**Lecture 4.** Influence of size effect on physical chemical properties of nanoparticles and nanomaterials.

The position of the atoms on a surface is geometrically and physically different from the position in a bulk of body. On a surface, the atomic reconstruction and another order of atoms arrangement take place. The surface composition does not correspond to the stoichiometric composition of chemical compounds in a bulk. The depth of this discrepancy occupies a several interatomic layers.

In addition, there are ledges, cavities and other irregularities for atoms on a surface of crystal grains of nanoparticle, causing additional differences between the surface and bulk properties of nanoparticles. The size effect defines the relationship between surface and bulk properties of nanoparticles, depending on a size of particles. Quantitatively, the size effect can be represented as a ratio between surface of nanoparticles (for spherical particles ) and their volume (), i.e Ssurf/Vvol value is inversely proportional to the radius or diameter of the particles, i.e. 1/r or 1/d. A ratio of the number of atoms (molecules) on a surface of nanoparticles (Nn) to the number of atoms in a bulk (Nvol) can be represented as:

, (1)

where determines the fraction of atoms (molecules) surface in relation to their number in a bulk of nanoparticles. In accordance with the formula for spherical nanoparticles, the is changed as shown in Table 1:

Table 1

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| The number of atoms in a bulk |  106 |  105 |  104 |  103 |  102 |
| β (fraction of surface atoms), % |  4 |  9 |  19 |  40 |  86 |

Decreasing the quantities of atoms in a bulk from 106 to 102 (decrease the size of nanoparticles) causes increase of surface atom fraction to 86 % , i.e. decreasing the size of particles dramatically results in increasing of the fraction of surface atoms compared to bulk. The number of atoms in a bulk equalled to 104 corresponds to lower size of nanoparticles (2-3 nm) which can form the dispersed phase particle.

In addition, the effect of size can be represented as a fraction of surface layer ΔV in the total volume of particles (V); this fraction for nanoparticles with diameters *a* and thickness of a surface layer *h* equals to:

 (2)

When the thickness of surface layer of *h* equal to 3-4 atoms of (0.5-1.5 nm), and at average size of nanoparticles of 10-20 nm, then about 50 % of the total mass of nanoparticles locate on the surface layer.

In general, the dependence of the fraction of surface atoms on bulk atoms is shown in Fig. 1.



Figure 1 **–** Dependence of the fraction of surface atoms (β) and the diameter of the nanoparticles () on the number of atoms in a bulk (Nvol)

Size effect is determined by quantitative ratio and qualitative feature of the surface of nanoparticles. Properties of atoms on surface differ from the properties of atoms in a bulk. Surface atoms connect the nanoparticles with the surrounding media. The atoms in a bulk are surrounded by same type of atoms. Due to the formation of unsaturated bonds on surface of nanoparticles the atomic recombination can occur and there is a different arrangement of atoms compared to bulk atoms. Atoms and molecules of a medium can be adsorbed on the surface of nanoparticles.

So, the first distinctive feature of nanoparticles is the size effect.

The peculiarity of fine disperse particles and nanoparticles is that their properties depend on both chemical composition of material and the particle size.

The size effects observed in disperse systems can be divided into two large groups.

1. Effects associated with the curvature of the surface of a liquid or gaseous dispersed particle:

a) the dependence of surface tension of liquid on a radius of the droplet or gas bubble in the liquid;

b) the dependence of the saturated vapour pressure (pr) on the radius and the sign of curvature (convex or concave) of liquid surface at the interface with the gas;

c) the dependence of the capillary pressure (pc) on the radius of liquid surface;

2. Changes of physical and chemical properties due to small size of dispersed particles:

a) crystal structure and the degree of symmetry of the crystal lattice;

b) thermodynamic parameters: heat capacity, melting point (crystallization), Debye temperature;

c) mechanical properties: strength and plasticity;

d) magnetic and electrical properties;

e) chemical properties, e.g. catalytic activity.

Size effects are especially significant for fine disperse systems, i.e. in the range of nanosize. This is one of the reasons for the great importance of nanosystems in contemporary science and high technologies.

It should be noted that size effects of nanoparticles have a quantum nature in some cases.

Let us consider several size effects characteristic for fine disperse particles.

*Thermodynamic properties.* *Decrease of melting point*. Decrease of solid dispersed particle size leads to a gradual decrease of melting point (Tm) of various substances. For metal particles the size effect manifests strongly in the range of sizes d <50 nm. For example, for gold particles the temperature difference ΔT = Tm,0 – Tm,d is noticeable at d < 20 nm (Tm,0, Tm,d – melting point of macroscopic sample and fine disperse sample, respectively) (Fig. 2). In the interval d <5 nm, the decrease of the melting point is hundreds of degrees; at d = 2nm we have ΔT = 1000 degrees. A significant decrease of the melting point was also observed for lead, bismuth, tin, and indium.



Figure 2 – Dependence of the melting temperature (Tm.d) of nanodispersed particles of gold on their size (d); the dotted line shows the change of the melting temperature of a macroscopic sample of gold

Thus, the size of nanoparticles can be regarded as a kind of temperature analogue. Therefore, when using the phase rule for fine disperse systems, it is necessary to enter an additional variable (degree of freedom).

Decrease of melting point of fine disperse particles is clearly explained by the following simplified model of the melting process. It is assumed that when the heat input, the crystal begins to melt when the amplitude (δ0) of the oscillations of atoms in the crystal lattice is commensurable with the interatomic distance (b). The melting point of macroscopic crystals corresponds at this scheme to the condition δ*0  ~ b*. For atoms on the surface of crystal, the amplitude of the oscillations is δd > δ0. Reducing the particle size leads to an increase in the relative fraction of surface atoms in a given particle. At d = 3 nm, this fraction already reaches 50%. As a result, condition δd ≥ bis achieved at a lower melting point.

For the theoretical description of size effects for melting the following equations are used:

, (3)

 = 1 – , (4)

 (5)

where Sm.0, Sm.d – the entropy of melting of a macroscopic and highly dispersed sample of the substance respectively, J/(mole·K); Hm,0 , Hm,d – the enthalpy of melting of a macroscopic and highly dispersed sample respectively, J/mole; R – universal gas constant; 2d0  - the minimum particle size at which there are no structural differences between a solid and a liquid: at the size d0 the differences in the enthalpy and entropy of the macroscopic phase and the dispersed particle equal to zero. Tm,d, K

Consider relatively large interval, when d/d0  >> 1, i.e. d > 5-10 nm. In this case:

Then at expanding the exponent of equation (9) in a row, it is sufficient to consider only the first two terms of the series:

 (6)

Equation (10) has a deep physical meaning. It shows that the change of the thermodynamic parameter (in this case, the melting enthalpy) is inversely proportional to the size of the dispersed particle d: ΔH ~ 1/d.

Such nature of size effects causes by the fact that the quantity 1/d = S/V, i.e. represents the ratio of a surface area of a particle S to its volume V; thus, the thermodynamic parameter is determined by the particle dispersion. Therefore, the smaller the size d, the greater is the fraction of surface atoms in a dispersed particle. This principle of changing the thermodynamic properties of dispersed particles (inversely proportional to their size d or radius r) is quite general in Colloid Chemistry. An example of such connection is given by Thomson (Kelvin) law for saturated vapour pressure above the curved surface of a liquid and the Gibbs-Ostwald equation.

The nature of the dependence of the melting temperature of dispersed particles on their size is essentially related to the aggregate state of the dispersion medium, which surrounds the particle. The effect of lowering the melting point with decreasing particle size is observed for aerosol disperse systems when the dispersion medium is a gas. In many technological processes the dispersed particles are distributed in thin pores of another solid phase. In such systems, both positive size effect and negative one are observed. For example, indium nanoparticles melt in the pores inside the iron at lower temperature (Tm,d < Tm,0). Inside the aluminium matrix there is an effect opposite in sign: indium particles melt at higher temperatures than macroscopic samples (Tm,d > Tm,0).

*Supercooling of droplets.* The size of dispersed particles has a strong influence on the crystallization process also. Highly dispersed droplets of different liquids can keep a liquid state for a long time at strong supercooling.

For liquid metals, the maximum supercooling (ΔTmax) of drops with a diameter of 2- 100 μm is shown in Table 2.

Table 2

|  |  |  |  |
| --- | --- | --- | --- |
| Metal | Temperature, oC | Metal | Temperature, oC |
| Mercury | 77 | Gold | 230 |
| Gallium | 76 | Copper | 236 |
| Tin | 118 | Manganese | 308 |
| Lead | 80 | Nickel | 309 |
| Silver | 227 | Platinum | 370 |

A significant supercooling is observed for droplets of other substances, for example water, organic liquids and melts of salts (degrees) (Table 3):

Table 3

|  |  |
| --- | --- |
| Compound | Temperature, °C |
| Carbon tetrachloride | 50 |
| Octane | 30 |
| Decane | 29 |
| Hexadecane | 14 |
| Lithium fluoride | 232 |
| Sodium fluoride | 281 |
| Sodium chloride | 168 |
| Potassium bromide | 168 |
| Cesium bromide | 161 |

*Heat capacity.* The size effect of metallic nanoparticles on a heat capacity is manifested sharply at very low temperatures. For example, for palladium clusters the temperature dependence of the heat capacity deviates from the corresponding dependence c=f(T) for macroscopic samples. These differences increase as the number of palladium atoms in the cluster decreases. Thus, the reduction of the size of dispersed particles affects their thermal properties similarly to a decrease of temperature.

*Mechanical properties.* The main mechanical property of solids - their strength. A quantitative characteristic of the strength of materials is the limiting stress (P), at which the sample (rod) ruptures under uniaxial tension. The limiting stress is defined by the equation

pc = fc/ S, (7)

where fc is the tensile force causing the rupture; S - cross-sectional area of the sample.

For samples with a sufficiently large cross section (diameter d > 0,1 mm) the strength depends only on the chemical nature of the substance. But for thin samples with diameter corresponding to the size of dispersed particles, obvious size effect is shown. It consists in the fact that the limiting stress increases as the diameter (d) of the rods, fibers, particles, etc., decreases. The dependence of the strength (pc) of glass threads on their diameter (d) illustrates this size effect (Table 4):

Table 4

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| d, mkm | 22.0 | 16.0 | 12.5 | 8.0 | 2.5 |
| pc, N/m2 | 220 | 1070 | 1460 | 2070 | 5600 |

The data presented show that the strength of thin threads increases sharply with their diameter decreasing. The size dependence pc = f(d) in this region is defined by the following equation

pc = pc,min + β/d (12)

where β is a constant, which depends on the chemical nature of the material, N / m. Thus, as for thermodynamic properties, there is an inverse relationship between the mechanical property of a dispersed particle (thread) and its size.

The strength of nanotubes is about 10 times higher than that of steel, although their ductility is 6 times smaller.

 The main physical reason for increasing strength at decreasing the diameter of the sample and the grain size is as follows. The limiting stress depends not only on the chemical nature of the substance, but also on the various structural defects. The so called linear defects, edge and screw dislocations, have the strongest effect on mechanical properties. The probability of finding in the sample of a dangerous defect responsible for its destruction; the lower probability, the smaller the diameter of the sample. The average distance between dislocations in crystals is about 10 nm. Therefore, strength growth is characteristic for samples of smaller sizes. This state is the basis for the production of high-strength composite materials. They are based on very thin fibers (filiform) which have increased strength.

Another remarkable mechanical property of nanoscale samples of some substances is their great plasticity. It was established that composite copper-niobium and copper-chromium wires with a diameter of 15-20 Nm with very strong cooling (in liquid helium) is deformed plastically, limiting elongation reaches 10 %. Massive samples of the same composition under these conditions are very fragile. Another example of the high strength of nanosized samples is carbon nanotubes.

*Magnetic properties*. The size effect favors the significant decrease of the Curie point which shows the transition temperature from the ferromagnetic state to the paramagnetic state. For iron, cobalt, nickel nanoparticles smaller than 10 nm, the Curie point is lower by hundreds of degrees than for macroscopic samples. The measurement of the magnetization of such type small particles is accompanied with a large spread of data (as at the measurement of the melting point). Therefore, Mossbauer spectroscopy is used to determine the Curie point of the nanoparticles.

Magnetic phase transitions also proceed in a larger (20-50 nm) dispersed particles. However, to carry out such transitions, the additional energy (in comparison with nanoparticles) needs. The source of this energy is internal stresses and defects that arise at obtaining the particles by means of topochemical reactions.

Palladium clusters have clear magnetic size effects. Macroscopic samples of palladium exhibit paramagnetic capability and their magnetic susceptibility is almost independent on temperature up to the temperature of liquid helium. The magnetic susceptibility of giant palladium clusters by several times smaller than that of a macroscopic metal, but they remain paramagnetic.

With a significant reduction of cluster sizes (up to tens of palladium atoms), they become diamagnetic. The size of dispersed particles also effects on the coercive field (Hc, A/m). This value characterizes the demagnetizing field at which the residual magnetization of the sample equals to zero. A coercive field represents an important characteristic of ferromagnetic materials. At Hc < 100 A/m, materials are considered as magnetically soft, at H > 100 A/m – magnetically rigid.

The coercive field of iron nanoclusters (d < 4 nm) is almost zero. Such low values of the coercive field is caused by thermal fluctuations. For small particles, their energy is sufficient to destroy the ordered orientation of the magnetic domains and to transfer the crystal to the paramagnetic state. At room temperature the value of the coercive field of iron is maximal for crystals of 20-25 nm. Therefore, nanocrystalline ferromagnets can be using to obtain storage devices with large memory.

Another important magnetic property of highly dispersed particles is a low magnetic anisotropy. In polycrystalline materials the minimum magnetic anisotropy of ferromagnets is observed at grain sizes of 10-20 nm. Losses due to remagnetization of such nanomaterials are small.

The nanodispersed magnetized particles with a diameter of about 10 nm are used for the preparation of ferromagnetic liquids. Ferromagnetic liquids are colloidal solutions in which the dispersed phase is nanomagnetic particles and the dispersion medium is a liquid, for example water or kerosene. When an external magnetic field is applied, the nanoparticles begin to move and activate the surrounding liquid. The prospect of industrial use of this effect is very high (for example, for cooling powerful transformers in electrical engineering and for magnetic enrichment of ores).

*Catalytic properties.* Nanodispersed solid particles of metals and metal oxides have a high catalytic activity which allows producing various chemical reactions at relatively low temperatures and pressures. Let us give some examples illustrating the catalytic properties of highly dispersed particles.

1. Gold nanoparticles with size of 3-5 nm have highly specific catalytic activity. The catalytic activity is connected with the transition of the crystalline structure of gold from the face-centered cubic in larger particles to the icosahedral structure of nanoparticles. The most important characteristics of these nanocatalysts (activity, selectivity, temperature) depend on the substrate material to which they are applied. In addition, even traces of moisture are very much affected. Nanosized gold particles effectively catalyze the oxidation of carbon monoxide at low (-70 oC) temperatures. However, they have a very high selectivity at reduction of nitrogen oxides at room temperature, if the gold particles are deposited on the surface of the alumina oxide.

2. A highly dispersed catalyst based on non-stoichiometric cerium oxide significantly decreases the temperature of sulfur oxide (IV) reduction under the influence of carbon monoxide. In addition, this catalyst has a higher stability than conventional cerium oxide catalysts with respect to the poisoning of the water vapor and carbon dioxide involved in the reaction

3. In addition to ultrafine particles, thin catalyst layers with thickness of several nanometers have a high catalytic activity. For example, for MoSi nanolayers the high catalytic activity is found under hydrodesulfurization reaction. The high degree of ordering of nanostructure of crystalline MoSi favors the maximum catalytic activity. The number of MoSi monolayers adjusts the selectivity of the catalyst. Catalytic selectivity can also be controlled by changing the structure of MoSi nanoparticles, that opens up a very promising direction in the heterogeneous catalysis of organic reactions.

Also, the extremely small nanoparticles (clusters) have the high catalytic activity. For example, giant palladium clusters consisting of several hundred (about 600) atoms exhibit the high selective catalytic activity in many organic reactions (oxidation with oxygen and nitrobenzene, carbonylation, hydrogenation, acetylation of carbonyl compounds, isomerization of olefins, etc.). At the same time, effective catalysis proceeds in relatively mild conditions - at temperatures and pressures, much less than at using conventional industrial catalysts.

The high catalytic activity of metal clusters is explained by their structure. As a rule, their surface has a rather complex structure: it has very sharp protrusions and flat areas. Local positive charges in a cluster are distributing differently. As a result, there are strong Lewis centers (at the vertices of the polyhedral structure) on the surface of the cluster cation, weaker Lewis centers (on the edges), and positively charged metal atoms with the lowest electrophilicity (on the faces).

*Biological properties.*

The high chemical activity of nanoparticles allows using them in many biological and medical processes. One of the most urgent areas is protection against certain types of biological weapons. For example, heat-resistant anthrax pathogens are effectively destroyed on air at room temperature by spraying nanoparticles of magnesium oxide. The smaller the size of the nanoparticles, the stronger effect.

**Revision questions:**

1. What is the size effect?
2. Which is affected by the decrease in particle size in the size effect?
3. Why conceptions of a surface and bulk have conditional character for nanoparticles?
4. Explain the change in a fraction of surface atoms (β) and diameter of nanoparticles (*a*), depending on the number of atoms in a bulk (Nvol).
5. What properties depend on size effect? Give the examples. Give examples of influence of size effect on thermodynamic properties.
6. How size effect influence on mechanical properties?
7. Describe the size effect in relation of catalytic properties.
8. What do you know about magnetic properties of nanoparticles?
9. Give the examples of size effect with respect to biological properties.