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LIQUID: LOCAL AND GLOBAL ORDER

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ABSTRACT

The local order in a dense system of atoms is described on the microscopical level. For a system where the local order is crystalline, models of the liquid state are discussed at different space scales. A special attention is paid for the definition of parameters and for the correspondence of the parameters of the theory and the initial atomic configuration

to those of finding that ideal figure Γ_k, which is nearest to the deformed physical structure. Each fluctuating structure can be thought of as a deformed ("excited") state of any of the patterns Γ_i. In order to recognize and classify the fluctuating structures one has to study the 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 a probabilistic character (see below). In general, the domains can overlap with each other.

Let us introduce local order-parameters—the irreducible multipole moments of the density [5, 6, 12]

$$T_{\alpha_1 \ldots \alpha_n} = \sum_{(a)} w(r^{(a)}) t^{(a)}_{\alpha_1 \ldots \alpha_n}, \tag{5}$$

where

$$t^{(a)}_{\alpha_1 \ldots \alpha_n} \equiv t_{\alpha_1 \ldots \alpha_n}(r^{(a)}), $$

and

$$t(r)_{\alpha_1 \ldots \alpha_n} = \overline{r_{\alpha_1} \ldots r_{\alpha_n}} \approx r^{2n+1} \frac{d^m}{dr_{\alpha_1} \ldots dr_{\alpha_n}} \left(\frac{1}{r} \right), \tag{6}$$

denotes the irreducible part of the Cartesian tensor $r^{(a)}_{\alpha_1} \ldots r^{(a)}_{\alpha_1}$. The summation in (5) extends over all the points $r^{(a)}$ of the configuration. The function $w(r)$ defines the weight of the contributions to $T_{\alpha_1 \ldots \alpha_l}$ from different coordination shells. 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 form 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 tensors $T_{\alpha_1 \ldots \alpha_l}$, $l = 0, 1, \ldots$, i .e. they are the independent scalars that can be constructed from the set $\{T_{\alpha_1 \ldots \alpha_l}\}$, $l = 0, 1, \ldots$

An 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. [12],

$$T_{lm} = \sum_{(a)} w(r^{(a)}) t^{(a)}_{lm}, \tag{7}$$

where

$$t^{(a)}_{lm} = Y_{lm}(\Omega^{(a)}), \tag{8}$$

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$\Omega^{(a)} = \{\varphi^{(a)}, \theta^{(a)}\}$ denotes the polar and azimuthal angles that fix the direction $r^{(a)}/|r^{(a)}|$ and $w(r)$ is a new weight function. $t^{(a)}_{\alpha_1 \ldots \alpha_l}$ and $T_{\alpha_1 \ldots \alpha_l}$ are linear combinations $t^{(a)}_{lm}$ of and T_{lm}, respectively.

The order-parameters (5), (8) 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 problems of recognition, as the feature space.

For the description and the classification of local structures it is sufficient to investigate a small number of low-rank invariants, i.e. the ones constructed from the parameters (5), (8) with a few smallest values of n. The reason for such a simplification is that the high-rank invariants are sensitive to the small-scale fluctuations of the atom positions.

The fluctuating structure is represented in the feature space by the probability distribution of fluctuations of the invariants Ψ, and can be described in terms of the probability density $p(\vec{\Psi})$. Let's study a finite collection $\{\Gamma_i\}$ of initial ideal patterns. Each distribution $p(\Psi)$ has at some distance in the feature space "neighbours" $p_n(\Psi)$ — the deformed states of ideal patterns Γ_n. By definition, the quantity

$$dw = p_n(\Psi^{(0)}; \xi)\, d\Psi^{(0)} \qquad (9)$$

is the probability of finding the values of invariants Ψ_l ($l = 0, 1, \ldots$) representing the fluctuations of the ideal pattern G_n in the vicinity $d\Psi^{(0)} = \prod_k d\Psi_k^{(0)}$, of the point $\Psi^{(0)}$. The solutions of the set of inequalities $p_n(\Psi) < \text{const}$ ($n = 1, \ldots$) are the domains in the feature space that represent deformed states of ideal patterns Γ_n. For small values of ξ the distributions do not overlap each other; any point Ψ representing the deformed state of some pattern Γ_i cannot simultaneously correspond to some other pattern Γ_j ($i \neq j$). In this sense, the division of the feature space into domains has deterministic character. When ξ increases the widths of the distributions increase, too; for $\xi > \xi^*$ the two neighbouring distributions overlap each other. In such a case the division of the feature space has a probabilistic character — some point Ψ can correspond to deformed states of two different patterns. For fluctuating structures it is necessary to introduce quantitative characteristics for the degree of overlap of the distributions. Let us assume that the fluctuating structure is the deformed state of those two patterns Γ_1, Γ_2 for which the value of $p(\Psi)$ is the bigger one. The total error E of recognition is

1. INTRODUCTION

Liquids (melts) and the melting transition have been intensively studied both experimentally and theoretically; for earlier reviews of this study see the books of Frenkel [1], Fisher [2], Ubellode [3]. The ideas of local order emphasized by Frenkel help to explain qualitatively the properties of liquids without strict definition of terms. To make the theory more adequate one has to define local order and describe it in terms of some order parameters. The volume where the order is to be treated as local contains many atoms, so the description in terms of order parameter fields is expected to be relatively universal and independent on details of atomic interactions. The experimental data rather support the concept of local order but give no unambiguous information about the nature of the order and the size of the ordered volume. In the theory, many figures where suggested for the part of the local structure of a simple liquid.

In recent papers (Patashinskii and Shumilo [4], Mitus and Patashinskii [5], Hess [6], Nelson and Toner [7]) it was assumed that the local structure of the melt resembles that of a crystal. Sachdev and Nelson [8] and Steinhardt, Nelson and Ronchetti [9] suggested the icosahedron to be 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 [10] and Zachariasen's model of a chaotic lattice [11]. Different models may, in principle, correspond to different types of the matter.

The local order in melts manifests itself in the presence of thermal fluctuations of atomic positions. These fluctuations are characterized by the parameter $\xi = \xi'/a$, where ξ' denotes the mean-square-root thermal displacement of atoms from their supposed ideal positions, and a denotes the mean interatomic distance. At the melting point $\xi = \xi_m = 0.07 \div 0.17$ is the Lindemann criterion. Every arrangement of N points can be treated as a fluctuation of any

other N-points configuration. The first step towards of a theory is to define the local order not only qualitatively, but quantitatively.

The melting temperatures T_m are high enough to allow a classical description of atomic positions exept for liquid He and probably H. One starts from Gibbs probability distribution

$$d\omega = Z^{-1} \exp\left\{-\frac{H(n)}{T}\right\} dn , \qquad (1)$$

$$Z = \int \exp\left\{-\frac{H(n)}{T}\right\} dn . \qquad (2)$$

The whole set of quantities for a microscopic state is denoted by $\{n\}$. For a classical system, the moments are distributed according to the universal Maxwell law, so we only study the configurational part of the energy H.

We only deal with degrees of freedom corresponding to the positions of atoms. To avoid complications we deal with a simple (or relatively simple) liquid. The model system with pair interaction of Lennard–Jones type

$$Z = \sum_{i \neq j} U_{LJ}(r_i - r_j) ; \qquad U_{LJ} = A\left[\left(\frac{a}{r}\right)^{12} - 2\left(\frac{a}{r}\right)^6\right] . \qquad (3)$$

is an example of such a system studied in many computer experiments.

2. PARAMETERS OF LOCAL ORDER

A physical configuration of N atoms is a set of points with coordinates $r^{(a)}$, $a = j, \ldots, N$. A description in terms of space order by definition means that the configuration $\widetilde{\Gamma}\{r^{(a)}\}$ build of points $r^{(a)}$ is to be represented as a deformed state of some ideal figure $\Gamma(r^{(a)})$ so that

$$r^{(a)} = r_0^{(a)} + \delta r^{(a)} . \qquad (4)$$

For a given physical configuration the problem of finding an ideal configuration may, in principal, have not a unique solution. The set of related ideal figures $\{\Gamma_n\}$, $n = 1, 2, \ldots$, is to be chosen on the basis of physical concepts. For a system of interacting particles, one may expect that ideal configurations are determined by minimal values of the interaction energy. For a close-packed system the clusters of CCF, HCP lattices and the icosahedon are possible candidates for the local structure.

Once the set of ideal figures Γ_i, $i = 0, 1, \ldots$, is chosen the problem reduces

$$E = \int \min\left[p_1(\Psi); p_2(\Psi)\right] d\Psi . \qquad (10)$$

The integration in (10) is carried out over the whole 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 Ψ_d such that $p_1(\Psi_d) = p_2(\Psi_d)$.

The crystal structure of most of the elements near their melting lines is a close-packed structure. 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. In Ref. [12] three 13-atom clusters were studied, namely the "crystallographic" ones corresponding to nuclei of fcc and hcp crystals and the icosahedron as candidates for the structural units of dense liquids. Each cluster has $N = 12$ "outer" atoms, equidistant from the central one located at the origin of the coordinate frame of the 3-D space. The distance from any of the atoms to the center is taken as a unit length. A computer simulation of the fluctuations of the structures was performed as follows. Each of the 12 atoms of the cluster was randomly displaced onto the surface of a sphere with radius ξ and with its center located at the atomic position in the ideal (i. e. nonfluctuating) cluster. No correlations of displacements of atoms were accounted for. The most related result to the problems discused here is the dependence of the probability of erroneous recognition E on ξ^2 (see formula (16)): $E(\xi^2)$ is very small for $\xi^2 \leq 0.01$, it reaches a value of order 10^{-2} at $\xi^2 \leq 0.02$ and then grows rapidly, and $E(\xi_b) \cong 1$ with $\xi_b \geq 0.02$.

Let us discuss the relation of the model to a physical system. The statistics of the atom displacements of an elastic system gives the mean square interatomic distance fluctuation in the form

$$\xi^2 = \frac{<(\delta r)^2>}{a^2} = AT . \qquad (11)$$

For temperatures higher than the Debye temperature as e. g. near and above melting of simple liquids thermal fluctuations of atomic positions are essentialy due to independent motions of the atoms. Therefore the statistics of cluster fluctuations used in simulations is as expected in real systems. The main assumption here is the existence of such clusters of locally ordered matter in the system. The assumpton is trivial for a crystal, but much less trivial for a liquid or an amorphous state. Let me emphasize two important facts about the dependance of E on ξ^2. The first one is that for $\xi \leq \xi_b \approx 0.02$ short-range fluctuations do not destroy the existing local order. It is well known from experiment that $\xi^2(T_m) \equiv \xi_m^2 \approx 0.01$ at the melting tempera-

ture T_m. The inequality

$$\xi_m < \xi_b$$

shows, that some part of the (PT)-plane corresponds to the equilibrium liquid state with a well-defined local order. The condition $\xi = \xi_b$ fixes the smooth boundary of the locally-ordered matter in (PT) plane. In elastic approximation one gets

$$\xi_b^2 = \frac{T}{T_m}\xi_c^2 \approx 0.01\,\frac{T}{T_m}\,.$$

The vicinity of the melting curve in the liquid state belongs to the locally structured liquid. Of course, to be more explicit one has to study the statistics of clusters in a macroscopic system of interacting particles. The simple simulation in [12] only determines the geometrical basis of the description, and gives the upper bound for the ξ_b.

In the liquid state for temperatures $T < T_b$ the local order in the good matter is frozen. In a first approximation one can neglect the fluctuations of invariants Ψ of the structural lowest rank tensors $T_{\alpha_1 \ldots \alpha_n}$ ($n \leq 10$) in clusters of good material.

The second result obtained in [12] is that for $\xi^2 > \xi_b^2$ the local order become ambiguous. A crystal lattice heated up to those temperatures can't keep the local order. It explanes the puzzle of the Lindeman criterium — the small value of $\xi_c \approx 0.01$. The described simulation support the possibility of local order in melt, but gives no answer on the next important question: what is the local order in the melt. In what follows we suppose it is crystalline.

3. LIQUID WITH CRYSTALLINE LOCAL ORDER

In what follows a liquid is suggested to be locally crystalline ordered. For an ideal crystal, this is the case for every small volume. Important topological properties of a lattice are the neighbourhood relations of its sites. A physical configuration of N points is said to have crystalline order if the points $r^{(a)}$ ($a = 0, 1, \ldots, N-1$) are represented as slightly shifted from their ideal lattice positions $r(a)$. More formaly we define the one-to-one mapping $\Gamma \to \Gamma'$: ($r^{(a)} \to r'^{(a)}$) of atomic positions onto sites of the chosen ideal lattice. The mapping preserves the nearest neighbourhood relations: images of nearest neighbours are nearest neighbours. Let us match the ideal lattice to the physical system. By definition the tangent position of the ideal lattice for a cluster containing N atoms is reached if:

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1. The image $r'^{(0)}$ of the central atom mahes the center $r^{(0)}$:

$$r^{(0)} = r'^{(0)}$$

2. The lattice is rotated from initial standard orientation in order to minimize the noncoincidence of images $r'^{(a)}$ and preimages $r^{(a)}$. There are $N-1$ vectors

$$\delta r^{(a)} = r^{(a)} - r'^{(a)}, \qquad a = 1, \ldots, N-1\,. \tag{12}$$

To define the minimal noncoincidence one has to consider the series of invariant combinations $\Delta_0, \Delta_1, \ldots,$ of vectors $\delta r^{(a)}$ and to minimize the invariants in the choosen sequence. There are 3 parameters (Euler angles) that are to be found for the tangent orientation $\widehat{g}(r^{(0)})$ of the lattice. One can take for simplicity

$$\Delta_0 = \sum_{a=0}^{N} (\delta r^{(a)})^2\,. \tag{13}$$

The tangent orientation of the lattice (or, in more physical terms, the orientation of the local lattice) is described by the rotation $\widehat{g}(r)$ that brings the ideal lattice in the tangent orientation from the reference orientation. The order in a cluster (a small part) of the system is crystalline if the mapping described above exists for limited $\delta r(b) \ll a$. In this case the rotation $g(r)$ is assined to the central point of the cluster, and this point belongs to good material. For an ideal crystal all atoms belong to good material, and therefore it is possible to map once all the atoms onto the ideal lattice supperimposed on the whole crystal. In this case the tangent lattice coinsides with the crystal lattice, and $g(r) = $ const. In 2-D crystals one has to proceed with a step by step mapping even for ideal crystal when $T \neq 0$.

Liquids are isotropic, and therefore a liquid must contain atoms of bad material — centres of clusters that cannot be mapped into the lattice in a unique way.

The most important next question is the form of the region occupied by good material (and by bad material as the complement of good material to the whole volume of the system). We assume the good material with the same local lattice to occupy most part of the volume, so liquid is in essence one multiply connected cluster of good material. The geometry of bad material has to make the system macroscopically isotropic. Note that the definition of local crystalline order given above is valid in principal for 2-D systems. A minimal disorder in the 2-D locally crystalline system that makes the system isotropic is a

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distribution of point defects. For the 3-D system, the minimal disorder is a finite density of infinite lines of bad material.

The next step of our construction is to map the whole system onto the lattice. To start with the mapping, one has to chose the initial cluster of good material and map all points of the cluster onto sites of the moveable ideal lattice. As described above, one superimpose the lattice on the cluster in tangent position, getting the local orientation $g(r)$, r being the centre of the cluster. The next step is to choose a new cluster with the central point r_1 being the nearest neighbour or point r, and to repeat the mapping procedure, mapping only new points and making minimal change of orientation to reach the new tangent orientation $g(r_1)$. The mapping at the second step is unique defined by the mapping at the first step. Continuation of the mapping along all paths through the good material define the local orientation field $\hat{g}(r)$. The mapping is one-to-one for every two consequent steps, but, in general, not one-to-one for a closed path. The procedure of mapping along paths is rather well known in dislocation theory as the Burgers—Frank procedure [13, 14]. Note that the mapping of points map the path through the system onto the path on the ideal lattice. The failure of the image contour is a whole number of elementary vectors of the lattice.

The idea of our construction is to describe a configuration of an atomic system, that is locally crystalline ordered but has no long-range order both translational or orientational. It is important to stretch that at few steps the change of atoms positions from those of a lattice sites and the change of orientation $g(r)$ is supposed to be small along the chosen path through the good matter cluster.

Consider quantities $b(r_0, r)$ and $g(r_0, r)$, defined as

$$b(r_0, r) = \sum_{path} \Delta \xi(r) \to \int \frac{\partial \xi_i}{\partial x_k} dx_k \quad (14)$$

$$\hat{g}(r_0, r) = \sum_{path} \Delta \hat{g}(r) \to \int \frac{\partial \hat{g}}{\partial x_k} dx_k \quad (15)$$

Here, $\Delta \xi = \xi(r+d) - \xi(r)$ is the displacement of an atom from its ideal position and $\Delta \hat{g}$ is the relative rotation

$$\Delta \hat{g} = \hat{g}^{-1}(r) g(r+d)$$

in the point r of the path, d is the shift from atom r to its nearest neighbour. The sum in (14), (15) is taken along the path. The continual form of $b(r_0, r)$ and $\hat{g}(r_0, r)$ is written in (14), (15) as path integrals.

The expected property of liquid configuration is that for a liquid there exist a finite correlation length r_{tr} of translational order and r_{or} of oriental order. In a crystal $r_{tr} = \infty$, $r_{or} = \infty$. For a path of a length l $(r_0, r) \gg r_{tr}$ one expects a result of a Brounian motion of $\xi(r)$ and $\hat{g}(r)$

$$|b(r_0, r)| \approx \left(\frac{l}{r_{tr}}\right)^{1/2}, \quad (16)$$

$$|\hat{g}(r_0, r)| \approx \left(\frac{l}{r_{or}}\right)^{1/2}, \quad (17)$$

It is expected (see below), that $l(r_0), r) \gg r_{tr}$. The important statement is that for a closed path in the configuration $r = r_0$ both $b(r_0, r_0)$ and $\hat{g}(r_0, r_0)$ are nonzero, and the mapping of the closed physical path onto the ideal lattice is not closed and has a failure

$$b(r_0) \equiv b(r_0, -r_0) = n^{(i)} \vec{e}^{(i)}. \quad (18)$$

which consists of whole numbers $n^{(i)}$ of elementary translation vectors e of the ideal lattice. For the rotation one returns to the initial point r_0 having an equivalent orientation of the tangent lattice, that means that

$$\hat{g}(r_0, r_0) = \prod (\hat{g}^{(j)})^{n_j}, \quad (19)$$

where $\hat{g}^j$ are elements of the rotational symmetry group of the lattice and n_j—whole members.

Circulations (14) and (15) are not changed by contraction of the contour of integration untill the contour crosses a line of bad material. The whole problem reduces to those of elementary circulations around defects, and the local characteristics of line defects are those of Volterra dislocations. Defect lines with $\hat{g}(r_0) = 0$ are well known dislocations. The failure $b(r_0)$ is the Burgers vector of the dislocation. It is constant on the moveable ideal lattice. As a physical quantity it has the form (18). Along the dislocation line, $b(r_0)$ rotate with the tangent lattice:

$$b(r') = \hat{g}(r') \hat{g}^{-1}(r) b(r). \quad (20)$$

Defect line that gives $\hat{g}(r_0, r_0) \neq 0$ is a disclination line. Instead of the Burgers vector for a dislocation the disclination is characterized by the direction of the rotation axes and the angle of rotation ω. The disclination axial vector $\vec{\omega}_d$ has the direction of the rotation line and the length ω. Along the disclination line $\vec{\omega}_d$ rotates with the tangent lattice:

$$\hat{g}^{-1}(r)\,\omega_d(r) = \hat{g}^{-1}(r')\,\omega_d(r'). \qquad (20')$$

From energy arguments one expects in the liquid only dislocations having smallest Burgers vectors b and disclination axial vector ω allowed by the ideal lattice symmetry.

To describe positions of atoms of a chosen cluster of good material homogeneous strain of the local lattice has to be introduced that brings the images $r'^{(a)}$ closer to the original points $r^{(a)}$. Small rotations and strains are described by rotation tensors $\omega_{ij} = -\omega_{ji}$ and strain tensors $U_{ij} = U_{ji}$ being respectively the antisymmetrical and the symmetrical parts of the distortion tensor β_{ij}

$$\beta_{ij} = \omega_{ij} + U_{ij},$$

$$\omega_{ij} = \frac{1}{2}(\beta_{ij} - \beta_{ji}), \qquad (21)$$

$$U_{ij} = \frac{1}{2}(\beta_{ij} + \beta_{ji}),$$

For liquid configurations we expect the strain to be small but the rotation to be rather large, so the representation (15) has to be generalized — see [4]. The best (tangent) orientation and the local deformation are to be determined by the minimization of the series of invariants described above.

The displacements $\delta \widetilde{r}^{(a)}$ of atoms from the tangent position of the deformed lattice are the short-range thermal fluctuations.

Now we are able to review the description of a configuration of a locally crystalline system. The configuration is described in terms of:

1. Good material:
   local orientation $\qquad\qquad \hat{g}(r)$,
   local strain tensor $\qquad\quad\; U_{ij}(r)$ $\qquad$ (22a)
   short range fluctuations $\quad \delta \widetilde{r}^{(a)}$

2. Bad material:
   dislocation lines $\qquad\qquad D_{tr}$
   disclination lines $\qquad\qquad D_{or}$ $\qquad$ (22b)

In our description point defects are to be considered such as vacancies and interstitials. These defects are local ones. The local topology of the configura-

tions described in terms of good and bad material is the same as that of a crystal with (possible) dislocation lines, so the recognition of a vacancy or an extra atom is to be based on the same principles. Formaly one can treat these point defects in a 3-D system as very small dislocation loops. The point defects may play an important part in the dynamics of defect lines where the necessity to deal with a concentration of vacances $n_v(r)$ and of interstitials $n_i(r)$ occur. To complete the list let me mention the concentrations of impurities. The description in terms of these parameters is justified if short rang fluctuations do not destroy the local order (see sect. 2), and if the density of dislocations is small enough and most part of the system belongs to good material. To proceed with the statistical theory one has to write the energy of the system in terms of parameters (22). In the elastic approximation this was the matter of the paper [4].

4. CHARACTERISTIC LENGTHS OF THE LIQUID

At the initial atomic scale a typical configuration of the liquid state is given in terms of atom coordinates $r^{(a)}$, $a = 1, 2, \ldots$ The energy has the form (3). The suggested local order allows the division of the matter into two parts — the good matter and the bad matter. The same configuration is described, with the help of the moveable ideal lattice and mapping procedure of atoms onto lattice sites, in terms of local orientations $\hat{g}(r)$, local strain $U_{ij}(r)$, the uncorrelated atom displacements from the sites of the local lattice, and the parameters of bad matter. The possibility of such a description exists only if the good matter occupies most part of the system and has the form of a multiconnected infinite cluster. The mean distance between two nearest dislocation lines l_d and the density of defect lines $n_d \sim l_d^{-2}$ has to obey the condition

$$\frac{l_d}{a} = \lambda_d > 1,$$

$$a^2 n_d < 1. \qquad (23)$$

Physical arguments that lead to (17) are the inelastic repulsion of defects at short distances and the loss of entropy for high densities of dislocations. There are no strict mesurements or computations of λ_d. The experimental data seem to be consistent with the values $\lambda_d \sim (3 \div 7)$ at the melting point. Let us treat λ_d^{-1} as a small parameter of the theory

$$\lambda_d^{-1} \ll 1, \qquad (24)$$

and go to the scale l_t

$$a \ll l_t \ll l_d \qquad (25)$$

for a coarse-grained description of a liquid configuration. At that scale the liquid is to be described in terms of smoothed fields of local orientation $\hat{g}(r)$, local strain $U_{ij}(r)$, and the bad matter parameters: positions $\{D_{tr}\}$ of dislocation lines, concentrations $n_p(r)$ of point defects, and diclination lines.

Let us first exclude disclination lines and describe the new infinite multiconnected cluster that include good matter, point defects and dislocations. The model of that part of the liquid is at scale lt a system $\{D_{tr}\}$ of strings with Burgers vectors $b(r)$, and a medium with local anisotropy of the local lattice elastically stressed by the dislocation strings. Locally this model is the model studied in the continuum theory of dislocations—see Kröner [15]. This model was studied in the dislocation theory of melting—see f. e. [5, 16, 17]

The local orientation $\hat{g}(r)$ is represented in the theory by the orientational order parameter. For the cubic local lattice it is the rank four tensor T_{ijkl} (see (6))

$$T_{ijkl}(r) = \sum_{\alpha=1,2,3} n_i^{(\alpha)} n_j^{(\alpha)} n_n^{(\alpha)} n_n^{(\alpha)} - $$
$$- \frac{1}{5}\left(\delta_{ij}\delta_{kn} + \delta_{ik}\delta_{jn} + \delta_{in}\delta_{kj}\right). \qquad (26)$$

Here $n^{(\alpha)}$ is one of three ($\alpha = 1, 2, 3$) basis vectors of the local ideal undeformed lattice. An essential change of local orientation due to dislocations demands some number of those defects. The standard configuration of small angle boundary that minimizes the necessary dislocation density under a change ΔP of orientation is known. The distance between dislocations in this boundary is (see [13])

$$b = \frac{\alpha}{\Delta \varphi}. \qquad (27)$$

One obtains the same change $\Delta\varphi$ of relative local orientation at the distance $\Delta r \gg b$ by shifting the dislocations randomly at distances $\delta r \le \Delta r$. For all the dislocations with density $n_d \approx 1/l_d^2$ having the same Burgers vector one gets the limitation for the orientation correlation radius r_{dr}:

$$H_{MFA} = - \nu \, T_{ijkl} \, h_{ijkl},$$

$$h_{ijkl} = \frac{\int T_{ijkl} \exp\left[-\beta\nu \, T_{ijkl} \, h_{ijkl}\right] dg}{\int \exp\left[-T_{ijkl} \, h_{ijkl}\right] dg}. \qquad (38)$$

The solution of (38) is studied in Ref. [5]. It gives a qualitative unterstanding of melting and crystallization, of surface melting [19] and other phenomena. In the crystal phase, $<T_{ijkl}> = h_{ijkl} \ne 0$, and $<\delta T_{ijkl}|>^2$ is relatively small at the melting temperature. At the same temperature in the liquid, $h_{ijkl} = 0$. For the defect line picture, it means the proliferation of defect lines, so that the defect density $n_d(T)$ at melting line is some dimensionless number in interatomic distance units. When the temperature increases, the density of defects increases slowly in the melt for $T \le T_d$. At the high-temperature boundary of the liquid state this increase is sharper as a function of temperature, and the density reaches the value $n_d \sim 1$, so that the description in terms of good and bad matter is no more adequate.

5. CONCLUSION

The picture of the liquid state described above explores two main assumptions one can't proof at the present time rigorously by theory or experiment. The first assumption is the existance of a crystalline local order in most small parts of the system, and the second one is the form of the cluster occupied by the good matter.

The real liquid, even the simple one, has a complex structure at all scales $r \le r_{or}$. One is able to study simple models of liquid (see eqs (37), (38)), and to understand at least qualitatively the properties of the system.

In this paper attention is paid to the description of atomic configuration. The statistical mechanics of the model of disclination lines interacting with local rotation field is beyond the frames of this paper, as well as problems of dynamics of the configuration. Assuming the local crystalline order in melt, one obtine some important properties from the geometry of the configurations: the existence of a relatively large length of $r_{or} \sim (10 \div 50)a$. A liquid has an anisotropy of a crystal in a volume containing thousands of atoms. The important part of liquid structure is a system of infinite disclination lines. The size of the core for a disclination is expected to be some a. One speculate that it is structureless and that the density in this core for a dense packed system is small.

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$$r_{or} \geq l_{or} = \frac{\gamma_d^2}{a} = a\,\lambda_d^2 \tag{28}$$

Let us take, as expected for the liquid at the melting temperature

$$r_{or} = \text{const} \cdot l_{or} . \tag{29}$$

For the supposed value $l_d \sim 3 \div 7$ one has

$$l_{or} \sim (10 \div 50)\, a . \tag{30}$$

This means that there exists a scale l_r for the liquid

$$l_d < l_r < l_{or} , \tag{31}$$

where the mean local orientation $T_{ijkl}(r)$ is a well defined quantity. From (28)−(30) one sees that the density of disclination lines is small. At scale l_r the liquid is in essence a system of disclination lines surrounded by continuum media having the anisotropy of the local lattice. The orientation order is represented by the field of orientation order parameter, in case of a cubic lattice this parameter is $T_{ijkl}(r)$. The media is plastically bended, this bending obey conditions (15), (20′) for paths around disclination lines:

$$\oint \frac{\partial \hat{g}}{\partial x_i}\, dl_i = \omega_d \tag{32}$$

In the static theory, one asks for the probability of a configuration of the local orientation field $T_{ijkl}(r)$. If written as

$$d\omega_{or} = A\,\exp\left\{ -\frac{H\,[\,T_{ijkl}(r)\,]}{T} \right\} D\,\hat{g}(r) , \tag{33}$$

it defines the effective Hamiltonian (local thermodynamical potential) of the local orientation. The probability distribution (33) can be obtained from the previous scale description, where the change of the local orientation could be written as a function of the dislocation and disclination lines configuration. Namely, one has to integrate the Gibbs distribution

$$d\omega_{or} = \exp\left\{ -\frac{H\,[D]}{T} \right\} d\{D\} \tag{34}$$

of dislocation lines over all states consistant with the long-wave orientation field $T_{ijkl}(r)$. The computations, even in a simplified version, are rather complicated — see [4]. The interactions of dislocations is known to be long

range. From the outer space at distance R, the action of a system of dislocation lines is equivalent to the action of one line with the resulting Burgers vector b_R, and the energy of elastic stress is

$$E_R \sim b_R^2 \ln R \ . \qquad (35)$$

An exeption is a dislocation wall mentioned above (see eg. (27)). We begin the description of the ensemble of dislocation line configurations for a given orientation field $T_{ijkl}(r)$ from a very special configuration where small angle boundaries (dislocation walls) divide the volume in crystalline cells of size l_{or}. For that configuration, the T_{ijkl} is constant in a cell. The interaction of dislocations is screened, and the energy density is the core energy density proportional to the dislocation density, plus the interaction energy density of dislocations in the wall. Small angle boudaries may cross at disclination lines. Let us start from this poligonized configuration and allow every dislocation to shift randomly at a distance $\delta r_d \sim l_g^2$. The energy of the dislocation system now has a part proportional to the dislocation density (core free energy), and a part that includes the interaction energy of dislocations over the screening length l_g.

Relations between this two parts depend on the parameter $p = l_g / l_{or}$. For $p \leq 1$ the amount of dislocations is the minimal one for the given long-range orientation field. The entropy is relatively small, and the effective Hamiltonian in (32) is of first order in ∇T_{ijkl}. For $p \geq 1$ the total density of dislocations exceeds essentially the minimal one.

The simple model Hamiltonian for the orientation ordering in a locally cubic system is proposed in [5]. The system is a help lattice. A configuration is given in terms of $T_{ijkl}(r)$, r being the sites of the help lattice. Independent variables are rotations $\hat{g}(r)$, and

$$T_{ijkl}(r) = \hat{g}(r) \, T_{ijkl}^{(0)} \ . \qquad (36)$$

The configuratiion $\{\hat{g}(r)\}$ has the energy

$$H\{\hat{g}\} = \sum_{r, r'} J(r - r' \, T_{ijkl}(r) \, T_{ijkl}(r') \ . \qquad (37)$$

Disclinations are included in (37) as lines of lines of help lattice sells with nonzero circulations of rotation changes (15), (32).

Models like (36), (37) are the simplest models of a liquid at the scale $l \sim l_{or}$. One can compare the ideas behind such a simple theory with those of Heisenberg or Ising models of magnets. In mean field approximation one obtaine from (37)

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Liquid: Local and Global Order

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Жидкость: локальный и глобальный порядок