

STRUCTURE AND PROPERTIES OF NANOSCALE AND MESOSCOPIC MATERIALS

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Concept of Size-Dependent Atomic Interaction Energies for Solid Nanomaterials: Thermodynamic and Diffusion Aspects

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Energy-related problems of solid nanoparticles and nanoscale materials concerning their stability and structure are investigated with a specifically targeting on nanocrystalline metallic systems. The new concept based on the atomic hypothesis about the size dependence of nearest atom–atom interaction energy and co-ordinated actions of atoms is offered. The verification is done for metallic thin films and nanoparticles on the basis of experimental results, theoretical approach, and molecular static simulations. As shown, for nanomaterials, the concepts of size-dependent interatomic interaction energies can be used for description of thermodynamic and kinetic properties.

Досліджено питання, пов'язані з енергією твердих наночастинок і нанорозмірних матеріалів, щодо їх стійкості та структури з акцентом на нанокристалічних металевих системах. У роботі пропонується новий підхід, який базується на атомній гіпотезі про розмірну залежність енергії міжатомової взаємодії найближчих атомів та узгоджені колективні дії атомів. Перевірку гіпотези було здійснено для тонких металевих плівок і наночастинок на основі експериментальних результатів, теоретичного наближення і молекулярно-статичного моделювання. Показано, що для наноматеріалів можна використовувати концепцію розмірної залежності енергії міжатомової взаємодії для опису термодинамічних і кінетичних властивостей.

Исследованы вопросы, связанные с энергией твёрдых наночастиц и наноразмерных материалов, относительно их устойчивости и структуры с акцентом на нанокристаллических металлических системах. В работе предлагается новый подход, основанный на атомной гипотезе о размерной зависимости энергии межатомного взаимодействия ближайших атомов и согласованных коллективных действиях атомов. Гипотеза была проверена для тонких металлических плёнок и наночастиц на основе экспериментальных

результатов, теоретического приближения и молекулярно-статического моделирования. Показано, что для наноматериалов можно использовать концепцию размерной зависимости энергии межатомного взаимодействия для описания термодинамических и кинетических свойств.

Key words: atom–atom interaction, size effect, thermodynamic properties, diffusion in nanomaterials, nanocrystalline structures.

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1. INTRODUCTION

Many quantities and physicochemical properties of nanosize metals and nanosolids, such as their melting, solubility, lattice parameter, and Young's modulus, remain no longer constant when their size becomes small [1–3]. One of the most commonly known size effect is related to the melting (transition) temperature T_m shift [4–6]. In a general form, the condition for the melting temperature can be written as:

$$T_m = T_\infty\{1 + \beta/L\}, \quad (1)$$

where T_∞ is the bulk melting temperature of the material, L is a characteristic size of a nanosystem (the radius R or the diameter d of a nanoparticle or the thickness h of the film, *etc.*). The coefficient β depends on the material data [6].

Nanomaterials' research related to the size effect is usually based on the increase of the excess surface energy of small systems (large part of grain boundaries and surface atoms). The decrease of the size leads to the situation when the phase with smaller surface free energy becomes more probable and stable. Such behaviour is found for many solid chemical elements and metallic systems (Mo, W, Y, Gd, Tb, Ho, Tm, *etc.* [7, 8]).

Due to the large part of grain boundary and surface atoms in solid nanomaterials, one should pay attention to the existence of defects (such as dislocations, dirt) that also leads to the difference in interaction between such defects and the bulk and surface atoms and results in size effects. Hereby, the main interest is related to the surface as the source of sink and barrier for moving defects [9–11] and self-organization of the matter like the self-cleaning, *etc.*

There is one more fundamental reason for size effects in multicomponent nanomaterials, where the first-order phase transformation starts from a nucleation and includes a change of composition or density. This is the less known so-called 'depletion effect' related to the conservation of matter. In the usual treatment of phase transition, it is assumed that there is no problem of matter supply during new phase formation. In a nanosystem, the amount of one of the components in

the entire nanosystem may be not sufficient for the construction of a critical nucleus of the different composition [12–14]. Moreover, in nanosystems, the well-known concept of equilibrium phase diagram has to be revised, due to the fact that the amount of matter is limited [15, 16]. Similar arguments may be applied for the case of grain boundary segregation problem as a successful approach to stabilize nanocrystalline materials against grain growth [17–19].

Another reason of the size effect in nanosolids appears because of quantum mechanics. The surface state of electrons may give the energy local levels yielding the size quantization, surface waves and the difference of the interaction with the light, dispersion and reflection changes, *etc.* The change of the dimension of a nanomaterial is also the reason for size effects explained mainly due to the quantum mechanical behaviour and dimension quantization. Basically, the quantum-mechanical explanation relies on the quantization of the phonon energy and anharmonicity of vibrations and atomic interaction around the nanomaterial crystal-lattice sites, which increases with the increase of the temperature and vice versa [20, 21]. This approach gives size effects within 0.1% for interatomic distances in intervals from about 1 nm to 10 nm at high temperatures (above the Debye temperature) and disappearing as the temperature becomes lower. Thus, the traditional quantum-mechanical scheme does not work at least for low temperatures.

Most of the physical quantities, such as the Debye temperature, the heat capacity, *etc.*, are related to the cohesive energy of atoms. That is why it is topical to check the atomic hypothesis related to the crystal energy optimization, collective effect of a group of atoms and space redistribution of atoms in a solid nanosystem even at the zero temperatures when the vibrations are absent. It is worth noting that such type of properties and behaviour can exist in many disciplines, say: in economics, there exist the so called ‘scale economy’ and ‘regional economics’ where one considers the effect of firm size on financial reliability and performance [22, 23]; in biology and descriptive statistics, one considers the statistical significance [24]; in mathematics education, relationship between class size and student achievements, *etc.* [25, 26]. In present communication, we show that there exist in physics and chemistry the similar fundamental reasons for size effects and one can offer the idea of the size-dependence of the cohesive energy on atomic level: the idea of the dependence of the energy of atom–atom interactions on the size of a nanosystem.

2. THEORY AND CALCULATIONS

In present work, we pay attention to one more fundamental reason for size effects in nanocrystalline materials—the size-dependent atomic

interaction energy, which means the dependence energy interaction of atoms with the co-ordination environment and the lattice on the size (for example, on the thickness of a solid nanofilm/nanolayer or the radius of a nanocrystalline particle). In other words, physicochemical properties become size-dependent and one can resume the atomic hypothesis: ‘the nearest atom–atom interactions and co-ordinated actions of atoms in a nanomaterial will be different depending on the size L : the change of a grain or crystal in size can lead to a redistribution of atoms in the lattice both on the surface and in the bulk and to the corresponding change in the interaction energy E of each atom on the surface and in the bulk with neighbouring atoms’.

The atomic hypothesis for nanomaterials can be described in the formula:

$$E = f(L). \quad (2)$$

Physical mechanism of proposed atomic hypothesis that leads to the change of the interatomic distance and dimensional change of the potential energy of interatomic interaction is based on the collective behaviour of atoms in nanosolids and existence of the non-symmetrical tails in the potential profile. The long-range part of the tail in nanosolids is cut off and leads to the changes of the number of atoms in interaction spheres and the distances between the atoms.

Recently, Liang [27] deduced that the cohesive energy of nanoparticles decreases with a reduction in size d . Therefore, nearly all thermodynamic quantities can be approximately expressed as a linear function of $1/d$ by general thermodynamics [28]. Noteworthy is the fact that the linear function of $1/d$ cannot be fully substantiated by the hypothesis of size dependence of atom–atom interaction energy. It may be the result of increasing the percentage of surface atoms in nanomaterials and averaging procedure. That is why it is important to prove that the proposed hypothesis is true not only for the surface atoms of a nanomaterial, but also for the internal ones.

Additionally, there are other factors such as the atomic radius and the shear modulus, which can modify the cohesive energy [29]. However, the nanoscale size seems to be the main factor influencing the interaction energy of atoms.

Let us verify the atomic hypothesis for nanomaterials on the basis of experimental results and our theoretical approach and simulations.

2.1. Theoretical Approach Based on Experimental Data and Microscopic Model

Let us first look at the experimental results on lattice parameter in nanocrystalline solids and give simple theoretical estimation. In most

experiments, an f.c.c. structure is observed, the densities of nano-materials and the lattice parameters have been found changed in the range of up to 1–2% [30–33]. With the sufficient degree of accuracy, one can write the approximation function of hyperbolic type for the crystal lattice parameter, observed in many experiments:

$$a(L) = a_{\infty}(1 + b/L). \quad (3)$$

Here, a_{∞} is an asymptotic value of the lattice parameter for macroscopic sizes, b is a fitting parameter.

Let us now make the theoretical estimation for the potential energy of atomic interactions. To describe the behaviour in metals, the pair Morse potential can be used [34–36]:

$$U(r) = U_0[\exp\{-2\rho(r - r_0)\} - 2\exp\{-\rho(r - r_0)\}]; \quad (4)$$

here, $U(r)$ is the potential of atom–atom interaction, $U_0 = |U(r_0)|$ is the parameter of the dissociation energy, and ρ is the degree of anharmonicity; r_0 —equilibrium distance between two atoms, r —the distance between the atoms and can be ranged from 0 to an unlimited distance.

The Morse potential function (4) correctly describes vibrational levels of b.c.c., f.c.c., and h.c.p. metals, covalent molecules, and defects in cubic crystals [37, 38]. Using the Morse pair potential (4) and the experimental result (3), we can estimate the dependence of the potential energy of the interaction between nearest atoms within the f.c.c. nanosystem on the size L . It is well known that the distance between two nearest atoms r_{opt} in the f.c.c. metals is equal to the lattice parameter divided by square root of two [39]. It means that we can use the relation $r_{\text{opt}} = a(L)/\sqrt{2}$ with the condition $a(L)$ according to formula (3). The simple algebra leads to the energy function of atom–atom interaction $E(L)$ in a first co-ordination sphere:

$$E(L) = U_0[\exp\{-2\xi(\eta + b/L)\} - 2\exp\{-\xi(\eta + b/L)\}] \quad (5)$$

with parameters $\xi = \rho a_{\infty}/\sqrt{2}$, $\eta = 1 - r_0\sqrt{2}/a_{\infty}$. The energy of the interaction of a single atom with all atoms in a first co-ordination sphere can be found due to the summation and is equal to the quantity of $W = ZE(L)$, where Z is the co-ordination number and $W_0 = ZU_0$.

For instance, for the f.c.c. Cu nanoparticles, $U_0 = 0.3249$ eV, $\rho = 1.3588 \cdot 10^{10} \text{ m}^{-1}$, $r_0 = 2.866 \cdot 10^{-10} \text{ m}$, $a_{\infty} = 3.615 \cdot 10^{-10} \text{ m}$, $Z = 12$ [31–33] yield the estimation values: $b = -2.1 \cdot 10^{-11} \text{ m}$, $L = R$, $W_0 = 6.2465 \cdot 10^{-19} \text{ J}$, $\xi = 3.474$, $\eta = -0.1212$, and the energy $E(R)$:

$$E(R) = 5.205 \cdot 10^{-20} \{ \exp(-6.947[-0.1212 - 0.021/R]) - 2 \exp(-3.474[-0.1212 - 0.021/R]) \}.$$

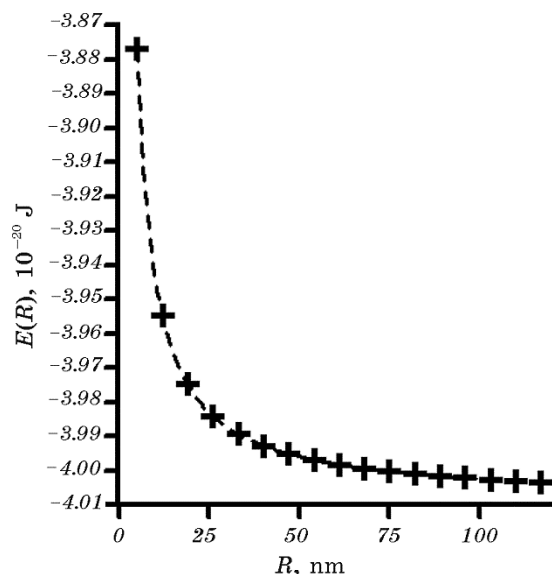


Fig. 1. Results of estimated calculations using Morse potential (5) and experimental data for lattice parameter (3) of isolated Cu nanoparticles: the dependence of the energy $E(R)$ on the radius of the nanoparticle.

Here, the energy $E(R)$ is calculated in Joules, the radius R of Cu particle is in nm. Graphical visualization is presented in Fig. 1. Thus, the result (5) explains the proposed atomic hypothesis on size-dependent physical properties of nanomaterials and presents new and important concept for nanoscience.

2.2. Verification by Molecular Static Simulations

The pair Morse potential function does not take into accounts the ion–electron–ion component of interaction. That is why we verified the proposed hypothesis by performing molecular static study based on the Sutton–Chen potential of atomic interactions for the solid monatomic thin films and nanoparticles of different metals in order to find out the stable structures and average atomic pair interaction energies inside the nanosystems and at the surfaces [40–42]. The Sutton–Chen potential is the many-body potential and, due to the reasonable agreement with experiments, is often employed for the description of the interaction between metallic atoms inside a metallic cluster or a nanoparticle [40, 43]. In Figure 2, we present the simulation results for Cu nanofilm of the thickness h , obtained due to molecular static simulations of energy optimization procedure for the whole nanofilm.

Let us look at the simulation results on thin Cu film (Fig. 2). One can

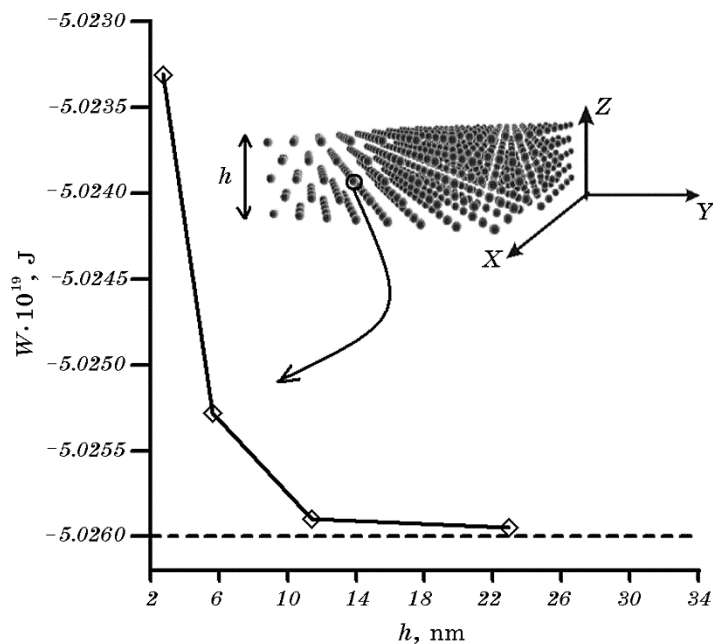


Fig. 2. Results of computer simulations using Sutton–Chen potential [40, 41] for Cu thin f.c.c. film in vacuum: the dependence of the energy of the interaction W of the internal atom within the nanofilm with neighbouring atoms on the different thicknesses.

see that the potential energy of atomic interaction demonstrates the size effect up to 20 nm. This is true for nanofilms and it is stronger for the case of nanoparticles, where we obtained the size effect for atoms up to 30 nm. Hence, simulations confirm the proposed concept of size-dependent energies of atomic interaction for nanomaterials.

3. RESULTS AND DISCUSSION

3.1. Application to the Thermodynamics of Nanosystems

As the example of the application of atomic hypothesis, we show the quantitative treatment emphasizing new physics: the methodology of phase diagram construction of binary nanosystems that may be furnished. Nanophase diagrams in this work mean the size-dependent isobaric temperature–composition phase diagrams of coexistence of different new nanosize phases.

For the first example, for a two-component nanosystem consisting A and B atoms, let us use well-known regular solution model and find the phase separation temperature T_{tr} (temperature, at which the binary

solid solution separates on two different phases) [12, 39].

Due to the abovementioned size effect for interatomic interaction energy within the scope of the thermodynamic approach for nanosolids, one can use the potential energy of the atom–atom interaction (5) in the form of a Taylor series, and, in the simplest case, it may be assumed by the following formula:

$$E(L) = E_{\infty}\{1 + \varepsilon/L\}. \quad (6)$$

Here, E_{∞} —potential energy of atomic interaction in bulk phase and ε is the energy fitting parameter. Then, for the two-component nanosystem, we can use the corresponding formula of the potential energies, E :

$$\begin{aligned} E_{AA}(L) &= E_{AA}(1 + \varepsilon_{AA}/L), \quad E_{BB}(L) = E_{BB}(1 + \varepsilon_{BB}/L), \\ E_{AB}(L) &= E_{AB}(1 + \varepsilon_{AB}/L). \end{aligned} \quad (7)$$

Hereby, the values $E_{AA}(L)$, $E_{BB}(L)$ and $E_{AB}(L)$ are the corresponding interaction energies of each sort of atoms (in a first co-ordination sphere) in a nanomaterial indicated by the corresponding subindexes A and B . The mixing energy

$$E_{\text{mix}}(L) = \{0.5(E_{BB}(L) + E_{AA}(L))\} - E_{AB}(L) \quad (8)$$

becomes size-dependent so that the phase separation temperature

$$T_{tr} = 2ZE_{\text{mix}}(L)/k_B \quad (9)$$

depends on the size L of a nanosystem and may vary from a few to hundreds Kelvins similar to equation (1). In equation (9), k_B is the Boltzmann constant. Simple algebra gives the condition for the phase transition temperature:

$$T_{tr} = T_{\infty}\{1 + \beta/L\}, \quad (10)$$

where $T_{\infty} = 2ZE_{\text{mix}}/k_B$ is the phase separation temperature, and E_{mix} is mixing energy in a bulk material, coefficient $\beta = \{0.5[E_{AA}\varepsilon_{AA} + E_{BB}\varepsilon_{BB}] - E_{AB}\varepsilon_{AB}\}/E_{\text{mix}}$.

For the second example, we apply the relations (6) and (7) to reconstruct the Gibbs free energy dependence for each nanophase in the nanomaterial. Using the Gibbs method of geometric thermodynamics (when the equilibrium concentrations in phases are determined by the rule of the common tangent drawn from curves of concentration dependences of the Gibbs free energy) and commonly used CALPHAD data for bulk phases and quantities E_{AA} , E_{BB} , E_{AB} , one can draw nanophase diagrams in a wide range of sizes and compositions, calculate the size de-

pendences of phase transition temperatures, solubilities of components, *etc.* Due to such technique, we calculated the nanophase diagram for thin Bi–Sn solid film giving adequate and coinciding with experiments results [44]. The size dependence of phase transition temperatures are found as following: $T_e = -161.5/L + 412$ K—the eutectic temperature of Bi–Sn thin film, $T_m^{\text{Bi}} = -279.5/L + 543$ K—the melting temperature of thin Bi film, $T_m^{\text{Sn}} = -187.3/L + 504.8$ K—the melting temperature of thin Sn film (the thickness L of the Bi–Sn film is taken in nm, and temperatures are in Kelvins). The approximation formulae for limit solubilities (solvus line) in Bi–Sn nanofilms have been found in the following form: $x_{\text{Bi}} = 0.1L^{-0.96} + 0.131$ —for Bi in Sn and $x_{\text{Sn}} = 61.8L^{-3.4} + 2 \cdot 10^{-3}$ —for Sn in Bi. It is worth noting that the limit solubility of Sn in Bi is equal to 0.024 for the 9 nm film at 395 K and 0.002 in a bulk material [45].

3.2. Application to the Diffusion in Nanomaterials

The aforementioned reasons allow us to make the conclusion that a size dependence of the kinetic coefficients in nanomaterials exists. It is evident from the consideration of the diffusion in terms of the energy-activated process, which follows the Arrhenius dependence:

$$D = D_0 \exp\{-Q/(k_B T)\}, \quad (11)$$

where D_0 is the frequency factor and Q is the activation energy for the diffusion process.

If we return to the idea that the size is important for bonding energy, then it becomes understandable that, first, depending on the diffusion mechanism (interstitial diffusion, or vacancy diffusion, *etc.*) bonding to the surrounding atoms may be different and, second, due to the relations (5)–(7) bonding energy and activation energy Q depend on the size of the nanomaterial.

Moreover, it can be understood from other viewpoint. On the one hand, it is well established that the correlation between the activation energy Q and the melting temperature T_m has the form:

$$Q \cong 18k_B T_m. \quad (12)$$

The diffusion parameters D_0 and Q are empirically correlated with the melting temperature and the proportionality factor is nearly a constant for a specific class of materials [46]. On the other hand, there exists a size dependence of the melting temperature in the form of equation (1). Taking into account the conditions (11), (12) and equation (1), one can find out the size dependence of the diffusion coefficient in the nanomaterial, which may be written as

$$D = D_0 \exp\{-18T_\infty(1 + \beta/L)/T\}. \quad (13)$$

One can see from equation (12) that the diffusion coefficient becomes a decreasing function of the size: it increases when the size L decreases and vice versa. The expression (13) explains the fast diffusion in nanoscale materials as compared with the bulk cases.

In addition, in polycrystalline materials compared to single crystals, diffusion is faster because of the grain boundaries [47]. In many cases, effective transport properties may be written due to diffusion coefficients in the form:

$$D = D_{\text{bulk}} + D_{\text{gb}}\delta/L, \quad (14)$$

where D_{gb} is the grain boundary diffusion coefficient, D_{bulk} is the bulk diffusion coefficient, and δ is the width of the grain boundary diffusion channel. It is worth noting that due to the proposed concept of size-dependent energies of atomic interaction for nanomaterials both quantities D_{gb} and D_{bulk} become size-dependent similar to equation (13).

Furthermore, there are other physical reasons for the existence of the size dependence of the kinetic coefficients related to the solubility limits in nanomaterials, *etc.* In this respect, the critical revision of many reactive diffusion problems (where a new phase appears due to interdiffusion processes) with regard for the size dependent diffusion at the initial stages of evolution (when the new phases are in a nm range) leads to new nonmonotonic solutions for rates of reactions and a time exponent and gives the new understanding of the old problems [48].

4. CONCLUSIONS

The paper presents the atomic concept in the following simple form: ‘the nearest bonding and co-ordinated actions of atoms in a nanomaterial are different depending on the size of it’. This is caused by the fact that in the nanosystem one has to take into account the change of a density and the limited number of atoms, while in a bulk material the last one is assumed to be infinite. We find it useful to compare size effect magnitudes using the pair Morse potential, experimental data on lattice parameter, and Sutton–Chen many-body potential. For the case of the solid thin film and nanoparticles, the effect of size on the energy of atomic interaction is found up to a few tens nm. The outlined in the paper nanophase diagram construction technique provides an acceptable explanation of the first order phase transition phenomenon. Our findings suggest that the size of the nanomaterial is important for diffusion of atoms and proposed atomic hypothesis may be the reason of the size-dependent diffusion in nanosize structures. It might be fruitful to further investigations of the atomic mechanisms in different

nanomaterials, through which the size translates into macroscopic behaviour and properties.

We believe that one can use the proposed concept to solve the inverse problem: the modification of the well-known pair potentials for real metals and chemical elements in nanosize states due to simultaneous taking into account the theoretical approach (4)–(7), experimental data, and computer simulations.

It is worth noting that new questions appear, say, when accepting system-size-dependent energy between nearest-neighbouring atoms, one should assume also position-dependence of the energy in the sample and include directional terms. This would be necessary to obtain end effects, say, in nanowires, whiskers, and transition metals.

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