Universal size dependence of the physical properties of nanomaterials

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Abstract. 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.

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, and others, 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).

2. Formulation of the problem
Currently there is no quantitative theory that allows to predict the desired properties of nanomaterials depending on the technological conditions. Therefore, even high quality models may help to avoid a large amount of routine, but expensive works.
In this paper we want to show that most of both internal and external dimensional effects described by one universal dependence. This makes it possible 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.

3. Theory
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 [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]:

$$T_m(r) = T_x\left(1 - \frac{d}{r}\right),$$  \hspace{1cm} (1)

where $T_x$ - the melting point of the bulk sample.

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

$$d = \frac{2\sigma u}{RT}.$$  \hspace{1cm} (2)

Here $\sigma$ - the surface tension of the bulk sample; $u$ - molar volume, $R$ - universal gas constant. When $r < d$, instead of (1) need to use the equation:

$$T_m(r) = T_x\left(1 - \frac{d}{d + r}\right).$$  \hspace{1cm} (3)

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

$$\sigma = 0.7 \cdot 10^{-3} \cdot T_x.$$  \hspace{1cm} (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. 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.

From (2) and (4):

$$d = 2.41 \cdot 10^{-4} \cdot \nu \text{ (M}^{-2} \cdot \text{моль)}.$$  \hspace{1cm} (5)

According to the (5), the thickness of the surface layer is defined by a single parameter $\nu$, i.e. 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 $\nu = 10.2 \text{ cm}^3/\text{mol}$ and the ratio of (5) gives $d = 2.45 \text{ nm}$.

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

$$\sigma(r) = \sigma_x\left(1 - \frac{d}{r}\right),$$  \hspace{1cm} (6)

where $\sigma_x = \sigma$ - 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:

$$\sigma(r) = \sigma_x\left(1 - \frac{2\delta}{r}\right),$$  \hspace{1cm} (7)

where $\delta$ 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).

4. Experimental results

Fig. 1 shows the size dependence of the luminescence intensity of the KCl-Tl phosphor, and Fig. 2 - size dependence of the magnetic susceptibility of magnetite.
Figure 1. The dependence of KCl-Tl luminescence intensity of the phosphor grain size [7].

Figure 1. The dependence of the magnetic susceptibility of the diameter of the magnetite grains [8].

In both these cases, depending describe with great accuracy the formulas:

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

5. Discussion
For most metals, the melting temperature of nanoparticles of various sizes are presented in Table 1.

| M  | \( T_\infty \), K | \( T_m \), K \( r = 1 \text{ nm} \) | \( T_m \), K \( r = 10 \text{ nm} \) | \( T_m \), K \( r = 50 \text{ nm} \) |
|----|----------------|----------------|----------------|----------------|
| Li | 452            | 188,3          | 396,5          | 440,1          |
| Na | 371            | 119,7          | 306,6          | 356,1          |
| K  | 337            | 71,7           | 246,1          | 314,1          |
| Rb | 312            | 60,0           | 219,7          | 287,7          |
| Cs | 302            | 48,7           | 198,7          | 273,6          |
| Be | 1558           | 556,3          | 1320,4         | 1558           |
| Mg | 923            | 225,1          | 704,6          | 869,1          |
Ca 1118  139,8  657,6  980,7
Sr 1030  110,8  562,8  883,6
Ba  983   99,3  520,1  834,5
Al  933   291,6  764,8  933
Ga 302,8  159,3  277,6  297,3
In  429   165,0  369,8  415,7
Tl  576   169,4  464,5  549,6
Si 1686  285,8  1131,5 1535,9
Ge 1231  246,2  879,3  1140,0
Sn  505   168,3  420,8  485,6
Pb  600   166,7  600,0  600,0
Se  493   170,0  414,3  475,0
Te  725   161,1  537,0  676,7
Cu 1356  411,0  1102,4 1296,4
Ag 1234  301,0  942,0  1162,0
Au 1336  310,7  1004,5 1253,3
Zn  693   277,2  602,6  672,8
Cd  594   204,8  499,2  572,3
Hg  234   127,7  216,1  230,2
Cr  2173  452,7  1574,6 2019,5
Mo  2873  383,1  1741,2 2542,5
W  3673  390,7  1996,2 3144,7
Mn 1517  399,2  1185,2 1436,6
Tc  2473  405,4  1637,7 2244,1
Re 3423  422,6  2001,8 2997,4
Fe  1808  441,0  1380,2 1702,5
Co  1763  464,0  1377,3 1670,0
Ni  1726  466,5  1359,1 1637,6
Ce  1077  168,3  699,4  972,0
Pr  1208  172,6  755,0  10,78,6
Nd  1298  175,4  791,5  1150,7
Sm  1325  181,5  812,9  1176,7

From Table 1 it is seen that the melting temperature of nanoparticles with sizes of 1 nm is much lower than the melting temperature of the bulk sample. Part of the metal at such sizes are thermally unstable at room temperature.

Table 2 shows the values of \( d \), calculated by the formula (5). From Table 2 it is seen 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.

Consider the account of the size dependence of the physical properties of small particles on the example of the theory of homogeneous nucleation of a new phase.

| M | d, nm | M | d, nm | M | d, nm |
|---|-------|---|-------|---|-------|
| Li | 0,7   | Sr | 5,8   | Sn | 1,4   |
| Na | 1,5   | Ba | 6,2   | Pb | 1,8   |
| K  | 2,6   | Al | 1,5   | Se | 1,3   |
| Rb | 2,9   | Ga | 0,6   | Te | 2,5   |
| Cs | 3,6   | In | 1,1   | Cu | 1,6   |
| Be | 1,3   | Tl | 1,9   | Ag | 2,2   |
The main provisions of the theory of formation of new phase nuclei were advanced by Gibbs and then
developed by Volmer, Becker and Doering, Stransky and Kaishev, Frenkel, 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.

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 $\Delta T$ [9]:

$$r_k = \frac{2Mq}{\rho q\Delta T},$$

(9)

where $M$ - molecular weight; $\rho$ - the density of crystal-nucleus; $q$ - heat of fusion; $T_0$ -
temperature equilibrium of the two phases of infinitely large radius, $\sigma$ - 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:

$$r_k = \frac{10Mq}{\rho q}.$$  

(10)

All values in the expression (11) (except $\sigma$) are determined experimentally with great precision and are
listed in directories. For pure metals surface tension value $\sigma_0$ 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 [10] 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 3. Critical radius of homogeneous formation of the pure metals [10]

| 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       |
| Na | 0,7       | Ba | 2,9       | Pb | 0,8       | Hg | 0,3       |
| K  | 1,2       | Al | 0,7       | Se | 0,6       | Cr | 1,3       |
| Rb | 1,4       | Ga | 0,3       | Te | 1,2       | Mo | 2,2       |
| Cs | 1,7       | In | 0,5       | Cu | 0,8       | W  | 2,8       |
| Be | 0,6       | Tl | 0,8       | Ag | 1,0       | Mn | 0,9       |
| Mg | 1,0       | Si | 1,6       | Au | 1,1       | Fe | 1,0       |
| Ca | 2,3       | Ge | 1,3       | Zn | 0,5       | Co | 0,9       |

Table 4 shows the experimental values of the critical range from [11].

Table 4. Critical radius of homogeneous formation of the pure metals [11]

| M  | $r_k$, nm | M  | $r_k$, nm |
|----|-----------|----|-----------|

5
| Element | Ga 0.9 | Ge 0.9 |
|---------|--------|--------|
| Sn      | 1.2    | Ag 1.2 |
| Cu      | 1.1    | Pb 1.1 |
| Bi      | 0.8    | Hg 0.8 |

Compare values from Tables III and IV 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.

6. Conclusion

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

\[
A(r) = A_s \left(1 - \frac{d}{r}\right)
\]  

(11)

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.

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