

## CRITICAL DIMENSION OF SMALL-SIZE PARTICLES

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**Keywords:** *particulate materials, micro-and nanoparticles, the critical size*

**Abstract.** The derivation of an equations for calculation of average and the largest critical sizes of micro- and nanoparticles in range of appearing their unique properties in comparison with the massive body

Study of the properties of materials in the nano-size (1–100 nm) range of its cluster formations, as well as nano- and microparticles leads to the development of new approaches and mathematical apparatus of nano-objects investigation. Above size range of nano-objects is presented as the results of experimental studies. However there is no theoretical justification for simple and complex substances, depending on the size of the atom and the linear size of the unit crystal lattice. Size of micro-and nanoparticles when the unique properties appear is important when the grinding and enrichment of mineral inorganic raw materials, synthesis of geopolymer binders and neocomposites [1, 2].

Critical size of micro-and nanoparticles obtained with ultrasonic, wet or dry mechanical grinding mean of grain materials and rocks is determined on the basis of appearing unusual changing of in comparison with ones in the massive body. We believe, unusual properties of small particles appear in the range of sizes, when the ratio of the number of elements of the discreteness in the surface layer is comparable or greater than the amount of volumetric ones, i.e. remoting to the center of their volume. At the same time, the congruence of product of volume ratio and the packing density of the surface and bulk elements of the matter discreteness respectively.

It is known, a decrease in particle size during crushing of rock materials. As a result, their specific surface area increases. With increasing of surface curvature of particles, which is due to decreasing their size, the relative number of surface atoms of crushing products increases, and their packing density decreases. It is associated with a decrease in the coordination number, increasing the Coulomb repulsion due to the increase in bond length between them within the particles at quantum-mechanical interaction. The superficial of discreteness (atoms or particles) are elements are located in two or more loose surface layers of clusters, microparticle aggregates or parietal layers of disperse or granular material in the container.

So, according to the literature sources [3] amount of loose surface layers increases to 3–4 layers when decreasing of the container volume with a granular material.

Key role in explaining the unusual properties of the materials obtained can play the structural topology of discrete systems. Mathematical apparatus of its study, based on the particle-geometric properties of discrete systems, consists mainly of some basic laws. The main one is a discrete distribution element of discreteness (atoms, molecules, balls, nano-, micro- or particulates, etc.) in size with a dense random (arbitrary) packaging in the system [4].

The equation for the critical dimensions and micro- and nano-particles as well as some of other equations and parameters of discrete systems are result from the general distribution of elements of discreteness in monodisperse disordered layer in the form of spherical solids and pores, densely filled by particles (balls) with appropriate size [4] according the following formula:

$$\frac{d_n}{d_1} = \left[ \frac{1}{10\eta_1(\sqrt{3}-1)^p} \right]^{\frac{m}{3(n-1)}} \quad (1)$$

where  $d_1, d_n$  – diameter of the largest particles (spheres) forming the packaging and diameter of particle (balls) with successively smaller size, filling the cavities formed respectively;

$\eta_1$  – random packing density of monodisperse particles layer (spheres, atoms – for simple substances), the atoms in the crystal cell ( $\eta_1 \leq 1$ ) – for complex substances;

$m$  – class of size distribution system of particles in the mixture, that determines the discontinuity in their sizes,  $m = 0 \dots 15 \dots (n+1)$ ;

$p$  – indicator that defines the separation or approximation of elements of discreteness (grains, particles, micro- or nano-particles, atoms) in the system:

$p = 3$  – is parameter for the random packing of grains, particles in the mixture;  $p \leq 6$  – for contacted and disaggregated solids (balls);  $p > 6$  – for penetrating one another and overlapping spheres.

Equation (1) describes the various classes of  $m$  particle size distributions at high-density packaging in a mixture with continuous ( $m < 3$ ), intermittent ( $3 \leq m < 6$ ) and continuous ( $6 \leq m \leq 12$ ) granulometry. From this equation also follows the expression for dimension (wall surface) of discrete system factor which depends on the ratio of the number of atoms (grains) in the surface layers of bulk or aggregates and their packing density to the rest of the number (volume) or the total number of atoms (particles).

Thus, decreasing the size of discrete bulk consolidation system promotes increasing the number of surface atoms (particles), and their packing density decreases up to value lower than the packaging density for bulk elements of material discreteness. This affects a number of physical properties of small particles.

Distribution by relative sizes of the particles (spheres) and pores between them in the expanded form (with  $m=3$  and  $p=3$ ) can be shown as following:

$$\frac{d_n}{d_1} = 1; \frac{2,549}{10\eta_1}; \left( \frac{2,549}{10\eta_1} \right)^2; \left( \frac{2,549}{10\eta_1} \right)^3; \left( \frac{2,549}{10\eta_1} \right)^4 \dots$$

In this distribution the expression for the size factor can be extracted from the ratio of the size of the largest prevailing pores in the random packing of globular particles of identical size to the balls size, filling the pores with a similar packing density as large volume in the layer. By others words, the shape and size of the pores doesn't not affect the packing density of particles (spheres) with smaller size. This is the nuclear with the smallest number of grains (balls) in any region of monodisperse layer when the packing density of the surface layers does not effects significantly on the total bulk packing density. Studies [4] of bimodal particle packets of round shape river quartz indicate this phenomenon takes place at the ratio of the largest prevailing relative size of pores ( $m=p=3$  and  $n=2$ ) (1) in random packing of monodisperse particles (spheres) layer to the relative size of pores or the compactly filling particles (balls) at  $n=12$  (1). This is the largest size of the fine particles (balls) most densely filling the free volume formed in random packing of monodisperse layer of large particles (spheres).

$$\frac{D}{d} \leq \frac{2,549}{10\eta_1} d_1 : \left( \frac{2,549}{10\eta_1} \right)^4 d_1 \leq \left( \frac{10\eta_1}{2,549} \right)^3 \leq \left( \frac{\eta_1}{0,2549} \right)^3 \leq 60,38\eta_1^3, \quad (2)$$

where  $D, d$  – is critical size of the atomic aggregates (clusters, nano-and microparticles) and the diameter of the atoms in the clusters or nanoparticles – for simple substances and the greatest linear dimension of the crystal cell – for complex ones or microparticles in aggregations of dispersed materials.

Equation (2) with the sign “ $\leq$ ” is the basic requirement for the average critical clusters and nanoparticles size. With a sign “ $\geq$ ” for the size factor, when the size of the container  $L$  consisting of granular disperse material has no effect on the packing density of particles with the size  $d$ , or when the linear dimension of the control samples of composite materials has no effect on their mechanical strength :  $L \geq 60,38 \cdot \eta_1^3 \cdot d$ .

Critical dimensions of growing spherical formations ( $n \geq 0$ ), including crystalline in interval of sphericity and the possible restructuring to limited crystal form ( $0 \leq n \leq 16$ ), the private expression (2) in the general follow form can be presented:

$$D = 60,38^{n/3} \eta_1^n d = 60,38^{1/3} \eta_1^n d = 3,923 \eta_1^n d, \quad (3)$$

where  $n=(0, 1, 2, 3-6) -9-12-15 \dots$

From the expression (1) at  $m=3$  and  $n=1$  it can be obtained an equation for the density of random packings of identical spherical particles of following form:

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

From this expression for  $p=3, p=0$  and  $p=6$  we obtain the first critical packing density  $\eta_{c1} = 0,2549$ , second one  $\eta_{c2} = 0,1$  for elements of substances discreteness respectively as well as the largest (theoretical) density of the random packing  $\eta_1 = 0,64976$ .

Since  $\eta_{c1} = \eta_1^{(9 \dots 10/3)}$  and  $\eta_{c1} = \eta_1^{(1 \dots 15/3)}$  are the first critical density of random packing and systematic (regular ) state of discreteness elements of the substance, the expression for the

size of an interval ( $n \geq 0$ ) and the average critical size ( $n=9...16$ ) of clusters and spherical nanoparticles will have the form:

$$D = 60,38\eta_1^{n/3}d, \quad \text{where } n = (0-3-6) - 9-15 \quad (4)$$

where  $n=9-10,5$  at  $0,6038 \leq \eta \leq 0,6403...0,64976$  – for medium critical particles dimensions of dispersed materials;

$n=10,5-11,5$  at  $0,64976 \leq \eta \leq 0,6802$  – for crystalline substances with space-centered crystalline lattice;

$n=11,5-12,4$  at  $0,6802 \leq \eta \leq 0,6981$  – for crystallites in the amorphous and liquid phases;

$n=12,4-15$  at  $0,6981 \leq \eta \leq 0,7405$  – for crystalline substances with hexagonal and side-centered lattice.

Substituting the expression (3) the known densities of systematic (regular) atoms packaging for simple substances as well as random (arbitrary) packings of spherical particles taking into account the density of their packaging and ball sectors in the hollows between them  $\eta_s$  at surface of the cross-section of the crystal for different packages, we obtain:

$$D \leq 3,923\eta_1^n d / \eta_s^{1/3}, \quad (5)$$

$$\text{for close packing} - \quad \eta_1 \leq 0,74048, \quad D \leq 3^n d, \quad (5a)$$

$$\text{for icosahedral packing} - \quad \eta_1 \leq 0,74048, \quad D \leq 2,905^n d / \eta_s^{1/3}, \quad (5b)$$

$$\eta_1 \leq 0,68834, \quad D \leq 2,70^n d / \eta_s^{3/4} \approx 2,7d / 0,9069^{3/4} \approx 2,905d, \quad (5c)$$

$$\text{for random packing} - \quad \eta_1 \leq 0,64976, \quad D \leq 2,549^n d / \eta_s^{1/3}, \quad (5d)$$

$$\text{for arbitrary packing} - \quad \eta_1 \leq 0,64029, \quad D \leq 2,512^n d / \eta_s^{1/3}, \quad (5e)$$

$$\eta_1 \leq 0,63716, \quad D \leq 2,50^n d / \eta_s^{1/3} \quad (5i)$$

$$\eta_1 \leq 0,63405, \quad D \leq 2,49^n d / \eta_s^{1/3} \quad (5j)$$

$$\eta_s^{1/3} = \pi/2\sqrt{3}^{1/3} = 0,9069^{1/3} = 0,96795, \quad \eta_s^{1/3} \approx \eta_1^{1/9} = 0,74048^{1/9} \approx 0,9672.$$

The expression for the size interval and average critical size ( $n = 9...16$ ) of growth clusters and spherical nanoparticles from the equations (4) likewise, we obtain:

$$D = 60,377\eta_1^{n/3}d / \eta_s^{1/3}. \quad (6)$$

From the expressions (5 b, c) for  $n = 1$ ,  $\eta_s^{1/3} = 1$  и  $\eta_s^{3/4} = 0,9293$ , respectively, should conclude the nuclear aggregation (cluster) consists of one surface atom layer. In the absence of the central atom the central pore size is  $0,9d$ , that corresponds to the size of the central pores in the icosahedral packing of atoms, contacting between them. So the vacancies in crystals and the

potential growth of the spherical aggregations are form. If there is a central atom in a single layer icosahedra cluster all of 12 of surface atoms are separated among themselves at equal distances.

The table shows the results of equation (4) and (6), where  $\eta_c \approx \eta_1^{1/9}$ , medium and minimum critical size of spherical nanoparticles is in the range of the possible restructuring and appearing of their unique properties compared with the massive body. Also the size of the growing crystal formations (3), (5), depending on the packing density of the discreteness elements (atoms of metals and other common substances), dimensional interval and average critical size of spherical nanoparticles with icosahedral atom packing  $\eta_1 = 0,68834$  in the absence of the central atom are given.

Table

**Dimensions of growing spherical and edged crystals and the critical size of micro- and nanoparticles in the range of appearing of their unique properties**

Index, <i>n</i> ----- <i>n</i>	Dimension of the micro - and nanoparticles $D \times d$ and packing density of the $\eta_1$ -structure elements in				
	0,7405 (Eq. 4, 6)	at $d = 0,3\text{nm}$	0,7405 (Eq. 4, 6)	0,6883 (Eq. 3, 5)	0,6403 (Eq. 4, 6)
1	2	3	4	5	6
0	<b>60–62</b>	<b>18–19 nm</b>	<b>1,0–1,1</b>	<b>60–63</b>	<b>60,4–63,0</b>
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
<b>9 ----- 3</b>	<b>24,5–25</b>	<b>7,4–7,5 nm</b>	<b>24,5–25,0</b>	<b>19,7–20,5</b>	<b>13,7–14,4**</b>
12---- 4	18–19	5,4–5,7 nm	71–73	<b>13,6–14,2</b>	10,0–10,5
<b>15---- 5</b>	<b>13–14(12,6)*</b>	<b>4,0–4,2 nm</b>	<b>206–213</b>	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
<b>27---- 9</b>	<b>4,0–4,2</b>	<b>1,2–1,3 nm</b>	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  $n = 10/3$

According the table and equations (4, 6) follows that the average size of nanoparticles, their unique properties are observed corresponds to the value  $n \geq 0$ , for  $n=0$  it will be equal to  $D = 60–63d$ . For example, at  $d \approx 0,3 \text{ nm}$  (for metal), we have  $D = 18–19 \text{ nm}$ , and at  $\eta_1 = 0,7405$  and  $n = 9, 15, 16$  we have  $D = 7,5; 4; 3,6 \text{ nm}$ . For disperse materials at  $d = 0,1 \mu\text{m}$  and  $n = 0$ , we obtain  $D = 6,0–6,3 \mu\text{m}$ , and at  $\eta_1 = 0,64976–0,6403$  and  $n=13,5–9$  the average critical size of microparticles is  $D = (14,0–14,4) d=1,40–1,44 \mu\text{m}$ .

As the size of the monomer silicate ion of silica (tetrahedra)  $d = 0,324 \text{ nm}$ , the size of nanoparticles of fresh sol at  $\eta_c \leq 0,7405^{3 \dots 5}$  will be equal to the 8,1–4,5 nm. Early studies show the nanoparticles of silica and other rocks with a minimum critical size of the 8,1–4,5 nm in water alkaline medium easily form gels.

The size of sustainable its aggregations at  $d = 8,1 \text{ nm}$ , will be equal to:

$$D_1 \leq 60,377\eta_1^{3 \dots 10/3} / \eta_1^{1/9} \cdot 8,1 \text{ nm} = 205 \dots 186 \text{ nm}.$$

Quartz nanoparticle size with dimension of crystal lattice  $a = 0,49$  nm,  $b = 0,49$  nm and  $c = 0,54$  nm and  $\eta_1 \approx 0,76$  is equal to:

$$D = 60,377 \cdot 0,76^{3 \dots 5 \dots 16/3} \cdot 0,54 / 0,76^{1/9} \text{ nm} = 14,7 \dots 8,5 \dots 7,8 \text{ nm.}$$

From the table we can also observe the average critical size of crystalline nanoparticles is in range of 7,5– 19 nm, and the minimum one is of 4,2 nm. For microparticle of dispersed materials at  $\eta_1 = 0,6403$  is equal to 14,4  $d$  respectively, and the highest average sizes are (60– 63)· $d$ . The critical sizes of nanoparticles of simple substances in the table are in bold.

For restriction of shape of growing spherical crystals in edged format suitable thermodynamic conditions, the minimum critical size is equal to (13–14)· $d$ , the average critical size is 25  $d$ , and the largest one is (60–62)  $d$ .

Use the above value of the second critical packing  $\eta_{c2} = 0,1$  for surface atoms in microparticles. As in the denominator of the expression (2) are tenfold values of the first critical packing density for random packing of substance discreteness elements, then to move to the largest and smallest critical dimensions of micro- and nanoobjects with atomic rough surface, this equation can be written by following:

$$\frac{D}{d} \leq \left( \frac{10\eta_1}{10\eta_{c2}} \right)^3 \leq \left( \frac{\eta_1}{0,1} \right)^3 \leq 1000\eta_1^3 \leq 1000\eta_c,$$

(7)

where  $\eta_c = \eta_{c1} \dots \eta_{c2} \approx 0,2549 \dots 0,1$

The largest and subsequent the critical dimensions of nano- and microparticles of metals and disperse materials with atomic rough and high-energy surface according to the obtained equations, (for example, if the diameter of the elements of their discreteness (atoms)  $d = 0,3$  nm) will be equal:

– with the closest systematic atom packing

maximum –  $D \leq (0,74048 / 0,1)^3 d \leq 406d \leq 122 \text{ nm,}$

medium –  $D = 1000 \cdot 0,74048^5 d = 223d = 67 \text{ nm,}$

the largest sphericity size –  $D = 60,38\eta_1^0 d / \eta_1^{1/9} = 60,38 \cdot 0,3 / 0,7405^{1/9} = 18 \text{ nm,}$

medium –  $D = 60,38 \cdot 0,7405^{3 \dots 5} \cdot d / 0,7405^{1/9} = (25 \dots 14)d = 7,6 \dots 4,2 \text{ nm,}$

minimum –  $D = 60,38 \cdot 0,7405^{23/3} d / 0,7405^{1/9} = 6,24d = 1,87 \text{ nm.}$

– with random (arbitrary) compact packing

maximum –  $D = 1000 \cdot 0,6403^{3 \dots 10/3} d = (262 \dots 226)d = 79 \dots 68 \text{ nm,}$

the largest sphericity size –

$$D = 60,38\eta_1^0 d / \eta_1^{1/9} = 60,38 \cdot 0,3 / 0,6403^{1/9} = 19 \text{ nm,}$$

medium –  $D = 60,38 \cdot 0,6403^3 d / 0,6403^{1/9} = 16,65d = 5 \text{ nm,}$

$$D = 60,38 \cdot 0,6403^{10/3} \dots 0,64976^{3,5} d / \eta_1^{1/9} = 14,4 \dots 14,0d = 4,3 \dots 4,2 \text{ nm,}$$

minimum –  $D \leq 60,38 \cdot 0,6403^5 \dots 0,64976^{16/3} d / \eta_1^{1/9} \leq 6,8 \dots 6,4 d \leq 2,0 \dots 1,9 \text{ nm.}$

The largest calculated size of microparticles for all types of packing of discreteness elements (atoms) with size  $d = 0,3$  nm, will be equal to:

$$D = 1000\eta^0 d = 1000d = 300 \text{ nm}$$

Taking into account the value of the second critical packing density of surface atoms is within the index of the amplitude of the random packing balls density  $0,1 \leq \eta_{c2} \leq 0,1076$ , then the expression (6) for the largest size for the matter microparticles can be written as following:

$$D \leq \left( \frac{\eta_1}{\eta_{c2}} \right)^3 \cdot d \leq \left( \frac{1}{\eta_{c2}/\eta_1} \right)^3 \cdot d \leq \left( \frac{1}{\eta_1^{n-1}} \right)^3 \cdot d \leq \frac{d}{\eta^{3(n-1)}}. \quad (8)$$

where  $n \leq 5$  – at  $\eta_1 \leq 0,64029$ ,  $n = 5,34$  at  $\eta_1 = 0,64976$ ,  $n = 6,0-6,17$  – at  $\eta_1 = 0,6802...0,6883$ ,  $n = 6,41$  – at  $\eta_1 = 0,6981$  и  $n = 7,67$  – at  $\eta = 0,7405$ .

Thus, it is possible to calculate the minimum, average and maximum critical size of spherical micro- and nano – particles on the base of the atoms diameter of simple substances and the size of a unit cell of complex substances where we can observe their unique properties.

These results obtained allow determine the possibility of synthesis of micro - and nanoscale geopolymeric composite materials (nonfired mineral binders of nonhydrated type of hardening) with wet grinding of mineral raw and industrial wastes [6].

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#### RESUME

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#### **Critical dimension of small-size particles**

The equation is obtained for the minimum linear container dimension with a granular (disperse) material for control size of sample based on the composite materials according to conditions of demonstration scale (parietal) factor, as well as the expression for the largest, middle and smallest micro- and nanoparticles where their unique properties compared to the massive body are appeared.

Sheets. 6, Table 1, Reference. 6