

Structural Topology of Products Resulting from Dry and Wet Finding of Mineral Raw

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Abstract: The topological analysis of processes and products resulting from dry and wet finding of mineral raw as well as equations described potentials and electrostatic interaction of micro- and nanoparticles in dispersed mineral systems are demonstrated.

Key words: Dispersed materials • Micro- and nanoparticles • Potentials and intermolecular forces

INTRODUCTION

Knowledge about intermolecular forces of micro- and nanoparticles (element of discreteness) of dispersed materials are need for development of theory of synthesis and real production of such geomaterials as fired and non-fired mineral binders and the based composites [1] using the products of mechanoactivation of silicate and aluminosilicate raw [2-5].

Main Part: Mechanical, ultrasonic and other modes of grinding of mineral components for non-fired (cementitious) binders with non-hydration type of hardening and based geomaterials lead to the results and topological states of dispersed systems represented in Fig. 1.

When reducing the particle size the electrical charge at their surface grows. Therefore particle interaction forces are increased and long-range particle repulsive forces work more intensively. Electrical charge on the particles charge distributed spherically. While, dispersed solid phase becomes more unconsolidated and bulk density and packing density of the particles are reduced. It leads to limiting mechanical finding in dry state. At this moment short-range particle attractive forces are equal and higher then their gravity sedimentation and integration of the particles to spherical aggregates with different size takes place. In this case average

particle packing density in dispersed system is critical ($\eta_{1c} \approx 0,2549$). Mechanical energy of grinding is mainly directed to destruction of the aggregate formed and finding of large -size particles.

Particle interaction is possible when $\eta_{1c} \leq \eta_1^3$ where $\eta_1 \leq 0,64029$ – packing density for grains of monodispersed fraction in milled component. Indicator of limiting dry grinding is the equation $\eta_{1c} \leq \eta_1^{1/3}$, thus $\eta_{1c} \leq (0,64029 \dots 0,63096)^{10^3} \leq 0,2625 \dots 0,22625 \dots 0,2512 \dots 0,2154$.

For $\eta_1 = 0, 62634 \dots 0,61875 \dots 0,60377$ we have:
 $\eta_{1c} = (0,62634 \dots 0,61875 \dots 0,60377)^{3 \dots 10^3} = 0,2457 \dots 0, 2102 \dots 0,2369 \dots 0,2018 \dots 0,2201 \dots 0,1860$.

Packing density of macro-, micro- and nanoparticles is determined as $\eta_1, \eta_{1c}, \eta_{2c} = \gamma / \rho$, where γ, ρ – bulk density of granular dispersed material, packed by bumping-down in container with dimension of (10...15) d_1 at least and its density respectively.

Ring mills, ball mills as well as roll and pendular mills are usually used and for ultra fine milling – jar and jet-type mills. Fineness degree i in this case is $I=d/d_2 \approx 100-10$ for grains of initial raw materials $d_1= 2$ mm and $d_2=0,1$ mm, where d_1 and d_2 are average particle size before and after milling [6].

Wet grinding in ball and colloidal mills allows increasing fineness degree in several times ($i=10$) up to colloidal state of dispersed system ($d_2 \approx 10 \dots 100$ nm) [6],

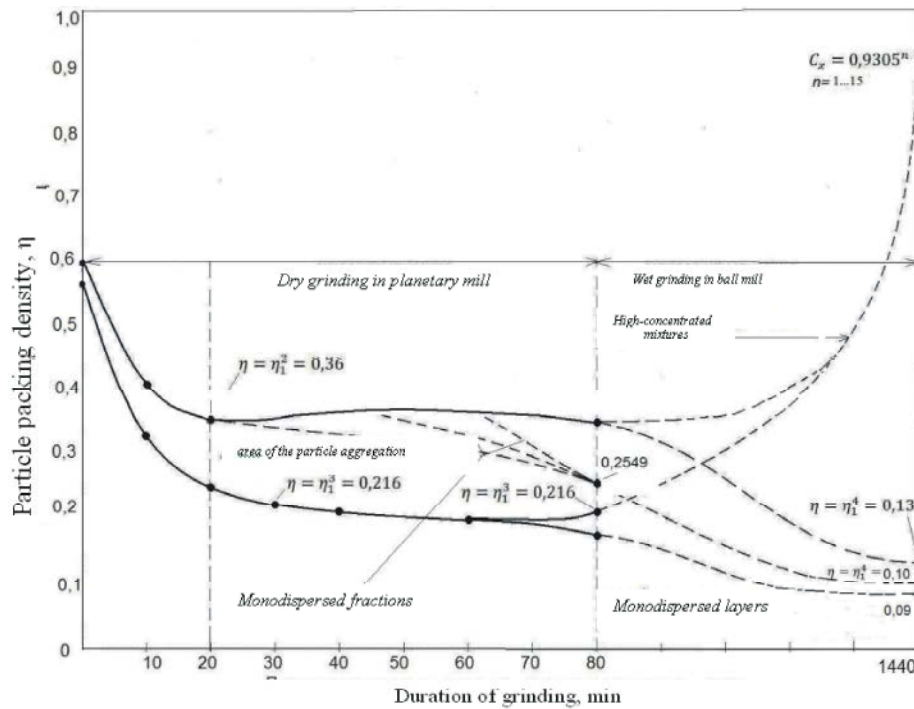


Fig. 1: Kinetics of quartz sand grinding, $d_1 \leq 0,315$ mm

where we can observe following:

- Partial charge shielding at the particle surface by dipole molecules of dispersive medium and forming of double-electric layer;
- The particle disaggregation due to certain longness of diffusion part with the same charge that leads to repulsive interaction as well as intensity reduction of coagulation for particles of dispersed phase and saving its high dispersity;
- Partial penetration of positive ion into diffusion layer in light-basic media when high concentration of solid phase as well as the layer thinning due to compensation of nuclear charge resulting to reducing of the system aggregative stability. For particle coagulation reduction it should to add surfactants, to change interfacial tension as well as stabilizers, plasticizers and others admixtures;
- Dissipation of micro- and nanoparticles of grinded silicates and aluminosilicates in light-basic media up to monomer and oligomers of hydrosilicic acids, silicates and aluminates with subsequent formation of silicagel, alumogel and sols. Dispersive phase removal leads to forming of coagulation, coagulation-condensation and coagulation-crystallization structures [7].

Wet ultra fine grinding allows production of solid polydispersed phase with high-density packaging ($\sigma_n \geq 0,65$) due to dosage of 10–20 % of initial raw during milling process as well as monodispersed particles with critical packing density ($\eta_{2c} \leq 0,1$ equivalent to dry powder) (Fig. 1).

Compressive strength of solid sol-gel silicate and aluminosilicate products is less then silicate glass and quartz ($R_{comp} \approx 500-2000$ MPa). Others significant disadvantages of the silica gels and alumogels are low alkali resistance, low water resistance and high sorption. When improving of those properties by introduction of metallic oxides of varied valence the based non-fired mineral cementitious materials and composites can be used for production of construction and special materials and structures.

It should be noted the above topological parameters of solid dispersed phase obtained by dry and wet grinding come out of principle of structural topology of granulated and dispersed systems as well as particle-size distribution when their high packing density in mixture [8-10]:

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

where η_i , d_i – packing density (part by volume) and dimension of identical discreteness elements of substance (atoms or molecules, particles);

d_n – average dimension of gradually less discreteness elements (particles); m – system class for particle-size distribution e.g. class of discontinuity of their average sizes, $0 \leq m \leq 12 \dots 16 \dots$; p – particle dissociation degree ($p \leq 6$) or overcoating degree ($p \geq 6$) of discreteness elements (atoms, spheres etc.); $n = 1, 2, 3 \dots$ – order number of particles with subsequently less dimension, which fill free space (e.g. formed pores of certain dimension) in arbitrary packing of grains with largest initial fraction.

According to (1), when $d_n = d_3$, where d_n is average particle size of fine fraction, $m = 3, n = 2, p = 0, 1, 2, 3$ it can be refined range of critical particle packing densities, including theoretical one ($p = 6$) of random packing of dimensionally identical spherical solids:

$$\eta_{pc} = \frac{1}{10(\sqrt{3}-1)^p} \quad (2)$$

where p is index of distance change between geometric centers of two neighboring monodispersed particles, $p < 6$ means particle disaggregation, $p > 6$ means approach of the particle (spheres) centers with their overcoating.

Results of calculation η_{pc} depending on value of p :

p	0	1	2	3	4	5	6
η_{pc}	0,1	0,1366	0,1866	0,2549	0,3482	0,4757	0,64976

Structural topology of discrete systems provides follow results of η_{pc} [6]:

$$\eta_c = \eta_i^n \text{ где } n = (9 \dots 16)/3, \quad (3)$$

where $n = 3$ is for weakly interacting particles of dispersed materials when $0,60377 \leq \eta_i \leq 0,6403$, $n = (10 \dots 15)/3$ is for interacting particles of dispersed solids during dry and wet grinding, where particle packing density of virgin granulated raw $\eta_i \leq 0,6403$ and limiting critical packing densities are followings:

$$\eta_c = 0,6403^{(10 \dots 15)/3} = 0,22625 \dots 0,1076,$$

$n = (10 \dots 16)/3$ is for atoms of discrete systems (inert gas and elementary systems in critical point and in λ – point) [11], where $0,64976 \leq \eta_i \leq 0,7405$.

Table 1: Values, calculated from equation (4), when $k_1 = 0,9758$

Value n	$C_3 \eta_i^5$	η_i	$C_3 = 0,2539 \eta_i^5$
$n = -1$	0,31623	0,626342	0,1
$n = 0$	0,1	0,630957	0,101479
$n = 1$	0,102477	0,634053	0,102477
$n = 2$	0,105026	0,6371635	0,103485
$n = 3$	0,107618	0,6402894	0,104503
$n = 6$	0,115815	0,64976	0,107618

If $\eta_i \geq 0,64976$, then $\eta_c = 0,64976^{10/3 \dots 16/3} = 0,2376 \dots 0,100$.

For each value $\eta_i \leq 0,7405$ we can obtain $\eta_c = 0,7405^{11/3 \dots 16/3} = 0,3323 \dots 0,2014$.

Experimental studies of D. Scott [12] devoted packing density of steel and lead rolls (when friction effect) in large spherical bottles when shakedown process and random feeling are shown, that:

$$\eta_i = 0,64 - 0,33\sqrt[3]{N}, \quad \eta_i = 0,60 - 0,37\sqrt[3]{N},$$

where N is total number of rolls in the bottle, when $N \rightarrow \infty$ $\eta_i = 0,64$ и $\eta_i = 0,60$.

Range of classical values of ζ_1 is defined from minimum of value of $\eta_{2c} = 0,1$ that is index of range of particle critical packing density $C_3 = 0,1$ (Table 1) as well as the largest value of experimental random packing density of spherical particles $\eta_i = 0,6402894$:

$$C_3 = \left(0,1/k_i^n\right)^{1/5} \quad (4)$$

where $k_1 = 0,634053/0,64976 = 0,9758269$, $k_2 = 0,634053/0,64029 = 0,9902597$.

Range of intermediate value ζ_1 for designing of schemes, presented levels of phase and topological states (PTS) for dispersed systems with random particle packing (Fig. 2) as well as experimental value of $\eta_i = 0,60$ can be calculated according to following equation:

$$\eta_i = \eta_{i\max} k_i^{n/2},$$

$$\eta_i = 0,6497595 \cdot 0,975827^n \cdot 0,618726; 0,6037693,$$

where $n = 1, 2, 3 \dots$

$$\eta_i = 0,640289 \cdot 0,99026^{n/2}; 0,634053; 0,630957; 0,627877; 0,624812; 0,62176; 0,618726; 0,615705; 0,61270; 0,609710; 0,60673; 0,6037693$$

Schemes, presented levels of PTS for dispersed systems consists of three followings sublevels:

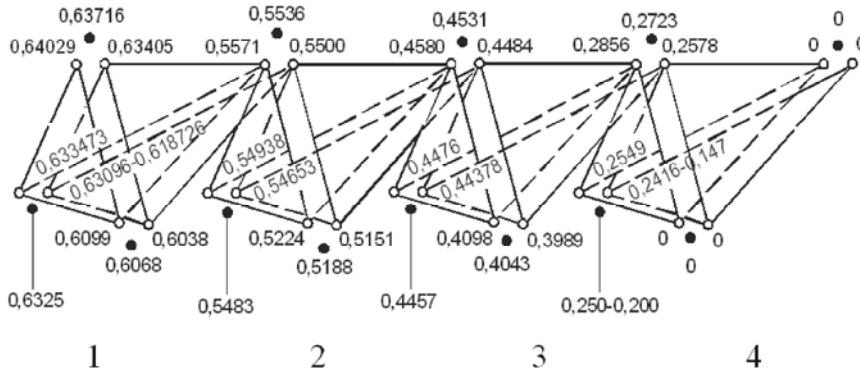


Fig. 2: Standard scheme of basic levels of PTS for disordered condensed discrete systems

- Top level presents homogeneous compact topological state;
- Middle level presents heterogeneous compact state;
- Lowest level presents homogeneous friable state.

Subsequent values at each sublevel are calculated according to the recurrence equation [8]:

$$\eta = \eta_l \left[1 - \frac{1}{3k \ln(120,754\eta_l^5)} \right], \quad (5)$$

where η_l , η are packing density (part by volume) of discreteness elements for substance in virgin and joint state of the system;

k is coefficient of discreteness element interaction: for interacting elements $k \neq 1$ and for noninteracting ones $k = 1$.

Schemes, presented levels of PTS (Fig. 2) allow determination followings topological states of dispersed systems:

- The 1st is pseudo-solid granulated one;
- The 2nd dispersed one;
- The 3rd pseudo-liquid;
- The 4th critical one.

It can be demonstrated, the particle interaction of in dispersed phase described well by the potential 2-4, that can be represented as [11]:

$$\varphi = \frac{n}{m-n} \varepsilon \left[\left(\frac{d_0}{r} \right)^m - \frac{m}{n} \left(\frac{d_0}{r} \right)^n \right] = \varepsilon \left[\left(\frac{d_0}{r} \right)^4 - 2 \left(\frac{d_0}{r} \right)^2 \right], \quad (6)$$

where $m > n$ and $m = 4, n = 2$ for the potential 2-4;

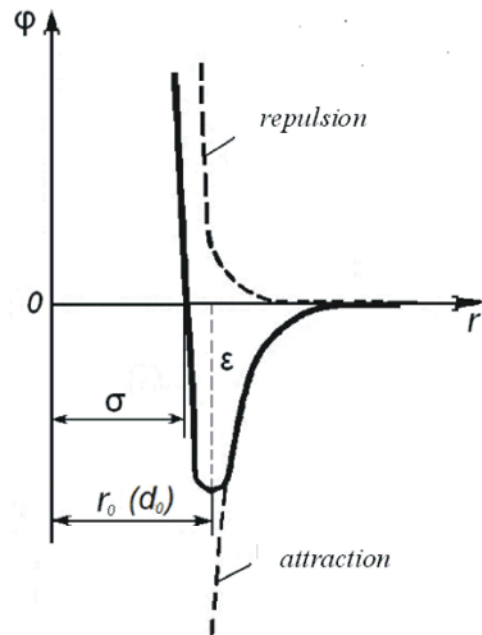


Fig. 3: Curves of influence of potential energy of interaction, attraction and repulsion of particles on distance between these ones and their parameters

d_0 is distance between the particles, determining the minimum position of potential energy of the particles interaction φ on the horizontal axis of potential curve (Fig. 3), r is current distance between the particles on the horizontal axis;

ε is minimum value of potential interaction energy φ for the particles on the potential curve (so-termed scale parameter in interaction).

The interaction potentials can be written with ε and σ parameters in general terms:

$$\varphi = \frac{n\varepsilon}{m-n} \left(\frac{m}{n} \right)^{\frac{m}{m-n}} \left[\left(\frac{\sigma}{r} \right)^m - \left(\frac{\sigma}{r} \right)^n \right],$$

Then for the potential 2–4 we have following:

$$\varphi = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^4 - \left(\frac{\sigma}{r} \right)^2 \right] = 4\varepsilon \eta^{2/3} (\eta^{2/3} - 1) \quad (7)$$

where σ is distance between contacted particles, attributed their diameter, is determined by the criteria of $r = \sigma$ и $\varphi(\sigma) = 0$:

$$\left(\frac{d_0}{\sigma} \right)^4 - \left(\frac{d_0}{\sigma} \right)^2 = 0.$$

According to this in equation it can be obtained following: $\frac{1}{d_0 = 2^2 \sigma}$ Application of this formula for d_0 in

equation (6) allows determination of the potential (7) over ε and σ parameters.

Electric interaction forces (particle attraction and repulsion) are determined by differential coefficient of $f = -d\varphi/dr$ (symbol “-” is deleted):

$$f = 8\varepsilon \left[\frac{\sigma^2}{r^3} - 2 \frac{\sigma^4}{r^5} \right] = 8\varepsilon \frac{\eta}{\sigma} (1 - 2\eta^{2/3}), \quad (8)$$

when $r > r_0$ interaction forces are negative (the particle attraction) and when $r < r_0$ interaction forces are positive (the particle repulsion). In position of $r = r_0$ and $f(r) = 0$ particle attraction forces are balanced by particle repulsion ones. Particle attraction forces are in maximum when $r = r_{00}$, ($d^2\varphi/dr^2 = 0$). Using equations (6) – (8) we can obtain following:

$$r_0 = \left(\frac{m}{n} \right)^{\frac{1}{m-n}} = 2^{1/2} \sigma, \quad r_{00} = \left[\frac{m(m+1)}{n(n+1)} \right]^{\frac{1}{m-n}} = (10/3)^{\frac{1}{2}} \sigma. \quad (9)$$

After modification of (9) to: $2^{1/2} \sigma / r = 1$ и $(10/3)^{1/2} \sigma / r = 1$.

As particle packing density is $\eta = (\sigma/r)^3$, then after cubing of these equations and using of η_1 for monodispersed phase besides 1, we can obtain the following:

$$\eta_{1c} = \eta_1 / \alpha_1^3 = 0,64029 / 2^{3/2} = 0,22638,$$

$$\eta_{2c} = \eta_1 / \alpha_2^3 = 0,64029 / (10/3)^{3/2} = 0,1052.$$

Structural topology [8] provides good correlation with experimental data:

$$\eta_{1c} = \eta_1 \alpha_1^3 = 0,64029 / 2^{3/2} = 0,22638,$$

$$\eta_{2c} = \eta_1 / \alpha_2^3 = 0,64029 / (10/3)^{3/2} = 0,1052.$$

The potential 2-4 is fully applicable for description of the particle interaction in metallic powders with atomic packing density in particles of 0,7405.

Critical particle packing density in powdery state is equal $\eta_{1c} = 0,7405^{(15...16)^3} = 0,2226...0,2014$. Then maximal particle packing density in powder depending on its size will be equal:

$$\eta_1 = (0,2226...0,2014) \cdot 2^{3/2} = 0,6297...0,5697$$

while, second critical packing density for fine-dispersed metallic particles will be equal: $\eta_{2c} = (0,6297...0,5697) / (10/3)^{3/2} = 0,1035...0,0936$

The above critical packing densities $\eta_{2c} = 0,1366$ and $\eta_{2c} = 0,1866$ are attributed to polymers, those can be described well by the potentials 2–5 and 3–5. For these potentials we can easily obtain relevant parameters (according to (9)):

$$r_0 = (5/2)^{1/3} \cdot \sigma, \quad \alpha^3 = 5/2; \quad r_{00} = 5^{1/3}, \quad \alpha = 5; \quad (10)$$

$$r_0 = (5/3)^{1/2} \cdot \sigma, \quad \alpha^3 = (5/3)^{3/2}; \quad r_{00} = (5/2)^{1/2} \cdot \sigma, \quad \alpha^3 = (5/2)^{3/2}. \quad (11)$$

Using equations (9) and (10), it is possible to calculate the value of packing density for macromolecules in amorphous polymers $\eta_1 = 0,1366 \cdot \alpha^3 = 0,1366 \cdot 5 = 0,683$. Experimentally obtained result is $\eta_1 = 0,681$ [13]. According to (5) for polymers, zones with amorphous phase have $\eta_{1min} = 0,6042$.

Using equations (10) and (11) and the term, that $\eta_{1c} = 0,1866$, packing density for macromolecules in linear amorphous polymers near the absolute zero is following:

$$\eta_1 = 0,1866 / (5/2)^{3/2} = 0,7376$$

More correct result can be defined, when $\eta_{1cp} = 0,74048$: of $\eta_1 = 0,7404805 \cdot 2 - 0,749224 = 0,73174$

Temperature extrapolation provides following: $\eta_1 = 0,731$ [13]. The same values of η_1 have crystals with hexagonal packing for atoms in position of average among η_1 values in supercooling position and hot pot, where:

$$\eta_1 = (0,749224 \cdot 0,726235)^{1/2} = 0,7376, \quad or$$

$$\eta_1 = \left(0,633473^{10/3} \right)^{1/5} = 0,7376,$$

where $\eta_1 = 0,726235$ and $\eta_1 = 0,749224$ is packing density for metallic atoms with face-centered lattice in supercooling position and hot pot [8].

Thus, mathematical apparatus technique of structural topology allows determination of topological state of dispersed materials, produced during grinding of granulated mineral raw up to formation of nanoparticles. It also allows estimation of limiting dimension of micro- and nanoparticles when dry and wet millings of mineral raw according to their packing density $\eta_{lc} \leq 0,2549$ and $\eta_{2c} \leq 0,1$ respectively.

When topological (and phase) transformation during grinding (or melting) of substance to next state of discrete system it is possible to identify a Grüneisen parameters from equation (1) as $\Delta\eta = \eta_1 - \eta$ and informational entropy change as $\Delta S = k_B \ln \Delta\eta$. Thus, for $\eta_1 = 0,64029\dots\dots 0,64976$:

$$\Delta S = k_B \ln \left[\frac{\eta_1}{3 \ln(120,75\eta_1^3)} \right] = k_B \ln \left\{ \frac{0,6403\dots 0,64976}{3 \ln[120,754(0,6403\dots 0,64976)^3]} \right\} \approx -2,5k_B,$$

where k_B – the Boltzmann constant.

CONCLUSION

Obtained calculated value ΔS has good correlation with experimental $\Delta S = -2,5k_B$.

The results, obtained in this study will make a contribution to development of up-to-date material science on products of dry and wet grinding of mineral raw, as well as theoretical and practical aspects of based geo-materials production.

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