**Lecture 7**.

**Molecular kinetic properties of nanoparticles. Brownian motion. Diffusion. Osmosis.**

*Brownian motion.* Nanoparticles as fine disperse systems are characterized by the molecular-kinetic phenomena such as Brownian motion, diffusion and osmosis. These phenomena are caused by molecular nature of gas and liquid dispersion media and kinetic energy of molecules.

Brownian motion is a continuous, chaotic motion of high dispersed particles (including nanoparticles), suspended in gases or liquids because of action of the molecules of the dispersion medium. The nature of this phenomenon: molecules of dispersion medium act (impact) due of kinetic energy on particles of dispersion phase (nanoparticles). These impacts (1020 per second) unequal by energy lead to a resultant force that cause the particles motion. The true way of particle is changing constantly, and it cannot be traced. Therefore, the shift of the particles which characterize the change of the particle coordinate in time is determined.

Mean displacement xavr., i.e. the average value of the coordinate x of the particle for particular time τ is equal to:

, (1)

where, R – universal gas constant; T – absolute temperature; – Avagadro’s number; τ – time;– viscosity of disperse media; r – radius of particles of dispersed phase.

According to formula (25) value characterize the molecular-kinetic properties of dispersion medium. In addition to the translational motion of the particles, the rotational motion is also observed for nanoparticles. It is associated with the geometric inhomogeneity of nanoparticles, especially for crystalline and two-dimensional nanoparticles. The mean square displacement of translational Brownian motion is equal to:

xavr.2= 2D (2)

where, D is the diffusion coefficient of translational motion.

The standard angular displacement:

avr.2= 2Dr. (3)

where, Dr. is the diffusion coefficient of rotational motion.

Diffusion coefficient D and Dr. characterize the translational and rotational Brownian motion in liquid and gas medium. Most nanoparticles have an irregular shape: protrusions and recesses on their surface contribute to the formation of rotational Brownian motion. It is determined by the angle which mean-square value is equal:

, (4)

where the mean square angle of the rotational Brownian motion with respect to the selected axis in time; Boltzmann constant; rotational mobility, which depends on the mass of the nanoparticle and equals to:

B = I/, (5)

where I – the number of revolutions of the rotary motion; density of nanoparticles; diameter of nanoparticles.

 According to calculations, the average number of revolutions (up to 28) due to Brownian motion is achieved within 5 minutes. In rough nanoparticles, in addition to their linear movement, the flicker effect is observed, which is inaccessible to the human eye. In a gaseous medium the nanoparticles can have the same translational energy as molecules, which allows to estimate the speed of Brownian motion ():

 (6)

1/2, (7)

where m – mass of nanoparticles, – average energy of particles in a gaseous medium.

Thus, Brownian motion of the nanoparticles is not differed from the fine disperse systems, studied in Colloid Chemistry. But there are some features of nanoparticle Brownian motion considering the size, shape and dimensions of nanoparticles.

*Diffusion.* Diffusion is a spontaneous process of substance distribution (ions, atoms, molecules, highly dispersed particles, including nanoparticles) from the area of higher concentration to an area of lower concentrations. Unlike Brownian motion, the diffusion is manifested not only in gas and liquids, but also in solids. For a stationary process with one-way diffusion (in one direction), the mass of the diffused substance is characterized by Fick's law:

 (8)

where diffusion coefficient; concentration gradient ( – the difference between the concentrations at a distance x from the object; – for this reason, the minus sign is placed in the right-hand side of the equation (since diffusion is always positive); S – area flow section; diffusion time; the diffusion coefficient (m2/s) quantitatively determines the diffusion efficiency when the gradient of concentration, area of flow section and time are equal to one. The diffusion coefficient of a nanoparticle depends on the medium in which the diffusion takes place. The approximate value of the diffusion coefficient: in gases 10-4 (at normal temperature and pressure), in liquids – 10-9 and in solids – less than 10-14 m2/s. In liquids, the diffusion coefficient depends on the type of diffusion (Table 1):

Table 1

|  |  |  |  |
| --- | --- | --- | --- |
| Type of diffusion | ionic | molecular | nanoparticles |
| Diffusion coefficient, m2/s  | 10-8 | 10-9 | 10-10 |

The larger the diffusion coefficient, the more effective the diffusion (see equation 8). In liquids and solids, the diffused particles (molecules, ions, atoms) transition occurs from one stable state to another. The temperature dependence of the diffusion coefficient is determined by the Arrhenius equation as follows:

 (9)

where – an apparent diffusion coefficient, numerically equal to the diffusion coefficient at an infinitely large temperature; – the activation energy of the diffusion process; Boltzmann constant; T – temperature.

The diffusion of nanoparticles manifests in different cases: in the case of nanoparticles as dispersed phase of dispersion medium; at alloying, that is, the injection of some substances into nanoparticles for giving of certain properties; diffusion of nanoparticles inside the crystalline nanoparticles.

The types of diffusion of crystalline nanoparticles at the interface with different surfaces are shown in Fig. 1.



Figure 1 – Scheme of different types of diffusion applied to crystalline nanoparticles (*c* - crystal grain of a nanoparticle*, s* - surface contacting with nanoparticles); types of diffusion: 1 - bulk, 2 - grain boundary, 3 - surface, 4 - boundary.

Four different types of diffusion for crystalline nanoparticles are present: 1 – bulk, in the bulk of a crystal of a polycrystalline body; 2 – grain-boundary between grains of crystals; 3 – surface over the crystal surface; 4 – boundary diffusion an the interface of the crystal *k* and the contacting surface *s*. Surface diffusion occurs as a result of the movement of atoms or molecules along the crystal surface within the molecular layer.

The different diffusion coefficients for a copper nanoparticle (diameter 10 nm, 293 K) is given in Table 2.

Table 2. The value of the diffusion coefficients of copper and other components in the composition of nanoparticles

|  |  |
| --- | --- |
| Diffusible substance | Diffusion coefficient, m2/s |
| D1bulk | D2grain-bound | D3surface |
| Cu | 4,0 10-40 | 4,0 10-24 | 2,6 10-20 |
| Ag\* | 8,0 10-33 | 8,0 10-20 | 4,8 10-17 |
| Au\* | 1,6 10-34 | 2,6 10-26 | 4,7 10-22 |
| Bi\* | 8,8 10-30 | - | 2,3 10-19 |
| \**Note: for copper nanoparticles containing Ag\*, Au\*, Bi\** |

As it is seen, the maximum diffusion coefficient is observed for surface diffusion, and the minimum for bulk diffusion, that is, D3  D2 D1 and for copper the coefficient of surface diffusion is by 20 orders of magnitude higher than the bulk diffusion, and for other types of diffusion it does not exceed by 10 orders of magnitude.

Increasing of the temperature leads to increase the values of diffusion coefficients. The surface diffusion is more intense, and the less intensive one is the bulk diffusion.

The activation energy of the diffusion process is quantitatively determined by the tangent of the slope of the straight line (Fig. 2):

 (10)



Figure 2 – The dependence of diffusion coefficient on reverse temperature

Diffusion processes play an important role in technology in particular at alloying – the introduction of substances into metal alloys to change the structure of alloys and give them certain physical, chemical and mechanical properties. Boron adsorbed on the surface of nickel increases the plasticity of nickel alloys due to grain-boundary diffusion. Diffusion of nanoparticles is accompanied with adsorption. Adsorption is associated with the deposition of metal nanoparticles on polymer surfaces and determine the possibility of creating nanocomposites.

*Osmosis.* Molecular-kinetic phenomena include osmosis. Osmosis is the phenomenon when the molecules of solvent 1 (dispersion medium) tend to pass through semipermeable membrane 2 into solution 3 (disperse system) or from more dilute solution 1 into more concentrated one 3. (Fig. 3, a).

The motion of the dispersion medium (solvent) is indicated by arrows in Fig.23. Solution 3 can be a colloidal solution, i.e., sol of nanoparticles. As a result of osmosis there is a pressure , called as osmotic pressure.

Reverse osmosis (Fig. 3, b) – the transition of water or other solvents through the semipermeable membrane from concentrated solution to less concentrated solution as a result of pressure P which exceeds the difference of osmotic pressures of both solutions (P> ).

In this case, the membrane passes the solvent, but does not pass some of the substances dissolved in a solvent.



Figure 3 – Scheme of osmosis (a) and reverse osmosis (b): 1 – solvent, dispersion medium; 2 – solution, including colloid solutions; 3 – membrane; 4 – movement of a solvent; – is the diameter of the nanoscale pores of a membrane

The osmotic pressure ( for an ordinary (molar) solution according to Van’t-Hoff equation is equal to:

, (11)

but for a nanoparticle as a colloidal solution:

 (12)

where C – concentration of solution; mass concentration of nanoparticle kg/m3; – radius of a nanoparticle; – nanoparticle density; – Avogadro's number.

The dependence of the osmotic pressure on the sizes of nanoparticle: , that is, the smaller the particle size, the greater the osmotic pressure.

For a nanoparticle commensurate with the molecular size at C = 10-1  kmol/m3, reaches 6×1025 particles per m3, and the osmotic pressure is 2.4·105 Pa (or approximately 2.4 atm.) that is great value. For a nanoparticle with a size of 100 nm, the osmotic pressure is about 10-3 atm, that is very insignificant.

The intensity of osmosis and reverse osmosis depends on the ratio between the channel diameters of the membrane (Fig. 23, a) and the thickness of the diffusion layer λ (Fig. 24). When , the diameter of the channels is much larger than the diameter of the ionic atmosphere, the efficiency of the process does not reduced. At decrease in the cross section of the channels and loss of the membrane capacity is observed. Simultaneously with the movement of the solvent, it is possible the motion of the diffusion layer ions that can also lead to a decrease of the productivity of the membranes.

The membranes can have cation-exchange and ion-exchange properties. Nanoporous polymeric and inorganic materials are used for reverse osmosis. They contain ions that can be replaced by ions in the solution in contact with the membrane, for example, OH groups.

**Revision question:**

1. What molecular-kinetic properties do you know?
2. What is the reason of Brownian motion?
3. What is the mean square displacement?
4. What factors influence on the mean square displacement?
5. What features of nanoparticle Brownian motion you can characterize?
6. Write the equations of translational and rotational average square displacements.
7. What is a diffusion?
8. Write the Fick’s law.
9. What is the diffusion coefficient?
10. What types of diffusion for nanoparticles do you know?
11. Why does surface diffusion coefficient exceed the grain-boundary and bulk diffusion coefficients?
12. How the temperature influence on diffusion?
13. How one can calculate the activation energy through diffusion coefficient?
14. What is the osmosis?
15. What is the reverse osmosis?
16. Write the Van’t-Hoff equation for nanoparticles and compare the osmotic pressure for ordinary solutions and sols?