

UDC 546.621

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Properties and behavior of nanoparticles

The methods of obtaining nanomaterials have been described, and the conditions for the formation of nanoparticles of a given size have been assessed. It has been shown that the surface energy of the nano-sized particles, due to a large portion of surface atoms, is significantly greater than the surface energy of the microparticles resulting in the non-equilibrium state of the former with the possibility to self-organize forming, in particular, strong and wear-resistant cladding films from the metallic nanoparticles on the friction surfaces. To explain the interaction of the nanoparticles, which are at the boundary of the quantum and classical states, with the environment, the main provisions of quantum mechanics have been used. The mutual interaction between the bare nanoparticles and between the nanoparticle and a surface, separated by the environment, has been considered. It has been shown that without the stabilization with surfactants, metallic nanoparticles will aggregate; in turn, the nature of the interaction between the nanoparticles with the solid substrates is determined by their dielectric constants. The paper presents an overview of the development of the nanotechnology industry, indicates the commercial demand for nanomaterials, marks the countries that are leaders in the production of nanomaterials, and lists the main elements used for the production of metallic nanopowders.

Keywords: *production methods, surface energy, non-equilibrium, self-organization, quantum behavior.*

Introduction. When the size of the substance changes along the one, two or three coordinates to the size of a nanometer scale, a new quality, new properties and characteristics appear [1]. Materials, containing structural elements whose dimensions do not exceed 100 nm in at least one dimension, are classified as nanomaterials.

In 1959, R. F. Feynman, who is considered the founder of nanotechnology, noted [2], “I am sure that by learning to regulate and control structures at the atomic level, we will obtain materials with completely unexpected properties and discover completely unusual effects.” In 1974, the Japanese physicist N. Taniguchi introduced the term “nanotechnology,” proposing to describe mechanisms with a size smaller than one micron. Physicists and chemists began to research the methods of obtaining nanomaterials and their special properties, and the achieved scientific results were awarded six times with Nobel prizes.

For all nanoparticles, a change in fundamental physical parameters is observed: a significant decrease in the melting temperature [3], an increase in strength [4] and a simultaneous increase in strength and ductility [5]. Compared to traditional materials, nanomaterials are characterized [1] by increased hardness (2...7 times), strength limit (1.5...8 times) and yield strength (2...3 times).

When silicon oxide particles with a diameter of 16 nm are applied to the surface, a superhydrophobic material is formed [6] with high wetting angles (up to 170°) and a small angle of inclination of the surface to the horizon (<5°). The use of nanomaterials in solar cells allows to obtain up to 80% of the energy of sunlight while existing solar cells can only use 20% [7]. The addition of nanoparticles to liquids improves thermal conductivity [8] and heat transfer [9]. Additive manufacturing (3D printing) provides new opportunities in the manufacture of ultralight components and machine parts using nanopowders [10]. Significant achievements in optics, electronics and computer technology are determined by the use of nanoparticles [11]. It is assumed that by the middle of the 21st century, nanotechnology will have been used in all spheres of human activity.

Problem statement. The work examines the features of the behavior of nanoparticles, determined by their production methods and structure; the mechanism of interaction between nanoparticles and the environment; the structure of production and the cost of nanomaterials.

1. Production of nanomaterials. All methods of obtaining nanomaterials can be conditionally divided into two large groups [1]: “bottom-up,” when nanomaterials are formed from individual atoms, and “top-down,” which act by cutting off excess material.

The physical and chemical methods of the first group provide for obtaining objects from individual atoms through the formation of particle nucleation centres. High-energy methods (plasma excitation, laser radiation, voltaic arc or thermal exposure [12]) achieve high temperatures and ensure the transition of substances into a gaseous state followed by condensation of products. Evaporation and condensation can occur in a vacuum, in inert gas or reactive gas.

At the heart of these methods is obtaining a critical nucleus and creating conditions that prevent the growth of the particle, or its removal from the formation zone. The formation of the nucleus is determined by the energy balance [13]:

1) increase in Gibbs potential of a system due to the formation of the surface s of the nucleus

$$\Delta G_s = \sigma \cdot s, \quad (1)$$

where σ is specific surface energy;

2) decrease in Gibbs potential of a system for an account of the combination of molecules into a phase with a lower chemical potential accompanied by the release of the heat of crystallization

$$\Delta G_v = (H_2 - H_1) - T(S_2 - S_1). \quad (2)$$

Changes in enthalpy and entropy are determined by the formulas [13]

$$H_2 - H_1 = -qV, \quad S_2 - S_1 = -\frac{qV}{T_k}, \quad T = T_k - \Delta T, \quad (3)$$

where q is the heat of fusion of a unit volume, V is the nucleus volume, T_k is the temperature of formation of the phase, and ΔT is the amount of supercooling.

From (2) we get,

$$\Delta G_V = -qV \frac{\Delta T}{T_k}. \quad (4)$$

Therefore, the total change in the Gibbs potential due to the fluctuating formation of the nucleus will be

$$\Delta G = \sigma s - q \frac{\Delta T}{T_k} V; \quad (5)$$

in the case of a spherical nucleus of a radius r , we obtain

$$\Delta G = 4\pi r^2 \sigma - q \frac{\Delta T}{T_k} \frac{4}{3} \pi r^3. \quad (6)$$

The critical size of the nucleus is determined by the condition $d(\Delta G)/dr = 0$, which gives

$$r_{cr} = \frac{2\sigma T_k}{q\Delta T}. \quad (7)$$

The resulting expression defines the critical nucleus: all nuclei of size $r > r_{cr}$ are unstable and disappear, and all nuclei of a radius $r > r_{cr}$ will continue to grow, because their growth process leads to a decrease in energy. We should note that the size of the critical nucleus decreases with an increase in supercooling ΔT .

Representative values for most materials are $\sigma \sim 0.1 \text{ J/m}^2$ and $q \sim 10^5 \text{ J/m}^3$, then as follows from formula (7), to create a critical nucleus with a radius $r_{cr} = 5\text{-}10 \text{ nm}$, it is necessary to create a significant supercooling $\Delta T \sim (0.1\text{-}0.2)T_k$, which is 10-20% of the evaporation temperature of the substance. The created critical nucleus begins to grow, and by regulating the processes of growth and removal of particles from the zone of formation, nanoparticles of a given size are obtained[14].

The widespread chemical sol-gel method is based on the quick introduction of the second reagent into the heated mixture of the primary reagent. As a result of the chemical reaction, a saturated solution of the compound is formed; nucleation (the formation of a nucleus) occurs quickly and nucleus growth begins. The size of the obtained nanoparticles is determined by the competition of the processes of nucleation and growth of the formed product.

Another method is based on the grinding of the material to the nanoscale level as a result of large deformations. The essence of this method is repeated intense plastic deformation in different directions, which leads to crushing into nanoelements [5]. For this, mills, hydrodynamic cavitation, conductor explosion, etc. are used.

Therefore, nanoparticles obtained by various methods are not in equilibrium, which is determined both by the non-equilibrium process of formation and by methods of preventing further growth. In addition, they have excess surface energy, a significant proportion of surface atoms, and a concentration of defects in the crystal structure, which determine their special properties and behavior.

2. Properties of nanoparticles.

2.1. The role of the surface. In ordinary macroscopic bodies, we deal in everyday life, the number of molecules on the surface is much smaller compared to their number in the volume. Therefore, all physical properties of macroscopic bodies are

determined by the features in the volume; for nanoparticles, the relative portion of surface atoms is significant.

Atoms near the surface differ geometrically and physically from the positions within the crystal, and the composition at the surface layer does not correspond to the stoichiometric composition of the chemical compound [15]. Therefore, a change in structure, breaking of translational symmetry, a change in the coordination number, the appearance of broken (unsaturated) bonds, point defects and dislocations are observed on the surface of crystalline bodies. The mobility of surface atoms and the ability to adsorb with phases that are in contact with the surface change significantly [16]. Restoration of the saturated bonds for surface atoms is possible due to the adsorption of atoms from the environment [17].

Thus, when the particle size reduces, the activity of the substance in the solid state and the speed of physicochemical interaction with the surrounding medium increase sharply due to the rise of the portion of atoms on the surface. The speed of such interaction is always proportional to the area of the surface.

In addition to the above, the electronic structure changes – donor or acceptor centres appear near the surface [17]. The presence of surface centres can lead to the charging of the surface, which also affects the interaction of nanoparticles with the environment.

We will evaluate [18] the portion of atoms (molecules) located on the surface of a spherical particle with a diameter d to the total number of atoms in the volume:

$$\frac{\Delta V}{V} = \left[\frac{\pi}{6} d^3 - \frac{\pi}{6} (d - 2\delta)^3 \right] \left(\frac{\pi}{6} d^3 \right)^{-1} \approx \frac{6\delta}{d}, \quad (8)$$

where δ is the thickness of the surface layer of a particle.

The thickness of the surface layer of nanoparticles δ is determined by 3-4 monolayers and has a value of ~ 0.5 nm. Then, for spherical particles of 50, 20 and 10 nm, the portion of surface atoms is 6%, 15% and 30%, respectively. Therefore, it is impossible to explain the behavior of nanoparticles without taking into account the role of surface atoms. An increase in the share of surface atoms (molecules) leads to the active interaction of particles located on the surface of a nanoparticle with the environment, playing a decisive role in the formation of their unusual physical and mechanical properties [19].

A decrease in particle size leads to an increase in the total surface energy and, hence, to a non-equilibrium state of nanoparticles. Simple calculations [19] show that when a spherical particle is broken into N small particles while maintaining the same volume $V = Nv$, we get

$$\frac{4}{3}\pi R^3 = N \frac{4}{3}\pi r^3 \quad (9)$$

where R is the radius of the initial particle and r is the radius of the formed particles. From this, we can find the ratio between the radii

$$r = N^{-\frac{1}{3}} R. \quad (10)$$

Since the surface energy is proportional to the surface area, the ratio of the generated surface energy to the initial one gives

$$\frac{w_r}{w_R} = \frac{N\sigma r^2}{\sigma R^2} = N \left(\frac{r}{R} \right)^2, \quad (11)$$

and, taking into account (10), we have

$$\frac{w_r}{w_R} = N \cdot N^{-\frac{2}{3}} = N^{\frac{1}{3}} = \frac{R}{r}. \quad (12)$$

Thus, the surface energy increases as many times as the particle size reduces, i.e., when micron-sized particles are replaced by nano-sized ones, the surface energy increases a thousand times, and the excess surface energy causes their non-equilibrium state. Hence, the thermodynamics of non-equilibrium processes [20] has to be applied to explain the behavior of nanoparticles.

Surface atoms form fewer bonds, and therefore their binding energy is lower compared to atoms in bulk. X-ray and neutron imaging studies of nanocrystalline Pd established [21] that the density of the substance at the interface is 20-40% less than the density of ordinary Pd, and the coordination number of an atom is less than the coordination number of an atom in an ordinary crystal.

The authors [21] measured the diffusion of tin in copper at a temperature of 1000⁰C and established the ratio between the volume diffusion coefficient D_v and the boundary diffusion coefficient D_s :

$$D_s/D_v = 8 \cdot 10^5. \quad (13)$$

This ratio increases when the temperature lowers. Therefore, surface atoms have a significantly higher diffusion coefficient, which greatly speeds up the process of the embedding of surface atoms of a nanoparticle into the body upon contact.

2.2. Quantum-mechanical behavior of nanoparticles. On a dimensional scale, nanoparticles are on the boundary of the quantum [22] and classical states, and this metastable and structurally heterogeneous state determines a unique complex of their physicochemical and mechanical properties. To understand their behavior, it is necessary to take into account the features that distinguish the behavior of classical and quantum particles [23]:

1. Heisenberg's uncertainty principle. The accuracy limit for the simultaneous determination of a pair of quantities described by non-commuting operators is limited. By measuring, for example, the coordinate and momentum of a particle, we get

$$\Delta x \cdot \Delta P > h, \quad (14)$$

where Δx is the uncertainty (measurement error) of the microparticle's spatial coordinate, ΔP is the uncertainty of the particle's momentum and h is Planck's constant. For a classical particle, both the coordinate and the momentum can be measured accurately (within the accuracy of the method).

In addition to coordinate and momentum, non-commuting pairs of operators include, for example, current and voltage, electric field intensity and magnetic induction, etc.

2. Wave-particle duality. The same representative of the microworld exhibits both wave and particle properties, therefore wave-particle duality is a general feature

of the behavior of a quantum particle. The propagation of a de Broglie wave is associated with the movement of the particle.

The de Broglie wavelength λ is determined by the values characterizing the particle

$$\lambda = \frac{h}{P} = \frac{h}{\sqrt{2mkT}}. \quad (15)$$

where P is the momentum of the particle, h is Planck's constant, m and T are the mass of the particle and its absolute temperature, respectively.

Estimation of the de Broglie wavelength for an atom at room temperature according to equation (15) gives a representative value

$$\lambda = 0.2 - 0.1 \text{ nm},$$

that is, the atoms located on the surface of nanoparticles behave like classical particles, and their motion is described by the equations of classical mechanics.

For electrons in metals, the de Broglie wavelength has a typical value of 1.0 nm. That is, the quantum nature of electron behavior can be exhibited for small particles or in thin films. For nanoparticles of semimetals (Bi) and semiconductors (ZnSb) [20], the effective mass of electrons $m \sim 0.01m_0$ and energy $E \sim 0.1 \text{ eV}$, then the value of the de Broglie wavelength is about 10 nm; that is, the manifestation of quantum effects for electrons of this type of nanomaterials is significant. For electrons of surface atoms, this estimate gives

$$\lambda = 5 - 10 \text{ nm}.$$

Therefore, in most cases quantum mechanics has to be used to explain the electron behavior in nanoparticles.

3. Probabilistic nature. Quantum mechanics only predicts the probability of processes. Thus, the probability of finding a microparticle of mass m in the volume dV surrounding the point \vec{r} at a certain time t is determined by the squared absolute value of its wave function $|\psi_{(r,t)}|^2$, which is found from the Schrödinger steady-state equation [22]

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + u_{(x,y,z)} \psi = E \psi; \quad (16)$$

here E is the energy of the particle and $u_{(x,y,z)}$ is the potential energy. Thus, in the quantum world, a particle's movement is characterized not by the trajectory but by the most probable trajectory.

The structural and electronic properties of surface atoms and molecules, including adsorbed ones, are described by the quantum-mechanical method of molecular orbitals. Molecular orbitals are obtained by linear combinations of atomic wave functions, which are found by solving the Schrödinger equation (16).

In the one-electron approximation, wave functions are found as a sum of radial and angular components [22]

$$\Psi_{nlm(r,\theta,\phi)} = R_{nl(r)} \cdot Y_{lm(\theta,\phi)}. \quad (17)$$

where $R_{nl(r)}$ are radial functions, $Y_{lm(\theta,\phi)}$ are spherical functions, the type of which depends on the quantum numbers n and l and characterizes the electron density distribution.

The wave function of the system of k electrons $\Psi_{(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_k)}$ is approximated by the product of k individual functions (9)

$$\Psi_{(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_k)} = \prod_{i=1}^k \Psi_{nlm_i} \quad (18)$$

in such a way, the electron density of the cluster is calculated.

The positions of surface atoms are different due to unsaturated electron bonds compared to nanoparticle atoms in bulk. Therefore, in the case of the surface of a nanoparticle, the orbitals can protrude beyond the object and bond with the environment. Due to the interaction with the environment, the orbitals are deformed and their energy changes. When the energy of the interacting orbital reaches the Fermi level [17] (the maximum energy of an electron in metal at $T = 0$), the electron moves to a vacancy in the metal zone upon contact. As a result, there is a Coulomb interaction between the nanoparticle and the metal. Due to attractive forces, configurations with a strong covalent or ionic bond or a weak van der Waals bond are formed [17].

4. Quantum states. The Schrödinger equation has a solution for the entire variable range if the eigenvalues of E belong to the discrete spectrum, i.e. a quantum particle can be in stable states which correspond to discrete energy values. It should be noted that a classical particle can have an arbitrary energy value not exceeding mc^2 .

Discrete values also take other physical quantities that characterize a quantum particle [22] and fundamentally distinguish it from a classical one. The transition of a quantum particle to other states occurs in a jump. If the external disturbance is not intense enough, the system will not change its state; the state can be changed only if the disturbance has sufficient intensity.

5. Tunnel effect. The probability of a quantum particle with an energy E to penetrate the region $[x_1, x_2]$ where the value of the potential energy $u(x) > E$ is determined from the expression

$$w = D = D_0 \cdot \exp \left[-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(u(x) - E)} \cdot dx \right] \quad (19)$$

As follows from the formula, when $E < u$, we get $w > 0$ (a quantum particle has a chance to pass through the barrier if its energy is less than the maximum potential energy; for a classical particle in this case $w = 0$); when $E > u$, $w < 1$ (for a classical particle in this case $w = 1$).

Examples of tunneling are the conductivity of points of the mechanical joint of conductors covered with a dielectric oxide film, the movement of dislocations in crystals [17], etc.

Therefore, electron tunneling from nanoparticles during interaction with the environment is quite probable. When electrons are tunneled from the surface of nanoparticles, an additional Coulomb interaction occurs between the nanoparticle and the environment accelerating the embedding of nanoparticle atoms [23].

Indeed, the formation of strong and ductile films on friction pairs has been observed [24] when nanosized powders of Cu, Ag, Bi, In, Sn and Pb are added to lubricants increasing the service life of friction pairs.

3. Self-organization. According to the laws of classical thermodynamics, the evolution of a physical system should lead to an equilibrium state, which corresponds to the complete absence of ordering. For an isolated system

$$dS / dt \geq 0, \quad (20)$$

and in the equilibrium state, the entropy S reaches a maximum. Therefore, the spontaneous formation of an ordered structure is not possible at the macroscopic level in an isolated system, because this process corresponds to a decrease in entropy [13].

If the system, which was in stable equilibrium, is affected by external factors that bring it out of this state, then according to Le Chatelier's principle [13], processes that occur in the system try to counteract changes caused by external action. With minor deviations from the equilibrium position, according to Onsager's hypothesis [25], there is a linear relationship between the emerging flows J and driving forces X_i

$$J = \sum_k L_{ik} X_i X_k. \quad (21)$$

However, when the deviation from the equilibrium state increases, as Prigogine [25] showed, the thermodynamic system loses stability, and then small fluctuations can lead to self-organization processes – the creation of new spatial and time structures that do not develop near the equilibrium state.

To describe the processes that occur in such systems, the concept of an open system is introduced. The change in entropy consists of two components [25]

$$dS = dS_V + dS_S, \quad (22)$$

where $dS_V < 0$ is the increase in entropy in the system due to the ongoing processes, and dS_S is the flow of entropy due to the exchange of energy or matter with the environment, and this term does not have a definite sign. In such an open system, called an “active element,” a redistribution of energy between its elements, leading to the decrease of entropy, is possible:

$$dS = (dS_V + dS_S) < 0. \quad (23)$$

That is, in open thermodynamic systems, transformations with a decrease in entropy can occur, leading to the system ordering due to the tendency of the system to reduce entropy through self-organization [25] of structures. Self-organization is a process that results in a new order in an open system that is far from thermodynamic equilibrium when the transition from chaotic motion and a chaotic state occurs due to an increase in the magnitude of fluctuations spreading to the entire system.

Self-organization of structures causes [26] the occurrence of self-oscillations, spatially inhomogeneous structures in physical and chemical processes, etc. Such examples in hydrodynamics [13] are the structuring of convective flows in cells – Rayleigh-Benard convection, and the emergence of symmetric vortex structures during turbulent flow around bodies – the Karman street.

We will evaluate the excess surface energy of spherical nanoparticles with a size of $r_0 = 10$ nm in a sample of a mass $m = 1$ g.

The average density has been taken as $\rho = 4 \cdot 10^3 \text{ kg/m}^3$; the volume of a given mass is $V = m / \rho = 2.5 \cdot 10^{-7} \text{ m}^3$.

The volume of a nanoparticle is $V_o = \frac{4}{3}\pi r^3 = 4.2 \cdot 10^{-24} \text{ m}^3$ and its surface area is $S_o = 4\pi r^2 = 1.26 \cdot 10^{-15} \text{ m}^2$.

Since the number of particles is $N = V / V_o = 6 \cdot 10^{16}$, their total surface area is $S = S_o N = 75 \text{ m}^2$ and total surface energy is $W = \sigma S = 7.5 \text{ J}$, where the specific surface energy has a representative value $\sigma \sim 0.1 \text{ J/m}^2$. If such energy is used to lift a given mass in the gravitational field, the lift will be equal to $\Delta h = w/mg = 750 \text{ m}$.

We should note that the specific surface energy increases as the size r of the spherical particle reduces [27]:

$$\sigma(r) = \sigma(1 + 2\delta/r)^{-1}, \quad (24)$$

here σ is the surface energy value for a flat surface, δ is the diameter of the molecules of the substance. For a nanoparticle with a size of 10 nm, we can assume $\sigma(r) = \sigma$.

Therefore, 1 gram of nanoparticles has a representative value of the total surface $\sim 10\text{-}100 \text{ m}^2$ and a characteristic value of excess surface energy $\sim 1\text{-}10 \text{ J}$.

The very process of nanoparticle formation is accompanied by self-organization processes. Due to the creation of a non-equilibrium state, self-organization first transforms the chaotic movement of atoms (molecules) in the gas phase into an oscillatory-translational movement during the creation of a critical nucleus. After that, self-organization leads to the formation of a crystal lattice in the nanoparticle itself. Since the formed nanoparticles have large excess energy, self-organization of the already formed nanoparticles can occur under appropriate conditions.

For example, when metal nanoparticles are added to the lubricant, high stresses and temperature gradients are achieved in friction pairs creating significant deviations from equilibrium. In these positions, nanoparticles are capable to self-organize [28]. This leads to the formation of a strong and wear-resistant cladding film that increases the service life of friction pairs.

4. Interaction between nanoparticles. Consider two spherical nanoparticles of equal radius R , separated by a distance D and interacting in the medium as shown in Fig. 1. The interaction between the particles is mainly determined by the Van der Waals force, which arises due to the dipole-induced interaction [29]. Van der Waals forces contribute to the aggregation or flocculation of particles. For short distances between particles (when $D < R$), the interaction energy is determined by the equation [30]

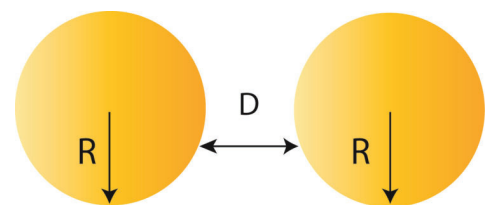


Fig.1. Interaction between two bare nanoparticles.

$$W = -\frac{AR}{12D}, \quad (25)$$

where A is the Hamaker constant, which, as a rule, has the order of 10^{-19} - 10^{-21} J and is a function of the properties of the material and the environment in which the interaction takes place. To estimate the Hamaker constant, an approximate formula is used [30]

$$A = \frac{3}{4}kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2; \quad (26)$$

here k is the Boltzmann constant, T is the absolute temperature, ε is the dielectric constant, and subscripts 1 and 3 refer to the particle and environment, respectively.

The Hamaker constant is an important parameter because its sign determines whether the interaction is repulsive or attractive, while its magnitude determines the strength of the interaction. It can be seen from equation (26) that for the case of bare nanoparticles, the value A always takes a positive sign indicating attraction. Therefore, bare metallic nanoparticles, which are dispersed in inert nonpolar liquids, will aggregate and form clusters, which leads to their instability. To prevent the aggregation of nanoparticles, researchers have developed two methods of increasing the stability of nanoparticle dispersion: electrostatic repulsion and steric repulsion [29]. Repulsion is usually carried out by the adsorption of surfactants on the surface of nanoparticles.

5. Interaction between nanoparticles and surfaces. In addition to the interaction between particles, the interaction of the nanoparticle with the surrounding body is important. An example when a spherical nanoparticle of radius R interacts with a substrate located at a distance D from the nanoparticle, as shown in Fig. 2, is determined by the formula [30]

$$W = -\frac{CR}{6D} \quad (27)$$

when $D < R$. An approximate formula is used to estimate the constant C

$$C = \frac{3}{4}kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right). \quad (28)$$

Subscripts 1, 2, and 3 refer to the particle, surface, and medium, respectively.

We should note that when $\varepsilon_2 > \varepsilon_1 > \varepsilon_3$ or $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$, and when $\varepsilon_3 > \varepsilon_2 > \varepsilon_1$ or $\varepsilon_3 > \varepsilon_1 > \varepsilon_2$, the constant C is always positive, which leads to the attraction of the nanoparticle to the surface.

When interacting with a metallic surface ($\varepsilon_2 \gg 1$), nanoparticles added to the lubricant (relative dielectric constant is low $\varepsilon_3 \sim 2-3$) will be attracted to the metallic surface if $\varepsilon_1 > \varepsilon_2$ and improve its tribological properties, which explains the effectiveness of nanoparticle additives in lubricants [19, 30].

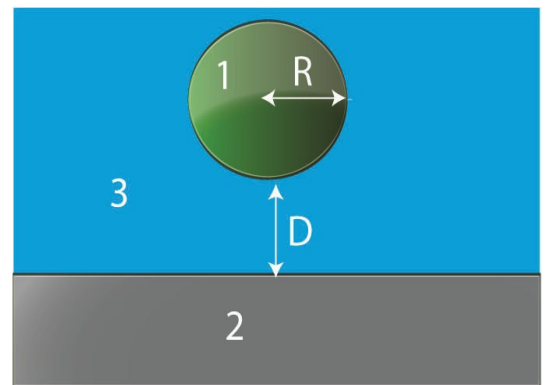


Fig.2. Interaction between the nanoparticle and surface.

However, when $\varepsilon_1 > \varepsilon_3 > \varepsilon_2$ or $\varepsilon_2 > \varepsilon_3 > \varepsilon_1$ (the medium has an intermediate dielectric constant), the C parameter will always be negative leading to the repulsion of the nanoparticle from the surface.

Thus, by changing the values of the dielectric constants of the involved materials and the environment, it is possible to manipulate the sign of C and, hence, the type of interaction of nanoparticles with contacting surfaces.

6. Production volumes of nanomaterials, their specifics and prices.

6.1. Development of the nanotechnology industry. In 2000, the US Administration launched the “National Nanotechnology Initiative.” In the same year, 500 million dollars were allocated from the US federal budget, and already in 2015, the US government increased the funding of scientific research in the field of nanotechnology to 3.7 billion dollars. Besides the USA, intensive research and development in the field of nanotechnology are conducted by Japan, China, Germany and Israel [31]. Fundamental research on the problems of nanotechnology is also conducted in Ukraine within the framework of the comprehensive program of the National Academy of Sciences of Ukraine “Nanostructural systems, nanomaterials and nanotechnologies.”

According to the calculations of the Lux Research consulting company, in 2012 the volume of the nanotechnology market in the world amounted to 190.3 billion US dollars and had increased to 569 billion dollars by 2021. The world leaders in the production of nanomaterials and their implementation are the United States (278.8 USD billion), Europe (147 USD billion) and the Pacific Region (29.4 USD billion, mainly Japan) [31, 32]. The United States leads by the volume of the commercial market, the number of publications (about 25,000), and nanotechnology patents (45% of all related ones.)

The industry demand for nanoproducts in 2020 (USD billion): manufacturing industry– 455, nanoelectronics– 390, the pharmaceutical industry– 234, ecology– 130 and transport –91. Unfortunately, the production capacity of nanomaterials can satisfy the demand of the industry by only 40%.

6.2. Structure of nanomaterial production. Metal powders and their oxides are the main type of products on the world market of nanopowders.

In the market of pure metallic nanopowders, the volume of production is as follows: nickel – 16.5%, copper – 16.5%, iron – 14%, aluminum – 13%, titanium – 13%, zinc – 10%, tungsten – 5% and molybdenum – 5% [31]. Metallic nanopowders are used to obtain various compounds and for additional charging in powder metallurgy to strengthen parts.

In the product group of metal oxides, 4/5 of the production volume is accounted for by the three most common raw materials: silicon dioxide – silica (SiO_2), aluminum oxide – alumina (Al_2O_3) and titanium dioxide (TiO_2). At the same time, silica occupies more than half of the total production, alumina – 18% and titanium dioxide – 10%. In addition, the most available oxides are oxides of iron, zinc, cerium, zirconium, copper, magnesium and yttrium.

Production of nanopowders by particle size: 22% with sizes less than 15 nm, 23% with sizes in the range of 16-30 nm, and 15% with sizes in the range of 31-60 nm. Therefore, more than half of all nanopowders (up to 60%) have a particle size of less than 60 nm, and about 45% less than 30 nm [32].

6.3. Cost of nanomaterials. Prices for nanomaterials vary and are determined by the following factors: manufacturers cooperate with specific industries, therefore, produce nanopowders with different characteristics (fractional composition, shape, purity, etc.); in the production of nanopowders with controlled properties the important indicator which determines the price is the volume of the batch.

The approximate cost of some common nanopowders in US dollars per kilogram is currently as follows: silicon dioxide – 60, iron oxide – 60, titanium dioxide – 70, zinc oxide – 75, barium oxide – 80, aluminum oxide – 95, cerium oxide – 150, zirconium oxide – 500, silver oxide – 1000 and indium tin oxide – 1500 [31, 32]. It should be noted that the high cost of nanopowders of zirconium oxide, silver oxide and indium tin oxide is determined by the high cost of raw materials and small production volumes.

The cost of manufacturers may differ from the specified by 25-50% and depends, in particular, on the size of the order and transport costs during delivery to the consumer.

The authors express their sincere gratitude to Professor V. Kalinchak and Professor O. Khliyeva for their sound advice and comments regarding the problems considered in the article.

Conclusions.

1. Methods of obtaining nanomaterials lead to their non-equilibrium state.
2. The imbalance of nanoparticles can initiate self-organization, which determines the effectiveness of their application.
3. Nanoparticles exhibit quantum properties, and quantum mechanics has to be used to explain their behavior.
4. An important role in the features of the behavior of nanoparticles plays a large portion of surface atoms.
5. Bare nanoparticles attract each other and their surface is covered with surface-active substances preventing aggregation.
6. It is possible to control the nature of the interaction of embedded nanoparticles with the environment by changing the dielectric constant of nanoparticles and the materials into which they are introduced.
7. Recent advances in nanotechnology have significantly reduced their cost and made them competitive in use. The industry demand for nanomaterials exceeds the capabilities of nanotechnology production.

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Властивості та поведінка наночастинок

АНОТАЦІЯ

У статті розглядаються методи отримання наноматеріалів та умови утворення наночастинок заданого розміру. Показано, що поверхнева енергія нанорозмірних частинок, завдяки великій частці поверхневих атомів, значно перевищує поверхневу енергію мікрочастинок, що призводить до нерівноважного стану перших із можливістю самоорганізації та формування, зокрема, на поверхнях тертя міцної та зносостійкої плакувальної плівки з металевих наночастинок, яка суттєво збільшує ресурс пар тертя. Для пояснення взаємодії з оточенням наночастинок, що знаходяться на межі квантового і класичного станів, використано основні положення квантової механіки. Розглянуто взаємодію між голими наночастинками та між наночастиною і поверхнею, розділених середовищем. Показано, що без стабілізації поверхнево-активними речовинами металеві наночастинки будуть агрегувати; у свою чергу, характер взаємодії наночастинок із твердою підкладкою визначається їх діалектичними константами. У статті наведено огляд розвитку наноіндустрії, вказано комерційний попит на наноматеріали, зазначено країни - лідери з виробництва наноматеріалів, приведені метали, що використовуються для виробництва основної продукції – металевих нанопорошків.

Ключові слова: методи виробництва, поверхнева енергія, нерівновага, самоорганізація, квантова поведінка.