Statistical polyhedral geometry analysis of the short range order transformations in disordered and nanostructured metallic phases using MD-simulation results and diffraction data

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Abstract. Using MD-simulation results and some diffraction data the detailed analysis of the short range order transformations initiated by a heat treatment in 3d-metal based systems (Fe, Co, Ni) and Si with different initial configurations was carried out. New information about the nature of nanophase formation and the structure evolution of modern nanofragmental materials was obtained.

1. Introduction
With rapid advancing of new tendencies in material technology such as producing of nanodisperse or clustered powders and design of nanostructures some actual problems appear. The main of them are connected with thermal stability of nanophase states and especially with the stability of structural units or short range order. These problems were traditional for amorphous and nanocrystalline alloys and became attractive again especially for nanostructured materials obtained using vapor-condensation method. The short order as phenomenon is inherent for all ordered and disordered materials independently on their nature. Detailed metric and topological information about possible kinds of short range order and their classification for disordered systems can be obtained as a result of combination of methods of molecular dynamics MD and statistical geometry of Voronoi polyhedrons. Moreover, structural changes in disordered materials could be described adequately by polyhedron types and their statistical distribution in addition to radial and angular correlation functions, structure factors and some physical properties sensitive to their structure.

Results of MD-simulation, some diffraction data and analysis of short range order transformations initiated by heat treatment in transition metals TM based systems (TM are Fe, Co, Ni and Mn) and Si with different initial configurations were combined and a new information about the nature of nanophase formation and structure evolution of modern nano-materials was obtained. Finnis – Sinclair procedure for many-particle potentials with appropriately parameterized interactions functions [1] was used. According to propositions of Frank, Bernal and Mackay and results of our previous MD-simulation (LAM 4, France 1980) the most probable short range orders in liquid and amorphous metals are either icosahedral or a combination of the first icosahedral shell with the hexagonal next shells.
The mentioned resemblance in main features of short range orders in liquid and amorphous metals stimulates their consideration as different states of a unified disordered phase with different deviations from the equilibrium state. Consequently, the relaxation processes can be interpreted as specific phase transitions in the space-time continuum. Therefore, it is interesting to find some homothetic structure units for above mentioned states analyzing short range ordering of vapor-condensed metallic nanophases.

2. Vapor-condensed nanophase structures: hybrid short order of spherical and chain coordinations

According to the ordinary classification of atomic aggregations, the aggregations of a size between 2 and 10 nm are classified as nanoclusters. The most interesting for chemical thermodynamics are spheroidal cation metallic clusters with number of atoms corresponding to well known Cini series [2] completed by Mackay’s anticosahedron, Dzugutov’s 38-atom octahedron and 75-atom decahedron having rather high thermal stability [3, 4]. However, basing on our MD-results [5, 6], in the processes of layer-by-layer completions of cluster shells in metals with specific atom bonds (for example in d-metals) both spheroidal and non-spheroidal nanoclusters (spirals, helicoids or their hybrids with spheroids, like icosahedron) can be formed.

A real vapor-condensation process is determined not only by thermodynamic but also by kinetic parameters. Their joint influence defines features of formed structures and energy spectra. In our work we consider unusual thermal dependences of dynamical properties and various structural transitions taking place while heating and melting of clusters (isomerization and quasimelting) and rapid quenching of liquid nanodroplets analyzing specific scale effects and influence of surface layer morphology.

3. Thermostability: isomerization and “quasimelting” processes.

The nature of structural transformations at the melting of nanoclustered materials is known very badly. First of all it’s necessary to take into account the difference in structural, energetic and dynamic features of the outer and inner cluster, especially the first because it determines the melting process. According to MD-results, some kind of isomerization with an appearance of “pop-out” and “pop-in” defects in surface layers, vice-versa coordination rearrangements “icosahedron-octahedron”, while nanocluster heating precedes the melting, Figure 1.

![Illustration of isomer-structural transformations:](image)

Figure 1. Illustration of isomer-structural transformations:

a) isomeral changing of 5-fold symmetry nuclear Ni clusters Niₙ (n > 20) at initial stage of nucleation & rise of nanophase (defects of “pop-out” and “pop-in” types);

b) isomeral transformation of fcc cluster structure into icosahedral one.

With subsequent heating up to $T_m/3$ ($T_m$ is the melting temperature) these rearrangements expand to the next inner shells with almost entire “fluidization” of 2 to 3 upper shells including surface one.
The deeper shells retain their “hard-like structure”. These transformations represent the initial stage of melting and are classified as “the quasi-melting stage”. Here the resulting atom momentum of surface shell differs from momentum of next inner shells and relative movement of atoms generates effect of mutual sliding of the neighbor shells.

The temperature of the “quasi-melting stage” depends on number of atoms in the nanocluster, its density, type of atomic bonds and heating rate. The most thermally stable nanoclusters are icosahedral ones with dominant tetrahedral coordinations or nanoclusters with electric charge distribution from excess negative in the surface shell to positive in the center.

4. MD simulation of short range order in undercooled liquids and bulk amorphous metals: from spherical to spiral and hybrid structures

Consideration of liquid metal structure as similar to dense non-crystalline packing of atoms was proposed by Ubellode as a result of his study of liquids deeply undercooled below their melting points. Analogous ideas appeared in Frank and Bernal’s reports about mechanical model investigation. For the systems with spherically symmetric atomic interaction it is reasonable to suggest existence of chains. They consist of several tetrahedrons or five-atom tetrahedron rings in the forms of bi-pyramids with the five-fold symmetry or two combined bi-pyramids with common vertex. In both the cases the icosahedron short range order structure corresponds to density values specific for the fcc or hpc crystal lattice but without long range order. This theory was supported experimentally only recently by Reichert H. et al.

However, our MD calculations have shown that independently on physical and chemical properties of a system under consideration, the morphology of nanocrystallite bounds and inhomogeneity of its inner structure is predetermined by its nanosize. In particular, for the most of crystals including metals, the fcc or hpc lattices provide dense packing of spherical particles on the short range order scale with forming the same long range order. Nevertheless, in a globally disordered system icosahedral polyhedrons provide a denser (of 8.4%) and energetically preferable stable local packing but without long range ordering. While cooling liquid transition metals below melting point irregular icosahedral atom groups join into rather large scale fragments. Using statistical geometry approach we studied the simulated nucleation and growth of nanophases formed by regular and truncated tetrahedrons conjugated on trigonal and pentagonal faces. In addition, efficiency of our analysis of the nanostructures was demonstrated not only in frames of Mackey’s globular clusters with polytetrahedral short range order and five-fold symmetry, but on the base of alternative ones, such as Friauf polyhedrons conjugated on hexagonal facets or Burdiik-Coxeter helicoidal chain of meso- and long range ordered Bergman nanofragments including up to 20 Friauf polyhedra [6]. Moreover, general structure features of scale dependence of the TM-isomeral cluster series differs of Cini-series by presenting of combined spiral (helicoidal) and spherical (polytetral, icosahedral) hybrid short range orders, Figure 2. [6, 7].

Figure 2. The types of short range order in nanoclusters of transition metals in a condensed state: clusterized spiral (helicoidal with non-integer symmetry axes) [7]) and spherical ordering of tetrahedral (a) and icosahedral atom groups (b) with fife-fold symmetry.
**Conclusion.**
According to our results, properties of substances characterized with cluster-fragmen
tal (or cluster-layered), carcass, network, layer-stratum or helicoidal-chain structures depend, on one hand, on com
mensurability of time-spatial scales of physicochemical phenomena. On the other hand, they are
determined by size correlations of studied objects and characteristic parameters of relevant coherent
hierarchic substructures.

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