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Molecular-dynamics Calculation of Nanostructures Thermodynamics. Research of Impurities Influence on Results

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1. Introduction

There is a need to emphasize a number of peculiarities occurring during the study of dynamic phenomena in nanostructures. First, the spatial scales: typical sizes of the nanostructures lie within the ranges from 10 to 1000 Å. Second, the governing parameters have the duration from parts of the molecular vibrations period and atomic vibrations in crystal structures, which is about 10^{-14} s, to the time of a disturbance wave passage over the characteristics scale in the space, i.e. up to 10^{-9} s. Such spatial-temporal scales of the dynamic phenomena make their experimental investigation difficult, at least now. Unique experimental equipment as a scanning tunnel microscope, scanning probe microscope, atomic force microscope created in recent years permits to break fresh ground along this line. Moreover, the experimental investigations are very money- and time-consuming. All these factors generate a need to study the above mentioned fundamental problems theoretically.

According to specialists research, the approaches of quantum mechanics can be used in the above spatial-temporal ranges to calculate electrical, electromagnetic and optical properties of the nanostructures, as well as the molecular dynamics method (MDM) can be utilized to study thermomechanical processes and calculation of respective characteristics and phenomena wherein quantum effects can be ignored.

This method permits, knowing nothing but the potential of interaction between the atoms in the system, which is calculated by the quantum mechanics method, to obtain the complete information about the system – the set of axes and pulses of all atoms at an arbitrary time point. It enables to solve the above mentioned fundamental problems. But the method has even more opportunities. By one or another way of information processing, we can transit from the micro-level to the next meso-level and obtain the system parameters for the concordance with the continuum mechanics macro-characteristics, which is the most important problem in the deformable body mechanics. To do this, it is necessary to research the dependence of the nanosystem characteristics on its parameters and to obtain an asymptotic value when the parameters do not depend on the sizes.

2. Validation of the molecular-dynamic approach to the calculation of the nanostructure state equation

Both the formation of the nanostructures in modern technologies (for example, condensation of nanoclusters from the gas phase, generation of nanofilms in CVD and ALD processes, etc) and their further functional utilization are frequently attended by considerable temperature loads (for example when the current passes through contacts in microelectronic circuits). For this reason, a demand arose to study the thermodynamic properties of nanostructures.

However their spatial and temporal scales make the experimental investigation difficult, at least today, and hence they should be studied theoretically, foremost by the molecular dynamics method.

At the moment, there are a great many works devoted to the study of individual thermodynamic properties of specific materials (see, for example Sekkal et al., 1998; Won Ha Moon & Ho Jung Hwang, 2003; Chen Jan et al., 2007; Berroukche et al., 2008).

Normally, under consideration are structural characteristics, elastic constants, internal energy change regarding the temperature, thermal capacity, thermal expansion factor, the dependence of the compression modulus regarding on the temperature, etc. As a rule, periodical boundary conditions are used. It results in the fact that the surface role is ignored, and volume thermodynamic properties are calculated alone. Few works (see, for example Bolesta et al., 2001; Bolesta et al., 2002; Golovnev et al., 2003; Bolesta et al., 2006; Golovnev et al., 2006 a; Golovnev et al., 2006 b; Alekseev et al., 2008) were devoted to the study of the particular influence of the surface on thermomechanical characteristics of the nanostructures.

But traditionally the thermodynamics is supposed to be developed for a certain system if any thermodynamic potential is found (free energy is the most common parameter in practice).

As it was mentioned above, the nanostructres differ from ordinary materials in that the quantity of surface atoms, their energy and energy of bond with volume atoms are comparable to similar characteristics of the volume atoms, for which, in the case of macrosystems, the phenomenology thermodynamic theory has been developed and respective thermodynamic characteristics have been found. At the same time, the properties of the surface atoms are very much unlike from the volume atoms properties. The most evident way is to construct the thermodynamics of the systems consisting of two sub-systems: the volume and surface ones. In this case, however, the traditional way is unfit because of the following reason. The thermodynamics contains the postulate of additivity: the energy of the thermodynamic system is the sum of its components energies.

The total energy of the nanostructure U_t can be presented as a sum:

$$U_t = U_{sa} + U_V + U_b ,\qquad\qquad(1)$$

where U_V is the energy of volume atoms; U_{sa} is the energy of surface atoms; U_b is the energy of these subsystems binding. To apply the traditional approach, i.e. to use the additivity postulate, the binding energy should be much less than the energies U_V and U_{sa}. This condition is however not satisfied for the case of nano-systems.

All these circumstances caused the investigations of the thermodynamic properties of the nanostructures with the detailed separation of the volume and surface atoms subsystems.

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Moreover, the formulation of the equation of nanostructure state is a fundamental challenge of independent importance.

2.1 The structure of solids state equation

The most reasonable approach to the formulation of the equation of an arbitrary system state in thermodynamically-equilibrium state is given by the statistical physics. With the Hamilton function of the system

$$H = \sum_{j=1}^{N} \left(\frac{p_{xj}^2}{2m} + \frac{p_{yj}^2}{2m} + \frac{p_{zj}^2}{2m} \right) + U(\vec{r}_1, ..., \vec{r}_N), \tag{2}$$

the statistical integral can be calculated as

$$Z = \int \exp\left(-\frac{H}{kT} \right) d\Gamma \tag{3}$$

and either free energy

$$F = -kT \ln Z \tag{4}$$

or internal energy

$$E_{in} = kT^2 \frac{\partial \ln Z}{\partial T} \tag{5}$$

can be found.

Having these thermodynamic functions, all thermodynamic characteristics of the systems can be described, and the equation of state can be formulated, too:

$$P = -\left(\frac{\partial F}{\partial V} \right)_T. \tag{6}$$

But this way has been successfully passed only for the calculation of gas thermodynamics. This method was used for solid bodies by Mie and Grüneisen (Mie, 1903; Gruneisen, 1926). When the solid body was considered as a system of classical 3D oscillators, they received the following expression for the free energy:

$$F = U_0(V) + kT \sum_{i=1}^{3N} \ln \frac{h\omega_i}{kT}; \tag{7}$$

Here $U_0(V)$ is the potential energy of atoms interaction at zero temperature, which can depend only on the solid-body volume; T is the temperature; N is the total amount of atoms in the system; ω_i is the atoms oscillation frequency in the crystal lattice. With the aid of Gibbs–Helmholtz theorem

$$E_{in} = F - T \left(\frac{\partial F}{\partial T} \right)_V \tag{8}$$

the expression for the internal energy was found, too:

$$E_{in}(V,T) = E_x(V) + E_T(V,T) \tag{9}$$

here $E_x = U_0(V)$ is the «cold» energy, and $E_T(V,T)$ - the thermal component of the internal energy, which can depend on the system temperature and volume. To the harmonic oscillator approximation, $E_T = 3NkT$.

Using the expression known from the thermodynamics, the authors found also the thermal equation of the solid-body state:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial U_0}{\partial V} - kT\sum_{i=1}^{3N}\frac{1}{\omega_i}\frac{\partial \omega_i}{\partial V}. \tag{10}$$

Evident that the total pressure also consists of the «cold»

$$P_x = -\frac{dU_0(V)}{dV} \tag{11}$$

and thermal components:

$$P_T = -kT\sum_{i=1}^{3N}\frac{1}{\omega_i}\frac{d\omega_i}{dV}. \tag{12}$$

But the dependence of the atoms potential energy and oscillations frequency on the solid body volume has still not been found, neither within the classical nor quantum model framework. For this reason, phenomenology theories based on a certain set of experimental data were developed within the whole XX century. The less phenomenology constants the theory required, and the broader was the parameter space wherein the theory gave reliable results, the better it was deemed to be. In the continuum mechanics, the sum in the last expression is normally replaced by some mean expression

$$\frac{3N}{V}\left\langle\frac{V}{\omega}\frac{\partial \omega}{\partial V}\right\rangle, \tag{13}$$

and the equation of state

$$P - P_x = \gamma\frac{3NkT}{V}, \tag{14}$$

is written through the Grüneisen constant

$$\gamma = -\left\langle\frac{V}{\omega}\frac{d\omega}{dV}\right\rangle, \tag{15}$$

which includes all phenomenology.

In (Stepanyuk, 2009), the direct calculation of the statistical integral with the aid of the molecular dynamics was realized. The authors however did not give any details on the preparation of the initial data for the nanostructure (coordinates and pulses at the zero time), nor on the boundary conditions. Moreover, the accuracy of the numerical model is

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extremely important for the direct calculation of the statistical integral (averaging on long times). The data on the numerical error for the energy and the method of the system temperature modeling should have been given.

2.2 The stages of the molecular-dynamic modeling
Though the Mie and Grüneisen theory has not enabled to calculate the solids thermodynamics from first principles, but it has given the structure of the thermal and caloric equations of state. This permitted to construct the molecular-dynamic approach to the calculation of solid nanostructures thermodynamics and finally, using the scaling peculiarities, of macroscopic solid bodies.

2.2.1. Since the properties of the nano-strctures depend on the shape and sizes, at the early stage the corresponding atomic structure with an ideal crystal lattice should be chosen; its properties are to be calculated. Below the example of the calculation of the cooper cluster shaped as a sphere of radius 20 Å will be presented.

2.2.2. Since the nanostructure has a very developed surface, its potential energy does not correspond to the potential energy minimum. Hence, at the second stage of the calculation one should find the global minimum of the potential energy of the structure at zero temperature. The found coordinates of atoms will be used as initial data for the third-stage calculation.

2.2.3. The isothermal process of the cluster compression by the controlled external pressure at $T = 0^o K$ must be modeled. This will enable to obtain such «cold» characteristics as the dependence of pressure and internal energy on the volume.

2.2.4. At the fourth stage, the nanostructure undergoes the isochoric heating. Such «cold» characteristics as energy and pressure retain constant. This allows to obtain the dependence of the thermal components of the internal energy and pressure on the volume and temperature (the caloric and thermal equations of state, correspondingly).

2.2.5. The free energy of the nanostructure is calculated from the equation of state with the aid of the Gibbs-Gelmgolc equation.

3. Modeling of the initial state of the nanostructures

3.1 Choice of initial coordinates
So far as the nanostructures properties depend on the shape and sizes, at the first stage the respective atomic systems with calculated thermodynamic properties is chosen. Below is given an example of the calculation of the copper cluster shaped as a sphere with the radius 20 Å. Fig. 1 shows the sample assignment of the initial coordinates of such a structure. First, the coordinates of the atoms in the ideal copper FCC-structure are assigned (the atoms in such a structure are located in the corners of a cube with the edge $a = 3,615$ Å and in faces centers). Then those are selected which radii are less than the assigned one (20 Å in our case). To simulate the interaction, we used the EAM Voter potential for copper (Voter & Chen, 1987; Voter, 1993).

3.2 Detection of the global minimum of the system energy
The nanostructure possesses an extremely developed surface and thus the constructed cluster does not lie within the potential energy minimum. To bring the system to the global minimum of the total potential energy, the artificial-viscosity method is used. It enables to

find the global minimum of the potential energy of the system at zero temperature. The method consists in the following: the atoms are continuously under the action of the dissipative forces $\vec{F_i} = -\nu \vec{p_i}$. Varying the viscosity factor ν , it is possible to accelerate or to decelerate the process of the system evolution in the state with the potential-energy minimum.
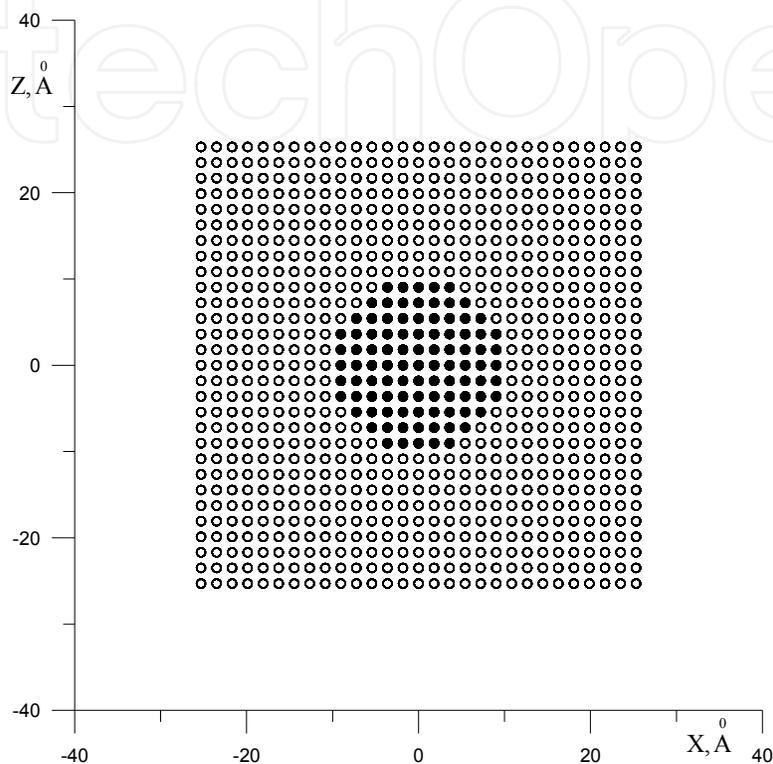

Fig. 1. Positions of the atoms in the XZ plane. Light bobbles – the atoms of cubic cluster; black bubbles – the atoms of the forming spherical cluster

4. Calculation of the «cold» characteristics of the nanostructure

To model the isothermal process of the nanostructure compression by the controlled external pressure at $T = 0^o K$, the following method is used.

The pressure P_0 is assigned on the surface as an external parameter. Evident that the problem of surface definities arises for the nanostructure case. Evaluation of the amount of the closest neighbors is the most common way. For the ideal FCC structure, this amount is 12 (first coordination sphere). Thus, in the nanostructure, those atoms which have the coordination number equal to 12, are referred to the volume atoms. The rest are referred to surface ones.

The forces f_a acting on the surface atoms and directed by the radius from the center (sphere extension) or toward the center (sphere constringency) are calculated by the formula

$$f_a = (S_t P_0) / N_s, \tag{16}$$

where S_t is the surface area, N_s is the total amount of the surface atoms.

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To damp the shock-wave processes in the sphere, the methods of linear force amplification f_a from zero to the assigned value and artificial viscosity are used. As a result, at the end of the calculation, the statically-equilibrium state is reached at $T \approx 0^o K$. Then, the finite coordinates of the system are used to calculate the necessary characteristics.

For convenience, the relative variation of the volume is chosen as an independent variable:

$$x = (V - V_{fr}) / V_{fr}. \tag{17}$$

This value is negative for the sphere constringency case, and positive for the sphere extension.

To test the results, the pressure P_c внутри inside the control sphere was additively calculated as follows. The sum of projections of the forces acting on the atoms inside some control sphere is calculated (in the calculations, the radius of this sphere r_c was chosen to be 10 Å) normal to the surface from the side of the atoms with radius above r_c. Then, to calculate P_c, this total force is divided to the area of the control sphere surface. Thus, in the calculations the pressure has the negative sign in the case of compression and positive – in the case of extension. Fig.2 presents the sample dependence of the external and control pressure in the cluster on the time pitches amount.
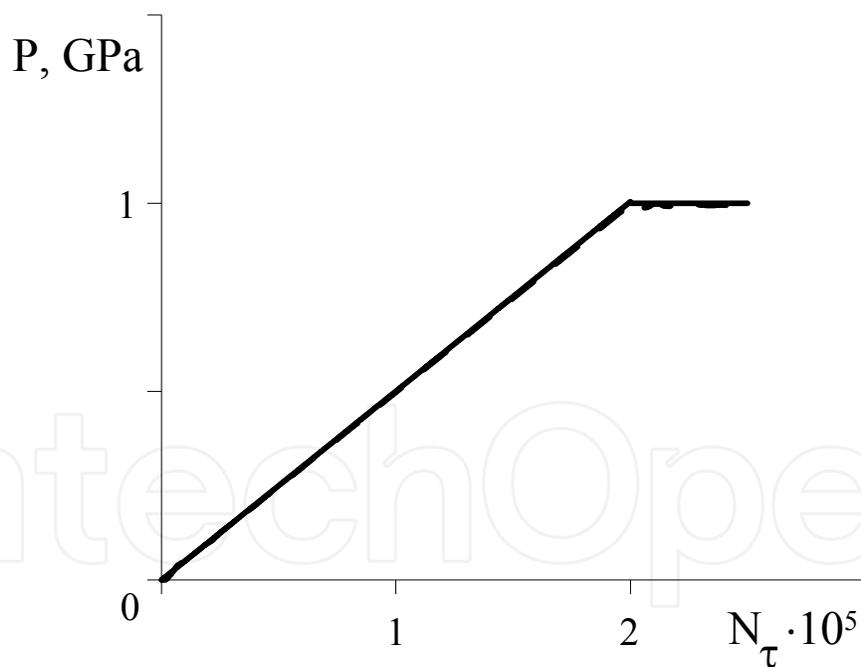

Fig. 2. External pressure (GPa – the solid line) and pressure in the control sphere (dotted line) vs the time pitches amount (10^5)

Fig.3 presents the dependence of the nanoclusters radius on the time pitches amount for the compression case.

Evident, that both the control pressure and radius take the asymptotic values. Final coordinates of the atoms are utilized then for the calculation of the cluster volume and potential energy.

The extension is calculated within the range from 0.1 to 12 GPa, and constringency – from 0.1 GPa to 20 GPa. The sphere state is analyzed in details as a whole unit, both its volume and surface parts. Index α in this case takes the values of t, v, s, respectively.
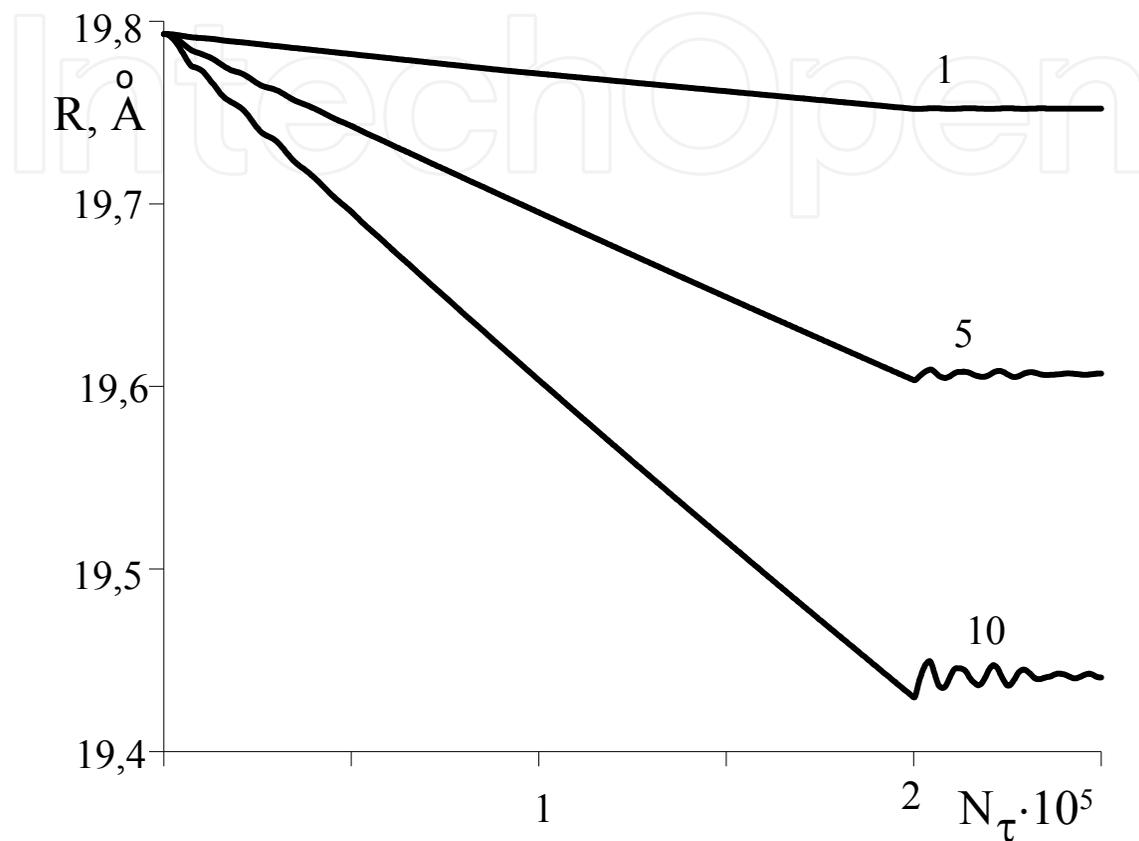

Fig. 3. Cluster radius (Å) vs the time pitches amount (10^5) for various compressing pressures (GPa)

4.1 Calculation of the nanostructure «cold» energy dependence on the volume

It is convenient to perform also the physical analysis of the energy characteristics for the potential energies variations in respect to the initial potential energy, which is the cooled-sphere energy:

$$\Delta U_\alpha = U_\alpha - U_{\alpha fr}. \tag{18}$$

The value of the index α is given above.

Fig. 4 shows such a dependence for the total energy of the system on the relative change of the volume.

The dependence is close to quadric, though it differs somehow from it. It results from the fact that for the high values of the external pressure, the deviations of atoms from the equilibrium state are big, and the non-linear part of the interatomic interaction potential has its effect.

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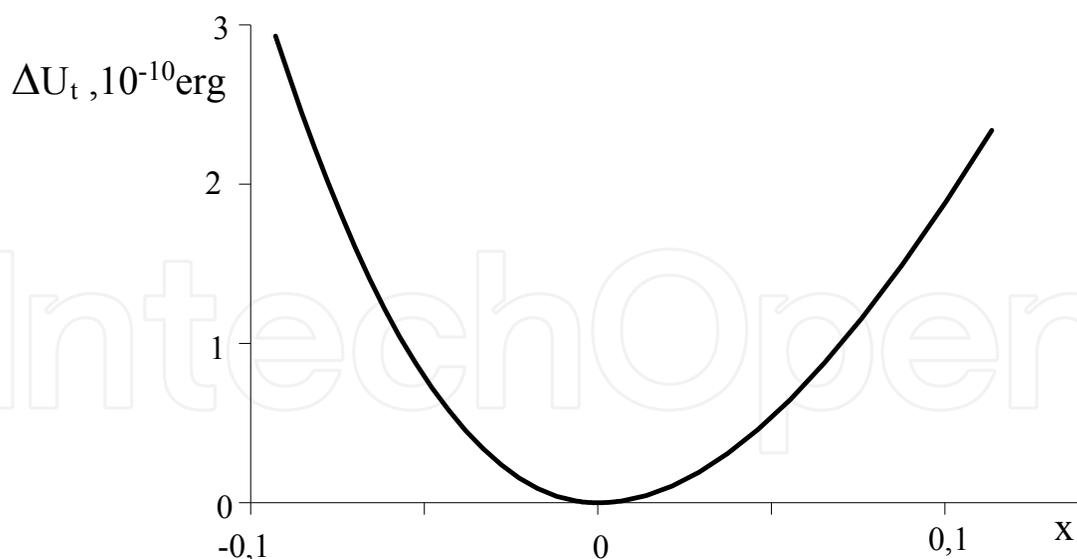
Fig. 4. Variation of the total energy (10^{-10} erg) of the cluster vs the relative change of the volume Title of figure, left justified

Hence, the performed calculations result in the dependence of the «cold» internal energy of the nanocluster on the volume. This characteristic is the most important one for the calculation of the thermodynamic properties of the nanostructures.

4.2 Calculation of the «cold» pressure dependence on the volume

The second most important «cold» characteristic is the dependence of the pressure on the volume at $T \approx 0^o K$. Fig. 5 presents the dependence of the external pressure on the relative variation of the total volume for the pressure range from -20 to 12 GPa. The non-linearity, similarly to the energy case, is caused by the non-linear character of the interatomic interaction potential. For convenience, Fig.6 presents the same graph for the external pressures varying from -1 to 1 GPa. The dependence is also convenient for evaluations.
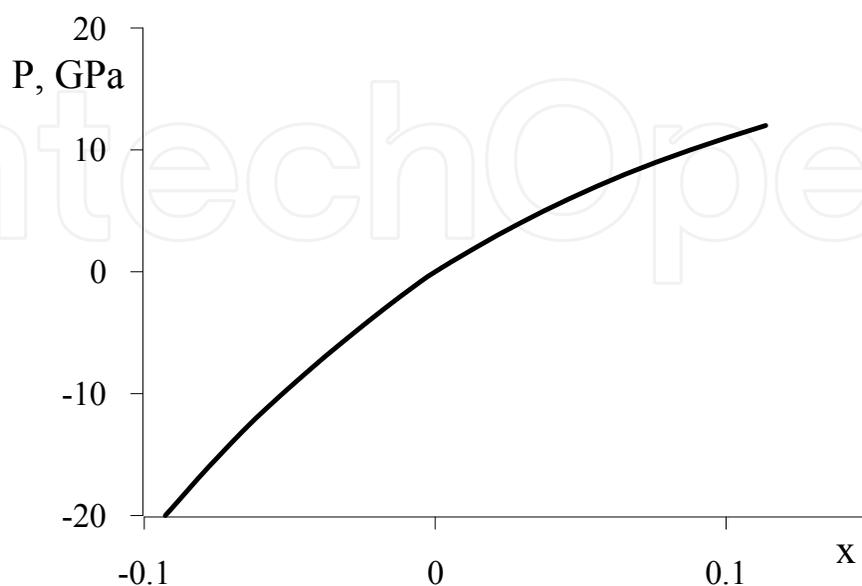

Fig. 5. The cold pressure (GPa) in the cluster vs the relative change of the volume
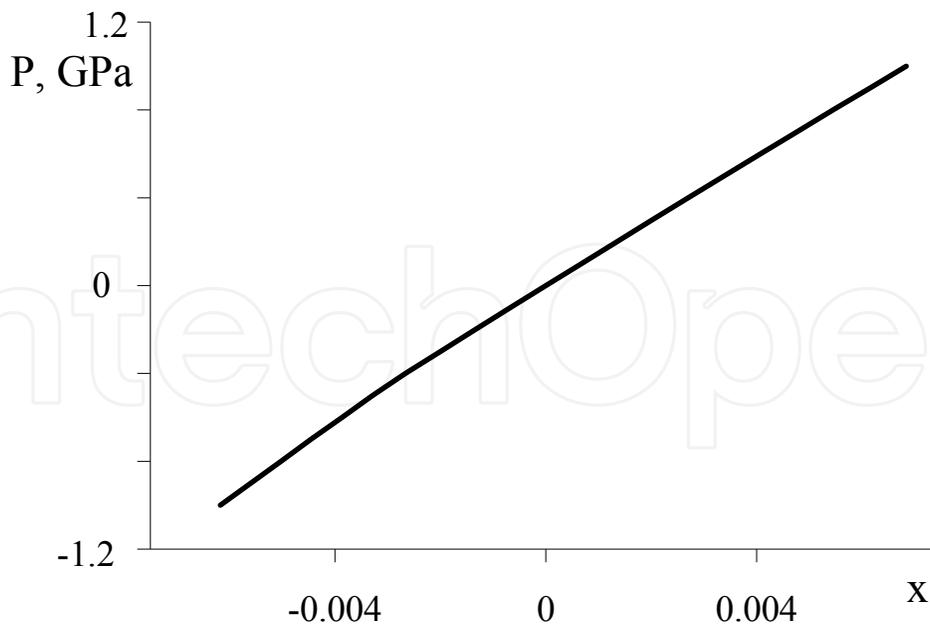
Fig. 6. The cold pressure (GPa) in the cluster vs the small relative change of the volume

Numerically obtained characteristics completely define the "cold" component of the thermal and caloric states of the nanostructure.

5. Molecular-dynamic modeling of the nanostructure heating

When it is necessary to assign the system initial state with $T > 0^\circ$ K, the stochastic forces method is used. Its idea is that atoms are under the action of chaotically directed momenta of constant amplitude. The parameters of the acting random force are: average impact frequency ω along each Cartesian axis and amplitude f_0, which provides the increment of the atom momentum component at one impact $\Delta p = f_0 \tau$. Since the atoms coordinates do not change at the impact, the heating speed in this case depends on the kinetic energy increment:

$$\frac{\Delta E}{\Delta t} = \omega \sum_{a=1}^{3} \sum_{i=1}^{N} \left(\frac{\left(p_i^a + \Delta p \right)^2}{2m} - \frac{\left(p_i^a \right)^2}{2m} \right) = \frac{\omega}{2m} \sum_{a=1}^{3} \sum_{i=1}^{N} \left(2 p_i^a \Delta p + \left(\Delta p \right)^2 \right), \quad (19)$$

Followed by the energy transport from kinetic to the potential component. The first item in parentheses in the right part of (5.1) turns into zero at adding, since the random forces and momenta are not correlated, so finally we have

$$\frac{\Delta E}{\Delta t} = \frac{3\omega N}{2m} \left(\Delta p \right)^2. \quad (20)$$

Hence the heating speed does not depend on the cluster energy and linearly depends on time. This is the major advantage of this heating method in contrast with the commonly used momentum scaling. The random force parameters are chosen according to the requirement of the equilibrium state of the cluster at each time point of the heating process.

6. Molecular-dynamic calculation of the nanostructure state equations

In line with the proposed method of the calculation of the nanostructure state equation, the finite states featuring the arrays of coordinates and moments which are obtained by comprehensive compression and extension at zero temperature, are used then as initial data at the system heating. The heating is carried out for each value of the external pressure and hence for the set of subsystems volumes values. The isochoric process is modeled by means of surface atoms location into the external harmonic potential, which does not allow the atoms to shift toward the area of big radii.

The second peculiarity of the heating process is the fact that over each range of $\Delta T = 25^o K$, the stochastic force is off, and the system relaxes into the thermodynamic-equilibrium state within the time range of $\Delta t = 10^{-12}$ s. All characteristics are averaged by thermal fluctuations on this time range. The temperature is determined by the energy of atoms chaotic motion:

$$\frac{3}{2} NkT_{kin} = E_{kin} = \sum_{i=1}^{N} \frac{\overrightarrow{\Delta p_i}^2}{2m}. \tag{21}$$

Here $\Delta \overrightarrow{p_i} = \overrightarrow{p_i} - m_i \overrightarrow{V_c}$ is the chaotic component of the i-atom momentum. ($\overrightarrow{p_i}$ is the i-atom momentum in the laboratory system of coordinates; m_i is its mass; and $\overrightarrow{V_c}$ is the velocity of the mass center of the system). The heating was performed within the range from 25 to 1000 K. According to this, below authors use the index of the calculation temperature grid i_T, with this value the corresponding chaotic temperature of the system $T_{kin} = i_T * 25$ (^{o} K) is found easily.
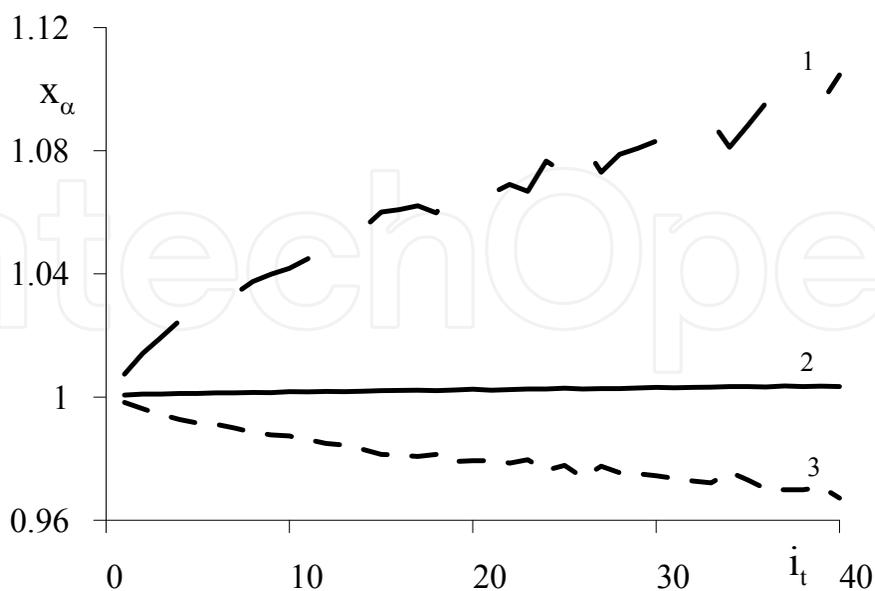

Fig. 7. Relative change of the volume at cluster compression vs the number of the temperature grid i_T for the external pressure $P = 5$ GPa: *1* – surface; *2* – whole system; *3* – volume

Additive restrictions which should be taken into account at the analysis of thermodynamic phenomena in the nano-systems are associated with the classical mechanics application. It is known that at the temperatures below Debye temperature the quantum effects must be regarded. Hence the conclusions obtained below are valid for the temperatures of $T \geq \Theta_D$. For copper $\Theta_D = 315^o \, K$ (Born & Huang, 1954).

6.1 Isochoric process modeling

To analyze the behavior of the subsystems volumes in the nanocluster, the best example is the ratio of $x_\alpha = V_\alpha / V_{\alpha 0}$ which varies with temperature. In the case of sphere constringency, Fig. 7 shows the dependence of this parameter on index i_T for the initial pressure 5 GPa.

It is evident that the total volume retains constant to a high accuracy and the process can be deemed to be isochoric. On the other hand, the growing x_S means that the surface layer volume increases during the heating, and the volume layer volume decreases, because x_V reduces.

In the case of extension, the similar pattern is observed but up to the external pressures of 1 GPa. For higher extending pressures, such a method of modeling of isochoric processes does not give proper results below about $300^o \, K$. At the temperatures above this value, x_t approaches to 1, and the process can be treated as isochoric.

6.2 Calculation of the caloric equation of the nanostructure state

The most fundamental value in thermodynamics is the total internal energy of the system E_{in} , which has the mechanical analog and involves both the potential energy of atoms interaction (including the «cold» one), and the energy of atoms chaotic motion E_{kin} .

The dependences of energy increments $\Delta U = U(T, V) - U_0(V)$ and E_{kin} of the whole system on the temperature grid number are linear for the case of the initial compression of the sphere. Their values are close to each other, which vindicates the presence of the equilibrium thermodynamic state. Similar situation is observed for the sphere extension.

The dependence of the total internal energy on the temperature grid number is given in Fig.8 for the initial constringency, for two values of the cold pressures of 0.5 and 5 GPa. Internal-energy dependence on temperature is also linear, and the graphs coincide within the whole pressure range, both for the compression and extension cases.

It was mentioned above that in the extension case for the pressures above 1 GPa, the dependence of the relation between the finite and initial volumes on the temperature differs dramatically from the case of pressures within the range from -20 to +1 GPa. At the same time it was found that the dependence of the internal energy for the cold pressures of 1 and 5 GPa on the temperature practically coincides, and linear graphs have the same angle of inclination (or nanostructure thermal capacity).

Hence, the internal energy has been found numerically within the wide range of system temperatures and volumes. It should be especially noted that this energy linearly depends on the temperature and satisfies the classical Dulong–Petit law. At the same time, the dependence on the volume is weak and can be neglected for the zero approximation.

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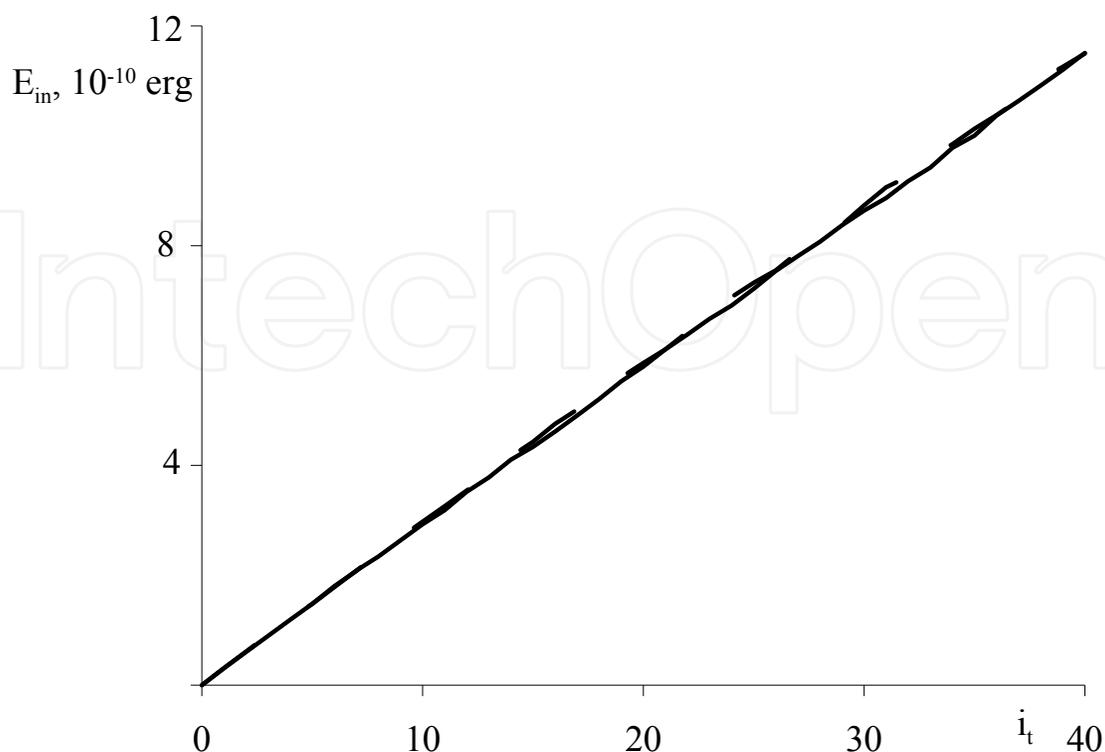
Fig. 8. The increment of the cluster internal energy E_{in} (10^{-10} erg) at the cluster compression vs the temperature grid number i_T for external pressures $P = 0.5$ GPa (solid line) and $P = 5$ GPa (dotted line)

6.3 Calculation of the thermal equation of the nanostructure state

When calculating the thermal equation of state, it is necessary, above all, to choose the model of the pressure calculation in the cluster. To do this, the formula for stress tensor components, obtained within the kinetic theory framework (see, for example, (Zimmermann, 1999; Zimmerman et al., 2009), is used:

$$\sigma_{\alpha\beta} = \frac{1}{V_c}\left[\sum_i \frac{p_i^\alpha p_i^\beta}{m} + \frac{1}{2}\sum_{i\neq j} F_{ij}^\alpha r_{ij}^\beta\right].$$ (22)

Here V_c is the volume of the studied system; p_i^α is the α-component of the i-atom momentum; m is atomic mass; r_{ij}^β is the β-component of the radius-vector between the i- and j-atoms. The summing-up is done by all atoms lying within the studied volume. The first item in the thermodynamically equilibrium state is rearranged in the form of (Allen & Tildesley, 1987):

$$P_{kin} = \frac{NkT}{V}.$$ (23)

Evident that the total pressure consists of the kinetic (similar to gases) and potential components:

$$P_T = P_{kin} + P_U,\tag{24}$$

and the potential component P_U also contains the «cold» pressure. Since the calculation of the kinetic component is not difficult, and the «cold» pressure has been found in the preliminary calculations, it is more convenient to use the expression $\Delta P_U = P_U - P_x$ to analyze the thermal effects.

The obtained data valid for t the coordinates of all atoms enabled to construct the dependence of pressure ΔP_U on the internal energy of a volume unit which is quite commonly used in the continuum mechanics. The obtained parametric dependence on the initial cold pressure is biunique bound with the relative volume variation. Thus, these data give the fundamental thermodynamic dependence $P_T(V, E_{in})$.

It is more usual for thermodynamics to use the thermal equation of state in the variables (P, V, T). Since all variables are calculated numerically, it is rather simple to construct the dependence of the changing thermal pressure ΔP_U on the temperature (Fig.9).
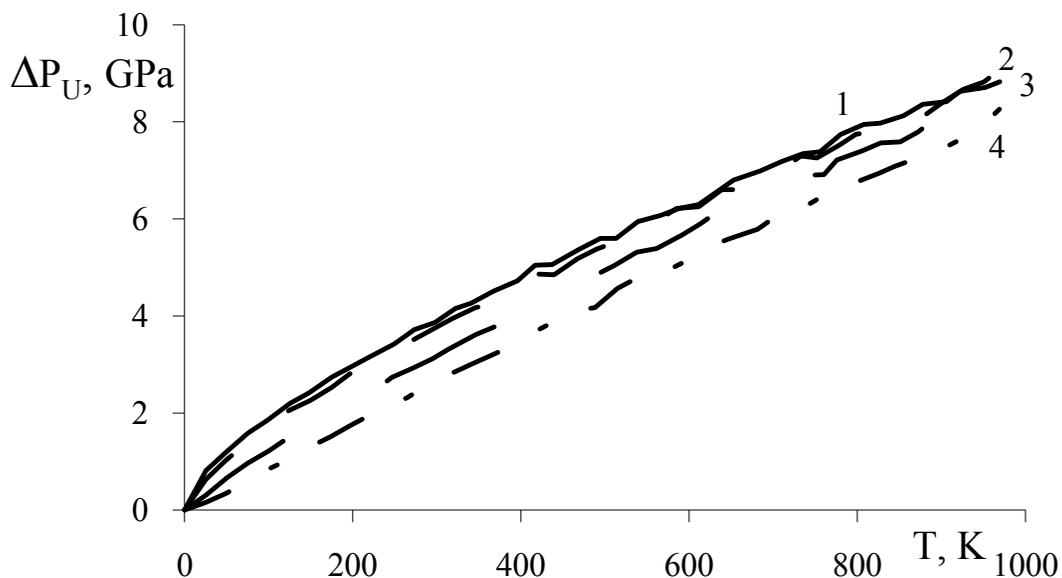
Fig. 9. Thermal pressure in the cluster ΔP_U (GPa) vs the temperature (compression case) for the cold pressure: 1 – 0.1 GPa; 2 - 1 GPa; 3 - 5 GPa; 4 – 10 GPa

Within the range from 0.1 to 1 GPa, the graphs almost coincide, and at higher pressures one can see the parametric dependence on the sphere volume. For the case of sphere extension, in the range of 0.1 – 1 GPa, the data for the cluster extension almost coincide. It should be noted that the dependence is close to linear at the temperature above 300 ºK.

6.4 Grüneisen constant calculation

In practice, the expression for the thermal equation of state with the Grüneisen constant is frequently used (see above). Since in the molecular-dynamic calculations the temperature, volume and pressure are found from the first principles, this constant can be found:

$$\gamma = \Delta P / (3NkT / V).\tag{25}$$

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Fig. 10 presents its dependence on the temperature for various values of the constringent cold pressure (or the same – on the value $x = V(P_x) / V_0$).
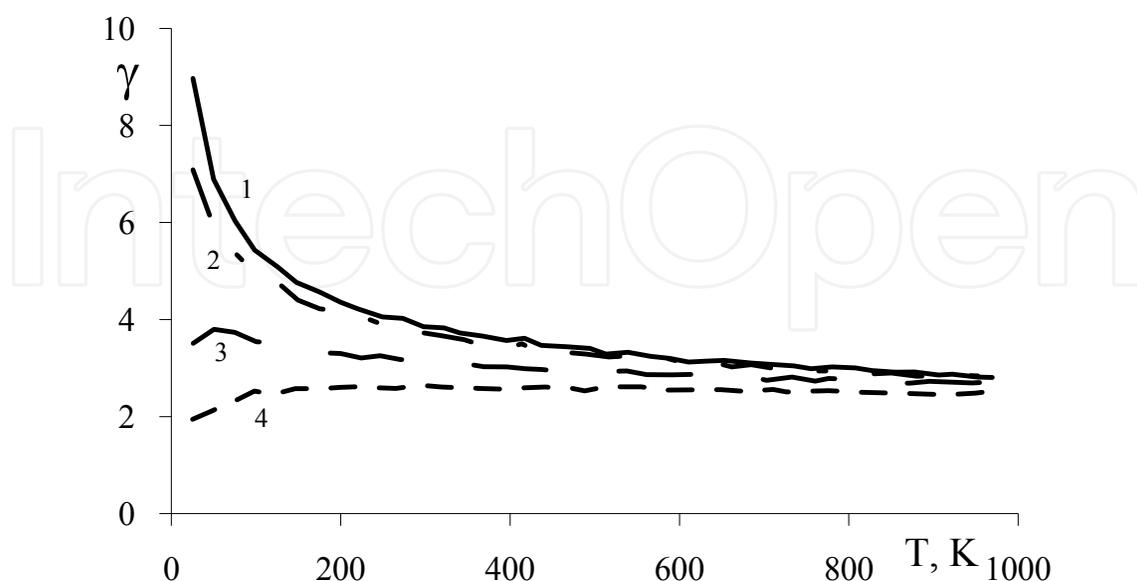

Fig. 10. Grüneisen constant vs the temperature (compression case) for the cold pressure:
1 – 0.1 GPa; *2* – 1 GPa; *3* – 5 GPa; *4* – 10 GPa

Evident that for the temperature of $T \geq 300^o$ K, the slight decrease of γ within the limits of 10 % is evidently observed. At the same time, one can see the strong dependence of this value on the initial cold pressure or on the system volume. For $T = 300^o$ K, the Grüneisen constant values differ almost twice from the case of the pressures of 0.1 and 10 GPa. At the same time, we see the strong dependence of this value on the initial cold pressure or on the system volume. For example, at $T = 300^o$ K, the values of the Grüneisen constant differ almost twice for the pressures of 0.1 and 10 GPa. It should be noted that the experimental magnitude of this value (the case of copper) found in the macroscopic experiments is 1.8. This is approximately twice lower than the similar value for the nanostructures at low pressures.

6.5 Free energy of nanostructures

As it is well known, any known thermodynamic potential gives complete information on the thermodynamics of the whole system. Before the internal energy was found in the variables (T,V) which are the eigen variables of the free energy. This is a typical situation when the internal energy is calculated from *ab initio* by statistical physics methods or, for example, inside of the dynamic method proposed here. In this context, the Gibbs–Helmholtz equation should be used at the following stage:

$$F(T,V) = -T\int \frac{E_{in}(T,V)}{\tilde{T}^2}d\tilde{T} + T\varphi(V),$$ (26)

which would enable to transit from the internal energy in the variables (T,V) to the free energy. Here, the internal energy is

$$E_{in}(T,V) = U(T,V) + E_{kin} \,, \tag{27}$$

where $U(T,V)$ is the total energy of the cluster and E_{kin} is the kinetic energy of the chaotic motion of the atoms.

The potential energy can be presented as

$$U(T,V) = U_x(V) + \Delta U(T,V) \,. \tag{28}$$

In return, the potential energy (the cold energy) of the cluster is a sum

$$U_x(V) = U_{0fr}(V_{0fr}) + \Delta U_x(V) \,. \tag{29}$$

of the potential energy of the cooled cluster without external pressure $U_{0fr}(V_{0fr})$ with the initial cluster volume V_{0fr} and positive addition to the energy $\Delta U_x(V)$, which occurs due to the compression by the external pressure to the volume V.

The addition to the potential energy $\Delta U(T, V)$ can depend in the general case on the temperature and volume, similarly to the thermal energy E_{kin}. As was shown before, both the internal energy and $\Delta U(T,V)$ weakly depend on the volume and this dependence can be ignored in the zero approximation, whereas the Dulong-Petit law $\Delta E_{in} = 3NkT$ can be used for the internal energy increment.

Hence, the internal energy of the cluster can be presented as:

$$E_{in} = U_{0fr}(V_{0fr}) + \Delta U_x(V) + 3NkT \,. \tag{30}$$

Substituting this in (26), we have:

$$F(T,V) = -T \int \frac{U_{0fr}(V_{0fr}) + \Delta U_x(V) + 3Nk\tilde{T}}{\tilde{T}^2} d\tilde{T} + T\varphi(V) \,. \tag{31}$$

Upon elementary transformations we obtain the expression for the free energy:

$$F(T,V) = U_{0fr}(V_{0fr}) + \Delta U_x(V) - 3NkT \ln\left(\frac{T}{T_0}\right) + T\varphi(V) \,. \tag{32}$$

With the thermodynamics generalities we obtain the expression for the pressure, its numerical values, on the other hand, are found *ab initio*:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{d(\Delta U_x(V))}{dV} - T\frac{d\varphi(V)}{dV} \equiv P_x(V) - T\frac{d\varphi(V)}{dV} \,. \tag{33}$$

To determine the unknown function $\varphi(V)$, the expression $\Delta P_T = P - P_x$ from the molecular-dynamic calculations should be analyzed; The pressure caused by the chaotic motion of the atoms

$$\Delta P_{kin} = T\frac{3Nk}{V} \,, \tag{34}$$

Depends linearly on the temperature and corresponds to the expression

$$P - P_x = -T\frac{d\varphi}{dV} . \tag{35}$$

Evident that the function $\varphi(V)$ can be presented as a sum

$$\varphi(V) = \varphi_{kin}(V) + \varphi_U(V) . \tag{36}$$

Of kinetic and potential components. Then

$$-T\frac{d\varphi_{kin}}{dV} = T\frac{3Nk}{V} . \tag{37}$$

Or, when transiting to the relative volume

$$x = \frac{V_{0fr} - V}{V_{0fr}} , \tag{38}$$

we have

$$\varphi_{kin}(V) = -3Nk\ln(1-x) . \tag{39}$$

To find the potential component of this function, the numerical molecular-dynamic calculations should be used. The dependence of ΔP_U on the temperature for various cold pressures (or volumes) is shown in Fig.9. For the temperatures above 300 ºK at which these calculations are valid, the pressure dependence is truly approaching to the linearity. In this case, the derivative is

$$\frac{d\Delta P_U}{dT} = \frac{d\varphi_U}{dV} . \tag{39}$$

The treatment of numerical calculations results enabled to construct the value $\frac{d\varphi_U}{dV}$ from the relative change of the volume $x = \frac{V_{0fr} - V}{V_{0fr}}$. (Fig.11.). The polynomial approximant is:

$$\frac{d\varphi_U}{dV} = 0,00755251 + 0,0324687x - 0,416867x^2 \equiv ax^2 + bx + c . \tag{40}$$

As a result, we have

$$\varphi_U(V) = \tilde{a}x^3 + \tilde{b}x^2 + \tilde{c}x + c_0 , \tag{41}$$

where

$$\tilde{a} = -\frac{V_{0fr}a}{3} ; \tilde{b} = -\frac{V_{0fr}b}{3} ; \tilde{c} = -\frac{V_{0fr}c}{3} . \tag{42}$$

Finally, the free energy of the nanoclusters is in the form of

$$F(T,V) = U_{0fr}(V_{0fr}) + \Delta U_x(V) - 3NkT\ln\left(\frac{T}{T_0}\right) + \\ + T\left(\tilde{a}x^3 + \tilde{b}x^2 + \tilde{c}x + c_0 - 3Nk\ln(1-x)\right)$$

(43)

The obtained expression and numerically found cold energy $\Delta U_x(V)$ together solve completely the challenge of calculation of the thermodynamic properties of the nanostructure.
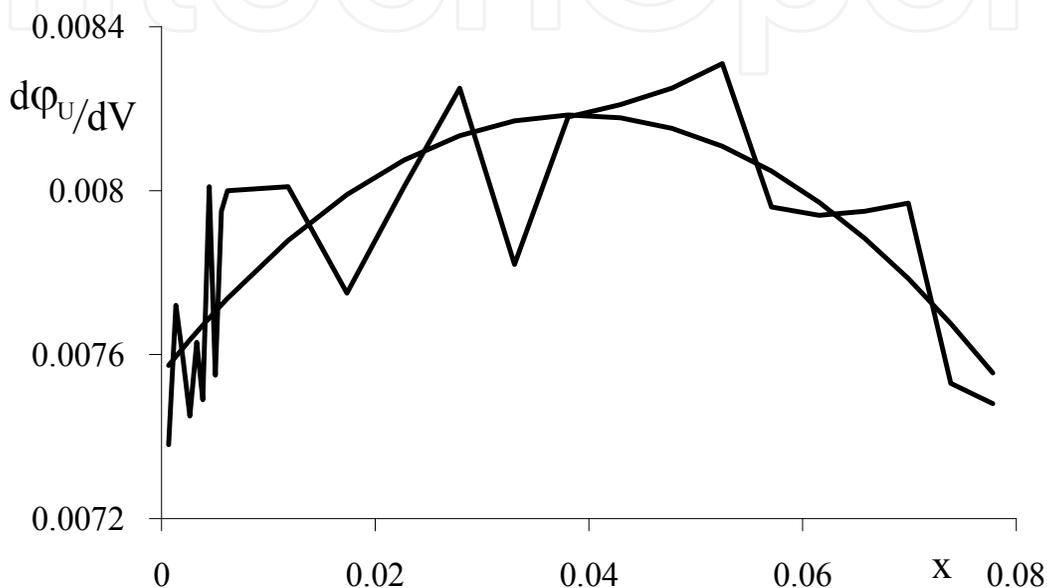

Fig. 11. Dependence of $\dfrac{d\varphi_U}{dV}$ on the relative change of the volume: fine solid line – exact calculations, heavy line – polynomial approximant

7. Analysis of the influence of admixtures on nanoclusters thermodynamics

The developed approach was applied to the study of nanoclusters thermomechancial properties by the molecular dynamics method. It permitted to find out the criteria of applicability of traditional methods to alloyed nanostructures, to investigate the influence of the stoichiometric coefficient on the thermomechancial properties. Moreover, scaling enables to extend the results of this work to macro-subjects and to obtain similar characteristics for the deformed body mechanics.

7.1 The physical model and basic calculation procedures

A copper sphere with the radius of 20 Å (Golovnev et al., 2006 a) was used to simulate a metal nanoculster with insertions. Then the copper atoms with specific numbers were replaced by silver atoms with the aid of the Monte-Carlo method. Total amount of the replaced atoms corresponded to the percentage of the silver atoms, which was used as the external controlled parameter. The content of the silver atoms in the nanoclusters varied from 1 to 8%.

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To take the copper-silver interaction into account, the Voter EAM potential for Cu, Ag, CuAg is used (Chen Jan et al., 2007; Berroukche et al., 2008). To prepare the initial data, the whole system was cooled with the help of an artificial viscosity method (Bolesta et al., 2001), similarly to the case of pure copper, and whereby the system of atoms was at the calculation end in the potential energy minimum. The finite arrays of coordinates and momenta obtained during the cooling were then used as initial data for the simulation of the sphere quasi-statical compression and extension. Fig.12 illustrated the influence of the silver concentration by the cluster radii dependence on time for the cooling process. Evident that as the silver concentration rises, the cluster radius increases. Below we give the results for the cluster compression within the pressure range from 0.1 to 10 GPa.
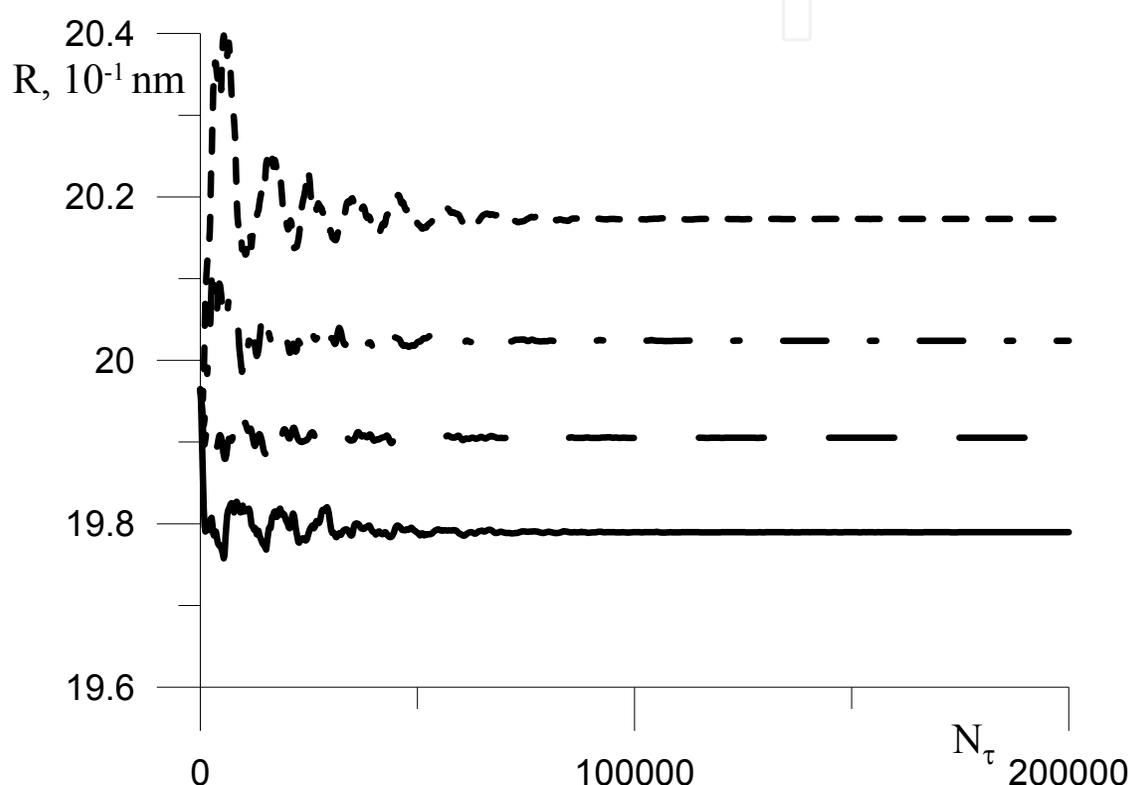
Fig. 12. Radii of nano-spheres varying with time during the cooling. Solid line – pure copper; dashed line – alloy Cu99%Ag1%, chain line – Cu96%Ag4%, dotted– Cu92%Ag8%

7.2 Simulation of the cooled nanosphere compression

Then the sphere was cooled similarly to the pure copper case (see paragraph 4).

The key thermodynamic characteristics of the system are the dependencies of the "cold" pressure P_x and internal energy U_{tx}, which is just the potential energy of the system at $T \approx 0^o K$, on the cluster volume.

In the frame work of the proposed method (Golovneva, 2007), the pressure P_x equals the external pressure, which is the parameter under control. The nondimensional value was used as the characteristics of volume:

$$x_t = 1 - \frac{V}{V_0}.$$

(44)

Here V_0 is the volume of cooled cluster without external pressure at the preset silver concentration. The magnitude of the value was taken on the asymptotic after static equilibrium fixing. The calculation results are presented in the Fig.13. The significant influence of the admixtures and abnormal behavior of the dependence (a sharp bend) are seen when the concentration of the silver atoms in the nanoclusters reaches the silver solubility limit in copper (8%).
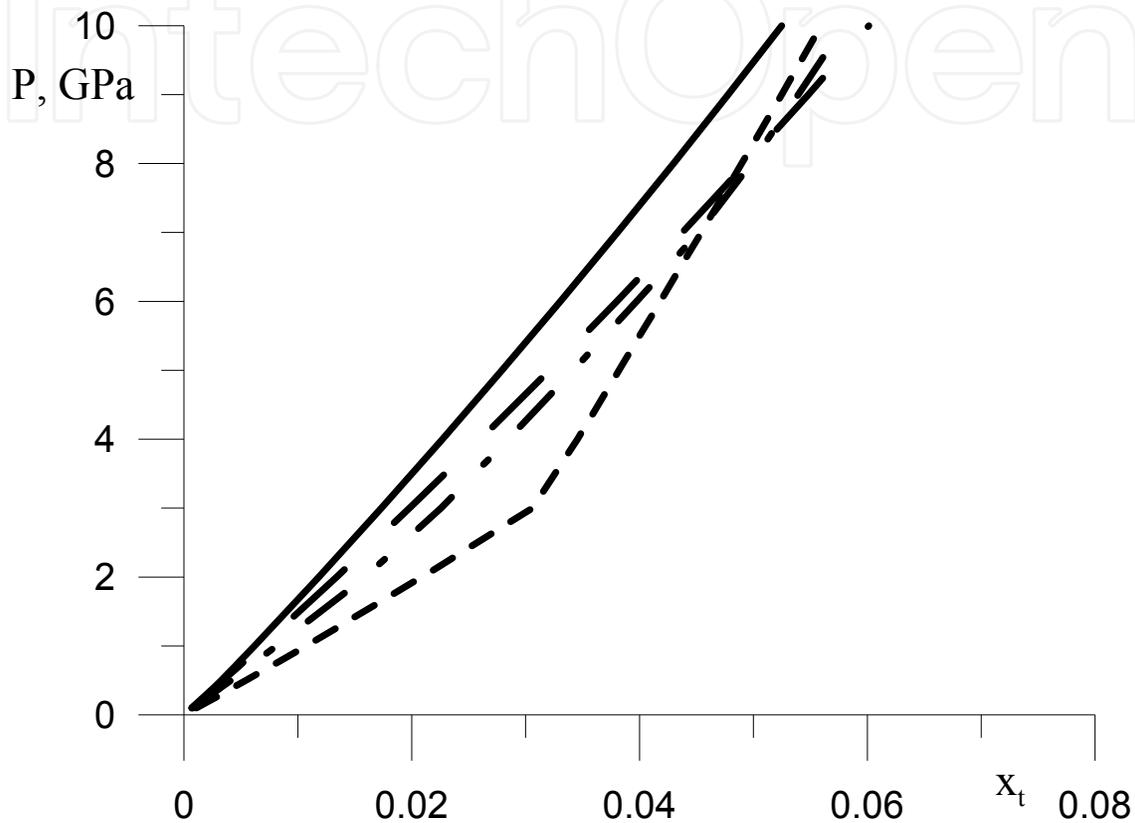


Fig. 13. Pressure vs the relative change of the Cu nanoclusters volume for various concentrations of silver. Solid line – pure copper; dashed line – alloy Cu99%Ag1%, chain line – alloy Cu98%Ag4%, dotted line– Cu92%Ag8%

For greater visualization below we present the dependence of the internal energy variation:

$$\Delta U_{tx} = U_{tx} - U_0 . \tag{45}$$

On the relative volume x_t. Here U_0 is the potential energy of cooled cluster without external pressure at the preset silver concentration. Likewise as in the previous case, the energy value U_{tx} and relative change of volume were taken in the equilibrium state at a certain pressure. The results are shown in Fig.14. Both for pure copper and for small silver concentrations, the dependence approaches to a parabolic one. Increasing concentration of silver causes the reduction of value ΔU_{tx}. However at the limit silver concentration in the alloy CuAg of 8%, the anomalous sharp bend and abrupt energy growth are observed.

To explain this phenomenon, the radial distribution function (RDF) of copper atoms in respect to silver atoms was studied. Fig.15-a presents the RDF with 2%silver for the case of no external pressure (solid line) and for the pressure of 10 GPa (dotted line). Evident that

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both the peaks size and shape are well preserved, only their centers are slight shifted. At the same time, at 8% silver (Fig.15-b), we see the considerable broadening of the lines and centers shift. In return, it brings many new atoms in the interaction sphere (its radius is 4.96 Å (the fourth peak)), change of the dependence $\Delta U_{tx}(x_t)$, and as consequence, the function

$P_x(x_t)$, since $P_x = \dfrac{dU_{tx}}{dV}$.

7.3 Calculation of caloric and thermal equations of state for the nanoclusters

The nano-sized spherical alloy was heated in the same way as in the pure copper case (see paragraph 6).

The obtained results enable to construct the equation of state in the Mie-Grüneisen form, which is written for the continuum mechanics as:

$$P - P_x = \gamma \frac{3NkT}{V}.$$ (46)

or through the internal energy

$$P = \gamma \frac{(E_{in} - U_{tx})}{V},$$ (47)

where E_{in} is the total internal energy of the cluster.
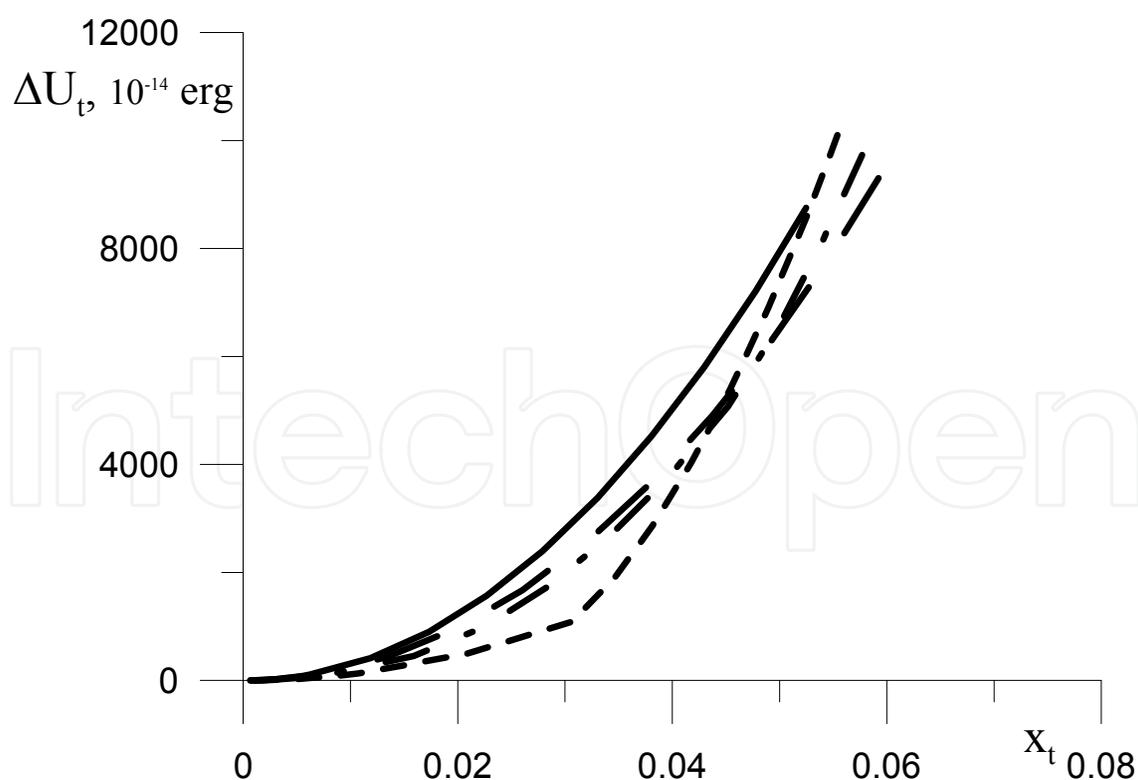
Fig. 14. Relative potential energy vs the relative change of the Cu nanoclusters volume for various concentrations of silver. Solid line – pure copper; dashed line – alloy Cu99%Ag1%, chain line – alloy Cu98%Ag4%, dotted line – Cu92%Ag8%
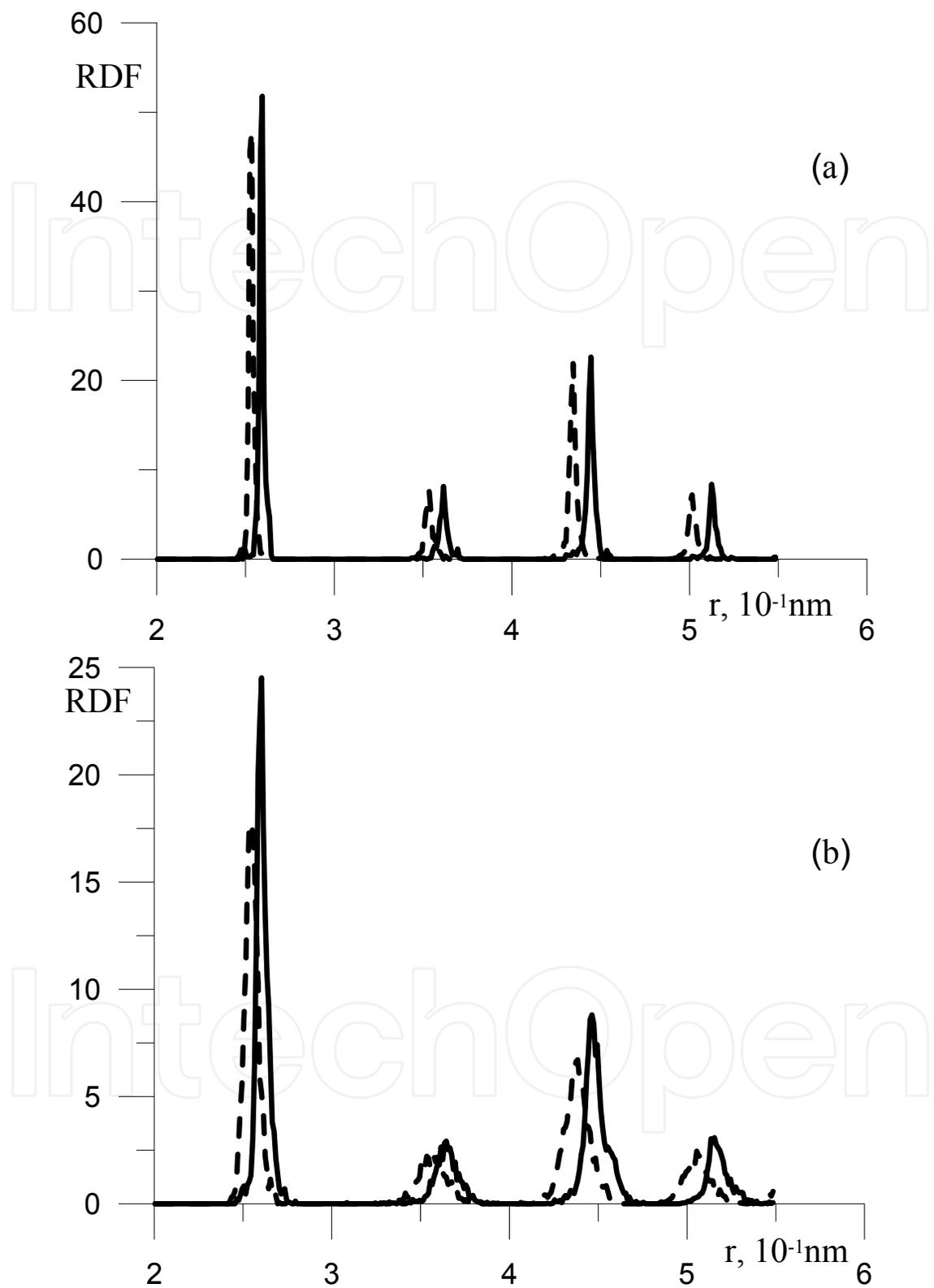
Fig. 15. Radial function of distribution (RDF) of copper atoms in respect to silver atoms regarding the distance at the cold nanocluster compression. Solid line – no external pressure, dotted line – the external prersure is 10 GPa. a) silver atoms concentration 2%; b) silver atoms concentration 8%

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It should be noted that in the modeled process, the volume of the total system retains constant during the heating, i.e. the pressure change is caused by the temperature increase alone. As an example, Fig. 16 presents the dependence $\Delta P = P - P_x$ on the temperature for the external pressure of 1 GPa.

The obtained set of such curves for the initial compression pressures from 0.1 to 10 GPa dictates the thermal state of the nanostructure $P(V,T)$.

The caloric equation determining the total internal energy E_{in} which is the temperature and volume function was calculated as a sum of ΔU and kinetic energy of the chaotic motion of atoms. The numerical dependence of the relative total internal energy $\Delta E_{in} = E_{in} - E_{in0}$ on the temperature for various silver concentrations was found. It is important that the inclination angle of nanostructure thermal capacity do not change as the silver concentration varies until it reaches 8%, and coincides with the classical Dulong-Petit law.

The obtained results completely describe the thermodynamic properties of the nanoclusters from pure copper and copper-silver alloy. But frequently it is convenient to use the analytical expression (46), with the complicated dependence of the processes on the volume and temperature being transmitted into the Grüneisen constant. Fig.17 shows such a dependence for the case of the initial external pressure of 1 GPa.

It should be stressed (refer above), that the results were obtained in the context of classical mechanics and can be used for the temperature above the Debye temperature. For comparison, the experimental value of the Grüneisen constant for macroscopic samples of copper is 1.84, for macroscopic samples of silver – 2.46 (22 Grigor'ev & Meilikhov, 1991).
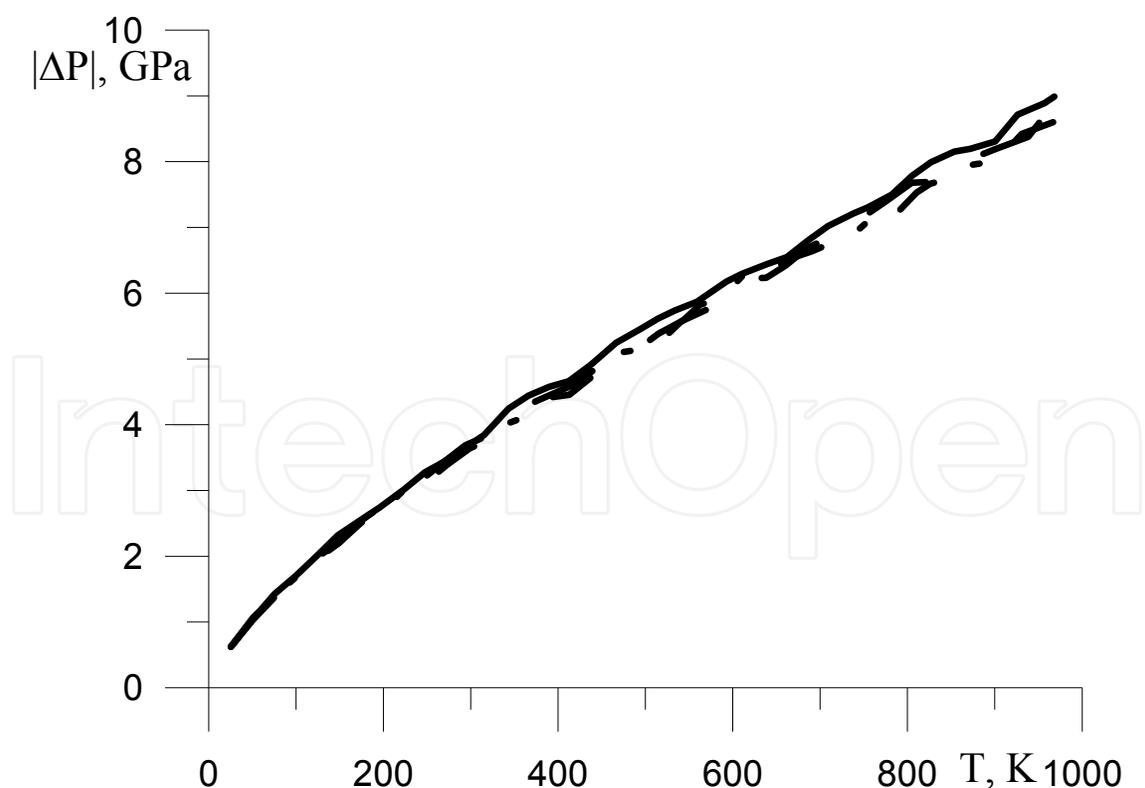

Fig. 16. "Hot" pressure vs the temperature at the external initial compressing pressure of 1 GPa. Solid line – pure copper; dashed line – alloy Cu98%Ag2%, chain line – alloy Cu96%Ag4%, dotted line – Cu92%Ag8%
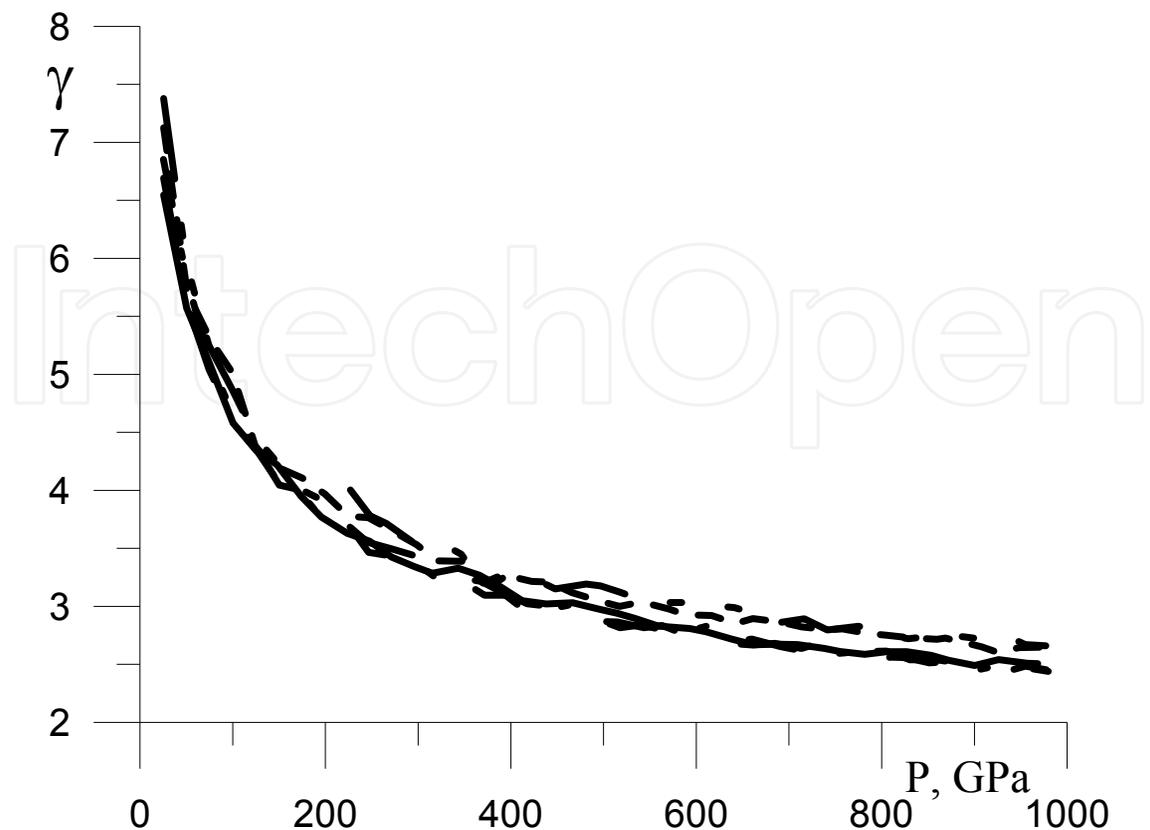
Fig. 17. Grüneisen constant vs the temperature at the external initial compressing pressure of 1 GPa. Solid line – pure copper; dashed line – alloy Cu98%Ag2%, chain line – alloy Cu98%Ag4%, dotted line – Cu92%Ag8%

8. Conclusion

In summary, the procedure of calculation of the thermodynamic properties of nanostructures *ab initio* is proposed and tested for the case of spherical copper clusters.

The study demonstrated that the results for the volume part of the system coincide with the results for macro-subjects. The difference between nanostructure and macrobodies properties results from the significant influence of the surface atoms in the nanostructures.

The proposed method enables to calculate the thermomechanical properties of the macrobodies by means of similar calculations for the microstructures when the influence of the surface atoms can be ignored.

Moreover, the developed method of the calculation of the thermodynamic properties by the molecular-dynamic method *ab initio* was tested on the nano-alloy Cu_xAg_{1-x} shaped as spherical clusters. Furthermore, a program system was produced which permits to calculate the thermomechanical properties of any alloy with known inter-atomic interaction potentialities.

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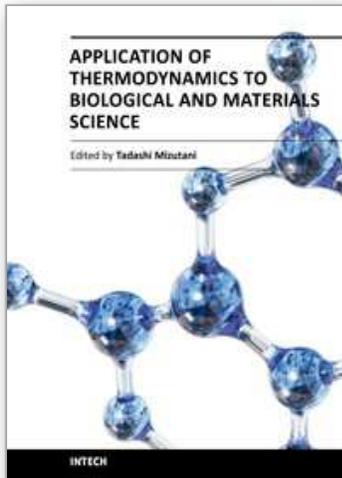
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