

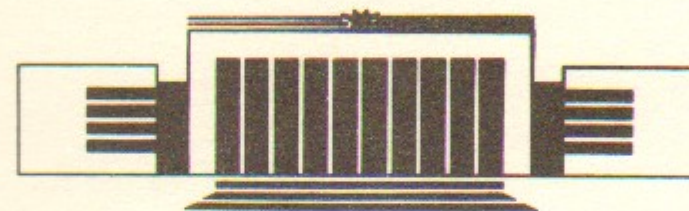


ИНСТИТУТ ЯДЕРНОЙ ФИЗИКИ СО АН СССР ⁹

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**STATISTICAL DESCRIPTION
OF THE LOCAL STRUCTURE
OF CONDENSED MATTER.
III. MACROSCOPICAL SYSTEMS**

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Institute of Nuclear Physics
Statistical Description of the Local
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III. Macroscopical Systems

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ABSTRACT

A method of a statistical analysis of local structure of liquids represented by an ensemble of configurations of atoms is proposed in the mathematical framework of structural invariants. The problem of the description of local structure of macroscopical volumes of liquids is studied. The statistical algorithms of the identification (classification and determination) of local structure of liquids are presented. The conditions of the recognition of macroscopical close-packed structures (fcc, hcp) in the presence of thermal fluctuations of their constituent atoms are studied.

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1. LOCAL STRUCTURE OF A LIQUID—STATUS OF THE PROBLEM

The physical concepts which assume the presence of a definite type of local structure in a melt (i. e. a liquid near its freezing temperature T_m) seems to be fruitful in theoretical investigations of properties of a wide class of liquids starting from simple theoretical models [1—9]. Unluckily, the character of local arrangement of atoms in small volumes of melt is not sufficiently well known. The experimental results do not yield firm conclusive answers to the question of the existence and type of local structure in melts. The ambiguities of the interpretation are due to the indirect character of available information concerning the instantaneous positions of atoms: the 3-d structure is characterized in terms of radial distribution function (RDF). This characteristic seems to be very sensitive to irregularities of the structure (see section 4). Meanwhile, it is reasonable to expect that the «good» local order is violated in some domains of the melt—in analogy to the case of an ideal crystal with dislocations. It was assumed earlier [9] that a melt consists of multiply connected regions of «good» matter and of domains where the local structure is violated. The latter ensure the isotropy of the melt, i. e. the lack of long-range correlations of local anisotropies of physical properties. The relatively small concentration n_b of atoms of «bad» matter is thus the main obstacle for the identification of local structure of melt (in presence of thermal fluctuations) with the help of RDF.

The strong sensitivity of RDF to small concentration n_b is probably the manifestation of the general tendency in structural prob-

lems. The anomalous strong dependence of mean-root-square deviation ξ of an atom from its supposed equilibrium position on n_b was discussed by us in [10].

On the other hand there exist quite a number of facts which support the concept of the local structure of melts. In particular, the results of X-ray, electron and neutron structural experiments show that, as a rule, the local structure of melt in volumes corresponding to at least two first coordination shells resembles that of the parental (or, maybe, some other) crystal, see e. g. in a hand-book [11].

The more detailed study of the structure of the melt can be made via computer experiments using the Monte-Carlo and (or) molecular dynamics methods. The ensemble of typical configurations of atoms thus obtained contains the full information about the instantaneous positions of atoms. In this way the noticeable progress in understanding the physics of melts, and in particular of their thermodynamics was achieved. Nevertheless, the results of the simulation of the structure of the melt are, from our point of view, inconclusive ones because of the lack of systematical approach to the problem of analysis of types of structures displaying noticeable thermal fluctuations of constituent atoms. The success of such analysis depends critically on the choice of appropriate set of parameters which should ensure the sufficiently detailed description of both topological and metrical properties of local structures (see [10]).

The aim of this paper is to propose a method for analysis the structure of a macroscopical configuration of atoms in order to study the problem of the existence and types of local order in melts.

2. LIQUIDS—PHYSICAL CONCEPTS. SOME DEFINITIONS

In this paper we study the local order in liquids—the characteristic of the arrangement of atoms in a small neighbourhood of an atom. The results of structural investigations [11] indicate that the local order in melts exists at least in few coordination shells.

A group of atoms (mentally) picked out of condensed matter (cluster) can be treated as a geometrical figure, characterized by the coordinates \bar{x}_i of centers of atoms. Such the detailed description

is superfluous in the study of structure of real physical systems. Note that the concept of the structure includes the possibility of any motion, not changing the interatomic distances. Small (thermal) fluctuations of atoms' positions lead to various geometrical figures corresponding to one «physical» structure. In other words, one configuration can be selected to represent this infinite set of figures. This configuration can be associated with the concept of «physical» structure; it displays usually some type of point symmetry and can be chosen as the ideal structure pattern. Suppose that the set of patterns is known. Then by definition the structure of a cluster coincides with that of a pattern which provides maximal coincidence (resemblance). Such the prescription is of no value when many patterns approximate the studied structure equally well. In particular, this is so when the temperature is sufficiently high [10]. Consequently, the set of patterns should consist only of structures as different from each other as it is possible. For the detailed account of the concepts of statistical description of the local structure of condensed matter see [12]. The choice of a set of patterns depends on physical concepts.

We suppose that a melt displays one (or few) type of local structure. There exists an opposite point of view on this subject (see e. g. [13]) based on the concept of local chaos which neglect the possibility of noticeable coincidence of local structures. The general concepts concerning the local order in melts have arisen in the twenties of our century (see e. g. in [14]); it was assumed that the small volumes with some type of arrangement of atoms—the so called subotaksis—exist in a melt. The general physical picture of the kinetics of liquids based on the notion of subotaksis was proposed by Frenkel [2]. In short, the subotaktic domains are supposed to be unstable i. e. they cannot be regarded as «nuclei» of some other phase; in particular, they cannot be identified with microcrystallites. A subotaksis has no physical boundary associated with the rapid change of parameters of state.

In general, a large variety of types of local order can be discussed, including both crystallographic and non-crystallographic point symmetries. In the latter case at least two different crystallographic elements are required to build 3-d quasi-periodic lattice [15]. In particular, Frank [3] assumed the existence of small icosahedral domains in supercooled liquids.

We assume that for a large variety of melts (including simple melts) the local crystal order hypothesis holds. According to this

hypothesis the statistical picture of ordering of atoms in small volumes of crystals coincides with those of the melts. The concept of local and global structures is associated with the so called «tangent» figures. By the definition [16, 9] the tangent position of an ideal structure to real physical system minimizes the degree of non-coincidence of atoms and their supposed pre-images (i. e. the sites of tangent figure). The choice of tangent figure is dictated by physical arguments. For example, the local crystal order hypothesis implies the choice of some crystal lattice as tangent figure. The appropriate local order-parameters were introduced by Hess [6] and in our paper [8]. Another example—the choice of tangent figure for the study of the structure of metallic glass. The local order is supposed to be icosahedral, with five tetrahedra (slightly distorted) sharing an edge. The local topology is the same as in {3, 3, 5} polytope which plays the role of tangent figure. The local order-parameters were introduced by Sethna [16] and Nelson and others [17].

The concept of tangent figure provides the possibility of consistent analysis of configurations of atoms of condensed matter. Each of them can be splitted into domains of «good» and «bad» matter. The former one is associated with slow rotation of tangent figure in space; the local structure of the latter differs strongly from that of tangent figure. For example, the domains of «bad» matter corresponding to local crystal order hypothesis are locally equivalent to dislocations [9] while for metallic glasses they correspond to disclinations of Frank—Kasper phase [4].

So far the ideal structure patterns (tangent figures) were supposed to be a priori known. Generally it is not clear whether the configuration of atoms of interest displays any type of local structure and, if so, which set of ideal structure patterns is the «proper» one. In the present paper we study some topics related to such the formulation of the problem of identification of local structure of condensed matter.

In general three types of local structure associated with different time scales can be distinguished in melts [18]. The instantaneous (*I*) structure is described by the set of coordinates of atoms at some fixed moment of time. The vibrational (*V*) structure is the averaged structure of an atom's neighbourhood over the period of time less than time of «settled» [2] life. In our language this means that the defects are immovable. Finally, the diffusional (*D*) structure arises when the defects are free to move. This paper is

devoted to the study of *I*-structures in order to obtain some knowledge of *V*-structures.

In order to study the resemblance of structures of two clusters some quantitative characteristics must be used [10, 12] (see also [19]). Let us introduce the local order-parameters—the irreducible multipole moments of the density [6, 8]

$$T_{\alpha_1 \dots \alpha_l} = \sum_{(a)} \omega(\vec{x}^{(a)}) t_{\alpha_1 \dots \alpha_l}^{(a)}, \quad (1)$$

where

$$t_{\alpha_1 \dots \alpha_l}^{(a)} = \overline{x_{\alpha_1}^{(a)} \dots x_{\alpha_l}^{(a)}} \quad (2)$$

denotes the irreducible part of the Cartesian tensor $x_{\alpha_1}^{(a)} \dots x_{\alpha_l}^{(a)}$. The summation in (1) extends over all the points $\vec{x}^{(a)}$ —the centers of the atoms that surround the central atom of the cluster. Function $\omega(\vec{x})$ defines the weight of the contributions to $T_{\alpha_1 \dots \alpha_l}$ from different coordination shells. 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 $T_{\alpha_1 \dots \alpha_l}$, $l=0, 1, \dots$, i. e. they are all the scalars that can be constructed from the set $\{T_{\alpha_1 \dots \alpha_l}\}$, $l=0, 1, \dots$

The equivalent set of local order-parameters (Nelson and Toner, see [7]) 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}

$$T_{lm} = \sum_{(a)} \tilde{\omega}(\vec{x}^{(a)}) t_{lm}^{(a)}, \quad (3)$$

where

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

$\Omega^{(a)} = \{\varphi^{(a)}; \theta^{(a)}\}$ denotes the polar and azimuthal angles that fix the direction $\vec{x}^{(a)}/|\vec{x}^{(a)}|$ and $\tilde{\omega}(\vec{x})$ is a new weight function. $t_{\alpha_1 \dots \alpha_l}^{(a)}$ and $T_{\alpha_1 \dots \alpha_l}$ are linear combinations of $t_{lm}^{(a)}$ and T_{lm} , 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. [20]. Some examples can be found in [10, 19, 21].

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 $\psi_l^{(k)}$ ($l=0, 1, \dots$; $k=1, \dots, 2(l-1)$) will be referred to as structural invariants [12] and the phase space $\{\psi_l^{(k)}\}$ will be referred to as the feature space.

For the sake of simplicity the upper index in $\psi_l^{(k)}$ will not be written out explicitly, i. e. ψ_l will be used instead of $\psi_l^{(k)}$. Any figure can be represented by a point in the feature space. Let us define also the dimensionless invariants $\varphi_l = \psi_l / \sigma_l$ [12], where σ_l^2 denotes the dispersion of the random variable ψ_l . The sets $\{\psi_l\}$ and $\{\varphi_l\}$ which are many-dimensional random variables (random vectors) will be denoted by $\vec{\psi}$ and $\vec{\varphi}$, respectively; the covariance matrix of random vector $\vec{\psi}$ will be denoted by $\vec{\sigma}$.

The structure of 13-atom close-packed clusters in the presence of thermal fluctuations of their constituent atoms at $T \approx T_m$ can be described by a few relevant structural invariants with small values of l [10]. The rest of the invariants describe the details of the structure and are of interest at lower temperatures corresponding to crystal phase. This important property of structural invariants makes them a promising tool for the systematical approach to the problem of analysis of types of structures displaying noticeable thermal fluctuations.

The local structure is identified as follows. The feature space is divided (at temperature T) into domains corresponding to the fluctuations of ideal structure patterns. In general these domains overlap one another, that leads to a probabilistic character of recognition. Any structure represented by a point in the feature space can be treated (with some probability p_i) as the fluctuation of the structure of any ideal pattern Γ_i (consisting of the same number of atoms). The concept of a definite type of local structure is thus meaningless unless $p_i \gg p_k$ for some i . The quantitative measure of the error of recognition is given by the degree of overlapping of the probability densities of invariants $\vec{\psi}$. The details can be found in our paper [12].

The formalism of structural invariants yields a convenient description of the local structure of macroscopic systems. Let us consider a configuration of atoms. For each atom \vec{x}' one finds his $N-1$ nearest neighbours which constitute together an N -atom cluster. The invariants $\vec{\psi}$ evaluated for this cluster define the field $\vec{\psi}(\vec{x})$ in the point $\vec{x} = \vec{x}'$. Fields $\vec{\psi}(\vec{x})$ characterize the local structure of the given configuration.

The program of the identification of local structure of liquids (and amorphous systems) presented below is rather time consuming. Thus, the clear understanding of the degree of rigorousness of mathematical treatment is necessary. In the next section this problem is briefly discussed.

3. STATISTICAL ANALYSIS OF LOCAL STRUCTURE OF MODEL LIQUIDS. BASIC CONCEPTS

In this section we present briefly the basic concepts of the statistical identification of local structure of condensed matter described via an ensemble of configurations of atoms. We suppose that this ensemble of semimacroscopic (containing $10^2 - 10^4$ atoms) configurations, i. e. of semimacroscopic I -configurations is known, e. g. from computer experiments. Taking into account the presumed equivalence of time and statistical averaging (ergodic hypothesis, see e. g. [22]) one can conclude that the ensemble represents the macroscopic I -structure.

The problem of the identification of local structure of a condensed system can be divided into two parts. The first one is, according to the terminology of Kendall [23], the classification of local structures of a macroscopic (or semimacroscopic) I -configuration into groups consisting of similar structures but different with respect to each other. Namely, a priori one knows neither the types of «good» and «bad» matter nor their numbers. The aim of the classification is to extract the statistically uniform domains (i. e. groups of atoms) in an I -configuration. The concept of statistical uniformity means the statistical equality of some parameters in this domain. The choice of these parameters is dictated by the behaviour of structural invariants in presence of thermal fluctuations and, in turn, determines how detailed the classification will be. The hypothesis of local crystal order states that the results of the classification are the same ones (in statistical meaning) for each of the semimacroscopic I -configurations of the ensemble.

In the second stage of the identification the classified structures are compared with the ideal patterns of structure (determination). The following formulations are of interest. I) — «quantitative» determination — where the statistical hypothesis that the structure of interest resembles that of one ideal structure pattern is verified. II) — «semiquantitative» determination — where it is assumed that the studied structure is one of a few known types; the determination is provided via the comparison of the moments of the invariants with these of ideal patterns. III) — «qualitative» determination — where the presence of some definite (but unknown) types of local order for macroscopic I -configuration is displayed. This formulation is technically simpler than the preceding ones and is thus

of main interest for the verification of the basic concepts concerning the local structure of melts.

In what follows we present the simplest algorithms for classification and determination of local structures. The reliability of the identification depends on the number of used informative invariants; in general the random vector $\bar{\psi}$ should be used. In some cases it may turn out that the use of only one informative invariant ψ_l is sufficient. Thus, the methods of both many-dimensional and one-dimensional statistical analysis are used throughout.

4. IDENTIFICATION OF STRUCTURE OF «COMPUTER» LIQUID: CLASSIFICATION

In this section the simple algorithm of classification of types of local structure of l -structure described by vector field $\bar{\psi}(\bar{x})$ is presented. The volume of the matter is divided into domains of «good» and «bad» matter using the density probability function ρ_l of random variable ψ_l . The classification of atom \bar{x} as an atom of a «good» matter depends on the radius R_g of the neighbourhood of \bar{x} which contributes noticeably to ψ_l . An atom belongs to a «good» matter only if all his neighbours are in «right» positions, i. e. the atom and its neighbourhood resemble an ideal pattern of structure. The defects like dislocations, vacancies etc. presented in this neighbourhood, make the atom a «bad» one. As a result, defects give rise to the region of «bad» matter with radius R_g . This is the origin of the strong susceptibility to defects of RDF at large (a few interatomic) distances.

We propose the following method of classification. One finds with the help of $\bar{\psi}(\bar{x})$ the empirical density probability functions $\rho_l(\psi_l)$. The typical functions ρ_l corresponding to some concepts of local structure of liquids are shown in Fig. 1. In particular, the case (a) corresponds to the presence of definite types of «good» and «bad» matters. The boundary $\psi_l^{(b)}$ splits the ψ_l axis in two parts in a «natural» way. Most of the clusters belong to the $\psi_l > \psi_l^{(b)}$ domain; by the definition their constituent atoms form the «good» matter. Equivalently, an atom belongs to a «bad» matter only if it does not belong to any cluster with $\psi_l > \psi_l^{(b)}$. Such the classification is suitable for the distinction of two types of noticeably different structures when one of them is dominant (Fig. 1,a). When two

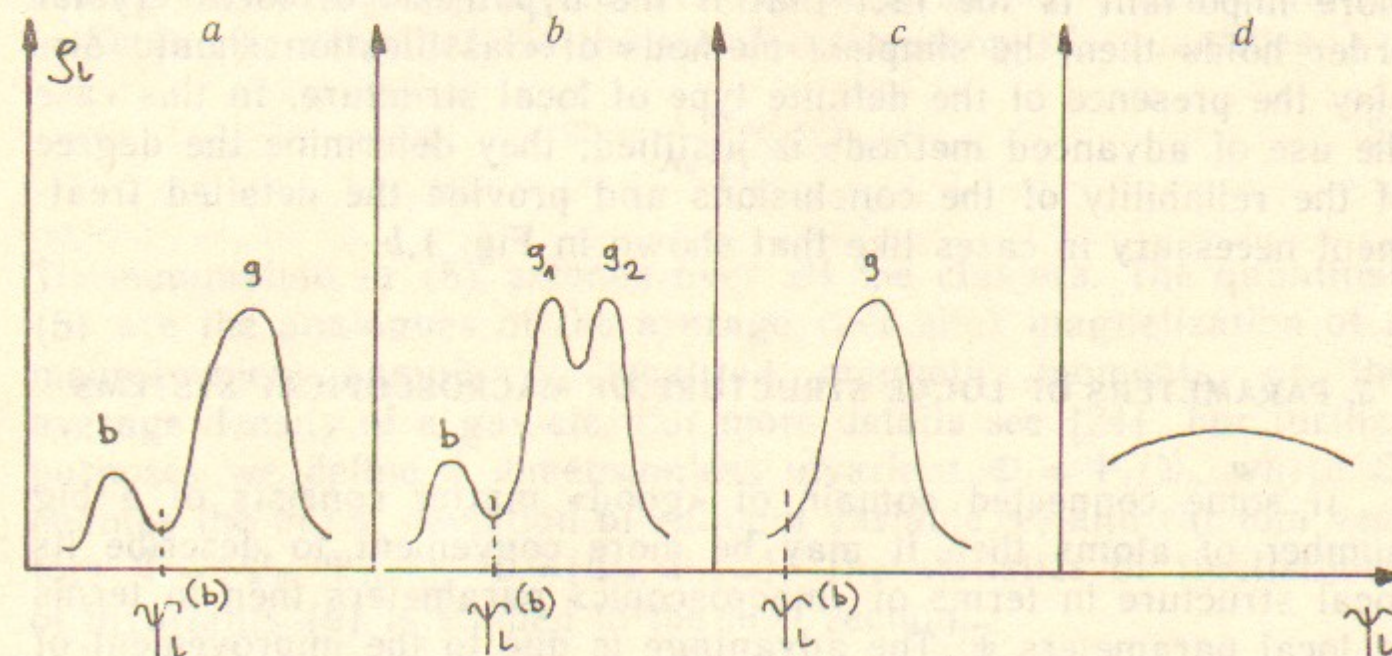


Fig. 1. Schematic plots of some typical functions $\rho_l(\psi_l)$; «g», «b» — «good» and «bad» matter.

types of similar structures are present (Fig. 1,b corresponding to some concepts of local structure of alkali metal melts [5]) one can, for the beginning, neglect this fact and apply the above algorithm to find the domains of «bad» and «good» matters. To this end the less informative invariants with higher values of l [10] can be used. In the case displayed in Fig. 1,d no definite type of local order exists.

The merits of the method are its simplicity and small volume of needed computer time. Its main shortage is due to the element of arbitrariness. Namely, one expects that the number of relevant invariants at the melting temperature is not less than 10 [10]. In this case any reasonable statistics is not sufficient to construct the probability density function $\rho(\bar{\psi})$ and the classification has to be done via the use of partial density function $\rho_l(\psi_l)$. It is natural to expect that the classifications resulting from the use of different ρ_l do not coincide. Next, in some cases the choice of $\psi_l^{(b)}$ is also arbitrary (see Fig. 1,c). Finally, this method offers no possibility to compare the differences between two different classifications.

In principal, the advanced methods of many-dimensional statistical analysis can be used to yield the algorithms free of these shortcomings. We do not present them here for the following reasons. Firstly, they are very (computer) time consuming. Secondly and

more important is the fact that if the hypothesis of local crystal order holds then the simplest methods of classification should display the presence of the definite type of local structure. In this case the use of advanced methods is justified; they determine the degree of the reliability of the conclusions and provide the detailed treatment necessary in cases like that shown in Fig. 1, *b*.

5. PARAMETERS OF LOCAL STRUCTURE OF MACROSCOPICAL SYSTEMS

If some connected domain of «good» matter consists of a big number of atoms then it may be more convenient to describe its local structure in terms of «macroscopic» parameters than in terms of local parameters $\bar{\psi}$. The advantage is due to the improvement of the conditions for the recognition of fluctuating structures. In this section we introduce such the description.

Macroscopical volume δV of «good» matter containing n_g atoms can be treated as a set of $N_0 = n_g/N$, N —atomic clusters; the parameters describing fluctuations of the shapes and orientations in space of two neighbouring clusters are supposed to be not too strongly correlated. The choice of N is a priori arbitrary since the «clusters» have no real physical boundary. To some degree, the analogous arbitrariness arises when the element of periodicity of an ideal crystal is to be chosen. The main difference is that for big values of N such that $N_0 \sim 1$ the «cluster» displays no resemblance to any crystallographic structure. The study of fluctuations of macroscopical structures with the help of such the large cluster though in principle possible is difficult due to the evident lack of a classification scheme for the choice of patterns Γ_i which form the basis in the space of structures [12]. For this reason it is convenient to use small volumes of melts which display noticeable similarity with some crystallographic (or non-crystallographic) structure. As stated in section 1 such the similarity holds in volumes corresponding to first coordination shells, containing $N_c \sim 10^1 \div 10^2$ atoms [11]. In such the case the choice of $\{\Gamma_i\}$ corresponds to the concept of crystallographic (non-crystallographic) point-symmetries. Evidently such the description is valid for systems where the mentioned above similarity holds in volumes containing more than N_c atoms.

Let us consider an arbitrary splitting of domain δV of «good» matter onto N -atom clusters. In general, some of the atoms may

belong to more than one cluster. The local structure of the matter in δV can be described via the set of «macroscopical» quantities

$$\Psi_i = \frac{1}{N_0} \sum_l \Psi_l(\vec{r}_i). \quad (5)$$

The summation in (5) extends over all the clusters. The quantities (5) are the analogues of the average (per site) magnetization of a macroscopical sample of localized magnetic moments, or the average density of a gas etc. For more details see [24]. For further purposes we define a dimensionless invariant $\Phi_i = \Psi_i/\Sigma_i$, where Σ_i denotes the m.r.s. deviation of random variable Ψ_i and random vectors $\vec{\Psi} = \{\Psi_0, \Psi_1, \dots\}$, $\vec{\Phi} = \{\Phi_0, \Phi_1, \dots\}$. The statistics of fluctuations of invariants (5) is studied in the next section.

6. IDEAL PATTERNS OF STRUCTURE: FLUCTUATIONS AND CONDITIONS FOR RECOGNITION

Determination of the structure of previously classified domains requires the description of the structure of presumed patterns in the presence of thermal fluctuations in terms of parameters (5).

The physical picture of the structure of a liquid accepted in this paper implies the existence of an equilibrium concentration of linear defects and deformations due to these defects. When the defects are immovable, the structure of average locations of atoms can be identified with the V -structure. The long range orientational order does not exist; when moving along the «good» matter the tangent lattice changes its orientation. This in turn leads, at the distances of a few coordination shells, to the deformation analogous to the elastic deformation in bent bar of an ideal monocrystal. The statistics of fluctuations of invariants reflects both the «quick» phonon-like movements corresponding to nearly independent fluctuations of atoms' positions in deformed local lattices, and the «slow» movements, corresponding to this deformation. The problem of the separation of the «phonon» and «defect» part of a deformation was studied in paper [9].

In what follows we discuss the statistics of fluctuations of invariants Ψ_i in the case of ideal crystal. In the space of structural invariants the fluctuations of some structure G_i are represented by the probability density functions $\Xi^{(i)}(\vec{\Psi})$ and $\tilde{\Xi}^{(i)}(\vec{\Phi})$. In order to

find these functions note that the local probability density functions $\rho(\bar{\psi}(\bar{r}))$ for N -atom clusters do not depend on \bar{r} : $\rho(\bar{\psi}(\bar{r})) = \rho(\bar{\psi})$.

At the temperatures exceeding the Debye temperature the relative thermal displacements of atoms are mainly due to the short-wavelength phonons. Thus for our high-temperature systems the fluctuations of atoms' positions can be treated as statistically independent (some correlations are present for the nearest-neighbours only, see e. g. in [25]); the fluctuations of parameters $\bar{\psi}_i(\bar{r}_i)$ and $\psi_i(\bar{r}_j)$ ($i \neq j$) of the structures of two neighbouring clusters are also statistically independent. Averaging (5) over the ensemble and taking into account the ergodic hypothesis one finds the parameters $\langle \Psi_l \rangle$ describing the fluctuating structure

$$\langle \Psi_l \rangle = \overline{\psi_l(\bar{r})} = \bar{\psi}_l, \quad (6)$$

where $\langle \dots \rangle$, $\overline{\dots}$ stand for statistical and time averages. Some examples of evaluation of functions $\bar{\psi}_l(\xi)$ can be found in [10, 19]. It should be stressed that quantities ψ_l are not linear functions of ξ ; this results in the dependence of $\langle \Psi_l \rangle$ on ξ . When the number of atoms is very large ($N_0 \gg 1$) the statistics of fluctuations is dominated by the configurations with $\Psi_l \approx \langle \Psi_l \rangle$. This is the simple consequence of the universal effect of the narrowing of the width of the density probability function $\Xi_l(\Psi_l)$ for the independent additive quantities ψ_l (see e. g. in [26]):

$$\frac{\Sigma_l}{\langle \Psi_l \rangle} = N_0^{-1/2} \frac{\sigma_l}{\langle \psi_l \rangle}. \quad (7)$$

For large values of N_0 the central limit theorem (see e. g. in [27]) states that the invariant Ψ_l is normally distributed:

$$\begin{aligned} \Xi_l(\Psi_l) &\sim n(\Psi_l; \langle \Psi_l \rangle, \Sigma_l); \\ \bar{\Xi}_l(\Phi_l) &\sim n(\Phi_l; \langle \Phi_l \rangle, 1), \end{aligned} \quad (8)$$

where « \sim » stands for «asymptotically». It was assumed that the two first moments of random variable ψ_l are finite. In the case of quadratic invariants the variables ψ_l are, with good accuracy, normally distributed [10]; then formula (8) holds for any value of N_0 . The parameters of the function $\Xi_l(\Psi_l)$ are, in accordance with (6) and (7)

$$\langle \Psi_l \rangle = \bar{\psi}_l; \quad \Sigma_l = \sigma_l / \sqrt{N_0}. \quad (9)$$

Let us study the conditions for the recognition of ideal structure patterns described via parameters $\bar{\Phi}$. We assume that the fluctuations of invariants Φ_l with different values of l are statistically independent. For normally distributed random vector $\bar{\Phi}$ this is so when the non-diagonal elements of covariance matrix vanish. It is also assumed that the quantities $\Sigma_l^{(i)}$ for the ideal patterns Γ_i satisfy the approximate relation $\Sigma_l^{(i)} \approx \Sigma_l^{(j)}$. Both these conjectures hold approximately for the 13-atom clusters studied in [10]. Then, the probability E of erroneous identification of the fluctuating structure via the maximum-probability decision rule is [12]

$$2E = 1 - \operatorname{erf} \left(\frac{\Delta_{12}}{2\sqrt{2}} \right), \quad (10)$$

where $\Delta_{12} = |\langle \bar{\Phi}^{(1)} \rangle - \langle \bar{\Phi}^{(2)} \rangle|$ denotes the distance between the centers $\langle \bar{\Phi}^{(1)} \rangle$, $\langle \bar{\Phi}^{(2)} \rangle$ of Gaussian distributions corresponding to structures 1 and 2 and $\operatorname{erf}(x)$ stands for error function:

$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$. Writing down formula (7) in terms of parameters $\bar{\varphi}$ and $\bar{\Phi}$,

$$\bar{\Phi} = \sqrt{N_0} \bar{\varphi}, \quad (7')$$

one finds

$$\Delta_{12} = \sqrt{N_0} \delta_{12}, \quad (11)$$

where $\delta_{12} = |\langle \bar{\varphi}^{(1)} \rangle - \langle \bar{\varphi}^{(2)} \rangle|$ denotes the distance between the centers $\langle \bar{\varphi}^{(1)} \rangle$, $\langle \bar{\varphi}^{(2)} \rangle$ of distributions corresponding to the fluctuations of N -atom clusters of structures 1 and 2. Formulas (10) and (11) give the possibility to study the conditions for the recognition of macroscopical structures via the characteristics of fluctuations of individual clusters.

As an example, let us study the conditions for the mutual recognition of close-packed structures: cubic (FCC) and hexagonal (hcp). These structures are the «natural» candidates for the ideal structure patterns of simple liquids. In Fig. 2 we present the plot of the function $E(\xi)$; function $\delta_{12}(\xi)$ (Fig. 3) was evaluated on the basis of data presented in our paper [10]. To be definite, in the case of quadratic invariants the data presented in Fig. 2 coincide with the data obtained from (10) for $\xi > 0.15$. For $\xi < 0.15$ the values of E are smaller (better recognition) than presented in

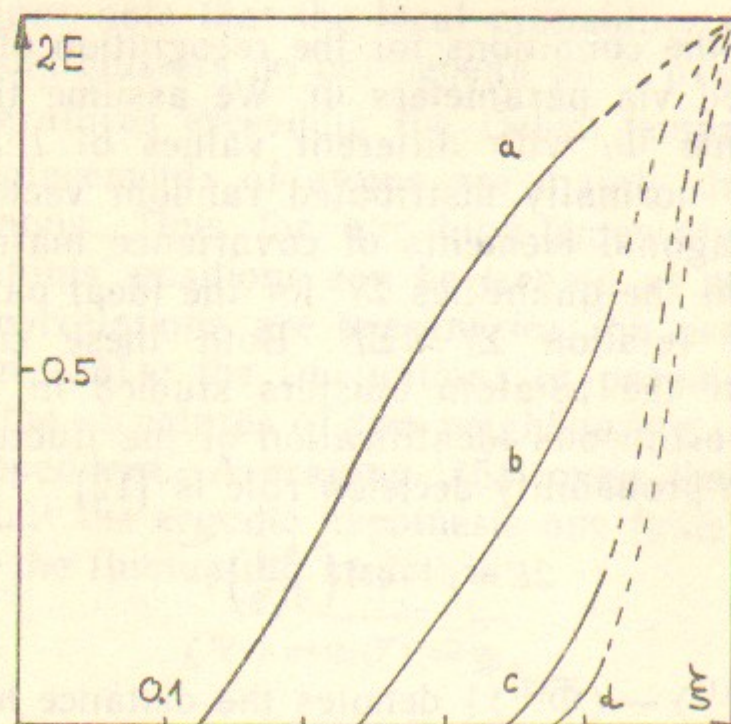


Fig. 2. Plot of the dependence of the error of recognition E on ξ for cubic (fcc) and hexagonal (hcp) domains of «good» matter. $N_0=1$ (a), 8 (b), 38 (c), 77 (d).

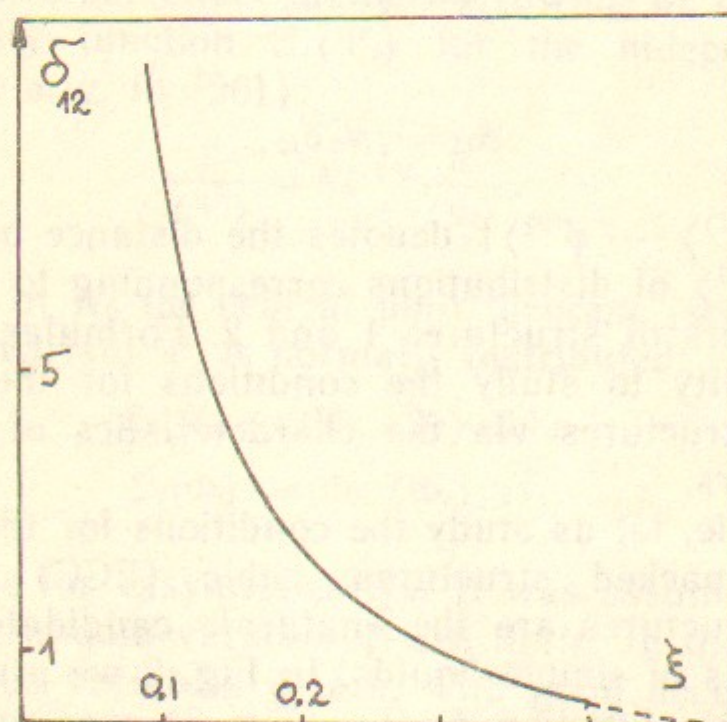


Fig. 3. Plot of the function $\delta_{12}(\xi)$ for cubic and hexagonal 13-atomic clusters.

Fig. 2. This reflects the fact that only the most informative invariants were used in [10] to find $\delta_{12}(\xi)$. For $\xi > \xi_c \approx 0.5$ the relation $\delta_{12}(\xi) = 0$ holds with the accuracy of computer experiment. With the same accuracy the function $E(\xi)$ tends to a non-symmetrical step function at $N_0 \gg 1$. Thus, the advantage of the use of invariants Ψ_i shows up at intermediate values of ξ : $0 < \xi < \xi_c$.

The modelling of the fluctuations at $\xi > 0.4$ needs probably better statistics. For this reason the results corresponding to $\xi > 0.4$ are presented by dashed lines in Figs 2, 3.

7. IDENTIFICATION OF STRUCTURE OF «COMPUTER» LIQUID: DETERMINATION

In this section we discuss the simplest variants of determination of local structure of liquids. The set of n samples (configurations of atoms) is given and each configuration is divided into regions of «good» and «bad» matters; the former is described via $\bar{\Psi}$. The determination of the structure is performed via the statistical analysis (see e. g. [28, 29]) of the sample $\bar{\Psi}^{(1)}, \dots, \bar{\Psi}^{(n)}$. As a rule we do not present the well-known algorithms in detail.

7.1 «Quantitative determination»

As pointed out in section 3 the statistical hypothesis stating that Ψ_i is normally distributed has to be verified. In the simplest version one uses the property of the asymptotically normal distribution of sample excess (ϵ) and asymmetry (A) of normally distributed population. If

$$|A/\sigma_A| \leq 3, \quad |\epsilon/\sigma_\epsilon| \leq 3, \quad (12)$$

where $\sigma_A = \sqrt{6/n}$ and $\sigma_\epsilon = 2\sigma_A$, then the hypothesis is accepted and the determination acquires semiquantitative character. The significance level of the test (the probability of making the error of the first kind) is $\alpha \approx 0.003$.

In the more rigorous approach the goodness-of-fit test χ^2 can be used; the values of $\langle \Psi_i \rangle$ and Σ_i are identified. If the value of the test χ^2 evaluated on the basis of sample $\Psi_i^{(1)}, \dots, \Psi_i^{(n)}$ satisfies the inequality

$$\chi^2 \leq \chi_{\alpha, r-3}^2, \quad (13)$$

where r denotes the number of domains onto which the Ψ_l axis is divided, α —the significance level, then the hypothesis is accepted. Here $\chi_{\alpha, m}^2$ denotes the α -percent point of χ^2 -distribution with m degrees of freedom [30]. The determination acquires semiquantitative character.

7.2. «Semiquantitative» determination

In the simple version one determines the type of fluctuating structure represented by point $\bar{\Psi}^*$ via the maximal-probability decision rule [12]. It states that the fluctuating structure is the deformed state of this of patterns « i » for which the value of $\Xi^{(i)}(\bar{\Psi}^*)$ is the biggest one:

$$\Xi^{(i)}(\bar{\Psi}^*) > \Xi^{(j)}(\bar{\Psi}^*), \quad (14)$$

The upper index denotes the type of the pattern. In assumption of the statistical independence of Ψ_l and of approximate equality $\Sigma_l^{(j)} \simeq \Sigma_l^{(i)}$ the function $\Xi(\bar{\Psi})$ is a product of functions $\Xi_l(\Psi_l)$, formula (8), and the probability E is given by formulas (10) and (11).

In another approach one finds the confidence estimates for mean values and dispersions of random variables Ψ_l . If Ψ_l is normally distributed then the confidence estimates with measure of reliability equal to $1-\alpha$ are (see e. g. [27]):

for $\langle \Psi_l \rangle$:

$$\left(\bar{\Psi}_l - \frac{S_l}{\sqrt{n}} t_{\alpha, n-1}; \bar{\Psi}_l + \frac{S_l}{\sqrt{n}} t_{\alpha, n-1} \right); \quad (15a)$$

for Σ_l :

$$\left(\frac{(n-1) S_l^2}{\chi_{\alpha/2, n-1}^2}; \frac{(n-1) S_l^2}{\chi_{1-\alpha/2, n-1}^2} \right). \quad (15b)$$

Here $\bar{\Psi}_l$, S_l^2 denote the unbiased estimates of mean value and dispersion evaluated from the sample $\Psi_l^{(1)}, \dots, \Psi_l^{(n)}$; $t_{\alpha, n} = \frac{1}{2} \alpha$ -percent point of Student's t -distribution [30]. If the parameters $\langle \Psi_l \rangle$ and Σ_l of some ideal structure pattern lie in intervals (15) then the I -structure can be treated with measure of reliability $1-\alpha$ as the fluctuation of that pattern.

In many-dimensional case the confidence estimates for the m -dimensional vector of mean value of $\bar{\Psi}$ are obtained with the help of the generalized T^2 -statistics of Hotelling [29]. In the assumption of the normal distribution of $\bar{\Psi}$ the probability to get the sample (of size n) with mean value $\bar{\Psi}$ and sample covariance matrix \bar{S} such that

$$n(\bar{\Psi} - \langle \bar{\Psi} \rangle)' \bar{S}^{-1} (\bar{\Psi} - \langle \bar{\Psi} \rangle) \leq T_0^2(\alpha), \quad (16a)$$

where

$$T_0^2(\alpha) = \frac{(n-1)m}{n-m} F_{m, n-m}(\alpha) \quad (16b)$$

is $1-\alpha$ [29]. Here $F_{m, n-m}(\alpha)$ denotes the α -percent point of F -distribution and $(\dots)'$ —a row. The principles of the determination are the same ones as in the 1-d case. The survey on confidence estimates for many-dimensional normally distributed variables can be found in [31].

7.3. «Qualitative» determination

In this formulation one verifies the statistical hypothesis stating that the density probability function of structural invariants is the same one in various domains of «good» matter. We deal with the physically interesting case when these domains correspond to individual (subsequent) configurations. To this end one verifies the hypothesis stating that two samples correspond to one parent population. No knowledge about the distribution of structural invariants is required. For each of the configurations one finds the sample $\psi_{l1}, \dots, \psi_{ls}$, where $\psi_{li} = \psi_l(\bar{r}_i)$ denotes the value of invariant ψ_l for a cluster with center \bar{r}_i and s —number of clusters in the configuration.

The decision is made with the help of non-parametrical goodness-of-fit tests (sign test, Van der Warden X -test, Wilcoxon test). Let us discuss the determination on the basis of Wilcoxon test (see e. g. [27]). The elements $\psi_{l1}, \dots, \psi_{ls_1}$ and $\psi'_{l1}, \dots, \psi'_{ls_2}$ of two samples are mixed together and then ordered by their magnitude. By the definition pair (ψ_{lk}, ψ'_{lk}) forms an inversion when $\psi'_{lk} < \psi_{lk}$. When the hypothesis is true then u —total number of inversions—should not differ noticeably from its mathematical average $\frac{1}{2} s_1 s_2$. The

hypothesis is rejected when $|u - \frac{1}{2}s_1s_2|$ exceeds a critical value u_α (α is the significance level). The quantities $u_\alpha(s_1, s_2)$ are tabulated e. g. in [27]. For big values of s_1, s_2 ($s_1, s_2 > 20$) the approximate formula holds

$$u_\alpha = z_\alpha \sqrt{\frac{s_1s_2(s_1 + s_2 + 1)}{12}} \quad (17)$$

where $2\Phi_0(z_\alpha) = 1 - \alpha$ and $\Phi_0(x)$ denotes the Gaussian distribution

function: $\Phi_0(x) = \frac{1}{\sqrt{2\pi}} \int_0^x e^{-t^2/2} dt$. If the hypothesis is true for any

pair of configurations than it can be concluded that the macroscopical structure has some (unknown) type of local order.

The analogous analysis can be done in terms of parameters Ψ_l .

8. CONCLUSIONS

The mathematical formalism presented in this and preceding [10, 12] papers gives the possibility of a consistent analysis of structures of «computer» liquid and amorphous systems both on local and semimacroscopical levels. The aim of the subsequent work is to apply it to the study of the local structure of the melt and, in particular, to verify the validity of modern concepts of this structure.

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III. Макроскопические системы**

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