l\}$, for each of the clusters. The case of $n_0=2000$ configurations was also studied; the results are, with good accuracy, the same ones. Each new configuration was obtained by the change of the locations of all the 12 outer atoms.

Preliminary results were published in paper [6].

3. RESULTS

3.1. 1-Dimensional Case

Let' verify the conjecture about the Gaussian distribution of fluctuations of the invariant , see formula (I.9b). To this end the non-normalized densities of the probability of fluctuations of two invariants, namely Q_6 and R_8 were found on the basis of the corresponding histograms, see Fig. 1. Q_6 and R_8 are the members of the set of most informative invariants, see below. The data presented in

Fig. 1,*a* were obtained on the basis of $n_0=2000$ configurations at $\xi=0.21$. The plots of the «experimental» densities of probability coincide, with an accuracy of a few percent, with the plots of the Gaussian distributions. We have verified the hypothesis of the Gaussian distribution of the fluctuations of invariant Q_6 for the hexagonal cluster. The χ^2-test holds at the level of significance $\alpha=0.1$.

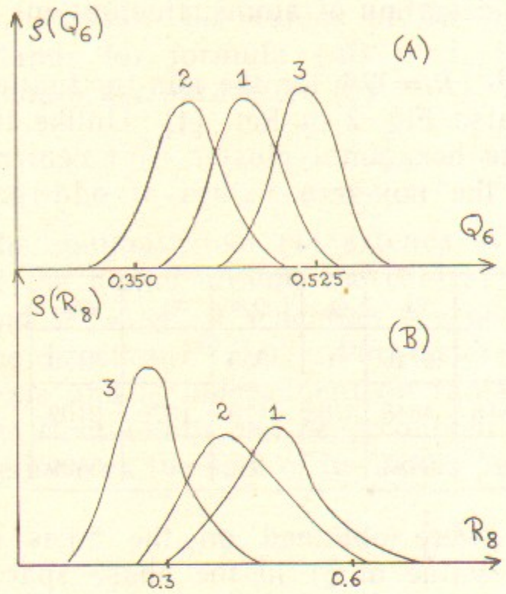

Fig. 1. Nonnormalized probability densities of fluctuations of invariants: $\rho(Q_6)$, $\xi=0.21$ (*a*) and $\rho(R_8)$, $\xi=0.135$ (*b*) (*1*—fcc, *2*—hcp, *3*—icosahedron).

The data presented in Fig. 1,*b* were obtained on the basis of $n_0=400$ configurations at $\xi=0.135$. The hypothesis of the Gaussian distribution of the fluctuations of invariant R_8 for the icosahedron is also accepted at $\alpha=0.1$.

These results show that the fluctuations of invariants Q_6 and R_8 can be treated, with good accuracy, as Gaussian ones. We assume that this conclusion holds also for all the other invariants. In Fig. 2 the mean values of invariants $\langle Q_l\rangle_i$, $\langle R_l\rangle_i/\sigma^{(l)}_{i,R}$ and the standard deviations $\sigma^{(l)}_{i,Q}$ and $\sigma^{(l)}_{i,R}$ ($l=3,\ldots,10$) are shown for a few values of parameter ξ. Index $i=1,2,3$ denotes the cubic and hexagonal clusters and the icosahedron, respectively; the indices Q, R refer to the spaces $\{Q_l\}$ and $\{R_l\}$. These quantities are the parameters of the Gaussian distributions, see (I.9). The values of these parameters corresponding to $l=1,2$ are, within the range of the «experimental» error, equal for the structures studied here.

The data presented in Fig. 2 make it possible to estimate the number $N_r(\xi)$ of relevant invariants. By definition, relevant invari-

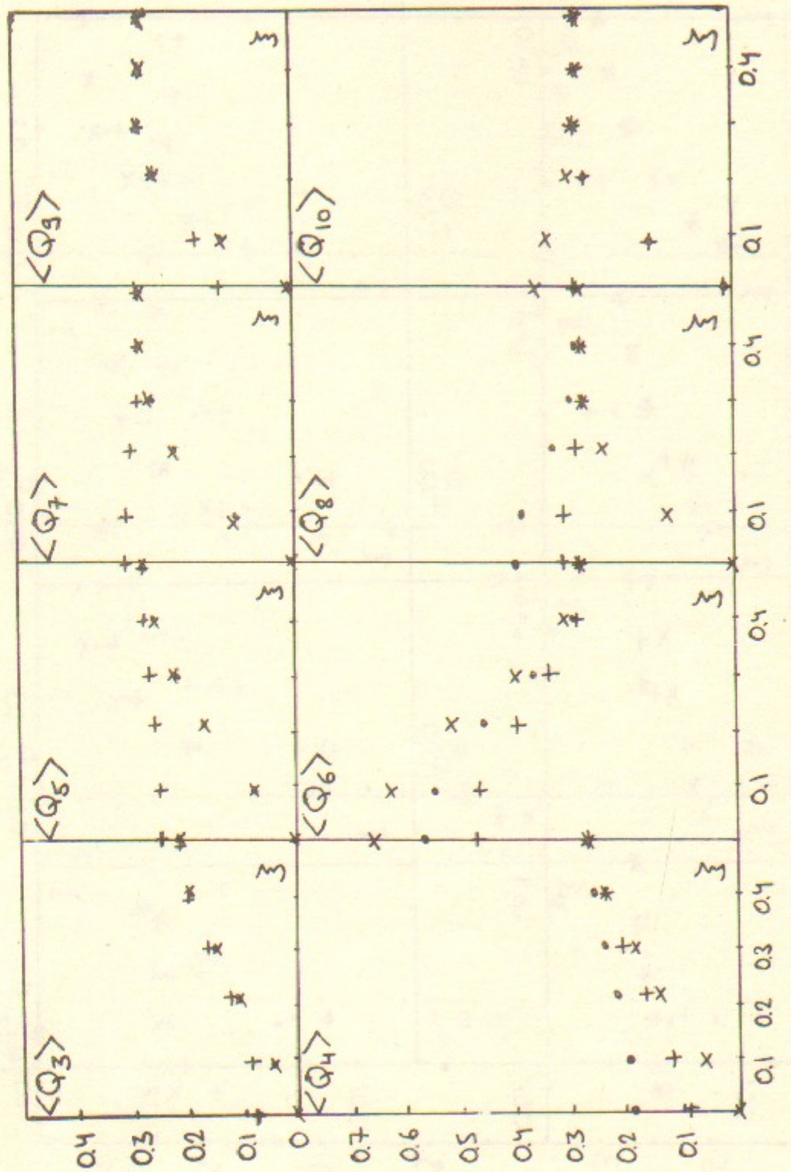

Fig. 2a. The dependence of $\langle Q_l\rangle_i$ on ξ; • —fcc, + —hcp, × —icosahedron.

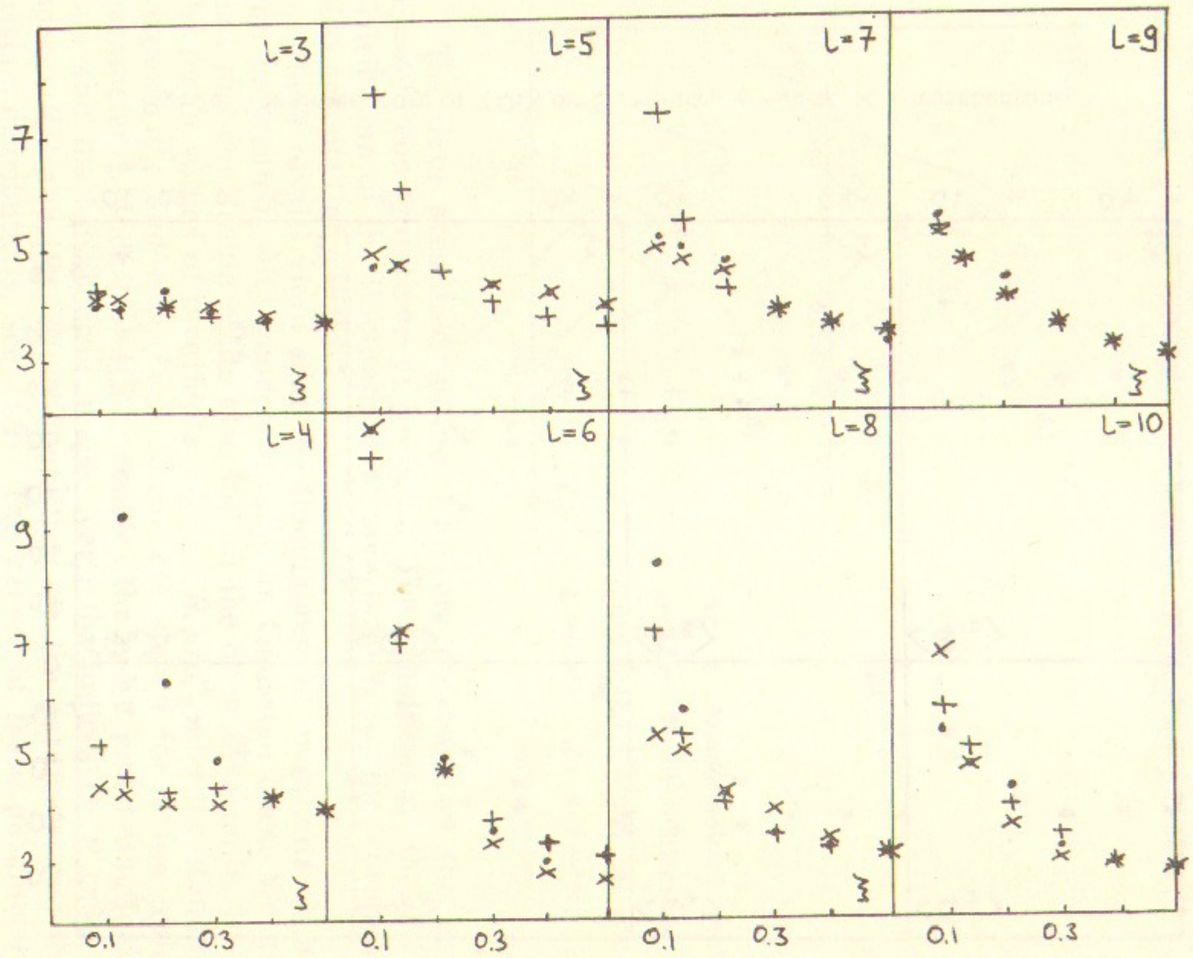

Fig. 2b. The dependence of $\langle R_l \rangle_i / \sigma_{i,R}^{(l)}$ on ξ; • — fcc, + — hcp, × — icosahedron.

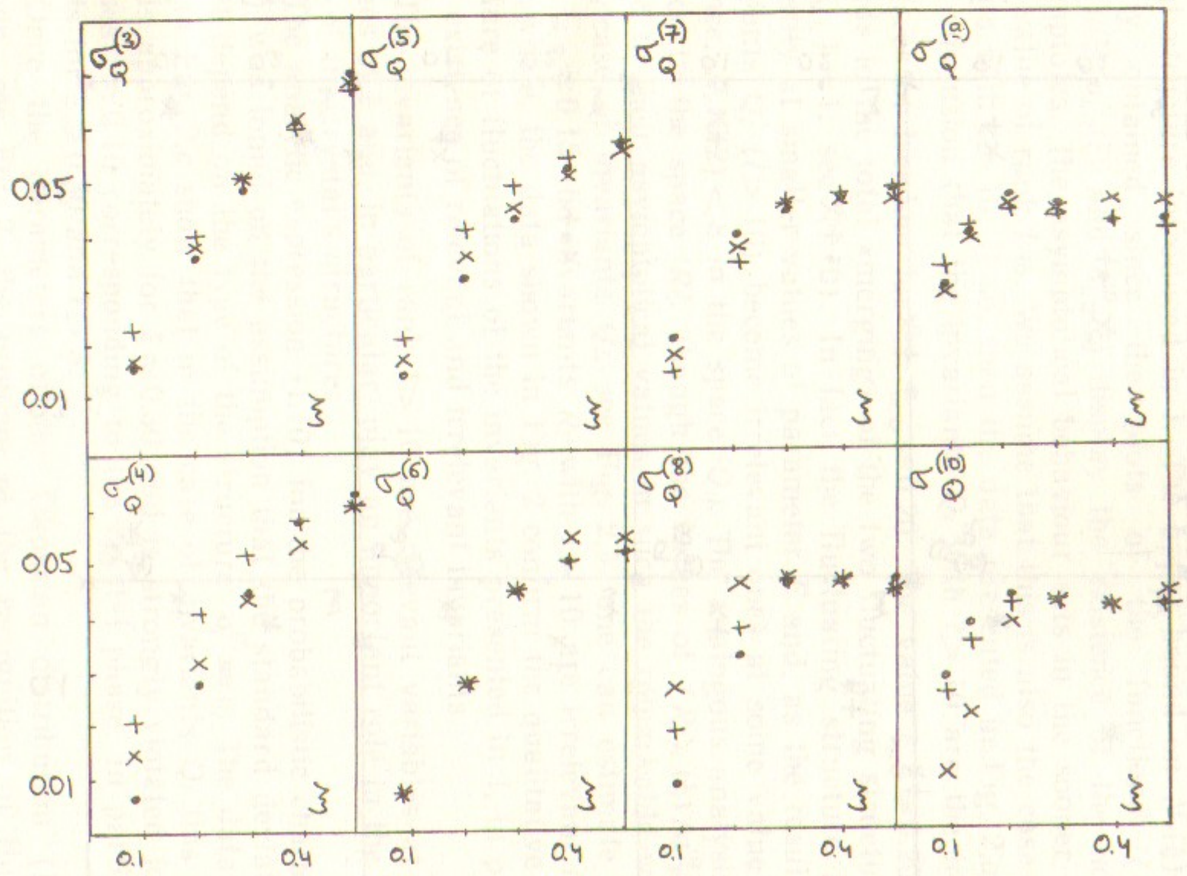

Fig. 2c. The dependence of $\sigma_{i,Q}^{(l)}$ on ξ; • — fcc, + — hcp, × — icosahedron.

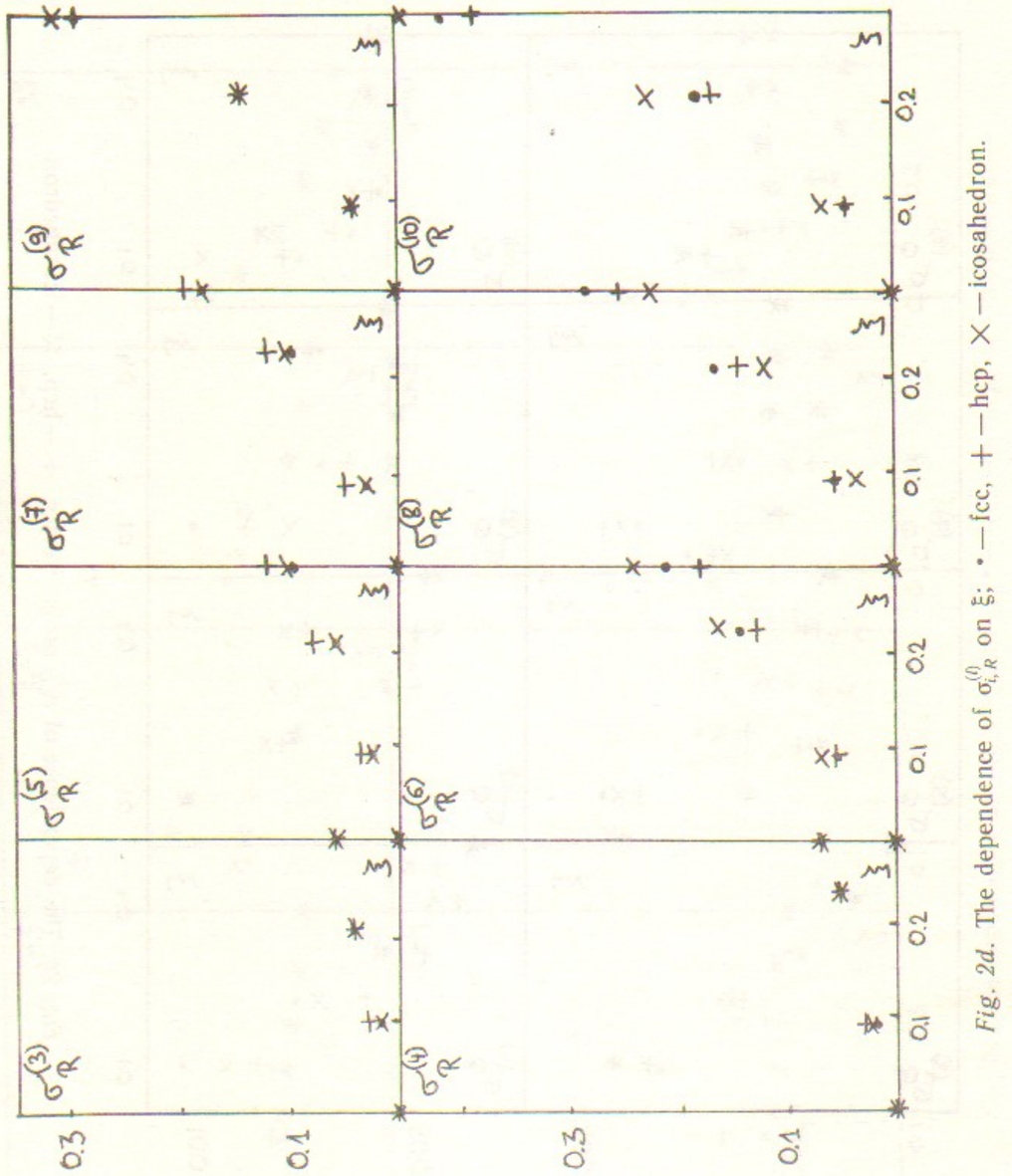

Fig. 2d. The dependence of $\sigma_{i,R}^{(l)}$ on ξ; • — fcc, + — hcp, × — icosahedron.

ants «distinguish» the fluctuating structures at the given value of ξ. The concept of relevant and irrelevant invariants has the probabilistic meaning in the same sense as has the characteristic $E(\xi)$ of the local structure introduced in I. The upper bound on $N_r(\xi)$ can be easily obtained since the plots of the functions $\langle Q_l \rangle_i (\xi)$, $\langle R_l \rangle_i (\xi)/\sigma_{i,R}^{(l)}(\xi)$ and $\sigma_{i,Q}^{(l)}(\xi)$ display the existence of the horizontal asymptotes. The asymptotical behaviour sets in the sooner the bigger value of rank l is. We assume that this is also the case of invariants with $l > 10$. If so, then the data presented in Fig. 2,*a* lead to the conclusion that the invariants Q_l with $l > 10$ are the irrelevant degrees of freedom for $\xi > \xi_{i,Q} \approx 0.20$. The value $\xi_{i,Q} = 0.20$ corresponds to the total «merging» of the two fluctuating structures, i. e. $E(\xi_{i,Q}) = 1$, see (I.10). In fact the fluctuating structure loses its identity at smaller values of parameter E and, as the result the invariants Q_l ($l > 10$) become irrelevant ones at some value $\xi < \xi_{i,Q}$. Hence, $N_r(0.2) < 8$ in the space $\{Q_l\}$. The analogous analysis can be made in the space $\{R_l\}$. Though the values of $\langle R_l \rangle_i (\xi)/\sigma_{i,R}^{(l)}(\xi)$ don't tend to their asymptotical values in such the remarkable way as in the case of invariants Q_l, see Fig. 2,*b*, one can estimate that for $\xi > \xi_{i,R} \approx 0.15$ the invariants R_l with $l > 10$ are irrelevant ones. On the whole, the data shown in Fig. 2 confirm the qualitative physical picture of fluctuations of the invariants presented in I, in particular the existence of relevant and irrelevant invariants.

The invariants of rank $l > 10$ are relevant variables at smaller values of ξ and, in particular, play an important role in the description of the crystal's structure.

The analytic expression (I.10) for the probabilistic characteristic $E(\xi)$ was found on the assumption that the standard deviations $\sigma_i^{(l)}$ don't depend on the type of the structure: $\sigma_i^{(l)} \equiv \sigma_l$ The data presented in Fig. 2,*c* show that in the case of invariants Q_l this equality holds approximately for $\xi \approx 0.30$ and is strongly violated for small values $\xi \approx 0.10$ corresponding to the crystal phase. In particular, it holds for $\xi \geqslant 0.30$ and $l > 5$.

Once the parameters of the Gaussian distribution (I.9) are known, see Fig. 2, the problem of the recognition of fluctuating structures can be treated quantitatively. An example of such the recognition is presented in Fig. 3 where the dependence of some of Ψ_l on displacement ξ is shown. For each value of ξ the bands correspond to the values Ψ_l such that $|\Psi_l - \langle \Psi_l \rangle_i (\xi)| < \sigma_i^{(l)}(\xi)$. Let's suppose for a while that the two fluctuating structures become indistinguishable ones when the corresponding bands intersect. Thus, in the

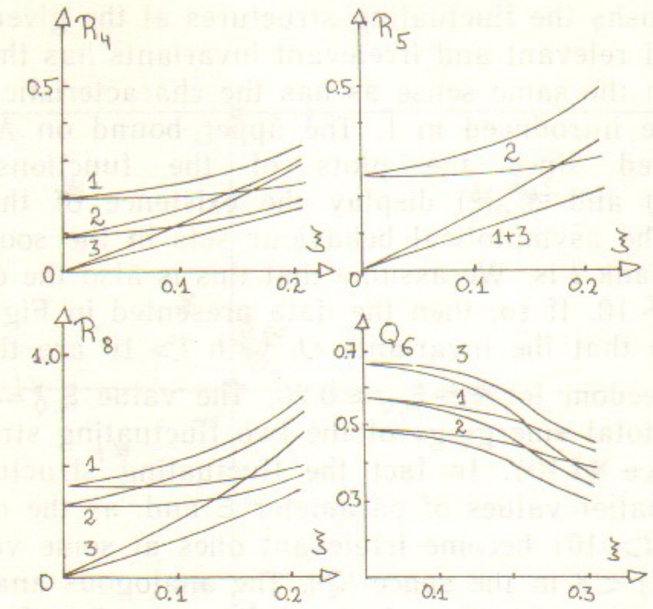

Fig. 3. The dependence of $\langle \Psi_l \rangle_l \pm \sigma_l^{(l)}$ on ξ for the most informative invariants Q_l and R_l (1—fcc, 2—hcp, 3—icosahedron).

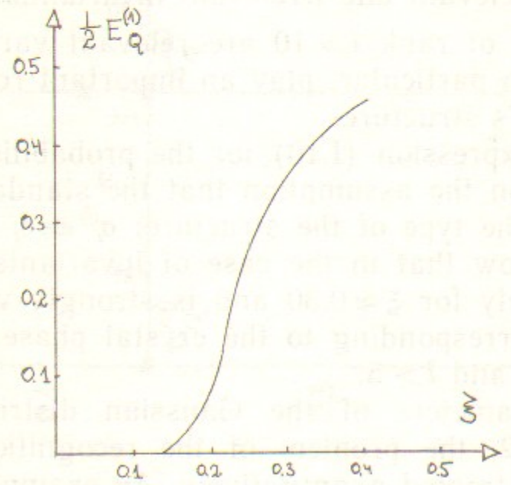

Fig. 4. The plot of the function $\frac{1}{2}E^{(1)}(\xi)$ for invariant Q_6.

Gaussian approximation (I.10) the probability $\frac{1}{2}E^{(1)}$ of the erroneous recognition of any of them is $\frac{1}{2}E^{(1)} = 0.16$. In what follows the functions $E(\xi)$ evaluated in the n-dimensional spaces $\{Q_l\}$, $\{R_l\}$ will be denoted by $E_Q^{(n)}(\xi)$ and $E_R^{(n)}(\xi)$, respectively.

The most informative of the calculated invariants are Q_6 for which the intersection of the bands occurs at $\xi = 0.21$ and Q_5 which distinguishes the fluctuating icosahedron for $\xi \leqslant 0.23$. In the space $\{R_l\}$ it's sufficient to restrict oneself to the study of invariants R_4, R_5 and R_8; the other ones give no new information about the similarity of the structures. The fluctuating fcc cluster remains distinct one until $\xi \leqslant 0.14$, the hcp one—when $\xi \leqslant 0.17$ and the icosahedron—when $\xi \leqslant 0.13$, see also in Ref. [6].

The recognition scheme presented in Fig. 3 can be repeated for various widths of the bands. The probabilistic characteristic $E(\xi)$ corresponding to invariant Q_6 was evaluated in the Gaussian approximation (I.10) and is shown in Fig. 4. Note that this case is an exceptional one since the standard deviations $\sigma_i^{(l)}$ don't depend on the type of the structure, see Fig. 2,*c*. The functions $E(\xi)$ describing the close-packed clusters coincide with one another.

The quantity $E^{(1)}(\xi)$ is an important characteristic of a fluctuating structure and determines the degree of its fluctuational «merging» with the other ones. Consider, for example, the problem of interpretation of the results of the computer modeling of liquid's structure with fcc local structure in the presence of thermal fluctuations corresponding to $\xi = 0.2$. One finds, see Fig. 4, that approximately 10% of the 13-atom clusters will be identified as icosahdral ones.

3.2. 2-Dimensional Case

When the n-dimensional space $\{\Psi_l\}$, $(l = 1, ..., n)$ is used to describe the fluctuations of the structure then the distinction of the clusters is, as a rule, better than in the 1-D case studied in Sect. 3.1, i. e. $E^{(n)}(\xi) \leqslant E^{(1)}(\xi)$. This is so for the following reasons.

Let's discuss the projections of the many-dimensional plot of the probability density of fluctuations onto the planes $Q_i - Q_j$ and $R_i - R_j$. In most of the cases these projections can be obtained on the basis of 1-D projections and thus are of no interest. Nevertheless, in a few cases, e. g. these of the sections $Q_8 - Q_{10}$, $R_6 - R_8$ and $R_8 - R_{10}$ the domains of the «structural stability» of the icosahedron

increase as compared to that found in the 1-D case. The distributions of probability corresponding to these «anomalous» projections merge in a different way than the «normal ones» do. The two types of the merging are shown in Fig. 5 for the projections $Q_6 - Q_8$ and $R_6 - R_8$. The shaded areas represent the volumes of the phase space of invariants accesible to the fluctuations with the density of probability exceeding some fixed value. In this sense they are analogous to the 1-D sections ($\xi = \text{const}$) of the bands in Fig. 3. In the first case, corresponding to the «normal» projections, see Fig. 5,*a*, the intersections of the 2-D and 1-D projections representing different structures take place at approximately the same value of ξ. On the contrary, in the moment of the intersection of the 2-D «anomalous» projections the 1-D projections display the noticeable overlap, see Fig. 5,*b*. The distance $\Delta^{(2)}(\xi)$ between the centers of the «normal» projections is approximately the same as the distance $\Delta^{(1)}(\xi)$ between the centers of one of 1-D projections. Hence, $E^{(2)}(\xi) \approx E^{(1)}(\xi)$, see (I.10). In the case of «anomalous» projections $\Delta^{(2)}(\xi) > \Delta^{(1)}(\xi)$ and $E^{(2)}(\xi) < E^{(1)}(\xi)$. In general, the distinction of two fluctuating structures is the better the more «essentially» non-zero components has the vector joining the centers of the distributions of probability corresponding to the fluctuating structures.

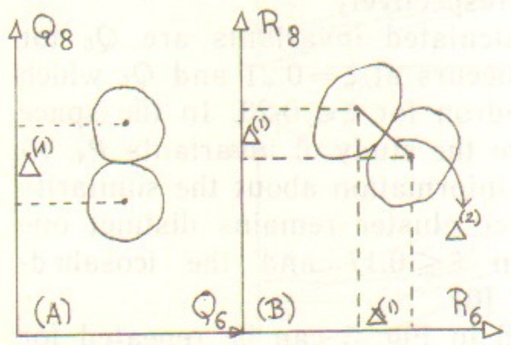

Fig. 5. The two types of «merging» of 2-D projections of probability densities of fluctuations of invariants: «normal» (*a*) and «anomalous» (*b*) projections.

3.3. Analysis in Many-Dimensional Space of Invariants

Let's study the mutual distinction of fluctuating structures in 10-dimensional space $\{\varphi_l\}$, $l = 1, \ldots, 10$. To this end we have evaluated the distances $\Delta_{ij}^{(10)}(\xi) = |\langle\vec{\varphi}\rangle_i(\xi) - \langle\vec{\varphi}\rangle_j(\xi)|$ between the centers $\langle\vec{\varphi}\rangle_i(\xi)$, $\langle\vec{\varphi}\rangle_j(\xi)$, see I, on the basis of the data presented in Fig. 2, and then, in the Gaussian approximation (I.10), the structural characteristics $\frac{1}{2}E_Q^{(10)}(\xi)$, Fig. 6,*a* and $\frac{1}{2}E_R^{(10)}(\xi)$, Fig. 6,*b*. For each fluctuating structure the functions $E_Q^{(10)}(\xi)$ and $E_R^{(10)}(\xi)$ characterize the error of recognition with respect to that one of other

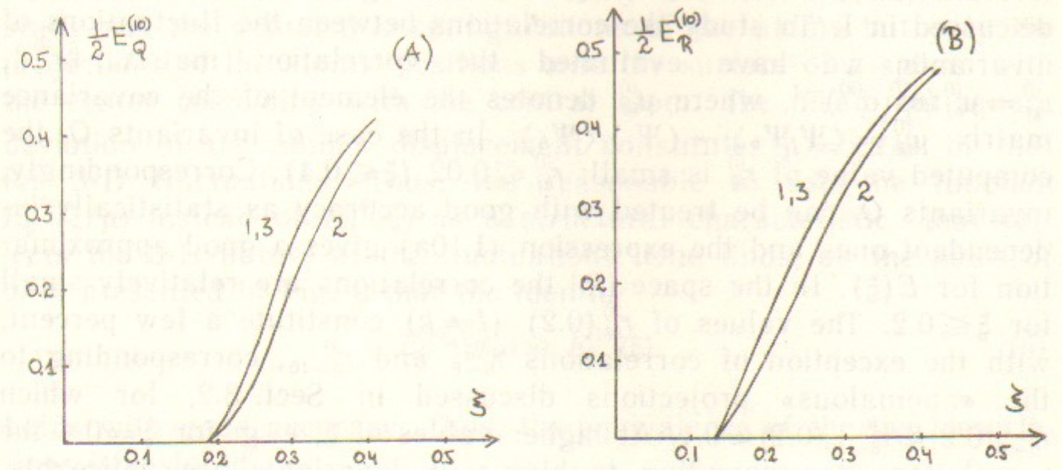

Fig. 6. The plot of the functions $\frac{1}{2}E_Q^{(10)}(\xi)$ (*a*) and $\frac{1}{2}E_R^{(10)}(\xi)$ (*b*) (*1*—fcc, *2*—hcp, *3*—icosahedron).

structures for which this error is the biggest. The role of invariants with $l > 10$ was discussed in Sect. 3.1. For $\xi > \xi_{i,Q}(\xi_{i,R})$ they are irrelevant degrees of freedom and, consequently, function $E^{(10)}(\xi)$ is identical to the structural characteristic $E^{(\infty)}(\xi)$ evaluated in the space of all independent invariants. One finds

$$E_Q^{(\infty)}(\xi) \equiv E_Q^{(10)}(\xi), \quad \xi \geqslant 0.20, \tag{4a}$$

$$E_R^{(\infty)}(\xi) \equiv E_R^{(10)}(\xi), \quad \xi \geqslant 0.15, \tag{4b}$$

One may expect, on the basis of arguments analogous to those presented in Sect. 3.1 that the identities (4) hold with good accuracy at much smaller values of ξ.

The use of $E^{(\infty)}(\xi)$ instead of $E^{(1)}(\xi)$ diminishes noticeably the probability of erroneous recognition of the structure at $0.20 \leqslant \xi \leqslant 30$. At higher values of ξ the difference between the values of these functions isn't so marked. The total «structural chaos» occurs at $\xi \sim 0.5$, i. e. when the concept of nearest neighbour loses its meaning.

The formulae (4) and Fig. 6 constitute an approximate solution to the problem of the recognition of the fluctuating close-packed structures with the help of quadratic structural invariants Q_l and R_l.

The structural characteristics $E(\xi)$ studied above were obtained in Gaussian approximation, see (I.9) and (I.10). Let's discuss

briefly the factorization of the probability density of fluctuations, formula (I.9), for invariants Q_l and R_l. In general,the problem was discussed in I. To study the correlations between the fluctuations of invariants we have evaluated the correlation matrix $\| r_{kl}^{(i)} \|$, $r_{kl}^{(i)} = \mu_{kl}^{(i)} (\sigma_i^{(l)} \sigma_i^{(k)})^{-1}$, where $\mu_{kl}^{(i)}$ denotes the element of the covariance matrix: $\mu_{lk}^{(i)} = \langle \Psi_l \Psi_k \rangle_i - \langle \Psi_l \rangle_i \langle \Psi_k \rangle_i$. In the case of invariants Q_l the computed value of $r_{kl}^{(i)}$ is small: $r_{kl}^{(i)} \leqslant 0.02$ ($\xi \leqslant 0.4$). Correspondingly, invariants Q_l can be treated with good accuracy as statistically independent ones and the expression (I.10a) gives a good approximation for $E(\xi)$. In the space $\{R_l\}$ the correlations are relatively small for $\xi \leqslant 0.2$. The values of $r_{kl}^{(i)}(0.2)$ ($l \neq k$) constitute a few percent, with the exception of correlations $r_{6-8}^{(i)}$ and $r_{8-10}^{(i)}$, corresponding to the «anomalous» projections discussed in Sect. 3.2, for which $r_{6-8}^{(i)}(0.2) \approx r_{8-10}^{(i)}(0.2) \approx 0.1$. At higher values of ξ, e. g. for $\xi = 0.4$ the correlations corresponding to high-rank invariants are noticeable: $r_{9-10}^{(i)}(0.4) \approx 0.4$. It means that the fluctuations of these invariants are no more statistically independent; instead, the appropriate linear combinations of R_l should be introduced. Consequently, at these values of ξ formula (I.10) isn't valid. Nevertheless, this fact doesn't influence the main results since for values of ξ bigger than $\xi = 0.2 \div 0.3$ the error of recognition is so big that the fluctuating structures are no more distinct ones, independently on the actual value of ξ. Another restriction on the use of formula (I.10) follows from the fact that our method of the simulation, see Sect. 2, results in the existence of an upper bound on the values of fluctuations of invariants. It was found that $|\varphi_l - \langle \varphi_l \rangle_i(\xi)| \leqslant \text{const} \approx 3$. Thus, the Gaussian approximation (I.10) for $E(\xi)$ isn't valid when the main contribution into $E(\xi)$, formula (I.6), give the values $\vec{\varphi}$ such that $|\varphi_l - \langle \varphi_l \rangle_i(\xi)| \sim 3$, i. e. for $E(\xi) < E^* \sim 1 - \Phi\left(\frac{3}{\sqrt{2}}\right) \sim 10^{-2}$. The error function $\Phi(x)$ was defined in I.

4. COMPARISON OF RESULTS: $\{Q_l\}$ vs $\{R_l\}$

The qualitative physical pictures of the fluctuational indistinctness of the close-packed types of local structure characterized by functions $E_Q(\xi)$ and $E_R^*(\xi)$, coincide. On the contrary, in the physically interesting interval $0.10 \leqslant \xi \leqslant 0.30$ the numerical results are different. This important methodological difficulty is solved as follows.

As stated in Sect. 2 invariant Q_l is sensitive to the specific 2-D fluctuations of the atoms' positions only. Namely, it's sufficient to study not the actual 3-D configurations of the atoms but only the projections of the atoms' positions onto the surface of a sphere with the center coinciding with the central atom. The mean-root-square deviation of the atom's displacement constitutes $\mu = \sqrt{2/3}$ of that for 3-D fluctuations. Thus, it's reasonable to use the function $E_Q^{(10)}(\xi/\mu)$ instead of $E_Q^{(10)}(\xi)$ as a structural characteristic that reflects the 3-D nature of the fluctuations. One finds, on the basis of data presented in Fig. 6 that the identity

$$E_Q^{(10)}(\xi/\mu) \equiv E_R^{(10)}(\xi) \tag{5}$$

holds with good accuracy. Thus, the equivalence of the two descriptions is restored.

So far, we have applied the formalism of structural invariants to find the probabilistic characteristic $E(\xi)$. Once this function is known, the quantitative treatment of some topics related to the local structure of matter is possible. In the next two sections we study some of these problems.

5. THE QUANTITATIVE FORMULATION OF THE CONCEPT OF THE CONDENSED MATTER

The formalism of structural invariants is intended for the analysis of the results of computer simulation of structure of crystals, liquids and amorphous solids. On the other hand, the results presented above make it possible to study the local structure of condensed matter from a new point of view. In particular, the qualitative concept of the local structure of dense liquids, see Ref. [2], can be formulated in a quantitative way.

The concept of condensed matter is, as a rule, used intuitively. In this paper the term «condensed matter» refers to matter with distinct type of local structure and, thus, has the statistical meaning. In other words, the total probability $\mathscr{E}(\xi)$ of the erroneous recognition of the local structure of condensed matter, see I, should not exceed some small value $\mathscr{E}_b$. Thus, the condensed state of matter exists for $\xi < \xi_{\max}$, where

$$\mathscr{E}(\xi_{\max}) = \mathscr{E}_b \,. \tag{6}$$

In this sense matter at $\xi \sim 0.5$ is structureless and corresponds to dense gas. The distinguished role of scale $\xi = 0.5$ was displayed in computer simulation of the structure of liquid argon by LaViolette and Stillinger [7].

Let's apply these ideas to the case of close-packed structures. On the melting line the mean-root-square deviation ξ_m for the close-packed matter is, as a rule, small. For example, for the rare-gas crystals (Ar, Kr, Xe, Ne), which display the fcc structure near the melting line, at the melting temperature $\xi_m = 0.09 \div 0.11$, see Ref. [8]. For these elements the local structure at melting temperature is well-defined since $E_R^{(10)}(\xi_m) \ll 1$. In the liquid phase the «memory» about the parental local structure gradually vanishes as the temperature (or equivalently ξ^2) increases. The noticeable concentration of clusters with some other type of local structure appears at bigger values of ξ than ξ_m, see Fig. 6. For example, at $\xi = 2\xi_m$ it constitutes approximately 20%.

Formally, ξ_{max} depends on $\mathscr{E}_b \in (0, 1)$. Physical arguments presented above imply that $\mathscr{E}_b \ll 1$. From our point of view it's reasonable to choose ξ_{max} as this value of ξ at which plot of $E_R^{(10)}(\xi)$, Fig. 6, changes from nearly horizontal to steep line, since at further small increase of ξ the error of recognition increases rapidly. In our case

$$\xi_{max} \approx 0.15 . \qquad (7)$$

Let's estimate value $\mathscr{E}_b = \mathscr{E}(0.15)$. For some fixed type of structure, denoted by 1, one has $\mathscr{E}(\xi) = E_2(\xi) + E_3(\xi) - E_{23}(\xi)$, where E_2, E_3 and E_{23} denote the probability of identification of structure 1 as structures 2,3, and «2 and 3», respectively. At $\xi = 0.15$ the distance $\Delta_{ij}^{(10)}$ $(i \neq j = 1, 2, 3)$ in 10-dimensional space $\{R_l/\sigma_l(\xi)\}$ is $\Delta_{ij}^{(10)} \approx 4$. Therefore, the overlapping of distributions is insignificant and $E_2 \approx E_3 \gg E_{23}$. Consequently, $\mathscr{E}_b = 2E_2(0.15) \approx 0.05$.

In order to estimate the width T_{max} of the temperature interval where exists condensed state of matter one has to study the dependence $\overline{\xi^2(T)}$ of the value of the mean-square displacement of an atom averaged over the sample, on temperature T. Here $\overline{\ldots}$ stands for «mean over the atoms». Let's discuss this problem.

In the presence of distinct type of local structure the short-wavelength oscillations of atoms with the wavelength of order of mean interatomic distance a resemble high-frequency phonons with wave-vector $|\vec{k}| \sim \pi/a$. Such the oscillations can be treated approxi-

mately in the standard formalism of the theory of elasticity. In our simulation the atoms fluctuate independently and one can expect that the fluctuations of the structure resemble the ones that occur in the presence of high-frequency phonons. The situation changes drastically when low-frequency shear deformations are accounted for since liquid starts to flow. Such the type of atomic motion doesn't affect, in the first approximation, the local structure. Consequently, function $\overline{\xi^2(T)}$ can be split into two terms

$$\overline{\xi^2(T)} = \xi_S^2(T) + \xi_L^2(T), \qquad (8)$$

where $\xi_S^2(T)$ denotes the contribution from short-wavelength oscillations of atoms that take place in domains of distinct local order («good matter») and $\xi_L^2(T)$ — the contribution from other types of atomic movements that occur mainly in domains of defective structure («bad matter»). Mathematical formulation of concepts of «good» and «bad» matter in liquid state can be found, e. g. in paper [9] of Patashinskii and Shumilo. The arguments presented above show that in the crude approximation the harmonic-approximation formula $\xi_S^2(T) \sim T$ is valid for «good» matter. Thus, using (7) and accounting that $\xi_m \approx 0.1$ one finds

$$T_{max} \approx 2T_m , \qquad (9)$$

where T_m denotes the melting temperature. The critical temperature T_c of rare-gas liquids constitutes $T_c = 1.8T_m$, see [10]. The qualitative phase-diagram of close-packed condensed matter is shown in Fig. 7. The shaded area represents the «condensed» state of liquid, i. e. the melt. Problem of the recognition in the vicinity of critical point remains open.

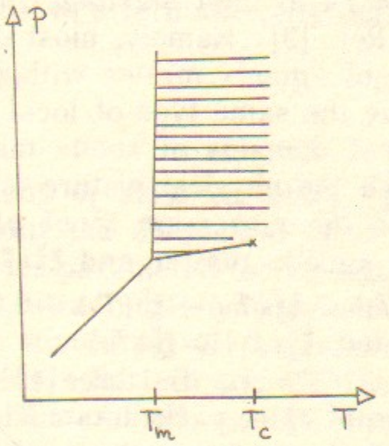

Fig. 7. The qualitative phase-diagram of the close-packed condensed matter. The shaded area represents the supposed «condensed» state of liquid, i. e. the melt, see text.

Numerical results (7) and (9) lead to the following physical picture of local structure of condensed matter. Big values of ξ_{max} $(\xi_{max}/\xi_m \approx 1.5)$ and T_{max} $(T_{max}/T_m \approx 2)$ imply that the domain (in p-T plane) where condensed state of matter exists spreads notice-

ably into the part of p-T plane corresponding to liquid phase. This qualitative result is of considerable importance for theoretical description of phenomena that occur near the melting line. In particular, it gives firm ground to microscopic [9] and phenomenological [11] theories of melting, in which the concept of local structure is used *a priori* to justify the introduction of the effective-hamiltonian formalism. Consequently, the foundations of more and more popular [12] concept of structural phase transition liquid-liquid accompanied by the change of the type of local structure [13] can be better understood.

On the basis of computer simulation results of liquid argon's structure LaViolette and Stillinger have pointed out in Ref. [7] that the value of standard deviation $\xi(T) \equiv (\overline{\xi^2(T)})^{1/2}$ changes nearly discontinuously in liquid from $\xi_m \approx 0.1$ to $\xi \approx 0.5$. Let's discuss briefly this problem. To this end we evaluate $\xi^2(T_1)$, $\xi_S^2(T_1)$ and $\xi_L^2(T_1)$ at $T_1 \approx T_m$ in melt starting from concepts of local structure presented in Ref. [9]. Namely, most of the atoms belong to connected domains of «good» matter with characteristic size $R \gg a$. These domains have the same type of local structure (tangent lattice). The structureless domains of «bad» matter contain small fraction n_i of atoms. Such the physical picture is self-consistent when $n_i \ll 1$. We assume that the dispersion ξ^2 of atom's displacement is $\xi_g^2(T_1) = \xi_m^2 = 0.01$ for «good» matter and $\xi_b^2(T_1) = 1$ for «bad» matter. If $n_i = 0.1$ then $\xi^2(T_1) = \xi_S^2(T_1) + \xi_L^2(T_1) = 0.01 + 0.10$ and $\xi(T_1) \approx 0.33 \approx 3\xi_m$. As expected, $\xi_L^2(T_1) \gg \xi_S^2(T_1)$.

At $T > T_m$ the three close-packed structures merge into a new type of close-packed «structureless» pattern. It can be expected that analogous phenomena exist for other, non-close-packed types of local structure. Consequently, the following hierarchic physical picture of structure of liquid emerges. In the close vicinity of the melting line each liquid is the melt with the defined pattern of local structure—the structure of this liquid. Different melts can display variety of patterns of local structures. At higher temperatures some of them become fluctuationally indistinguishable. The classification of structures is still possible in terms of new classes of structures, containing the merged «old» ones. The «fluctuational crystallography» of melts will be studied elsewhere.

6. SLOW VARIABLES

In phase spaces of invariants φ_l and Ψ_l the mean values $\langle \vec{\varphi} \rangle_i$ and $\langle \vec{\Psi} \rangle_i$ are represented by curves parametrized by ξ. Value $\xi = 0$ corresponds to ideal structure for which some of φ_l tend to infinity. For $\xi > 0.50$ these curves terminate in fixed points $\vec{\varphi}^*$, $\vec{\Psi}^*$, where $Q_l^* \approx 0.28$ and $R_l^*/\sigma_{l,R}^{(l)}(0.5) \approx 0.3$ ($l = 3, \ldots, 10$), see Fig. 2,*a*,*b*. The process of overlapping of two distributions is determined by velocity of relative approach of their centers $\langle \vec{\varphi} \rangle$. Let's translate and rotate the coordinate frame so that new axis 1 coincide with direction of the vector $\vec{w}_{ij}$, $\vec{w}_{ij} = \langle \vec{\varphi} \rangle_i - \langle \vec{\varphi} \rangle_j$. The linear combination

$$\varphi_{sl} = \sum_k \alpha_{1k}(\xi)\, \varphi_k , \tag{10}$$

where $\alpha_{ik}(\xi)$ denotes elements of the rotation matrix, defines the slow variable of our problem. In terms of Ψ_l's formula (10) reads

$$\varphi_{sl} = \sum_k \frac{\alpha_{1k}(\xi)}{\sigma_k(\xi)} \Psi_k . \tag{10'}$$

Distributions of probability of fluctuations of slow variables (10), (10′) give the maximal information about the distinction of structures, see below. Quantity φ_{sl} is the order-parameter for structural phase transition melt-melt. Concept of «structural hydrodynamical mode» agrees with results of computer simulation of relaxation of «structured» liquid presented by Hess [14]. In 1-D and 2-D cases corresponding to invariants Q_l, see Sect. 3.1 and 3.2, $\varphi_{sl} \sim Q_6$. In general, in many-dimensional space variable φ_{sl} doesn't coincide with any of variables φ_l. The difference between φ_{sl} and any of φ_l displays itself in the difference between $E_{Q,R}^{(\infty)}(\xi)$ and $E_{Q,R}^{(1)}(\xi)$, see Figs 4 and 6. Slow variable is effectively 1-D characteristic. It follows from its definition that $E_R^{(\infty)}(\xi) \equiv E_{\varphi_{sl}}^{(1)}(\xi)$.

Coefficients α_{1k} in (10) depend, in general, on value of ξ. It's a consequence of the fact that the high-rank invariants become irrelevant ones when ξ increases, i. e. when the values of corresponding components of vector $\vec{w}_{ij}$ become small quantities. The way in which a new slow variable appears in the system when ξ changes is presented schematically in Fig. 8. At $\xi < \min(\xi_1, \xi_2)$ $\varphi_{sl} \equiv \varphi_\beta$ while at $\xi > \max(\xi_1, \xi_2)$ $\varphi_{sl} \equiv \varphi_\alpha$.

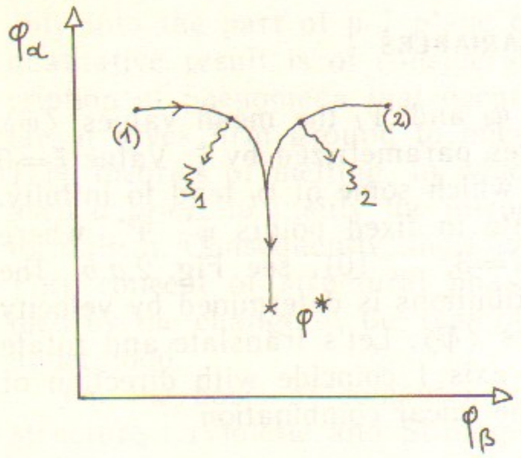

Fig. 8. The qualitative physical picture of the functional dependence of slow mode φ_{st} on value of ξ, see text. The solid curves *1*, *2* describe the trajectories $\langle\vec{\varphi}\rangle$ parametrized by ξ, corresponding to the fluctuations of two structures 1 and 2.

7. CONCLUSIONS

In this and previous (I) papers we have presented the formalism of structural invariants intended for recognition of structures in the presence of thermal fluctuations of constituent atoms. Structural characteristics of fluctuating clusters have probabilistic meaning. This formalism was applied to describe fluctuating 13-atom close-packed clusters (fcc, hcp, icosahedron) and, in particular, to estimate the domain (in p-T plane) of existence of «structured» liquid, i. e. the melt.

We have studied here quadratic invariants only, see (3). The more sound understanding of the fluctuations of structure of condensed matter will arise when cubic, quartic etc. invariants of parameters (1) and (2) and, in particular, the invariants constructed from Q_{lm} and R_{lm} with different values of l are taken into account in a systematic way. Recall that the irreducible tensor of rank l has $2(l-1)$ independent invariants $\Psi_l^{(k)}$, $k=1, \ldots, 2(l-1)$, see I. One can expect that among all those invariants there are new relevant ones leading to further increase of degree of structural stability of fluctuating clusters. The discussion of these problems is beyond the scope of this paper.

Our formalism is intended mainly for the analysis of results of computer simulation. The configurations of atoms of model liquids and amorphous solids can be generated via molecular dynamics and Monte Carlo methods. The study of the statistics of clusters in the manner proposed in this paper, though even it constitutes the noticeable computational task, would contribute strongly to understanding of structure of condensed matter.

Let's review briefly some of the topics related to local structure of condensed matter that can be studied via the formalism of structural invariants.

1. Investigation of hierarchic picture of local structure of liquids at various temperatures («fluctuational crystallography» of condensed matter).
2. Study of new hydrodynamic modes in melts, related to invariants with various ranks l.
3. Study of effects that might occur in the critical point of structural phase transitions melt-melt.
4. Investigation of restrictions on computer simulation of local structure. Some of these problems are at progress now.

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