

# SIZE FACTOR SELECTION MODIFIERS FOR FUNCTIONAL NANOCOMPOSITE MATERIALS BASED ON POLYMER MATRICES

## РАЗМЕРНЫЙ ФАКТОР ВЫБОРА МОДИФИКАТОРОВ ДЛЯ ФУНКЦИОНАЛЬНЫХ НАНОКОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ ПОЛИМЕРНЫХ МАТРИЦ

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**Abstract:** *On the basis of modern concepts of condensed matter physics and quantum physics considered the criteria for inclusion of dispersed particles of different composition, structure, and technological background to nanomodifiers of polymeric, oligomeric and combined matrices. There were proposed an analytical expression for the evaluation of limiting size of the dispersed particles  $L_0$ , which characterizes the manifestation of a particular energy state - nanostate. There was implemented the analysis of experimental and literature data confirming the adequacy of the calculated value of the size of particles in nanostate obtained using relation  $L_0 = 230 \cdot \theta_D^{-1/2}$ , where  $\theta_D$  - Debye temperature. It is shown that the provision of effective modification of macromolecular matrices necessary and sufficient condition is the presence of dispersed particles of different composition and structure of nanoscale structural fragments of the surface layer, which ensure the implementation of synergies through a combination of energy and mechanical factors in the formation of boundary layers of the optimal structure.*

**KEYWORDS:** DISPERSED PARTICLE, NANOSTATE, SIZE FACTOR, DEBYE TEMPERATURE, NANOSIZED FRAGMENTS. SURFACE.

### 1. Introduction

In the first half of the last century, in the scientific paradigm of condensed matter physics, including materials science, underlie the notion that the physical properties of the substances assessed by parameters characteristics affect their structural and chemical characteristics, environmental factors and individual characteristics of structure of concrete objects, called defects. Defects are considered as deviations of atomic structure and mutual configuration from their average structures called ideal structural models [1, 2]. The numerical values of the characteristics of the properties of substances called parameters given in the table without specifying the size of the sample on which they are defined. But in certain size ranges of particulate matter values of characteristics of the physical properties begin to differ from the parameters of bulk material analogs, and often fine particles acquire new properties, which allows them to achieve new effects, including in materials science and other practical applications.

For example, nanoparticles are not only provided the basis for the miniaturization of microelectronic components and shaped the direction of nanoelectronics, but also began to be used as functional additives to conventional substances used in materials science as matrices. Such additives are responsible for structural changes of matrices at different levels, which leads to a significant effect of improving performance parameters: tribological, deformation-strength, thermal and others. [3]. Intensively began to develop methods of producing nanoparticles, as well as the creation of composite materials, in which these particles are included as a modifying components. There are new terms: nanostructures, nanotechnology, nanomaterials, nanophysics et al. [4, 5]. It should be noted that the effect of particle size on the parameters of the various materials and their incorporation has been known for a long time. Nanomaterials in the form of glass, painted metal colloidal particles, produced in ancient Egypt. Light scattering such glasses studied Michael Faraday. In 1906-1910 P. Veimarn research found that "... between the world of molecules (atoms, ions) and microscopically visible particles there is a special form of matter with a complex of the physical and chemical properties inherent to this form - ultrafine or colloidal state, produced when the degree of dispersion (fragmentation) in  $(10^5 \div 10^7) \text{ cm}^{-1}$ , wherein the films have a thickness and fiber and particle size diameter in the range of  $(1,0 \div 100) \text{ nm}$ " [6].

Nanotechnology, as a branch of colloid chemistry, known from the middle of the XIX century. In 1935, W.J. de Haas and T. Birmash found that the thermal conductivity of the low-dimensional particles

is different values macro sized counterparts values. In 50-ies of XX century, it was confirmed by R. Berman, and attempt was made by R. Peierls to explain these results [7]. At the turn of XX and XXI centuries, the amount of basic knowledge of physics, chemistry and related sciences has led to the realization that the prefix "nano" actually forms new research areas that are of great practical significance [8].

### 2. Nanoparticles (definition)

Despite the fact that in recent years nanophysics and nanotechnology achieved unquestionable success, up to date no generally accepted definition of the term "nanoparticle" [4, 5]. Probably one of the first sources that indicated the dimensional boundaries of nanoparticles  $1,0 \div 100 \text{ nm}$  is above cited paper P. Weimar [6]. Follow-known studies have not paid enough attention to the justification of the size range of nanoparticles. Moreover, this dimension of the boundary between the nano- and macro-particulates adopted the same regardless of the composition and structure of matter. This approach lacked a sufficient physical justification. With the same 'success' can take any temperature as the melting temperature for all substances. At the convention dimensional border  $100 \text{ nm}$  indicated in a number of papers (eg, [9]). In this monograph when considering the impact of size on the properties of the dispersed particles rather cautiously said that "the effect of significant changes in the properties appears when the grain size is less than  $100 \text{ nm}$ , and is most clearly seen when the grain size is less than  $10 \text{ nm}$ ". Boundary  $100 \text{ nm}$  can be applied to characterize the nanocrystal when describing it in a general way. We proceed from the fact that not everyone nanoobject is nanoparticle.

Nanoparticle must have at least two major features (taxa). Firstly, the nanoparticles should have a developed surface. Second, the performance parameters in the nanoparticle physical properties (S) depend on its linear dimensions (r), i.e. nanoparticles of various substances exists characteristic function  $S(r)$  (Figure 1). For the nanoparticle concept of the surface is crucial. Nanoparticles regarded as an independent object which can be isolated from a mixture with other substances by mechanical, chemical or other means. Therefore, the nanoparticles can be regarded as a kind of nanophases with its specific features due to the composition, structure, technology acquisition and others factors.

A number of studies [4, 5, 8] suggested that the main role in the formation of specific properties parameters of nanoparticles plays their surface. In the macroscopic objects of atomic and molecular

mutual configuration in the surface layer is different from that which is structurally identical characteristic surface atomic planes in the crystal [9, 10]. It is believed that the influence of the surface as a two-dimensional defect applies to 5 - 7 atomic layers [11-13].

The concept of "surface" for macroscopic and low-dimensional particle has a different physical meaning. For macroscopic objects 'surface' is treated as an imaginary infinitely thin film on one side of which there are atoms of a specific substance, and on the other side - they do not exist. Of course, the surface atoms vibrate, but the amplitude of the thermal vibrations is so small compared to the size of macroobject that it is neglected. The surface at the equilibrium state of the real object is treated as a static system. Surface to be regarded as a dynamic system in the transition to the nano-sized objects. Since the period of atomic vibrations immeasurably less time any experiment, it is necessary to speak of the surface layer. If we consider that in addition to the surface atoms mutual atomic configuration changes just adjacent to the outer nuclear layer, this surface layer can be commensurate with the size of the particle itself. With further decrease the size of the concept of the surface loses its meaning. A particle moves in atom-cluster state [13]. It must be noted that the surface can be absent not only in low-dimensional particles, but also the objects of a size reaching hundreds of meters or more. For example, in the strict sense, surface did not exist for such macroscopic objects as clouds.

The dependence of the numerical values of the parameters of the physical properties of the particle size is observed by many investigators [1, 2, 8, 14-18]. The average (idealized) dependence of the parameters of the physical properties of the particle size ( $S(r)$ ) is shown in Figure 1.

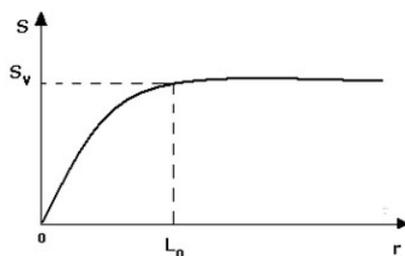


Figure 1 - The dependence of the parameter  $S$  of the physical properties of particle of size [ $S(r)$  function]

Figure 1 shows that a decrease in the size of the sample to a certain value  $r = L_0$  the numerical value of the physical property  $S(r) = S_v = const$ , where  $S_v$  - value characteristic of the bulk sample (table). If the  $r < L_0$  parameter  $S(r)$  decreases monotonically and if  $r \rightarrow 0$  then  $S(r) \rightarrow 0$ .

Analytical dependence of the function has the form

$$(1) S(r) = \frac{S_v}{\exp\left[\alpha\left(\frac{L_0-r}{r}\right)^{3/2}\right]} = \frac{S_v}{\exp\left[\alpha\left(\frac{1-x}{x}\right)^{3/2}\right]},$$

where  $L_0$  - dimensional boundary between nanostate ( $r < L_0$ ) and macrostate ( $r > L_0$ );  $\alpha$  - parameter depending on the analyzed physical properties.

Equation (1) shows that when  $x = 1$  ( $r = L_0$ ) value  $S(r) = S_v$ . Further  $x$  decreases ( $r < L_0$ )  $S(r)$  function decreases monotonically and  $\lim_{r \rightarrow 0} S(r) = 0$ .

If the value  $r > L_0$ , that is  $(1-x) < 0$ , the exponent becomes an imaginary quantity. As

$$(2) \left| e^{ia} \right| = \left| e^{ia} \cdot e^{-ia} \right|^{1/2} = 1$$

then  $x > 1$  the value of the function  $S(r) = S_v = const$ .

The presence of a sufficiently large amount of experimental data allows you to check the consistency of the proposed phenomenological formula (1). For this purpose, is used the following method.

After taking the logarithm of the formula (1) and substituting

$$(3) \begin{cases} Y = \ln \frac{S(r)}{S_v}; \\ X = \left( \frac{1-x}{x} \right)^{3/2}; \end{cases}$$

for the site  $r < L_0$  ( $x < 1$ ) we obtain

$$(4) Y = \alpha X.$$

In [18] the results of the analysis of the literature data. Distribution  $X$ ,  $Y$  points corresponds to a linear regression with a correlation coefficient  $C > 0,70$ , with more than 60% of the pixels have a correlation coefficient  $C > 0,90$ . Reducing the linear correlation due to the fact that the particles have investigated nanoobjects unequal size, and was such that part of the distribution area included in  $r > L_0$  [19]. The described method allows determining the  $\alpha$  ratio in formula (1).

All of the above makes it possible to confirm the presence of dimensional boundaries between nano- and macrostate particles of condensed matter. However, it remains unclear why this boundary  $L_0$  lies in the nanometer range, and how to influence the  $L_0$  parameter individual properties of nanoparticles substance.

### 3. Calculation dimensional boundaries between nano- and macro-state.

The formula for calculating the parameter  $L_0$  should, in our view, meet three basic requirements:

- Firstly, the formula should be derived based on the basic concepts of condensed matter physics and quantum physics, known facts and theories;
- Secondly, it should include parameters characteristics of the substance which determine its basic properties;
- Thirdly, the formula should be simple enough for practical use, and easily verified experimentally.

Obviously, if the parameter  $r$  passes through the dimensional limits  $L_0$  of variation of the parameter is not sharp. This fact was rightly pointed out in [19], which states that "... the boundary of nanometers in size may not be correct criteria nanostructured state of matter ..." as well as a number of studies [20].

The more  $r$  different from the  $L_0$  value, the more manifest the properties of the respective state. It can be concluded that when in a substance  $r = L_0$  there are any changes in the mechanisms of physical processes, or changing the structural characteristics of the energy-fine particles compared to the bulk counterparts.

From the theory of thermodynamics it is known that the molar heat capacity at constant volume of all substances is  $C_v = 3R$ , where  $R = 8,3144 \text{ J}/(\text{K} \cdot \text{mol})$  - the universal gas constant. The  $C_v$  parameter does not depend on the temperature  $T$  to determine its value ( $\theta_D$ ). Then  $C_v$  decreases monotonically and when  $T = 0 \text{ K}$   $C_v = 0$ .

Dulong and Petit law, which establishes the connection  $C_v$  and  $R$  parameters the ratio  $(C_v)_\mu = 3R$  is obtained based on classical statistics Maxwell-Boltzmann-Gibbs when using the ideal gas model. Einstein and Debye P. came to the conclusion that the temperature is lowered to a certain value classical statistics should be replaced by quantum. Atoms must be seen not as a colliding balls, but as quantum oscillators. Einstein proposed the condition that all the oscillators for monatomic substances have the same  $\omega_E$  frequency. P. Debye model is considered in which frequencies are

allocated according to the law  $P(\omega) \propto \omega^2$  up to a certain frequency  $\omega_D$ . When the ratio of the model is  $\omega > \omega_D$  applicable to describe the classical statistics.

Upon cooling agent treble "freeze." If the substance is heated from a low temperature, the low frequency "burn out." The theory of Debye to describe model systems were accurate Einstein's theory. In condensed matter physics began to use the concept of value of the Debye  $\omega_D$  - frequency,  $E_D$  - energy,  $\theta_D$  - the temperature [21].

The  $C_V(T)$  dependence is different for different substances. The resulting function  $C_V = f(T/\theta_D)$  has been set, the graph of which is shown in Figure 2. When in Formula (1) take  $x = T/\theta_D$ ,  $C_V = const$  ( $C_V$  at  $T \gg \theta_D$ ), then as shown in [18], the analytical relationships  $S(r)$  and  $C(T)$  coincide.

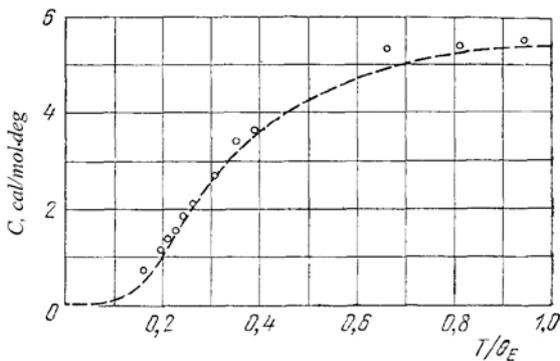


Figure 2 - The function  $C_V = f(T/\theta_D)$  in the P. Debye's theory of heat capacity [18]

Debye temperature ( $\theta_D$ ) as the parameter  $L_0$  is not strictly a sharp boundary, but this option is entered in the modern physical paradigm and used in the Mendeleev periodic system to describe its elements.

Debye theory of heat capacity indicates that the transition frequencies of quantum oscillators across the border  $\omega_D$  there is a change in the mechanisms of the processes of substance. The atoms as quantum oscillators vibrate at a certain frequency. At low volumes on the geometrical dimensions of the frequency spectrum is influenced not only the structure of the substance, and the particle size. Vibrations of atoms to create a dynamic field that oscillates the electrons in the electron cloud with the same frequency.

As part of the one-electron adiabatic approximation, we introduce the concept of Debye pseudo impulse  $P_D$ . We believe that the effective electron mass equal to the mass of a free electron. In this case

$$(5) P_D = \sqrt{2mE_D}$$

According to the formula of de Broglie Debye pseudo impulse  $P_D$  allows you to calculate the value of the Debye length (wave):

$$(6) \lambda_D = \frac{h}{P_D}$$

Wavelength Debye defines the scope of the electron on the surrounding areas of the sample [7]. Consequently, when  $r \ll \lambda_D$  the adiabatic model of a free electron is not applicable. It should be replaced by a model of "electronic jelly" [22].

Dynamic processes describes the flow of phonons, the mean free path which is commensurate with the  $\lambda_D$  [23, 24]. If values

$r < \lambda_D$  we can talk about a kind of "phonon vacuum" as a phonon can pass from one end to the other particles, followed by the process of flipping the border. When particle sizes  $r < L_0$  and  $r > L_0$  in the former case requires to consider model of "electronic

jelly" and "phonon vacuum" in the second case, the substance exists in a macroscopic phase.

As an example of the effect of particle size on the performance parameters of its properties shows the width of the plasmon peak for spherical gold particles (Figure 3).

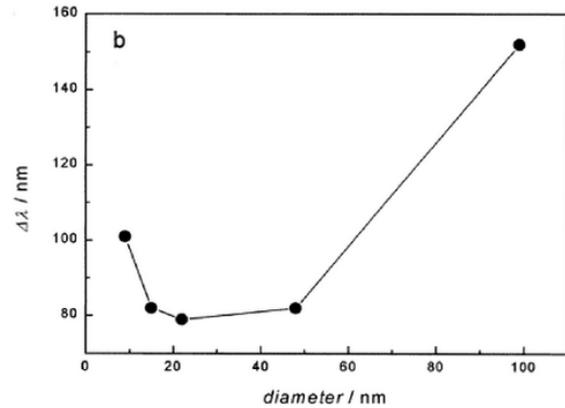


Figure 3 - Dependence of the maximum width of the plasmon ( $\Delta\lambda$ ) on the diameter of the spherical gold nanoparticle [5]

Consequently, the Debye length  $\lambda_D$  is the dimension of the boundary between the nano- and macrostate ( $L_0 = \lambda_D$ ) substance in the condensed state.

Debye parameters  $\omega_D$ ,  $E_D$ ,  $\theta_D$  are related to each other by the equations [22]:

$$(7) E_D = \hbar\omega_D = k\theta_D = \frac{P_D^2}{2m} = \frac{h^2}{2m\lambda_D^2}$$

where  $\hbar$ ,  $h$  ( $h = 2\pi\hbar$ ) - Planck's constant,  $k$  - the Boltzmann constant,  $m$  - mass of the electron.

Note that in these terms the Debye length and the de Broglie wavelength coincide. Condition (7)

$$(8) k\theta_D = \frac{(P_x^2 + P_y^2 + P_z^2)}{2m} = \frac{h^2}{2m\lambda_D^2}$$

For an isotropic medium  $P_x^2 = P_y^2 = P_z^2$ . In this case, the parameter of the Debye length  $\lambda_D$ , for example, along the axis x (y or z) is defined by the expression:

$$(9) L_0 = \lambda_D = \frac{\sqrt{1,5}h}{\sqrt{km}} \theta_D^{-1/2}$$

After substituting the numerical values of physical quantities ( $h$ ,  $k$ ,  $m$ ) received:

$$(10) L_0 = 2,3 \cdot 10^{-7} \left[ m \cdot K^{-1/2} \right] \cdot \theta_D^{-1/2} [K] = 230 \cdot \theta_D^{-1/2} [nm]$$

It is this formula has been used by us to calculate the  $L_0$  parameter of the experimental results obtained by many researchers [5, 5, 17].

Note that  $\theta_D = 170$  K for gold. Therefore, the value  $L_0$  is equal  $L_0 = 17,6$  nm to the gold particles, which agrees well with the results presented in [5], and given in Figure 3.

Debye temperature  $\theta_D$  - table setting. Experimental dependences for the  $S_V(r)$  characteristics parameters of the various physical properties are described in the literature. The experimental plots easy to determine the  $L_0$  value. This dimension corresponds to the start point of the  $S(r)$  deviation from the values of macroscopic matter. The parameter values  $L_0$  obtained experimentally and calculated by the formula (10) to coincide with an error not exceeding 10%. Therefore, we can say that when  $r = L_0$  there is a

kind of transition to the macroscopic phase of nanophase particulate matter [3, 25].

The proposed analytical expression (10) allows the evaluation of characteristics of the dispersed particles used in functional materials science to create composites based on metal, ceramic, silicate, organic macromolecular matrix. By scanning electron microscopy (SEM), it can be shown that the dispersed particles of micron dimensions range obtained with different technologies, are clustered structures containing nanoscale components (Figure 4). Nanocomponents whisker, plate and a spherical habitus characterized for inorganic particles obtained by dispersing (mechanical crushing) of natural semi-finished products - tripoli

(Figure 4 a), clay (Figure 4 b), shungite (Figure 4c), and the oxide sublimation products melts carbon and alloy steels (Figure 4 d), carbon nanotubes (Figure 4e) and polytetrafluoroethylene (Figure 4 f). Therefore, when assessing the effectiveness of modifying action of the dispersed particles in matrices of various kinds need to take account of their tendency to cluster formation and morphology and specific parameters of the surface layer comprising nanoelements. Obviously, significant role ratio of the surface layer particles and nanocomponents total since physico-chemical and structural processes occurring at the interface "matrix - the modifier" depend on a set of various factors affecting the kinetics of adsorption, crystallization and adhesion interaction.

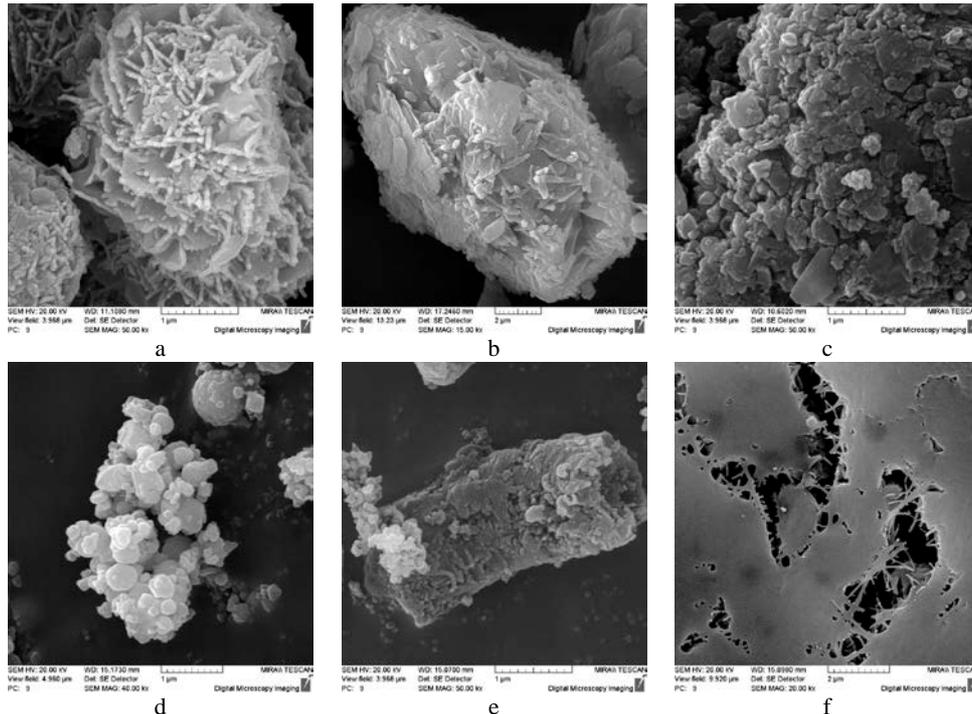


Figure 4 - A typical particle morphology tripoli (a), clay (b), shungite (c) metal oxide (d), carbon nanotubes (e), polytetrafluoroethylene (f)

#### 4. Conclusion

The experimental parameters depending on the characteristics of the numerical values of physical properties of substances from the sizes of the particles shows that these values correspond with tabular particle sizes  $r > L_0$  where  $L_0$  - dimensional macroscopic phase boundary between the state and nanophase particulate matter.

As part of the one-electron approximation for adiabatic electron with  $m$  mass can introduce the concept of the Debye pseudo impulse  $P_D$  and Debye wavelength  $\lambda_D$ . The relationship between Debye parameters: energy  $E_D$ , frequency  $\omega_D$ , temperature  $\theta_D$ , pulse  $P_D$ , wave length  $\lambda_D$ , is given by:

$$E_D = \hbar\omega_D = k\theta_D = \frac{P_D^2}{2m} = \frac{3P_x^2}{2m(\lambda_D)_x^2} = \frac{3\hbar^2}{2m(\lambda_D)_x^2}$$

For an isotropic medium  $L_0$  value proposed is calculated as:

$$L_0 = \lambda_D = \frac{\sqrt{1,5}\hbar}{\sqrt{km}} \theta_D^{-1/2} = 230 \cdot \theta_D^{-1/2}$$

When the particle size  $r > L_0$  is possible to use the classic one-electron adiabatic model. If  $r < L_0$  you must to use the model of "electronic jelly". The proposed formula allows the estimation of the modifying action of the dispersed particles in the parameters of the surface layer of the particle morphology formed by nanocomponents of different habitus.

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