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HOW TO DISTINGUISH THE LOCAL STRUCTURES OF THE MELTS

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How to Distinguish the Local Structures of the Melts

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ABSTRACT

We study the conditions of the mutual distinction of the structures of the 12-atoms close—packed clusters (FCC, HCP, icosahedr) in the presence of thermal fluctuations via the analysis of the distribution function in the space of structural invariants. It is shown that the close-packed types of local structure remain distinct well above the melting point.

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1. The concept of the local crystal-order in melts makes it possible to understand and to study many of phenomena connected with the melting and the melts [1—4]. No matter what the local order in melts is, it manfests itself in the presence of the thermal fluctuations. To characterize these fluctuations one defines the Lindeman ratio Li, $Li=\xi/a$, where ξ is the mean-square deviation of the thermal displacements of atoms from their supposed ideal positions and a denotes the interatomic distance. In the melting point $Li=Li_c=0.07-0.17$ [5]. The aim of this paper is to study the conditions of the mutual distinction of some patterns of the local structure of the condensed matter in the presence of the thermal fluctuations of the atoms. These patterns are the candidates for the structural units of the simple liqulds.

In order to study the configurations of the atoms of the melt one has to treat each of the «virtual» clusters, constituting the part of the configuration, as a fluctuation of an ideal pattern. The set of the ideal patterns $\{\Gamma_n\}$ is a priori known. Next, one has to define the quantitative characteristics ψ_i, $i=1, 2, \ldots$ of the cluster's form. To each configuration of the cluster's atoms corresponds a point ψ in the $\{\psi_i\}$-space. When the thermal fluctuations are small, the study of the distribution of the ψ points in the $\{\psi_i\}$-space makes it possible to find unambiguously the ideal pattern Γ_k, the fluctuations of which generate points ψ. When Li increases, the distributions in the $\{\psi_i\}$-space generated by the fluctuations of some ideal patterns Γ_i, Γ_j $(i\neq j)$ cover each other. In such the case the patterns Γ_i, Γ_j become fluctuationally indistinguishable. The general lines of our approach were described in [6].

2. The structure of the cluster can be characterized by the lo-

cal-order parameters, chosen here as

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

where

$$t^{(a)}_{\alpha_1\ldots\alpha_n}=\frac{\partial^n}{\partial r_{\alpha_1}\ldots\partial r_{\alpha_n}}\frac{1}{r}\Big|_{\vec{r}=\vec{r}^{(a)}}. \tag{2}$$

The summation in (1) extends over all the points $\vec{r}^{(a)}$ — the centers of the atoms that surround the central atom located in the origin of the coordinate frame. $w(\vec{r})$ is the weight function, defining the contributions from different coordination shells. $T_{\alpha_1\ldots\alpha_n}$ are irreducible multipole moments of the density function of cluster's atoms. From the mathematical point of view, $T_{\alpha_1\ldots\alpha_n}$ form the basis of the irreducible representation of the rank n of the 3-d rotation group O_3. The characteristics of the cluster's form have to be both rotationally and translationally invariant ones. They can be obtained via the contraction of the indices of $\{T_{\alpha_1\ldots\alpha_n}\}$, $n=0,1,\ldots$, i. e. are all the scalars that can be constructed from the set $\{T_{\alpha_1\ldots\alpha_n}\}$, $n=0,1,\ldots$

Mathematically equivalent are the local-order parameters constructed with the help of another basis of the irreducible representation of the O_3 group, namely that of spherical harmonics Y_{lm}:

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

where

$$t^{(a)}_{lm}=Y_{lm}(\Omega^{(a)}). \tag{4}$$

$\Omega^{(a)}$ denotes the polar and azimutal angles of the point $\vec{r}^{(a)}$ and $w(\vec{r})$ is a new weight function. $T_{\alpha_1\ldots\alpha_n}$ and $t_{\alpha_1\ldots\alpha_n}$ are the linear combinations of T_{lm} and t_{lm}, respectively. The invariants of T_{lm} can be constructed using the 3-j, 6-j etc. symbols technique [7]. In this paper we study the quadratic invariants of the parameters (1) and (3).

3. We have studied three 13-atom clusters, corresponding to the closest packing of hard spheres in 3-d space, namely the first coordination shells of the FCC and HCP lattices, and the icosahedral cluster. The crystal structure of most of the elements near the melting line is close packed. Such the structures were studied in the computer modelling of the structure of the melt [2, 8]. The icosahedral cluster is included as a candidate for the main structural

unit of simple liquids, according to [8]. Each cluster has $N=12$ atoms, equidistant from the central one. The distance from any of the atoms to the center is taken as the unit of length. The problem of the classification of the fluctuating structures in the liquid near its melting line is the cruicial one in understanding the phenomenon of the liquid-liquid structural phase transition [4]. The calculations were done as follows. Each of the 12 atoms of our clusters was displaced in the random way onto the surface of the sphere with radius r located in the atom's position in the ideal cluster. No correlations of the displacements of different atoms were accounted for. Two weight functions $w(\vec{r})$ were used. In the first case we obtain the bond-order parameter [9]

$$Q_{lm}=\frac{1}{N}\sum_{(a)} Y_{lm}(\Omega^{(a)}). \tag{5}$$

Parameter Q_{lm} characterizes the angular correlations and is independent on radial fluctuations of atoms. Such the fluctuations can be accounted for by the space-order parameter, defined as a sum of harmonic polynomials

$$R_{lm}=\frac{1}{N}\sum_{(a)} Y_{lm}(\Omega^{(a)})\,|\vec{r}^{(a)}|^l. \tag{6}$$

We have studied the invariants

$$Q_l^2=\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|Q_{lm}|^2, \tag{7a}$$

$$R_l^2=\frac{4\pi}{2l+1}\sum_{m=-l}^{l}|R_{lm}|^2, \tag{7b}$$

for $l\leqslant 10$.

The statistics of independent fluctuations of atoms, used here to find the distribution function in the space of invariants is different from the statistics of the thermal fluctuations of the cluster's atoms in a large system, where the correlations are present due to the interactions. We assume that for fixed value of Li such the characteristics as the half-width of the distribution function do not depend on the details of the statistics of the fluctuations of atoms too strongly.

The dependence of Q_l, R_l on r is shown in Fig. 1. For each cluster 400 configurations were generated (the case of 1000 configurations was also studied; in both the cases the results are, with good accuracy, the same). These data yield the sufficient conditions of the mutual distinction of the fluctuating structures (or the necessary conditions on which they can't be told one from the other). The sufficient conditions on which the fluctuating structures are no longer distinct ones can be found via the study of the intersections of the distributions themselves and not of their projections. It's the simple consequence of geometry. Namely, the m-dimensional projections ($m=1, 2, \ldots k-1$) of the k-dimensional distributions may intersect while the distributions themselves remain distinct ones.

For a given value of r the bands in Fig. 1 correspond to the values I of the invariants such that $|\langle I\rangle - I| \leqslant \sigma$, where $\langle I\rangle$ denotes the mean value of I and σ denotes the mean-square deviation. We present the results for $l=6$ from the $\{Q_l\}$-space and for $l=4, 5, 6, 8, 10$ from the $\{R_l\}$-space. The invariants with other values of l yield no new information about the fluctuating structures. Unlike the cubic and icosahedral clusters, the hexagonal cluster isn't the central-symmetric one, which leads to non-zero values of odd-rank tensors.

The most informative of the calculated invariants is Q_6 for which the essential intersection of the projections of the distributions takes place at $r=0.21$. In the space of invariants $\{R_l\}$ the fluctuating FCC cluster remains distinct until $r \leqslant 0.14$; the HCP one — when $r \leqslant 0.17$; the icosahedr — when $r \leqslant 0.13$.

The distinguished behaviour of invariant Q_6 is due to the specific geometry of the clusters under consideration. In general, to each pair of clusters there corresponds a combination of invariants which characterizes their mutual distinction in the «best» way. This combination is the order parameter in the phase transition with the change of the corresponding local structures (see [4, 6]).

4. Consider the problem of the mutual distinction of the three clusters under consideration in a melt near its melting line. On the melting line the mean-square deviation ξ for the close-packed matter is, as a rule, small. For example, for the rare-gase crystals (Ar, Kr, Xe, Ne), which display the FCC structure near the melting line, in the melting point $\mathrm{Li}_c = 0.09 - 0.11$ [10]. In what follows we take $\mathrm{Li}_c = 0.10$. One finds from Fig. 1 that the fluctuating structures maintain distinct ones when crossing the melting line. This property is independent on the choice of the set of invariants ($\{Q_l\}$, $\{R_l\}$). As stated in sect. 3, the domain of such the «structural stability» is larger

than found from Fig. 1. We'll not deal with this problem here, since the main goal is achieved by using the 1-d projections of the distributions.

5. Our results support the concepts of the local order in melts [11]. This, in turn, gives firm ground for the understanding of the phenomenon of the structural phase transition liquid-liquid [4]. The above considerations and the data presented in Fig. 1 lead to the conclusion that the temperature interval in the $p-T$ plane where the melt may display some fixed type of local structure is of the order of magnitude of that of the existence of the crystal phase. The configurations of atoms of model liquids and amorphous solids can be generated via the molecular dynamics and Monte Carlo methods. The study of the statistics of clusters in such the systems in the manner proposed in this paper would contribute strongly to our understanding of the structure of the condensed matter.

The more profound understanding of the fluctuations of the structure of the condensed matter will arise when quartic etc. invariants of parameters (1), (3) and also the invariants, constructed from T_{lm} with different l are taken into account in a systematic way. The discussion of these problems is beyond the scope of this paper.

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REFERENCES

1. *A.C. Mitus, A.Z. Patashinskii.* ZhETF 80 (1981) 1554 (Sov. Phys. JETP 53 (1981) 798); *A.C. Mitus, A.Z. Patashinskii.* Phys. Lett. 87A (1982) 79.
2. *S. Hess.* Physica 127A (1984) 509.
3. *A.Z. Patashinskii, B.I. Shumilo.* ZhETF 89 (1985) 315 (Sov. Phys. JETP 62(1) (1985) 177); *A.Z. Patashinskii, B.I. Shumilo.* Preprint INP 84-160 (1984).
4. *A.C. Mitus, A.Z. Patashinskii, B.I. Shumilo.* Phys. Lett. 113A (1985) 41.
5. *Yukalov V.I.* Oxford University Preprint 23/81 (1981).
6. *A.Z. Patashinskii.* Preprint INP 84-64 (1984).
7. *L.D. Landau, E.M. Lifshits.* Quantum Mechanics (Nauka, Moscow, 1974) (in Russian).
8. *P.J. Steinhardt, D.R. Nelson, M. Ronchetti.* Phys. Rev. B28 (1983) 784; *P.J. Steinhardt, D.R. Nelson, M. Ronchetti.* Phys. Rev. Lett. 47 (1981) 1297.
9. *D.R. Nelson, J. Toner.* Phys. Rev. B24 (1981) 363.
10. *T. Paszkiewicz.* The Physics of Phonons, to be published.
11. *A.R. Ubbelohde.* The Molten State of Matter (J. Wiley and Sons Ltd, 1978).

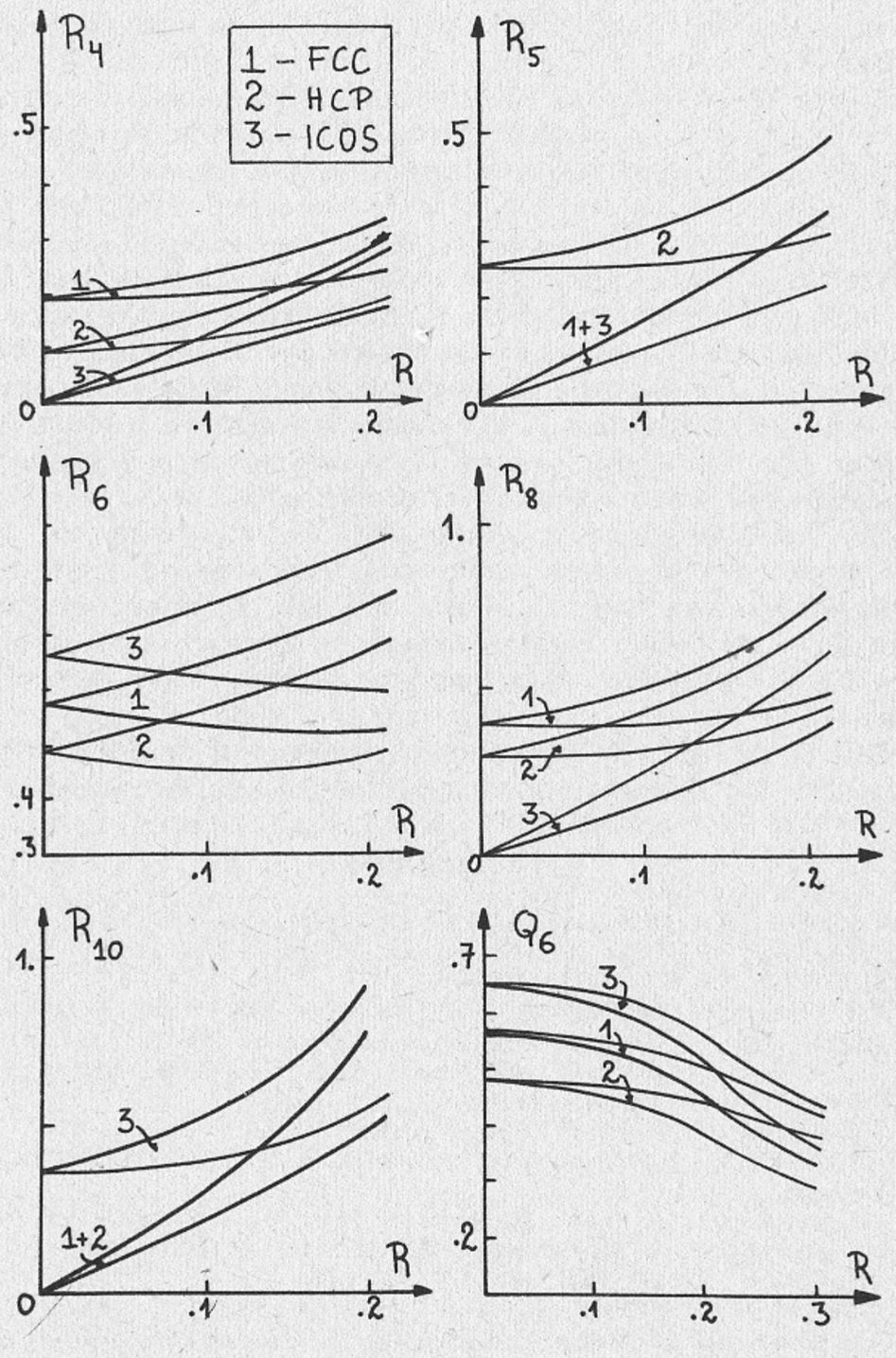

Fig. 1. The dependence of some of Q_l and R_l on r.

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