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Research Article

Nano- and Micro-Sized Discreteness Levels of Substance

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ABSTRACT
The calculation of discreteness level is presented for simple substances and model of sequential arrangement of atoms in clusters as well as clusters into blocks and blocks into crystal formations when its fusion. The separation method of crystal formations into discreteness elements of substance with interface between them to achieve the critical size for clusters, micro- and nanoparticles including in hydration and geopolymer binders is demonstrated.
Keywords: disperse and crystal substances, clusters, Nano- and micro particles, critical size

INTRODUCTION
Main discreteness levels of substance earlier were determined with critical sizes of discreteness elements in the following range (equation (1)), where n = 0, 1, 2, 3…:

$$(3.923\eta_1)^n \cdot d \leq D \leq 3.923^n \eta_1 d \tag{1}$$

The critical sizes of micro- and nanoparticles are included in this range. They can be determined with using the critical packing density, measured easily during the «dry» and «wet» ultimate material grinding as well as calculated using a packing density η_1 for monodisperse large spherical particles with diameters d or known value of η for simple materials, for example, metals with different types of ordered atoms packaging with diameter d.
Dimensions of initial and followings cluster formations in model of atoms sequential arrangement of «clusters in cluster»-type can be determined using a critical packing density of discreteness elements of substance $\eta_{c1} = \eta_1^{(9...15)/3}$ [1] applying by following equations:

$D_1 \leq 60{,}38\ \eta_{c1}\eta_1^k d \ \leq \ 60{,}38\ \eta_1^{n'}\eta_1^k d.$	(2)
$D_2 \leq 60{,}38\eta_{c1} \cdot D_1 \ \leq \ 60{,}38^2\eta_1^{n'}\eta_2^{n'} d.$	(3)
$D_2 \leq 60{,}38\eta_{c1}\eta_i^k \cdot D_1 \ \leq \ 60{,}38^2\eta_1^{n'}\eta_2^{n'}\eta_i^k d.$	(4)
$D_2 \leq 60{,}38\eta_{c1}\eta_1^k \cdot D_1 \ \leq \ 60{,}38^2\eta_1^{n'}\eta_2^{n'}\eta_1^k\eta_2^k \cdot d,$	(5)

where $\eta_i^k = \eta_1^k$ is a critical packing density in case of ordered atoms packaging of discreteness elements; $\eta_i^k = \eta_2^k$ is critical packing density in case of random atoms packaging of discreteness elements: coefficient k = 0 if the fusion of clusters into a big cluster is realized; k = 1 if the clusters separation up to ordered or random packing takes place.

On the base of left part of the equation (1) at n = 0, $\eta_1 = \eta_2 = \eta_i$ the *zero level of substance discreteness takes place*. $\boldsymbol{D_0 = d}$, d is diameter of atom.

First level of substance discreteness.

At η_1 = 0.7405, η_1 = 0.6403 and η_1 = 0.64976, with parameter n' = 5, n' = 10/3 and n' = 3,5 in the equation (2) the first level of discreteness of substance with size of nanoparticles demonstrated unusual change of physical properties can be calculated:

$D_1 \leq 60.38 \cdot 0.7405^5 \cdot 0.3$ nm $\leq$ **4 nm**.

$D_1 \leq 60.38 \cdot 0.64976^{10.5/3} \cdot 0.3$ nm $\leq$ 4 nm.

$D \leq 60.38 \cdot 0.7405^5 \cdot 0.64976 \cdot 0.3$ nm $\leq$ 2.62 nm.

$D \leq 60.38 \cdot 0.7405^{3.5} \cdot 0.64976 \cdot 0.3$ nm $\leq$ 2.60 nm.

Second level of substance discreteness.

$D_2 \leq 60,38^2 \eta_1^{2n'} d \leq 3645 \cdot 0.7405^{10} \cdot 0.3$ nm $\leq$ **54 nm.**

$D_2 \leq 60,38^2 \eta_1^{2n'} \eta_1^k d \leq 3645 \cdot 0.7405^{11} \cdot 0.3$ nm $\leq$ **40 nm.**

$D_2 \leq 60,38^2 \eta_1^{2n'} \eta_2^k d \leq 3645 \cdot 0.7405^{10} \cdot 0.6403 \cdot 0.3$ nm $\leq$ 34.7 nm.

$D_2 \leq 60,38^2 \eta_1^{2n'} \eta_2^k d \leq 3645 \cdot 0.7405^{10} \cdot 0.64976 \cdot 0.3$ nm $\leq$ 35.2 nm.

A size of micro particles at third level of substance discreteness according to the equations (2–5) is in range of 0.256 μm $\leq D_3 \leq$ 0.730 μm; at fourth level it is in range of 2.55 μm $\leq D_4 \leq$ 9.79 μm.

Firth level of substance discreteness.

$D_5 \leq 60,38^5 \eta_1^{5n'} d \leq 8.02334 \cdot 10^8 \cdot 0.7405^{25} \cdot 0.3$ nm $\leq$ **0.132 mm**

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^k d \leq 8.02334 \cdot 10^8 \cdot 0.7405^{26} \cdot 0.3$ nm $\leq$ 0.098 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_2^k d \leq 8.0233 \cdot 10^8 \cdot 0.7405^{25} \cdot 0.6403 \cdot 0.3$ nm $\leq$ 0.085 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^k \eta_2^k d \leq 8.023 \cdot 10^8 \cdot 0.7405^{26} \cdot 0.6403 \cdot 0.3$ nm $\leq$ 0.063 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^{2k} \eta_2^k d \leq 8.02 \cdot 10^8 \cdot 0.7405^{27} \cdot 0.6403 \cdot 0.3$ nm $\leq$ 0.046 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^{3k} \eta_2^k d \leq 8.02 \cdot 10^8 \cdot 0.7405^{28} \cdot 0.6403 \cdot 0.3$ nm $\leq$ 0.034 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^{4k} \eta_2^k d \leq 8.02 \cdot 10^8 \cdot 0.7405^{29} \cdot 0.6403 \cdot 0.3$ nm $\leq$ 0.025 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^{4k} \eta_2^k d \leq 8.02 \cdot 10^8 \cdot 0.7405^{29} \cdot 0.6498 \cdot 0.3$ nm $\leq$ 0.026 mm

$D_5 \leq 60,38^5 \eta_1^{5n'} \eta_1^{5k} d \leq 8.02 \cdot 10^8 \cdot 0.7405^{30} \cdot 0.3$ nm $\leq$ 0.0295 mm

On the base of these calculations we can conclude the following:

– firth level is ultimate sizes of mesh aperture for screen analysis to study disperse materials such as clay particles, fly ash (for geopolymer production) etc.;

– Coulomb interaction of substance discreteness elements (particles) is finished at sixth level with size range of 0.25 mm $\leq D_6 \leq$ 1.77 mm.

A critical packing density of substance discreteness elements $\eta_{c2} = \eta_i^{n''} = 0,1$ [1] is used for calculation the size of Nano- and micro particles at levels and sublevels in the systems of «sequential arrangement»:

$D_1 \leq 60,38\ \eta_{c2} \eta_1^k d \leq 60,38\ \eta_1^{n''} \eta_1^k d.$	(6)
$D_2 \leq 60,38 \eta_{c2} \eta_1^k \cdot D_1 \leq 60,38^2 \eta_1^{n''} \eta_2^{n''} \eta_1^k \eta_2^k d,$	(7)
$D_2 \leq 60,38 \eta_{c2} \cdot D_1 \leq 60,38^2 \eta_1^{n''} \eta_2^{n''} \eta_2^k d,$	(8)

where a coefficient n'' = (18; 18.5; 19; 23)/3 is for ordered arrangements of a substance discreteness elements with a packing density $\eta_1 = 0.6802$; 0.6883; 0.6981; 0.7405, respectively; a coefficient n'' = (13.5; 15; 16)/3 is for random arrangements of a substance discreteness elements with packing density $\eta_1 = 0.60377…0.63716…0.64976$, respectively, where

$$D \le \left(\frac{10\eta_1}{10\eta_{c2}}\right)^3 d \le \left(\frac{\eta_1}{0,1}\right)^3 d \le 1000\eta_1^3 d \le 1000\eta_{c1} d.$$

Equations (7, 8) at $\eta_1 = \eta_2 = \eta_3 ... \eta_n$ are followings:

– without an interface between clusters; $k = 0$, $\eta_1^k = \eta_2^k = 1$:

$$D_2 \ge 3645{,}4 \cdot \eta_1^{2n''} \cdot d. \tag{9}$$

– without an interface between clusters; $k = 1$, $\eta_1^k = \eta_2^k = ... \eta_i$:

$$D_2 \ge 3645{,}4\eta_1^{2n''}\eta_1^k\eta_2^k \ge 3645{,}4\eta_1^{2(n''+1)}d. \tag{10}$$

– with division only a big block or clusters in less ones:

$$D_2 \ge 3645{,}4\eta_1^{2n''}\eta_1^k d \ge 3645{,}4\eta_1^{2n''+1}d, \tag{11}$$

where η_1, η_2 is a packing density of initial discreteness elements (atoms, molecules) in initial clusters and a packing density of initial clusters, respectively;

η_i is a density of dividing of larger discreteness elements in less elements with ordered a packing density for metals $\eta_i = \eta_1$ = 0.7405……0.6802 and random packing density for discrete materials $\eta_i = \eta_2$ = 0.64976; 0.6403; (0.63716; 0.634053).

Coefficient 3645.4 is equal of a wave length value for line spectrum of hydrogen atom λ = 3645.6 Á (limit value of the Balmer series) [2].

First level of substance discreteness.

At η_1=0.7405; n = 23/3 and d=0.3 using the equation (6) the size of second a substance discreteness elements of first level can be calculated by following:

$D_1 \ge 60{,}38 \cdot 0{,}7405^{23/3} \cdot 0{,}3$ nm = **1.8 nm.**

$D_1 \ge 60{,}38 \cdot 0{,}7405^{23/3} \cdot 0{,}64976 \cdot 0{,}3$ nm = 1.18 nm.

On the base of the equations (6–11) the sizes of nanoparticles from second level are followings:

Second level of substance discreteness.

$D_2 \le 3645.4 \cdot 0.7405^{2(23/3)} \cdot 0.3$ nm = **10.9 nm.**

$D_2 \le 3645.4 \cdot 0.7405^{2(23/3+1)} \cdot 0.3$ nm $\le$ 6 nm.

$D_2 \le 3645.4 \cdot 0.7405^{2\cdot 23/3+1} \cdot 0.3$ nm $\le$ 8 nm.

In case of two-stage enclosing of «less clusters into bigger cluster» the presence of interface of smaller clusters reduces a size of larger cluster up to 6 nm and a size of smaller clusters is reduced to 1.2–1.8 nm. The appearance of unusual change in physical properties of smaller and larger clusters as a result of its 2- and 3-layerage (1.18 nm/0.3 nm $\approx$4; 1.81 nm/0.3 nm = 6; 6 nm/1.18 nm $\approx$ 8/1.81 = 4.47 and 10.9 /1.81 = 8/1.18 $\approx$ 6) is possible. In clusters consisting of 3–12 atomic layers the Coulomb interaction is significant: $D_2 = (12\cdot 2+1)\cdot 0.3$ nm = 7.5 nm is a second level of substance discreteness.

Third level of substance discreteness.

It is in interest when production of structures with three-stage enclosing. A size of clusters from third level of structure formation is following:

$D_3 \leq 60{,}38^3 \eta_1^{n''} \eta_2^{n''} \eta_1^k \eta_2^k \cdot D_2 \;\leq\; 60{,}38^3 \eta_1^{n''} \eta_2^{n''} \eta_3^{n''} \eta_1^k \eta_2^k \eta_3^k d \leq 220096 \cdot \eta_1^{3(n''+1)} d.$	(12)
$D_3 \leq 60{,}38 \eta_1^{n''} \cdot D_2 \;\leq\; 220096 \eta_1^{3n''} d \;\leq\; 220096 \eta_1^{3n''} d.$	(13)
$D_3 \leq 60{,}38 \eta_1^{n''} \cdot D_2 \;\leq\; 60{,}38^3 \eta_1^{n''} \eta_2^{n''} \eta_3^{n''} \eta_2^k \eta_3^k d \leq 220096 \cdot \eta_1^{3n''+2} d.$	(14)
$D_3 \leq 60{,}38 \eta_1^{n} \cdot D_2 \;\leq\; 60{,}38^3 \eta_1^{n''} \eta_2^{n''} \eta_3^{n''} \eta_3^k d \;\leq\; 220096 \eta_1^{3n''+2} d.$	(15)

Scale factor 220096 is included into the equation of the gas Avogadro hypothesis [2]. A size of clusters from third level of structure formation of «sequential enclosing» according to the equation (12–15) at η_1=0.7405 and d=0.3 is following:

$D_3 \leq 220096 \eta_1^{3(n''+1)} d$ = 220096·0.7405$^{(3\cdot 6/3)}$ ·0.3 nm = 26.7 nm.

$D_3 \leq 220096 \eta_1^{3n''} \cdot d$ = 220096·0.7405$^{(3\cdot 23/3)}$ ·0.3 nm = **65.8 nm.**

$D_3 \leq 220096 \eta_1^{3n''+2} d$ = 220096·0.7405$^{3\cdot 23/3+2}$ ·0.3 nm = 36.1 nm.

$D_3 \leq 220096 \eta_1^{3n''+1} d$ = 220096·0.7405$^{3\cdot 23/3+1}$ ·0.3 nm = 48.8 nm.

A size of clusters from fourth level of structure formation of «sequential enclosing» at η_1=0.7405 and d = 0.3 nm is in range of 119 nm $\leq D_4 \leq$ 397 nm

Ninth level of substance discreteness.

$D_9 \leq 60{,}38^9 \eta_1^{9(n''+1)} d \;\leq\; 1{,}0662 \cdot 10^{16} \cdot 0{,}7405^{9(23/3+1)} \cdot 0{,}3$ nm $\leq$ 0.21 mm.

$D_9 \leq 60{,}38^9 \eta_1^{9n''} d \;\leq\; 1{,}0662 \cdot 10^{16} \cdot 0{,}7405^{9\cdot 23/3} \cdot 0{,}3$ nm $\leq$ **3.2 mm**.

$D_9 \geq 60{,}38^9 \eta_1^{9n''+8} d \;\leq\; 1{,}0662 \cdot 10^{16} \cdot 0{,}7405^{9\cdot 23/3+8} \cdot 0{,}3$ nm $\leq$ 0.29 m.

On the base of calculated data the Coulomb interaction of particles in disperse raw materials is finished at ninth level of substance discreteness. In this case a particle size is varied in range of 0.21–3.2 mm depending of a size of initial discreteness element and a density of substance. A particle size at tenth level of substance discreteness is in range of 0.95–19 mm and a size of crystal blocks with maximum a packing density is 1.28 mm. A particle size at twelfth level of substance discreteness in structure formations of « sequential enclosing» are in range of 2.6 cm $\leq D_{12} \leq$ 7 m; an average size of blocks is $D_{12} \leq$ 6.3 cm.The calculations demonstrate a size of nanoparticles obtained from metal gas-vapour phase (0.4928$\geq \eta_1 \geq$0.3619) is $D \leq$ 20…5.2 nm and obtained from metal liquid phase (0.6655$\geq \eta_1 \geq$0.4928) it is $D \leq$ 113…31 nm.

Thus, a size of growing spherical metal nanoparticles can be calculated with the equations (2–6) in case of the dominant part of their atoms is placed in surface layers. At n = 1, 2; $\eta_1 = \eta_2 \leq 0.7405$ and d = 0.3 nm this parameter is following:

$D \leq 60.38 \cdot 0.7405^{3\ldots 10/3} \cdot d \leq 24.5\ldots 22.2 d \leq 7.4\ldots 6.7$ nm.

$D \leq (60.38 \cdot 0.7405^{3\ldots 10/3})^2 d \leq (600\ldots 492) \cdot 0.3$ nm $\leq 200\ldots 147$ nm.

$D \leq 60.38 \cdot 0.7405^{3\ldots 10/3} \cdot 60.38 \cdot 0.7405^{2\ldots 7/3} \cdot d \leq 811\ldots 734 d \leq 240\ldots 220$ nm.

A nanoparticle size demonstrated unusual changes of physical properties at first and second level of a substance discreteness are determined with the equations (2–5, 6, 8) at n = 1 and as well as by using the indexes for the first and second a critical packing density of discreteness elements:

$D \leq 60.38 \cdot 0.7405^{5\ldots 23/3} \cdot d \leq 13.4\ldots 6 \cdot d \leq 4.03\ldots 1.81$ nm

$D \leq (60.38 \cdot 0.7405^5)^2 \cdot 0.7405^4 \cdot 0.6403 \cdot d \leq 34.8 \cdot 0.3$ нм ≤ 10.4 nm

$D \leq 60.38{\cdot}0.7405^{5\ldots23/3}\,60.38{\cdot}0.7405^{(5\ldots23/3)-1}{\cdot}d \leq 244\ldots109{\cdot}d \leq 73\ldots32.8$ nm

The calculations demonstrate a packing density for atoms and micro particles in aggregations included in the first free layers around the central atom is not more then 0.64976; in case of 10–12 at least the parameter $\eta_1 \leq 0.74048$.

When dry grinding of grain materials the aggregation of micro particles followed by formation of spherical clusters and loose structure as a result of redistribution of electric charge is observed [3].

As a rough approximation a micro particles size when its aggregation and critical grinding can be determined. Thus, on the base of the equations (2) and (6) at η_1=0.455…0.545…0.64976 for quartz sand with size of discreteness elements in form of silicon oxide tetrahedral is 0.324 nm we can calculate this parameter for:

– a first critical point (when dry grinding) by following:

$$D_{c2} \leq \left(60.38\eta_1\right)^{3\ldots10/3} \cdot d \leq \left(60.38 \cdot 0.55\right)^{3\ldots10/3} \cdot 0.324\text{nm} \leq 12...38\mu\text{m}$$

–a second critical point (when wet grinding) by following:

$$D_{c2} \leq 1000\eta_1^{10/3} \cdot d \leq 1000 \cdot 0.6403^{10/3} \cdot 0.324\text{nm} \leq 73\text{nm}$$

$$D_{c2} \leq 1000\eta_1^{10/3} \cdot d \leq 1000 \cdot 0.545^{10/3} \cdot 0.324\text{nm} \leq 43\text{nm}$$

$$D_{c2} \leq 1000\eta_1^{(9\ldots10)/3} \cdot d \leq 1000 \cdot 0.455^{(9\ldots10)/3} \cdot 0.324\text{nm} \leq 30.5...23.5\text{nm}$$

Experimental value of D_{c2} is 27…30 nm [4].

Thus, aggregation effect of micro particles when dry grinding of quartz sand appears when its size achieves ≈ 25 µm. When wet grinding the average critical size of a sand micro particles is ≈ 40–25 nm.

The equations presented in this study allows calculation critical sizes of Nano-and micro particles as well as their aggregations for some pigments and construction materials such as channel black, ultramarine, titanium dioxide in form of rutile and anatase as well as quartz, calcite in form of chalk stone; calcium hydroxide and quicklime; Portland Cement and reactive silicate and aluminosilicate aggregations in geopolymers. Calculation data are in agreement with experimental and literature data in area of finely and ultra disperse components [5].

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