

# Physical principles of nanoscale criterion selection for disperse particles

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The article discusses the analysis of dimensional boundary between the nano- and macrostate and mathematical description of the nanoparticle term. Nanoparticle is a part of the substance, which has two main properties. First, the nanoparticle has a surface, and in a mixture with other substances it can be mechanically separated. The second characteristic feature of nanoparticle is the dependence of the numerical values of the physical properties on its size. When reducing the size of homogeneous material object, the parameters of its physical properties do not depend on the size up to a certain  $L_0$  value. If the size  $r < L_0$ , the parameters of the physical properties begin to change. Hence, there is a dimension boundary  $L_0$  between the macroscopic and nano-sized state.

**Keywords:** Nanoparticle, Debye temperature, quantum dimension effect, scale diapason

## Introduction

Nanomaterials have become the modern paradigm of materials science. They consist of structural elements of nanometer size, and nanotechnology allows modifying the traditional technical materials, giving them unusual properties and new functions. Thus, for example, it is possible to increase the efficiency of chemical reactions catalysts, films for microelectronics, protective coatings, magnetic systems and medical technologies. Theory and practice of materials science has accepted new terms with the prefix “nano”.

In principle, their introduction would not be essential if not yet obsolete classification of material objects at the macro-, micro-, and quantum objects or systems. The feasibility of developing new terminology usually occurs when the some phenomena are detected whose description by traditional conceptual apparatus is impractical or does not adequately reflect their new properties. Nanomaterials in the form of glass, stained with colloidal metal particles, produced in ancient Egypt. The scattering of light by such glasses studied Michael Faraday. Nanotechnology as the technology of colloidal chemistry has been known since the middle of the XIX century (Pauling and Pauling, 1978). Just at the turn of the XX and XXI centuries, the accumulated amount of fundamental knowledge in physics, chemistry, and related sciences was recognized as the scientific basis for a fundamentally new engineering technology called nanotechnology. It is believed that nanoparticle consists of a small amount of the basic substance and commensurate with it the surface layer, which to large extent determines the properties of the nanoparticles.

The aim of the work is the analysis of dimensional boundary between the nano- and macrostate and mathematical description of the nanoparticle term.

## The concept of “nanoparticle”

At present, it is assumed that the nanoparticle is atomic molecular system that retains its shape and has a linear dimension of less than 100 nm. It is sometimes said that the nanoparticle represents an object whose dimensions are measured in nanometers, and it contains a small number of atoms. There are other additions to these definitions which, in our opinion, are not justified.

The size of an object can be expressed in standard units, e.g., nanometers. Defining the common upper limit of the size for any nanoparticle is impossible. With the same “success” one can a common melting point for all substances. The notion that the nanoparticle generally contains a small number of atoms also needs to be clarified.

Let the radius of the spherical metal nanoparticle is 10 nm. The average radius of the metal atoms does not exceed  $r=1.5\text{\AA}$ . If the packing coefficient of atoms in the particle is equal to  $K$ , the number of atoms in the nanoparticle is

$$N = \left(\frac{R}{r}\right)^3 \cdot K. \quad (1)$$

To the densest packing  $K=0,74$ , i.e.  $N \approx 3 \cdot 10^5$  atoms. Such a particle can hardly be considered consisting of a small number of atoms. In addition, we should distinguish the nanoparticle and nanoobject concepts. Nanoobjects can assume any atomic-molecular system with dimensions at the nanoscale. For example, nanoobjects may be a cluster in a liquid or some other part of the substance compared to the basic matrix. Nanoobject may not have an interface with other components of substance. A nanoparticle necessarily has a surface and can be isolated from the mixture by mechanical means.

An important feature of the nanoparticle suggests a dependence of numerical values of physical properties of the substance from the size of nanoparticle. Most contemporary literature indicates the parameters of the physical properties regardless from the substances' particles size, believing that no dependence exists. It is believed that the particle size has no effect on these parameters; so, the substance is regarded as a continual medium. These parameters correspond to the macroscopic volume phase ( $S_v$ ) (Batsanov, 1985).

### Dependence of numerical values of substance physical properties from the particles size

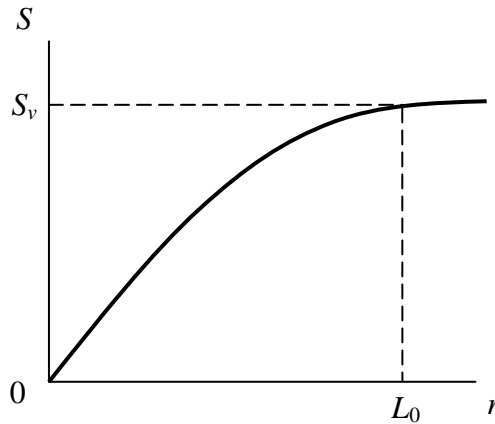
Even in the first half of the last century it was found experimentally that the specific heat of substances ( $C_v$ ) depends on their particle size (Kittel, 1967). Particularly noticeable interest in low-dimensional objects has increased after the famous report of R. Feynman in 1959 (Feynman, 2002). Studies of the properties of nanoscale particles have been performed by various authors (Gusev, 2007; Ajayan, Schadler, and Braun, 2004; Poole and Owens, 2005; Roldugin, 2004; Stoscio and Dutta, 2011). It was found that the numerical values of physical properties of various substances remain constant up to a certain size of particle  $r = L_0$ . If the size  $r < L_0$ , the parameter values  $S = S(r)$ , that is they are dependent on particles size. A typical dependence is shown in Figure 1.

Given curve with sufficient accuracy  $S(r)$  is described by the formula

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

Where,  $S_v$  - the bulk macroscopic value of the studied physical properties,  $\alpha$  - a parameter depending on the studied properties,  $x = r/L_0$ .

FIGURE 1. S PARAMETER DEPENDENCE OF THE PHYSICAL PROPERTY OF THE MATERIAL FROM ITS PARTICLE SIZE  $r$   
 $S_v$  - parameter bulk value,  $L_0$  - the maximum size of the nanoparticle



Analysis of numerous studies shows that the value  $L_0$  lies in the nanometer range, and its value depends on the substance. Therefore,  $L_0$  is the dimension of the boundary between the macroscopic and nano-sized state. If the particle size is  $r > L_0$ , the exponent becomes an imaginary quantity, and  $S(r) = S_v$ ,  $|\exp i_\tau| = 1$  as for any real value of  $\tau$ . The values  $S(x)$  and  $L_0$  are determined experimentally. Then, it opens the possibility of determining the  $\alpha$  value.

Let us introduce the values:

$$\ln \frac{S_v}{S_0} = Y, \quad \frac{1-x}{x} = X,$$

Now the condition (1) is converted into a linear function

$$Y = \alpha(X), \quad (3)$$

which points are known from the experiment.

It is obvious, when  $x = L_0$   $X = Y = 0$ , the value of  $\alpha$  - is the slope. We have performed calculations for different degrees  $\left(\frac{1-x}{x}\right)$  (see (2)). The highest correlation coefficient corresponds to a  $\frac{3}{2}$  degree. In some cases, experimental linear function (3) does not pass through the origin. This can be explained by the fact that not mono-sized particles are studied, and the statistical distribution of particles includes particles with  $r > L_0$ .

### **The calculation of dimensional boundary $L_0$ between macro- and nanoscale states**

In the study of the properties of various objects with large size their surface is viewed as an infinitely thin shell: one side of which contains the atoms (molecules) of the studied object, and the other does not have them. It is considered that atoms of the surface layer are in different state in comparison with the inner carbon atoms, and influence of the surface layer atoms extends over several inner layers (5-7) (Dunken and Lygin, 1980). However, the thickness of the surface layer is less than the size of the sample, so that it can be neglected. It is assumed that the surface is completely rigid and fixed in space.

The spectra of the wave functions of electrons, photons and other particles are discrete linear. With the decrease of particles size, relative sizes of the surface layer increase. The lines in the spectra begin to blur into bands, which leads to a change in the numerical values of properties. With further decrease the size of the band continue to expand, which is accompanied by the subsequent changes of  $S(s)$ . These changes are monotonic, as is observed in the experiments. This qualitative model explains why  $L_0$  is not a sharp boundary between the nano- and macrostate, but it does not allow calculating of this value.

In our view, the formula for calculating the  $L_0$  value must meet several requirements. First, it must be supported by well-known, proven physical principles. Secondly, it is necessary that it should take into account properties of the substance. Third, it must be fairly simple, and, most importantly, such formula should correspond to the experiments.

Let us refer to the Figure 1. If instead the  $S(r)$  on the ordinate axis we assume the heat for various substances temperatures  $T$  (which values are debugged on the abscissa), than instead  $L_0$  we should indicate the Debye temperature  $\theta_D$ . Constancy of  $C_v$  in  $T > \theta_D$  is explained in the framework of classical thermodynamics, based on statistical representations of the Maxwell-Boltzmann-Gibbs. When  $T < \theta_D$ , as shown by A. Einstein and P. Debye, you need to escape from the interaction of atoms only by collisions. It should be taken into account that the atoms are quantum oscillators that have the same frequency (according to A. Einstein), or are described by  $P \omega \sim \omega^2$  distribution of frequencies (by P. Debye). Both of these approaches correspond to the dependence  $C_v = f(T)$ . But the Debye theory turned out as more appropriate to the experiment. When  $T = \theta_D$ , there is a change in the process mechanism in the substance. The greater are the inequalities  $T > \theta_D$ ,

or  $T < \theta_D$ , that more motivated the use of an appropriate description of the processes in the analyzed material.

Along with the Debye temperature it is used the concept of the Debye frequency ( $\omega_D$ ), momentum ( $P_D$ ), wavelength, or more precisely the Debye wave ( $\lambda_D$ ), as well as the Debye energy. All these quantities are interrelated:

$$E_D = \hbar\omega_D = k\theta_D = \frac{P_D^2}{2m} = \frac{h^2}{2m\lambda_D^2}, \quad (4)$$

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

Processes in materials are usually divided into two types: electronic and lattice. In electronic processes the electromagnetic interaction occurs. Lattice processes include diffusion, thermal vibrations of atoms, mechanical waves (e.g., acoustic) excitations. In the first case, the interaction carriers are photons, in the second - phonons. Emerging of streams of other quasi-particles (excitons, plasmons, vacancy, etc.) is also possible. This aspect is not critical, since ultimately the interaction of various objects in substances performs due to electrons that can cause and movement of ions (atoms). This may explain the fact that in the equations (4) occur both the phonon ( $\omega_D$ ) and electronic ( $m$ ) characteristics.

The greatest interest is the Debye length ( $\lambda_D$ ). For electrons  $\lambda_D$  determines the size of the area in the matter covered by the influence of a single electron. When  $r > \lambda_D$ , a single-electron adiabatic approximation is correct. When  $r < \lambda_D$ , it is necessary to use the model of the “electronic jelly”.

The Debye length is an important parameter of the phonon processes, since  $\lambda_D$  - is the average mean of phonon free path (Reissland, 1975). That is, when  $r < \lambda_D$ , the particle is characterized by a “phonon vacuum” state; and physical processes taking place in it are different from the bulky ones.

Consequently,  $L_0 = \lambda_D$  limits the size of particles with macro properties. New mechanisms of physical processes suggest that the numerical values of parameters changes depending on the size.

Let us consider the equality

$$k\theta_D = \frac{P_D}{2m}. \quad (5)$$

Since  $\lambda_D$  is defined along a particular direction (along the path  $x$ ), then it is necessary to analyze the momentum component along this direction. For simplicity, we assume that  $P_x = P_y = P_z$  that is  $P^2 = 2P_x^2$ . But,  $P_x = \left(\frac{h}{\lambda_D}\right)_x$ . Therefore

$$k\theta_D = \frac{3P^2}{2m} = \frac{3h^2}{2m\lambda_D^2}. \quad (6)$$

The index  $x$  is omitted, since the  $\lambda_D$  vectors and the  $P_x$  component in (6) are collinear.

From (6) follows

$$\lambda_D = \frac{\sqrt{1,5}h}{\sqrt{km}} \theta_D^{-1/2} = C\theta_D^{-1/2}. \quad (7)$$

After substitution of the numerical values of the physical constants in the condition (7) we get:

$$C = 2,3 \cdot 10^{-7} \left[ \text{M} \cdot \text{K}^{1/2} \right].$$

Consequently,

$$L_0 = \lambda_D = 2,3 \cdot 10^{-7} \theta_D^{-1/2} [\text{M}] = 230 \cdot \theta_D^{-1/2} [\mu\text{M}]. \quad (8)$$

This formula is completely in line with many results published by various authors.

The Debye frequency is determined by the formula

$$\omega_D = \bar{u} (6\pi^2 n)^{1/3}, \quad (9)$$

where,  $\bar{u}$  - the average phonon velocity (speed of sound),  $n$  - the number of atoms per unit volume.

If the speed of sound is anisotropic quantity, and frequency ( $\omega_D$ ), length ( $\lambda_D$ ), and the Debye temperature become anisotropic values. In this case,  $\omega_D$  should be considered in a certain direction (e.g., along the x-axis):

$$\omega_D^{(x)} = k u^{(x)} n^{(x)} (6\pi^2)^{1/3}, \quad (10)$$

where,  $n^{(x)}$  - the linear density of the atoms. Hence

$$\theta_D = k u^{(x)} \cdot n^{(x)} (6\pi^2)^{1/3}, \quad (11)$$

Thus, the boundary between the macroscopic and nanostructured states determines the difference in the mechanisms of physical processes progress in the particles: when size  $r > L_0$  does not affect the value of the parameter and physical properties and when the particle size  $r < L_0$  provide the influence on the value (Liopo, Struck, and Nikitin, 2010).

### The lower limit of the size of the nanoparticles

From (2) describing relationship of the parameter value of the physical properties on the size of the nanoparticles follows that

$$\lim_{r \rightarrow 0} S(r) = 0. \quad (12)$$

But this contradicts the general physical concepts. Indeed, a single atom has size  $d > 0$ , but is not a nanoparticle as it has no surface and concept of the substance physical property for it becomes meaningless. Therefore, there must be a dimensional boundary  $B$  such that an object in condition  $L_0 > r > B$  behaves as a nanoparticle; and when  $r < B$  it should be considered as an atomic (molecular) cluster the properties of which cannot match the properties of nano- and macrophase. Particle will not be an aggregate, which includes the first coordination sphere. With further growth of this aggregate, starting with the  $n$ -th coordination sphere, the object acquires the properties of the particle. The  $n$  value may not be the same for all substances.

At small particle sizes, outside atoms oscillation amplitude ( $\delta$ ) may be commensurate with the size of the particle. Object size  $d$  is a some mean value, since it varies in time interval  $d \pm \delta$ .

Let us consider the behavior of an electron in a particle with a  $d$  size, not counting vibrations of atoms of the surface layer (the model of an infinitely deep potential well). The Schrödinger equation for the electron is:

$$-\frac{\hbar^2}{2m_e} \frac{d^2\psi}{dx^2} = E\psi \quad (13)$$

or

$$\frac{d^2\psi}{dx^2} + q^2\psi = 0, \quad (14)$$

wherein  $q = \frac{P}{\hbar}$ , as the momentum  $P = \sqrt{2m_e E}$ .

The solution is sought in the form

$$\psi = \psi_0 \sin qx.$$

Function  $\psi(x) = 0$  at  $x = 0, x = d$ .

Consequently  $qd = n\pi$ . That is  $q = n\pi/d = \frac{P}{\hbar} = \frac{2\pi P}{h}$ .

Since taking into account fluctuations of the surface atoms, the uncertainty of the electron position can be assumed to be equal to  $d$ , and the uncertainty of momentum  $\Delta P = P_{\max} - P_{\min}$ , we have (when  $n = 1$ )

$$\Delta P = P_{\max} - P_{\min} = \frac{h}{2} \left( \frac{1}{d - \delta} - \frac{1}{d + \delta} \right) = \frac{h}{d}. \quad (15)$$

Let introduce designation  $\delta/d = \Delta$ . In this case (15)

$$\frac{\Delta}{1 - \Delta^2} = 1. \quad (16)$$

The solution of this equation is the golden ratio  $\tau = 0,5(\sqrt{5} - 1)$ . Hence

$$d = \frac{\delta}{\tau}. \quad (17)$$

It must be noted that in this model it is assumed that the coordinates on the object surface changes for  $\pm\delta$ , and the other surface is fixed and is in the point  $x = 0$ . To account atoms vibrations on opposite surfaces the dimensional boundary must be calculated according to the formula

$$B = \frac{2}{\tau} \cdot \delta = 3,25\delta. \quad (18)$$

If the amount of atomic (molecular) object  $d > B$ , it can be regarded as a particle. Unless  $d < B$ , that is the atomic-molecular cluster. As  $L_0$  the dimensional boundary  $B$  is not strictly defined, that is accurate. The more  $d$  is different from  $B$ , the more is the reason to note the object has state of nanoparticle or cluster (Liopo, 2012).



## Conclusion

Nanoparticle is a part of the substance, which has two main properties. First, the nanoparticle has a surface, and in a mixture with other substances it can be mechanically separated. The second characteristic feature of nanoparticle is the dependence of the numerical values of the physical properties on its size. When reducing the size of homogeneous material object, the parameters of its physical properties do not depend on the size up to a certain  $L_0$  value. If the size  $r < L_0$ , the parameters of the physical properties begin to change. Hence, there is a dimension boundary  $L_0$  between the macroscopic and nano-sized state. This boundary depends on the properties of matter and related to the fundamental parameter of the solid state physics - with the Debye temperature. Deduced and physically justified dependence  $L_0 = f(\theta_D)$  is  $L_0 = 230\theta_D^{-1/2} [nm]$ . Calculated using this formula  $L_0$  values are fully consistent with the available in the literature data on the properties of nanoparticles study. The numerical value of physical properties parameter depending on the size of the object described by the condition

$$S(r) = \frac{S_v}{\left[ \exp \left[ -\alpha \left( \frac{1-x}{x} \right)^{3/2} \right] \right]}, \quad (19)$$

where,  $S_v$  - the bulk (macroscopic, ie, a tabular), the value of the parameter,  $x = r/L_0$ ,  $\alpha$  - coefficient depending on the property under consideration.

When reducing the size of the particles to very small values, the term “nanoparticle” disappears, as the surface of the objects disappears and the concept of “physical property” is meaningless. Dimensional boundary between nanostate and atomic cluster system ( $B$ ) is determined by the vibrations of the surface atoms. This factor “blurs” the surface, transforming it into the surface layer. Value ( $B$ ) is defined

$$B = 3,2\delta,$$

where,  $\delta$  - the amplitude of the vibrations of the atoms in the outer nuclear layer of the particle.

We note, in our view, an unusual feature of the  $S(r)$  function. If  $(1-x)/x = \tau$ , then the  $S(r)/S_v$  ratio is different from the golden ratio of 0.003 by less.

To determine the dimensional boundary between the macro- and nanoscale states, it is necessary to consider the Debye temperature, which is determined by the structural and chemical properties of the substance. When calculating the dimensional boundary between the nano- and atomic cluster states there is a need to know the parameters of the spatial fluctuations of the atoms of the outer coordination sphere ( $\delta$ ). Quantity  $\delta$  is not a tabular, as it can vary depending on

reciprocal configuration of atoms in cluster and external conditions (temperature, pressure and environmental features, etc.).

The paper does not consider the issue of calculating the  $\delta$  value as a parameter of the surface atoms position change. But the record of this quantity at small sizes of the particles allowed substantiating the existence of the dimensional boundary between nanostate and atomic cluster state ( $B$ ). If the size  $d$  is in the range  $B < d < L_0$ , the object is a nanoparticle. For values  $d < B$  a group of atoms (molecules) forms a cluster. However, this object does not have a fixed surface, i.e. loses the main feature of the particle. The boundary  $B$ , as  $L_0$  is not sharp, precisely fixed and depends not only on the cluster substance, but also on other factors.

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