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THE SIZE DEPENDENCE OF THE PHYSICAL PROPERTIES OF NANOPARTICLES AND NANOFILMS

Yurov V.M.¹, Eremin E.N.², Guchenko S.A.¹, Laurynas V.Ch.¹

¹E.A. Buketov Karaganda State University, Kazakhstan, exciton@listl.ru

²Omsk State Technical University, Russia, weld_techn@mail.ru

Dimensional analysis of the experimentally observed dependence of the physical properties of nanoparticles, nanofilms and nanomaterials showed that there is a universal equation that accurately describes the observed size effects. It is shown that the size factor is also a universal value and is determined only by the atomic structure of the nanomaterial. Discovered universal relationships enable us to calculate the physical properties (mechanical, electrical, magnetic, thermal, etc.) of small particles and thin films based on knowledge of the properties of bulk materials. Based on the example of the nucleation of a new phase it is shown that the classical theory are applicable, taking into account the size dependence of the surface tension. The calculation of the temperature field of plate nanometer thickness showed that it is necessary to take into account the size dependence of all physical parameters of the theory (coefficients of thermal conductivity, etc.).

Keywords: nanoparticle, nanomaterial, size effect, the surface layer, the melting temperature, heat of fusion, surface tension, thermal conductivity.

1. Introduction

A characteristic feature of the nanoparticles and nanomaterials is the size dependence of their physical properties. To distinguish two types of size effects [1]: own, or internal, associated with changes in properties such as melting temperature, heat capacity, etc., and the external, which is the size-dependent response to the external action of the forces that are independent of the internal effect (electric conductivity, magnetic susceptibility and others).

In this paper we want to show that most of both internal and external size effects described by one universal dependence.

2. The melting point of fine particles

The physical nature of reducing the melting point of the particles with decreasing size is as follows: with a decrease in particle size increases the proportion of surface atoms, which is less than the binding energy of atoms than in volume, so that less energy is required for the thermal motion of the phase transition solid-liquid. However, to find a quantitative relation between the melting point of the nanoparticles and their size was not easy (see. the review [2]). The melting point of the most accurate for the gold nanoparticle size dependence was defined in the pioneering work [3]. A similar relationship was observed by many authors later for some other metal nanoparticles. It was found that the experimental curves are well described by the equation [4]:

$$T_m(r) = T_\infty \left(1 - \frac{d}{r} \right), \quad (1)$$

where T_∞ - the melting point of the bulk sample.

The parameter d is determined by the formula [4]:

$$d = \frac{2\sigma}{RT} \quad (2)$$

Here σ - the surface tension of the bulk sample; u - molar volume, R - universal gas constant.

In Table 1 are presented the melting temperature of nanoparticles of various sizes for most metals the periodic table.

Table 1 - The melting point of pure metal nanoparticles (M - metal)

M	T_{∞} , K	T_m , K r = 1 nm	T_m , K r = 10 nm	T_m , K r = 50 nm	M	T_{∞} , K	T_m , K r = 1 nm	T_m , K r = 10 nm	T_m , K r = 50 nm
Li	452	188.3	396.5	440.1	Cd	594	204.8	499.2	572.3
Na	371	119.7	306.6	356.1	Hg	234	127.7	216.1	230.2
K	337	71.7	246.1	314.1	Cr	2173	452.7	1574.6	2019.5
Rb	312	60.0	219.7	287.7	Mo	2873	383.1	1741.2	2542.5
Cs	302	48.7	198.7	273.6	W	3673	390.7	1996.2	3144.7
Be	1558	556.3	1320.4	1558	Mn	1517	399.2	1185.2	1436.6
Mg	923	225.1	704.6	869.1	Tc	2473	405.4	1637.7	2244.1
Ca	1118	139.8	657.6	980.7	Re	3423	422.6	2001.8	2997.4
Sr	1030	110.8	562.8	883.6	Fe	1808	441.0	1380.2	1702.5
Ba	983	99.3	520.1	834.5	Co	1763	464.0	1377.3	1670.0
Al	933	291.6	764.8	933.0	Ni	1726	466.5	1359.1	1637.6
Ga	302.8	159.3	277.6	297.3	Ce	1077	168.3	699.4	972.0
In	429	165.0	369.8	415.7	Pr	1208	172.6	755.0	1078.6
Tl	576	169.4	464.5	549.6	Nd	1298	175.4	791.5	1150.7
Si	1686	285.8	1131.5	1535.9	Sm	1325	181.5	812.9	1176.7
Ge	1231	246.2	879.3	1140.0	Eu	1175	126.3	642.1	1007.7
Sn	505	168.3	420.8	485.6	Gd	1585	184.3	900.6	1376.0
Pb	600	166.7	600.0	600.0	Tb	1631	191.9	932.0	1418.3
Se	493	170.0	414.3	475.0	Dy	1680	195.3	954.5	1458.3
Te	725	161.1	537.0	676.7	Ho	1734	197.1	974.2	1500.0
Cu	1356	411.0	1102.4	1296.4	Er	1770	201.1	994.4	1531.4
Ag	1234	301.0	942.0	1162.0	Tm	1818	216.4	1044.8	1583.6
Au	1336	310.7	1004.5	1253.3	Yb	1097	146.3	664.8	970.8
Zn	693	277.2	602.6	672.8	Lu	1925	209.2	1057.7	1653.8

Table 1 shows that the alkali metal nanoparticle size (1-5) nm melt at negative celsius temperatures. Unlike the alkali metal, alkaline earth metal nanoparticles may be stable at 10 nm in size, and beryllium nanoparticles - and 1 nm. Melting point reduced by a larger amount than in the case of alkali metal $-\Delta T \approx (700-1000)^\circ\text{C}$.

From Table 1, which are stable at room temperature and thallium alumina nanoparticles of 10 nm gallium nanoparticles are unstable in sizes up to 100 nm. Lowering the melting temperature of the boron subgroup nanoparticles is ranging from 140 K to 640 K. The differences are significant in the subgroup of carbon. Silicon and germanium - semiconductors and have similar values ΔT . The same is observed for typical metals - tin and lead. The nanoparticles of 10 nm in both cases are stable under ordinary conditions. The melting point of lead 10 nm size nanoparticles is already equal to the temperature of the massive substance. In case also chalcogen nanoparticles of 10 nm in both cases are stable under ordinary conditions.

For metals copper subgroup stable at room temperature, are nanoparticles of 1 nm. The well-known and frequently cited paper [3] for the gold the size of 1 nm is obtained experimental value of the melting temperature of nanoparticles - (305÷310) K, which practically coincides with our values. This speaks in favor of the proposed in this paper methods for calculating the melting temperature of the nanoparticles. Cadmium and zinc nanoparticles 10 nm in size, as most of the above metal nanoparticles are stable at room temperature and above.

Nanoparticles subgroups chromium, manganese and iron 1 nm are stable at room temperature and above. Changing the melting temperature is very significant. Lanthanide nanoparticles of 1 nm are unstable at room temperature. When $r < d$, instead of equation (1) need to use the equation:

$$T_m(r) = T_\infty \left(1 - \frac{d}{d+r} \right). \quad (3)$$

Equation (1) allows you to experimentally determine the surface tension of the solid-state σ [5]. Processing of the experimental curves by means of (1) has shown that for metals with great precision the relation:

$$\sigma = 0,7 \cdot 10^{-3} \cdot T_\infty. \quad (4)$$

In other words, between the value of the surface tension and pure metal melting point there is a simple universal dependence (4). Note that the relationship (4) was also obtained in [6] in another way.

3. The thickness of the surface layer atomically smooth metal

When $r > d$ melting temperature tends to the value characteristic of the bulk sample. Therefore, the parameter d is naturally called the thickness of the surface layer of metal. For some metals, these values are given in Table 2.

Table 2 - Surface layer thickness d pure metals (M - metal)

M	d, nm	M	d, nm	M	d, nm	M	d, nm	M	d, nm	M	d, nm	M	d, nm
Li	0.7	Sr	5.8	Sn	1.4	Cd	1.3	Fe	2.2	Gd	5.3	Ac	3.5
Na	1.5	Ba	6.2	Pb	1.8	Hg	0.6	Co	2.0	Tb	5.3	Th	6.7
K	2.6	Al	1.5	Se	1.3	Cr	2.7	Ni	1.9	Dy	5.3	U	2.9
Rb	2.9	Ga	0.6	Te	2.5	Mo	4.6	Ce	3.8	Ho	5.5	Nb	1.8
Cs	3.6	In	1.1	Cu	1.6	W	5.8	Pr	4.2	Er	5.5	Pu	1.9
Be	1.3	Tl	1.9	Ag	2.2	Mn	2.0	Nd	4.5	Tm	5.2	Am	4.5
Mg	2.2	Si	3.4	Au	2.4	Tc	3.6	Sm	4.4	Yb	4.6	Bk	3.6
Ca	4.9	Ge	2.8	Zn	1.1	Re	4.6	Eu	5.8	Lu	5.7	-	-

Table 2 shows that the thickness of the surface layer of pure metals is not more than 10 nm. This means that the surface layer is a pure metal nanostructure. From (2) and (4):

$$d = 2,41 \cdot 10^{-4} \cdot v \text{ (m}^{-2} \cdot \text{mol)} \quad (5)$$

According to the formula (5), the thickness of the surface layer is defined by a single parameter - v , ie the atomic structure of the metal. Equation (5) also allows you to estimate the thickness of the surface layer of metal on the known value of u . For example, for gold $v = 10.2 \text{ cm}^3/\text{mol}$ and the ratio of (5) gives $d = 2.45 \text{ nm}$. This value is slightly different from the table 2 (2.40 nm).

4. The size dependence of the surface tension

In [5] to the surface tension of the nanocrystal obtained by the following expression:

$$\sigma(r) = \sigma_{\infty} \left(1 - \frac{d}{r} \right), \quad (6)$$

where $\sigma_{\infty} = \sigma$ - the surface tension of the bulk sample, the parameter d has the same meaning as in the previous cases.

Formula (6) in the form coincides with the formula Gibbs - Tolman - Koenig - Buff:

$$\sigma(r) = \sigma_{\infty} \left(1 - \frac{2\delta}{r} \right), \quad (7)$$

where δ is called the Tolman constant or Tolman length [6].

It is believed that this option can not be determined experimentally. In this case, a constant Tolman $\delta = d/2$, which can be determined experimentally. Formula (6) coincides with the mathematical formula (1).

5. External size effects

Figure 1 shows the size dependence of the luminescence intensity of the KCl-Tl phosphor, and Figure 2 - size dependence of the magnetic susceptibility of magnetite. In both these cases, depending describes with great accuracy the formulas:

$$I = I_0 \left(1 - \frac{d}{r} \right), \quad \chi = \chi_0 \left(1 - \frac{d}{r} \right). \quad (8)$$

Here the parameter d is calculated by formula (2) and determines the corresponding surface of the material layer thickness. In the coordinates $I/I_0 \sim 1/r$ dependence in Fig. 1 and 2 give a straight tangent of the angle which is equal to d . This makes it possible to determine the surface tension of the dielectric and magnetic materials.

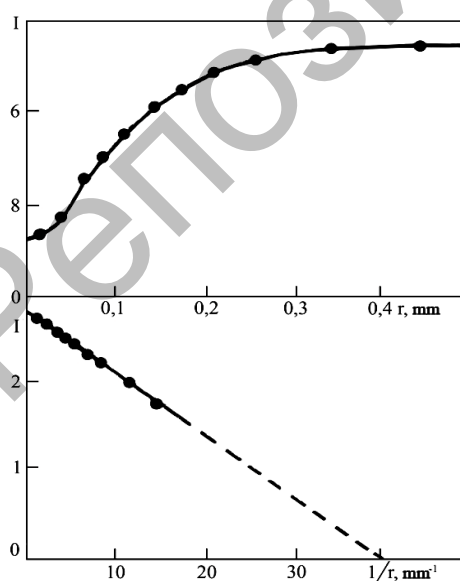


Fig.1. The dependence of KCl-Tl luminescence intensity of the phosphor grain size [7].

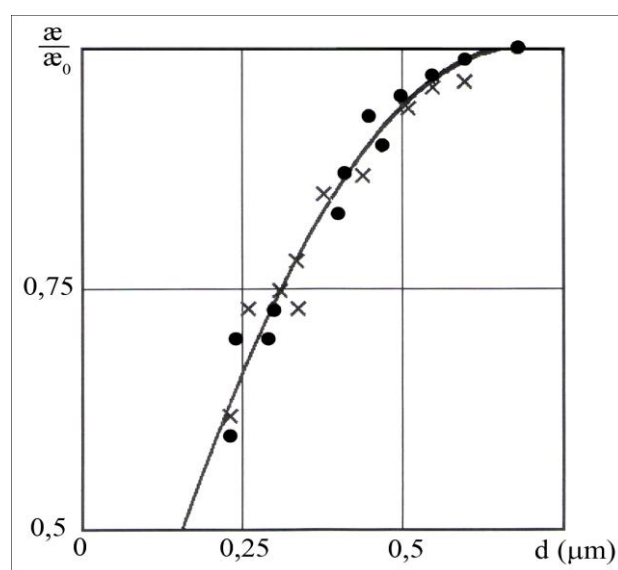


Fig. 2. The dependence of the magnetic susceptibility of the diameter of the magnetite grains [8].

6. Universal size dependence of the physical properties of nanomaterials

From the above it follows the following dependence of the physical properties of nanomaterial $A(r)$ on its size r :

$$A(r) = A_{\infty} \left(1 - \frac{d}{r} \right). \quad (9)$$

Consider some examples of the account of the size dependence of the physical properties of small particles and thin films. The main provisions of the theory of formation of new phase nuclei were advanced by Gibbs and then developed by M. Volmer, A. Becker and J. Doering, I. Stransky and R. Kaishev, I. Frenkel, Ya. Zeldovich et al [9].

Despite various modifications and refinement of classical nucleation theory, and it is quite correct qualitative description of nucleation process, it is still far from matching the experimental and theoretical data. This is due to the following circumstances:

- theory is based on the assumption that the microscopic clusters of atoms exhibit macroscopic characteristics and, more generally, the equilibrium thermodynamic parameters;
- almost all the works devoted to the initial stage of nucleation of a new phase (including the more recent work [10-12]), the formation of the metastable phase is considered to be instantaneous;
- theory (and its modifications) contains a number of parameters that do not have a strictly quantitative solutions.

7. Results and discussion

Example 1. Homogeneous nucleation of crystals

According to the classical theory of nucleation of a new phase in the old metastable phase is considered as a fluctuation process. In the case of the crystallization of a supercooled melt critical radius of a nucleus can be expressed in terms of supercooling ΔT [9]:

$$r_{\text{c}} = 2M\sigma T_0 / \rho q \Delta T, \quad (10)$$

where M - molecular weight; ρ - the density of crystal-nucleus; q - heat of fusion; T_0 - temperature equilibrium of the two phases of infinitely large radius, σ - interfacial tension of crystal-nucleus.

In most studies it is considered that homogeneous nucleation of metal crystals begins with the supercooling $\Delta T = 0.2T_m$ of the melting temperature. Assuming that $T_0 = T_m$, we obtain:

$$r_{\text{c}} = 10M\sigma / \rho q. \quad (11)$$

All values in the expression (11) (except σ) are determined experimentally with great precision and are listed in directories. For pure metals surface tension value σ_0 is defined in [4]. The interfacial surface tension at the crystal - melt is approximately equal to: $\sigma \approx 1/3\sigma_0$. Then the calculation of the classical formula (11) gives a value for the critical radius of the order of a micron or a fraction of that in the three orders of magnitude the experimentally observed values. In [13] takes into account the size dependence of all the quantities in the equation (11) and calculated the critical radius of nucleation of solid phase of pure metals (Table 3).

Table 4 shows the values of the critical radius of the homogeneous nucleation of some pure metals obtained experimentally in [14]. Compare values from Tables 3 and 4 show good agreement, which speaks in favor of the developed approach. From the above discussion, it follows that in the classical theory does not take into account the size dependence of the surface tension, the melting

point and other physical properties of small particles. Therefore, the discrepancy between theory and experiment is so impressive, despite the fact that the approach is based on fluctuations of no objection to the theory.

Table 3 - Critical radius of homogeneous formation of the pure metals [13]

M	r_k , nm	M	r_k , nm	M	r_k , nm	M	r_k , nm	M	r_k , nm	M	r_k , nm	M	r_k , nm
Li	0.5	Sr	2.8	Sn	0.7	Cd	0.6	Fe	1.0	Gd	2.5	Ac	2.3
Na	0.7	Ba	2.9	Pb	0.8	Hg	0.3	Co	0.9	Tb	2.4	Th	3.2
K	1.2	Al	0.7	Se	0.6	Cr	1.3	Ni	0.9	Dy	2.5	U	1.4
Rb	1.4	Ga	0.3	Te	1.2	Mo	2.2	Ce	1.8	Ho	2.5	Np	0.9
Cs	1.7	In	0.5	Cu	0.8	W	2.8	Pr	2.0	Er	2.5	Pu	0.9
Be	0.6	Tl	0.8	Ag	1.0	Mn	0.9	Nd	2.1	Tm	2.4	Am	2.1
Mg	1.0	Si	1.6	Au	1.1	Tc	1.7	Sm	2.1	Yb	2.2	Bk	1.7
Ca	2.3	Ge	1.3	Zn	0.5	Re	2.7	Eu	2.7	Lu	2.7	-	-

Table 4 - The critical radius of homogeneous formation of some metals [14]

M	r_k , nm	M	r_k , nm	M	r_k , nm	M	r_k , nm
Ga	0.9	Ge	0.9	Cu	1.1	Pb	1.1
Sn	1.2	Ag	1.2	Bi	0.8	Hg	0.8

Example 2: Thermal field plate nanometer thickness

Consider the problem of thermal field of unlimited plate thickness x . For ease of comparison, and confine ourselves to the stationary case. Then the heat equation will look like:

$$\frac{d}{dx} \left(\lambda \frac{dT}{dx} \right) = 0. \quad (12)$$

In a classic case of $\lambda = \text{const}$, and in our equation (3) - $\lambda = \lambda_0(1 - \alpha/x)$. Here, the size factor d is denoted by α , not to be confused with the sign of differentiation. Taking into account the size effect, the equation (12) takes the form:

$$\frac{x}{x + \alpha} \frac{dT}{dx} = \frac{C_1}{\lambda_0}. \quad (13)$$

Here, C_1 - a constant of integration. The solution of equation (13) has the form:

$$T(x) = \frac{C_1}{\lambda_0} (x + \alpha \ln x) + C_2. \quad (14)$$

If in (12) $\lambda = \text{const}$, then we have a classical solution of the problem for an infinite plate:

$$T(x) = C_1 x + C_2. \quad (15)$$

In contrast to the classical problem in the equation (14) there is a logarithmic term. This leads to a divergence in the origin. Therefore, the boundary conditions do not need to ask for $x = 0$ and at $x = x_{dB}$ - the length of the de Broglie wavelength of electrons. Only in this case the classical meaning is of the heat equation.

It is also significant that, according to (14), a thermal field nanoplates depends on the material of the plate through the bulk sample thermal conductivity λ_0 , and on the size factor α . In the classical case such dependence no. Since the surface layer of the solid body, as we have seen above (Table 2) represents nanostructure, the heat conduction (electrical conductivity, diffusion) will vary greatly from processes in volume.

Thus, for small particles and thin films, and also for composite nanomaterials stationary even temperature distribution depends on the nature of the material and the size factor. For example, the surface layer of the earth's crust (1.0 - 1.5 m) with respect to the Earth's radius ($\approx 6.4 \cdot 10^6$ m) is "apparent" thickness of about 0.1 microns, i.e., at the level of size effects, which we discussed above. For the analysis of the thermal field of the Earth is better to use equation (13) which including thermal conductivity material (granite, basalt, and others.) In contrast to the classical tasks which do not contain such information [15].

8. Conclusion

In recent decades, in our vocabulary, our minds quickly entered terms and concepts directly include the prefix "nano". So there are nanophysics, nanochemistry, nanobiology etc. All these areas of natural science are not only fundamental nature, but, above all, linked to the progress of nanotechnology, with their penetration not only in the scientific community, but also in the normal life of millions of people on our planet.

In this paper, we have touched on only some of the issues related to the physical properties of nanomaterials. But it is already possible to assert that there is a universal size dependence of these properties, which are described by equation (9) for $r > d$, and the equation of the type (3) when $r < d$.

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