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Dimensional Interval and Critical Sizes of Non-Legand Nano- and Microparticles

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Abstract. The derivation of the equation for the calculation of the critical size of clusters and nanoparticles in the range of appearing of their unusual properties in comparison with the massive body as well as the equation for the calculation of the growth of spherical crystallites and aggregations is presented in the article.

1. Introduction

The main characteristic of a substance with granular structure is discreteness of corpuscular formations and the substance structure at different scale levels. Quantitative accumulation of the sources of the individual properties of the substance leads to a qualitative change in the system of its microparticles with the appearance of unusual properties and to formation of aggregations. Change in the material dispersity when transfering to macro-level in the process of nuclear clusters assembly of nano- and microparticles, or when shifting to micro-level during milling process with using 'sol-gel' technology brings about changing in the topological state of the disperse layer and appearance of unusual properties of nano- or microparticles. *Discreteness level (degree of fragmentation) of the substance with the appearance of the critical state of its disperse layer or with demonstration of unusual properties changing in its microparticles which are different of those of massive body can be considered a critical dispersity.* Metal nano- and microparticles raise a profound scientific interest taking into account their unusual physical and other properties that are not found in massive bodies.

When the number of atoms in a microparticle is equal or more than 13, packing density can be achieved if each atom is a surfacial one. When increasing the size of the microparticles, two types of atom packing take place: the inner one that is close to the crystal packing and external one that is a surfacial, loose in a near-wall layer. Surface atoms have lower coordination numbers than inner ones. Their electron shells are strongly polarized, their bonds are directed only inside of the particle. For such particles, more stable configurations occur with five bonds between atoms (five-order symmetry

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axis), which is not valid for macrocrystals. There is a certain critical size of microparticles above which the pentagonal (icosahedral) structures become less stable than crystalline atom packing.

It is believed that the transformation from icosahedral to a crystalline structure is kinetically difficult to achieve due to the need to reorganize the structure and increase the number of atoms around. That explains saving of pentagonal shapes for relatively large (10–30 nm) metallic microparticles. However, a theoretically limited size of microparticles having a structure with stable pentagonal symmetry has not been found so far, because for this to be done, it is necessary to calculate free energy of huge number of isomers. For these particles, clear faceting characterizing crystals are still unstable and there is a tendency to form microparticles with spherical shape, where the corners and tips get round, and the edges are protruded. According to the data of Y. Petrov [2], in the range of 151–21100 the anomalies of physical properties are observed for a number of atoms in microparticles that results in transition region, where the center of microparticles gains more and more inner layers, where the package corresponds to the structure of the given compact metal. Metal ligand-free microparticles (cluster formations) have the following characteristics: surface and internal energy of a single cluster are comparable with number of atoms in a bulk. Structure of the cluster differs from the metal sample, where the packing density of crystal is absent. Interatomic distance is increased; melting temperature as well as Debye temperature of cluster formations is lower than that of massive metal, etc. Shape and structure of microparticles are in non-equilibrium state and correspond to the state, which is different from the minimal energy state. In this state, microparticles of metals, alloys and other simple mineral substances can exist.

It is known that as the consequence of spraying the metal vapor on a cold substrate (in cold helium) stable clusters with a magic number of atoms are formed. Ligand-free nanoparticles (cluster formation) of metals have been comprehensively studied. In such a way, for plumbum the most stable clusters consisting of 7, 10, 13, 17, and 19 atoms were obtained [3]. With 13 atoms in the clusters, the single-layer hexagonal and cubic close packing (η_1=0.7405) and icosahedral packing are formed (η_1=0.68834). In the first two packings the permanent groups of 3–5 atoms in the cluster are formed on the surface of the central atom. They contacts with each other and with the central atom, whereas in the icosahedral packing all 12 surface atoms with diameter d are separated from each other by an equal distance:

$$l = [(1/0.905)^{1/3} - 1]\, d \qquad (1)$$

They only contact with the central atom forming 6 axes of 5th order. It is intermediate structure between crystalline inorganic solids and developing organic bodies that are typical of the most viruses. Mechanisms of interaction of isolated 'cold' atoms and formation of such structures are not established yet. One of the interesting results in this field is establishment of an important role of states of electron of the surfacial atoms in metal clusters.

These states are characterized by the lack of electron density in comparison with bulk states. In this regard, increasing of electron work function of the cluster in comparison with a large metal crystal is observed. In such a way, the difference for 13 atom cubooctahedral clusters in transition metal is 2 eV. In addition, for clusters the properties of bond unsaturability and orientation between the atoms are presented weakly or are completely absent. Up-to-date studies of small particles using computational and empiric methods (neutron scattering and slow electrons diffraction) found the existence of specific vibrations localized near the surface within a few atomic layers. The vibration spectrum is shifted to lower frequencies compared to the infinite lattice of microcrystals. The amplitude increases for surfacial atoms in particular [3]. In our opinion, the length of p and d electron orbitals in 'cold' atoms

is reduced. Cluster assembly of 'cold' atoms and homogeneous crystalline (icosahedral) structures in inert medium and medium without charge carriers are based on a weakened quantum mechanical attraction and enhanced lateral Coulomb repulsion of the atoms according to two principles.

The first principle is the principle of close packing, it can be interpreted as a decrease of internal energy of cluster atoms or molecule collection in close packing as a result of attractive forces. Single 'hot' atoms or atoms in dense areas of fluctuations that come into contact with each other due to forces of attraction and in accordance with the quantum and mechanical compatibility of overlapping atom orbitals and permitted symmetry herewith in their translational stacking, tend to occupy the minimal volume and the densest packing fills in free space .

The second principle is the principle of Coulomb uniformity of distribution of the 'cold' atoms in nano-aggregations, it can be considered a result of Coulomb repulsion forces which are a homogenous distribution of atoms in a free assembly and free space around the central atom. Coulomb uniform distribution of atoms in the cluster formations leads to decrease in the density of their packing, the coordination number and the bond strength between them. Growth of metal nanoparticles according to the first principle of free holes filling in by single atoms formed by the surfacial atoms, as well as by increasing of density of their packing and coordination number, lateral or radial overlap of external p or d electron orbitals in accordance with the quantum and mechanical compatibility, formation of cuboctahedral or icosahedral structures in the presence of the central atom into the cluster or hollow clusters with formation of stray vacancies in there. The low packing density of surfacial atoms reduces bond strength between them as a result of Coulomb repulsion force and uniformity of their distribution in the surface layers. The growth of spherical crystals occurs when the packing density of atoms in the surface layers is equal to $0.4098^{2/3} \leq \eta \leq 0.64976^{2/3}$, where $\eta \leq 0.4098$ is the value indicating the impossibility of topological transition to a dense condensed state of substance [4]. Upon reaching the bulk packing density $\eta \geq 0.64976$, the quantum and mechanical interaction of atoms in compact packaging with high strength connection between them starts working. Quantum and mechanical compatibility of orbitals determines the type of symmetry and atomic structure with a minimum internal energy of the crystals. When putting the second layer of 6 atoms over, there is a possibility to reorganize the first layer with icosahedral structure of a cluster into a closest cubic packing density with formation of a stable octahedral shape. There are 19 atoms with a maximal coordinate number with up to 7 surfacial atoms in it.

$$\eta = V_0/V = (19\pi d^3/6)/0,4714 \cdot (3d)^3 = 0,7816$$

where V_0 , V – an occupied volume of atoms and the volume of octahedra with the size of an edge of $3d$, excluding the volume of cone in the tips of the octahedron.

When reorganizing the first layer of balls (atoms) with icosahedral packing in a hexagonal packing for the formation of its first faceted shape of a cluster, obtained on the basis of packing, it is necessary to have 17 balls (atoms) of the size. A trigonal bipyramid herein formed consists of 30 balls, where the maximal coordination number is 9:6 balls. 6 balls are placed in the octahedral holes between 4 balls, 6 balls are in the wells between 3 balls; 5 balls are on the tips. Whereas for the formation of polyhedon with cuboctahedral and icosahedral shapes the number of balls of the second layer according to (5) with n=2 has to be equal to N=42. The total number of balls of the three-layer polyhedron is 147 and is calculated according to S.P. Gubin equation [5]:

$$N = 1 + \sum_{1}^{n}(10n^2 + 2) \qquad (2)$$

The packing density of balls in a multilayer small polyhedron is unknown. It is assumed that it is η_1=0.7405. Then the diameter of the circumscribed sphere of cuboctahedron (η_1=0.7405) consisting of 147 balls, will be equal to $D \geq (147/\eta_1)^{1/3} d \geq 5.8d$ and (η_1=0.68834) is $D \geq (147/\eta_1)^{1/3} d \geq 6d$ for icosahedron. The packing density of balls in the circumscribed sphere with a single cuboctahedron and icosahedron η_1=13d^3/(3d)^3= 0.4815 and a hollow icosahedron when filling in pores in it, a ball's appropriate size would be 12.90 / 24.51 = 0.5264. In the absence of the central globe it is, respectively, the following:

$$\eta_1 = 12d^3 /(3d)^3 = 12/27 = 0,4444$$

$$\eta_1 = 12d^3 /(2,9d)^3 = 12/24,515 = 0,4895$$

Consequently, the low packing density of atoms in the clusters with icosahedral or cuboctahedral shape without the central atom is a condition for further growth, first of all, in the form of icosahedral, that is, spherical crystals with formation of vacancies in their cell or restructuring of a faceted crystal shape.

The study about the substance in the nano-scale range (1–100 nm) of its cluster formations, nano- and microparticles is related to the development of mathematical apparatus to describe them. The given size range of nano-objects is summarized according to empiric data, however, there is no theoretical justification depending on the size of an atom of simple substance and size of a unit of the crystal lattice of complex substances. The size range of micro- and nanoparticles when their unusual properties begin to appear is important when production and milling of minerals and inorganic raw materials as well as synthesis of geopolymer binders with non-hydration type of hardening and neocomposites occur [6, 7].

Regardless of the preparation method and structure of nanoparticles, the effects of their use in chemical and technological processes are promising to improve the quality of raw materials and construction composites during structure formation process. Major and fundamental aspect in the developing science about nanodispersed objects is the matter of dimension, structure and topological state of bulk and surface layers of nanoparticles, when their unusual properties appear, which differ from those of the massive body. It is believed that the unusual properties are associated with the relatively large proportion of surfacial atoms [8, 9]. It is known, when the formation of more loose atom packing in the surface layers than in the core of their clusters or crystal packing, the micro- and nanoparticles, generally rounded with atomicrough surface, are formed when cooling process. Under the conditions of supercooling of the molted mass, the crystalline shape becomes profitable. Packing density of atoms in atomic rough surface layers of micro- and nanoparticles can reach the critical value for the given substance.

Since the difference between the phases in critical point disappears, their specific surface free energy and the difference in thermodynamic (chemical) potentials go to zero. In this case, increasing in the size of nanoparticles is stopped for a while. As a result, the principle of close packing is observed when the interaction of atoms in nanoparticles occurs, starting from the deep of the layers. Direction of its action depends on the preparation conditions (formation) of the nanoparticles as well as on the size transition from Coulomb interaction to quantum-mechanical interaction. If it outgrows a structural-topological sphericity barrier, the growth of micro-crystals with faceted shape takes place. Differential characteristics of microparticles are explained by different distribution of electron density in the surfacial layer of atoms compared to the bulk atoms, which manifested in size effects. The size effect is associated with near-wall factor of discrete systems, which is determined by different packing

density and number of atoms in the surfacial layer and in the bulk layer of nano- and microparticles. Parietal factor takes place at the macro level: the granular layer and in aggregations of microparticles in composite materials with granular filler and other materials with a granular structure. A critical size of micro- and nanoparticles, obtained by ultrasonication, dry or wet mechanical dispergation of granular materials and rocks can be determined by a certain size, when unusual changing of one or a complex of characteristics of the particles occurs in comparison with the massive solid body. It is well known that the decrease in particle size during milling process of rocks and materials leads to increasing in their specific surface. With the increase of surface curvature of such particles motivated by decrease of their size, a relative quantity of surfacial atoms of milling products has a tendency to growth and their packing density reduces because of reducing of coordination number and enhancing of Coulomb repulsion due to bigger bond distance between the atoms in the range of quantum-mechanical interaction. As surface elements of discreteness such as atoms and particles can be considered those atoms and particles, which located into two or more loose surfacial layers of clusters, microparticles aggregations or in near-wall layers of in a volume of dispersed or granular materials in a container. According to research data [10], the number of loose surfacial layers increases to 3–4 layers, when the container dimensions with the granular material in it decrease.

2. Experimental part and results

In order to solve one of the main issues of micro- and nanodispersed particles, it may be helpful to apply a simple research apparatus of applied science, that is, discrete topology [11] of random condensed systems, since a common factor for them is discreteness of the investigated subjects. Discrete topology of random condensed systems, having discreteness at a different dimensional scale, (i.e. macro- and microscale) uses mostly two basic characteristics – random packing density of elements of discreteness and their coordinate number that determines a topological condition of a system. Mathematical apparatus for the investigations is based on corpuscular-topological properties of discrete systems and basically consists of some fundamental principles [11]. The main principle is a relationship between discrete distributions of elements of discreteness (atoms, molecules, balls, nano-, micro- or macroparticles, etc.) in dimensional order with random close density in a system [11]:

$$\frac{d_n}{d_1} = \left(\frac{1}{10\eta_1(\sqrt{3}-1)^p}\right)^{\frac{mn}{n}} \tag{3}$$

or, at p = 3 and *m* = 3 - for random packing eq.3 takes the following form:

$$\frac{d_n}{d_1} = \left(\frac{2{,}549}{10\eta_1}\right)^n = \left(0{,}2549/\eta_1\right)^n = \left(\eta_{c1}/\eta_1\right)^n \tag{4}$$

where, d_1, d_2 – diameter of the biggest particles (balls), forming a packing and diameter of the particles (balls) with consistently smaller size, filling in the existing voids in the packing.

η_1 – random packing density of monodispersed layer of particles (balls, atoms – for elementary substances), atoms in a crystal cell ($\eta_1 \leq 1$) – for complex substances;

m – class in the system of particle size distribution, determining discreteness in their size, *m* = 0…15 … (*n*+1);

p – factor, determining short or long distance of elements of discreteness (granules, micro- or nanoparticles, atoms) in a system:

$p = 3$ – for random packing of mixed granules and particles; $p \leq 6$ – for contacted and free stayed solid particles (balls); $p > 6$ – for covering and penetrated to each other spherical particles.

The calculations made with formula 4 for critical radius of microparticles depending on packing density of metallic atoms in them are listed in table 1.

From eq. 3 at $m = 3$ and $d_n / d_1 = 1$, the following formula for random packing density of identical spherical particles can be obtained:

$$\eta_1 = \frac{1}{10(\sqrt{3}-1)^p} = \frac{0,1}{(\sqrt{3}-1)^p}$$

From the equation mentioned above, at $p = 3$, $p = 0$ and $p = 6$ we have the first $\eta_{c1} = 0.2549$ and the second $\eta_{c2} = 0.1$ critical packing density of elements of discreteness of a substance and the maximal theoretical random packing density $\eta_{c1} = 0.64976$.

From eq. 3 follows the equation for dimensional near-wall factor of discrete systems from the ratio of maximal voids (pores) size at $m = 3$, $n = 2$ in random packing ($p = 3$) to particles (balls) size ($m = 12$), which fill in all the voids or free volume in the system more compactly:

$$D \leq \left(\frac{10\eta_1}{2,549}\right)^3 \leq \left(\frac{\eta_1}{\eta_{c1}}\right)^3 \leq \left(\frac{\eta_1}{0,2549}\right)^3 \leq (3,923\eta_1)^3 \leq 60,377\eta_1^3 d \qquad (5)$$

where D, d – critical size of atom aggregations (clusters, nano- and microparticles), particle aggregations of dispersed materials and the diameter of atoms in clusters, nano- or microparticles respectively for elementary substances and the most linear size of elementary crystal cell for complex substances. It is also a critical particle size for dispersed materials.

The results of calculation of critical radius for microparticles, depending on packing density of metal atoms in them using formula 4 are presented in table 1.

Table 1. Size of particles, obtained from liquid and crystal phases of metals.

Packing density of atoms in microparticles, η	Radius of microparticles, A (0,1 nm)					
	Zn	Pb	Sn	Au	Hg	Fe
	Radius of atom, Å (0,1 nm)					
	1,39	1,75	1,58	1,44	1,57	1,26
Crystal phase						
η = 0,7405	34,1	42,9	38,7	35,3	38,5	30,9
0,70323	29,2	36,7	33,2	30,2	33,0	26,5
0,68527	27,0	34,0	30,7	28,0	30,5	24,5
Liquid phase						
0,6370	21,7	27,3	24,7	22,5	24,5	19,7
0,63347	21,3	26,8	24,3	22,1	24,1	19,3
0,62634	20,6	26,0	23,4	21,4	33,3	18,7
0,60830	18,9	23,8	21,5	19,5	21,3	17,1
0,54100	13,3	16,7	15,1	13,8	15,0	12,0
0,49277	10,0	12,6	11,4	10,4	11,3	9,10
0,43406	6,96	8,76	7,91	7,21	7,86	6,31
0,4098	5,77	7,27	6,56	5,98	6,52	5,24
0,4040	5,53	6,97	6,29	5,73	6,25	5,01

A good correlation between the computed values of critical sizes for microparticles and empirical data can be taken as confirmation of formula 5. According to the empirical data given by A.S. Chizhik et al.[12], the radius of critical particles for the first four elements obtained from metallic molted mass is in the range of 20…30 Å. The data from the range has a good correlation with the calculated results using formula 5 for solid crystal and liquid phases of metals.

In compliance with eq. 5, the critical size of nanoparticles and number of atoms in forming aggregations from liquid phase depends on packing density of atoms in them. The critical size of dispersed particles from solid and liquid phase is not only a regular geometric parameter. According to the data given by S.L. Chizhik et al. [12], with decreasing of the size of metal microparticles, produced from molten mass, volume effect of super cooling disappears and latent heat gets equal to zero. At the critical diameter of microparticles, the difference between liquid and crystal condition comes out. The first class of phase transformation becomes continuous. The value of particle critical radius corresponds to the size in the field of short-range order in the liquid phase. Thus, the frozen density fluctuations in liquid at fast cooling are, to some extent, the nucleation centers of microparticles and crystal microphase. If the size of a microparticle dispersed from metal molted mass is extremely small, its volume consists of the compacted fluctuation zone. Depending on the size of microparticles cooled in the liquid metal phase, there is a probability of formation of different structures like loose amorphous and crystal structures. Critical size of nanoparticles with crystal structure produced from metal molted mass for the element presented in table 1 is in the range of 4…8.6 nm.

If the first critical random packing density of particles of dispersed materials is equal to $\eta_{c1} = \eta_1^{(9…10,5)/3}$ where $= \eta_1 \leq 0.6403…0.6498$ and a regular packing density of elements of discreteness of a substance is of $\eta_{c1} = \eta_1^{(11…15)/3}$ [11], where $\eta_1 = 0.6802…0.68834…0.6981…0.7405$, then the formula for dimensional range and for average critical size of clusters ($n= 9…15$) and spherical nanoparticles is the following:

$$D = 60{,}38\,\eta_1^{n/3}\,d\,, \qquad n = (0\text{-}3\text{-}6)\text{-}\mathbf{9…12…15} \qquad (6)$$

where, $n = 9–10.5$ at $0.60377 \leq \eta_1 \leq 0.64976$ – for critical particle size of dispersed materials.
For the critical size of nano- and microparticles of crystal substances with different crystal cell:
$n = 10.5 – 11.5$ at $0.64976 \leq \eta_1 \leq 0.6802$ – volume centered;
$n = 11.5 – 12$ at $0.6802 \leq \eta_1 \leq 0.68834$ – icosahedral;
$n = 12 – 12.4$ at $0.68834 \leq \eta_1 \leq 0.6981$ – trigonal;
$n = 12.4 – 15$ at $0.6981 \leq \eta_1 \leq 0.7405$ – compacted hexagonal and face centered cubic cells.

The critical sizes of growing spherical new formations ($n \leq 0$), including faceted crystals in the interval of sphericity and potential reorganization of structure to their different unique form ($0 \leq n \leq 15$) can be taken from Eq. 4 as:

$$D = 60{,}38^{n/3}\,\eta_1^{n}\,d\,/\,\eta_s = \left(60{,}38^{1/3}\,\eta_1\right)^{n} d\,/\,\eta_s = \left(3{,}923\,\eta_1\right)^{n} d\,/\,\eta_s \qquad (7)$$

where $n = (0,1,2,\mathbf{3})\text{-}6\text{-}\mathbf{9}\text{-}\mathbf{12}\text{-}\mathbf{15}…$.

$\eta_s = \eta_1^{1/9}$ – packing density of atoms in surface profile of interatomic layers. General equations for determination of the size of growing nano- and microparticles can be obtained from eq. 3 at $n = 2$, $p = 3$:

$$\frac{D}{d} = d_1 \Big/ \left(\frac{2{,}549}{10\eta_1}\right)^{m/3} \quad d_1 = \left(\frac{10\eta_1}{2{,}549}\right)^{m/3} = (3{,}923\eta_1)^n, \quad n = m/3 \tag{8}$$

Table 2 presents the calculation results obtained using eq. 6, 7 for average and minimal critical size of spherical nanoparticles in the interval of potential reorganization of structure and appearance of their unusual properties in comparison with a massive solid body. Therein presented the dimensions of growing crystal new formations (6), which depend on packing density of elements of discreteness in them (metal atoms and other elementary substances), dimensional interval and an average critical size of spherical nanoparticles with icosahedral atom packing ($\eta_1 = 0{,}68834$).

Table 2. Dimensions of a growing crystal and the critical size of micro- and nanoparticles in the range when their unusual properties appear.

Index of power, n-n	Micro- and nanoparticle size $D \times d$ with packing density of structural elements in them, η_1				
	0,7405 (12,7)	at $d = 0,3$ nm	0,7405 (12,8)	0,6883 (12,7)	0,6403 (12,7)
1	2	3	4	5	6
0	**60 – 62**	**18 –19 nm**	**1,0 – 1,1**	**60 – 63**	**60,4 – 63,0**
3….1	45 – 46	13 – 14 nm	2,9 – 3,0	42 – 43	38,6 – 40
6 ….2	33 – 34	9,9 – 10 nm	8,4 – 8,7	28,6 – 29,8	24,8 – 26
9….3	**24,5 – 25**	**7,4 – 7,5 nm**	**24,5– 25,0**	**19,7 – 20,5**	**13,7 – 14,4****
12….4	18 – 19	5,4 –5,7 nm	71 – 73	**13,6– 14,2**	10,0 – 10,5
15….5	**13 – 14(12,6)***	**4,0 – 4,2 nm**	206 – 213	9,3– 9,7	6,5 – 6,8
18….6	9,9 – 10	**3,0 – 3,1 nm**	601 – 621	6,4 – 6,7	4,0 – 4,2
21….7	7,4 – 7,6	**2,2 – 2,2 nm**	1745 – 1804	4,4 – 4,6	2,7 – 2,8
24….8	5,5 – 5,7	**1,6 – 1,7 nm**	5071 – 5243	3,0 – 3,1	1,7 – 1,8
27….9	4,0 – 4,2	**1,2 – 1,3 nm**	growing	2,1 – 2,2	1,1 – 1,15
30….10	3,0 – 3,1	**0,9 – 0,93 nm**	growing	1,4 – 1,5	–

*– at $n = 16/3$, **– at $n = 10/3$

From table 2 and eq. 6, 7 it can be assumed that the maximal size of nanoparticles, when their unusual properties appear, corresponds to the value $n \geq 0$, at $n = 0$ will be equal to $D = 60 – 63d$. For example, at $d \approx 0.3$ nm (for metals) we have $D = 18 – 19$ nm, and at $\eta_1 = 0.7405$ and $n = 9;15$ the value of $D = 7.5; 4$ nm. For dispersed materials at $d = 0.1$ μm and $n = 0$, the value of $D = 6.0 – 6.3$ μm and at $\eta_1 = 0.64976 – 0.6403$ and $n = (10.5 – 10)/3$ respectively, the critical size of microparticles is equal to $D = (14.0 – 14.4) d = 1.34 – 1.37$ μm. From table 2 it follows that the average critical size of crystal nanoparticles is in the range of 7.5 – 19 nm, at the same time, the minimal critical size, when unusual changing of physical properties can appear is 4.2 nm. For microparticles of dispersed materials at $\eta_1 = 0.6403$, the critical size is equal to 13.7 d and their maximal average dimensions are $(60 – 63) d$. The data of the critical size for nanoparticles of elementary substances (metals) are marked in table 2 with bold type.

For reorganization of the shape of growing spherical crystals into faceted crystals at appropriate thermodynamic conditions, the minimal critical size of elementary substances should be equal to $(13 – 14)d$, with the average critical size of 25 d and the maximal critical size of $(60 – 62) d$.

Since the size of monomer of a ion of silica (tetrahedron) $d = 0.324$ nm [13], the size of nanoparticles of freshly prepared sol at $\eta_c \leq 0.7405^{3...5}$, will be equal to 8.1 – 4.5 nm. Experience has

shown that nanoparticles of silica and others rocks with minimal critical size about $8.1 - 4.5$ nm form gel easily from liquid alkaline medium. The size of its stable aggregations at $d = 8.1$ nm equals to:

$$D_1 \leq 60,38 \eta_1^{3...10/3} / \eta_1^{1/9} \cdot 8,1 nm = 205...186 nm$$

Critical size of quartz nanoparticles, having a size of crystal cell with given parameters $a = 0.49$ nm, $b = 0.49$ nm и $c = 0.54$ nm and $\eta_1 \leq 0.76$ equals:

$$D = 60,38 \cdot 0,76^{5...16/3} \cdot 0,54 nm / 0,76^{1/9} = 8,5...7,8 nm$$

Incorporating in eq. 7 the known values of regular packing densities of atoms for elementary substances and random packing of spherical particles, taking into account their packing densities in the surface of cross-section area of crystal formations with filled in atom voids upper and lower layers in the form of truncated ball segments ($\eta_s \approx \eta_1^{1/9}$) for different packing, we obtain:

for closest packing – $\eta_1 \leq 0.74048$, $\quad D \leq 3^n d$

for icosahedral packing – $\eta_1 \leq 0.74048$, $D \leq 2,905^n d / \eta_s^{1/3}$

$$\eta_1 \leq 0.68834, \quad D \leq 2,70^n d / \eta_s^{3/4} \leq 2,70^n d / 0,9069^{3/4} \leq 2,90^n d$$

for random packing – $\eta_1 \leq 0.64976$, $D \leq 2,549^n d / \eta_s^{1/3}$

(general packing) – $\eta_1 \leq 0.64029$, $D \leq 2,512^n d / \eta_s^{1/3}$

$$\eta_1 \leq 0.63716, \quad D \leq 2,50^n d / \eta_s^{1/3}$$

$$\eta_1 \leq 0.63405, \quad D \leq 2,49^n d / \eta_s^{1/3}$$

where $\eta_s^{1/3} = \left(\pi / 2\sqrt{3}\right)^{1/3} = 0,9069^{1/3} \approx 0,968, \eta_s^{1/3} \approx \eta_1^{1/9} = 0,74048^{1/9} \approx 0,9672$.

From the equation for icosahedral packing $n = 1$, $\eta_s = 1$ and $\eta_s^{3/4} = 0.9293$ respectively, it follows that icosahedral atom aggregation (cluster) consists of one surface atom layer. Without central atom, the size of a central pore equals $0.9d$ that corresponds to the size of the central pore in an icosahedral packing of atoms, contacting each other. This way, vacancy defects form that gives an opportunity for growing of spherical aggregations. With the presence of the central atom in one-layered icosaherdral cluster, all 12 surface atoms contacting with it have an equal distance between each other.

Equations for dimension interval and for the average critical size ($m = 0...1...2...3$) of growing ($n = \infty...0$) clusters and spherical nanoparticles can be obtained from eq. 6, 7 in the following form:

$$\frac{(3,92\eta_1)^n d}{\eta^{1/9}} \leq D \leq \frac{(60,38\eta_{c1})^m d}{\eta^{1/9}} \tag{9}$$

$$\frac{1000\eta_1^n d}{\eta^{1/9}} \geq D \geq \frac{(60,38\eta_{c2})^m d}{\eta^{1/9}} \tag{10}$$

where $\eta_{c1} = \eta_1^{(11,5; \, 12; \, 12,4; \, 15)/3}$, $\eta_{c2} = \eta_1^{(18; \, 18,4; \, 19; \, 23)/3}$ at $\eta_1 = 0.6802$; 0.6883; 0.9681; 0.7405 respectively for systematic atoms packing (balls) in crystal structures, $\eta_{c1} = \eta_1^{(9; \, 10; \, 10,5)/3}$ and $\eta_{c2} = \eta_1^{(13,5; \, 15; \, 16)/3}$ – for random particles packing of dispersed materials at $\eta_1 = 0.6038$; 0.64029; 0.64976 respectively.

Both parts of equation 4 or 6, 7, including η_s take the cube and times $\pi/6$. After conversion we have a critical number of elements of substance discreteness for the corresponding packing:

$$N \leq \frac{(3{,}923\eta_1)^n}{\eta^{1/3}},$$

$$N = \frac{60{,}38\eta_1{}^n}{\eta_1{}^{1/3}}$$

3. Conclusion

The obtained formulas 9, 10 give a number of elements of discreteness in spherical aggregations and do not determine their number in coordination polyhedrons such as cubooctahedrons and icosahedrons.

Equations 9, 10 describe ($m \geq 0$) critical sizes of elements of substance discreteness for the main level of discreteness, even at critical condition of a substance.

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