

**MOLECULAR-DYNAMIC CALCULATION OF THERMAL EXPANSION COEFFICIENT
FOR COPPER NANOCLUSTERS**

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Abstract

The paper presents the molecular-dynamic investigation of thermal expansion linear coefficient (TLC) for copper nanoclusters of spherical shape in the wide size range. To do this, the nanoclusters was heated by the stochastic forces method, and a number of characteristics were calculated in a certain amount of time pitches. In particular, the linear sizes of the studied nanostructure, its volume and system temperature were derived. Then the TLC magnitudes were found by the known expressions with the interpolation method; the TLC dependencies on the nanostructure size were plotted. It was shown that the TLC depends on the nanostructure size. As the size increases, the calculated thermal expansion linear coefficient tends to its experimental value.

Key words: Molecular dynamic modeling, copper nanocluster, thermal expansion coefficient

1. INTRODUCTION

The thermal expansion linear coefficient is one of the most important thermodynamic features of materials, and until recently, it was found from experimental studies only. As high-performance (powerful) computer systems, the method of molecular dynamics has been developing; under the condition of thoroughly calculated potentials of inter-atomic interaction, this method enables to calculate theoretically this characteristic, too. Until now, however, the TLC was detected by the molecular-dynamic method for the systems on the approximation of periodical boundary conditions (see, for example, Sekkal et al., 1998, Moon and Hwang, 2003, Berroukche et al., 2008). It means that the macrosystem was modeled and the founded coefficient does not describe the properties of nanostructures. But the authors of (Gubernatorov et al., 2007) analyzed experimental data and assumed the governing role of the difference between the thermal expansion coefficients for liquid and solid phases of metals during crystallization. They proposed the following crystallization mechanism. Crystal clusters of the size about nanometers which are grains of crystallization, as was shown experimentally (Geld et al., 1971), have the thermal expansion coefficients approximately one order higher than the same characteristic of the liquid phase. As the melt temperature decreases, the nanoclusters reduce in size more intensively than the ambient liquid phase. It causes the occurrence of the stress gradient within the volume, which changes the process of atoms diffusion from the liquid phase toward the crystal cluster. This, in turn, significantly influences the crystallization process.

Thus, testing of this hypothesis conditioned the necessity to calculate the thermal expansion coefficient of the nanostructures, i.e. the structures with the developed surface which has a decisive impact on every characteristic of this system. At the first stage of this work, the results were obtained for spherical copper nanoclusters with a free surface.

2. PHYSICAL SYSTEM

To study the influence of nanostructure size and shape on thermodynamic properties, the molecular-dynamic calculation of the thermal expansion coefficient of spherical copper clusters was carried out. The nanospheres radii varied from 20 to 90 Å. It correlates with the amount of atoms from 2899 to 258725. Atomic interaction was described by a multiparticle potential obtained by the embedded atom method (Voter, 1993).

3. INITIAL DATA PREPARATION

Initial data were found as follows. First, the coordinates of the atoms of an ideal copper FCC lattice were 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 with the radius below the assigned one are selected. Fig. 1 shows the projection of an ideal crystal and selected sphere with the radius of 20 Å.

All calculations were done by the molecular-dynamic method with the fast modification Verlet (Allen and Tildesley, 1987). The time pitch was 10^{-16} s.

Then we found the minimum of the system potential energy by the artificial viscosity method (Golovnev et al., 2003). Obtained coordinates and atoms pulses were used as the initial data. Fig. 2-a presents the system temperature dependence during the cooling, Fig. 2-b shows the dependence of the variation of the system potential energy. The dependence of the nanosphere radius during the cooling for $R = 20$ Å is shown in Fig. 3.

Then, the nanostructure was heated above the melting temperature by the stochastic forces method (Bolesta et al., 2001). The heating was paused in every 25 K, and the system relaxed within 10^{-12} s to the thermodynamic equilibrium state. All necessary characteristics were calculated and averaged by thermal fluctuations within this interval. Hence the dependence of radii, edges lengths and clusters volumes on the temperature was determined.

4. CALCULATIONS RESULTS

Fig. 4-a shows the relative variation of radii $\Delta\tilde{R} = (R - R_0)/R_0$ vs the temperature for various initial cluster sizes. It should be noted that in the case of spherical clusters, we observe the strong dependence of the inclination angle tangent on the initial structure size up to 80 Å. The inclination angle decreases as the radius increases. For the spheres with the radii of 80 and 90 Å, the dependencies $\Delta\tilde{R} = (R - R_0)/R_0$ on the temperature virtually coincide. Hence it can be concluded that at further increase of the radii, the dependencies will end up with the asymptote which corresponds to the similar characteristics of macrobodies.

At the next calculation stage, the linear temperature interpolation was performed for each specified initial magnitude of the linear cluster size. Fig. 4-b presents the comparison of the obtained linear polynoms with the results of the molecular-dynamic calculation for specific initial structure sizes.

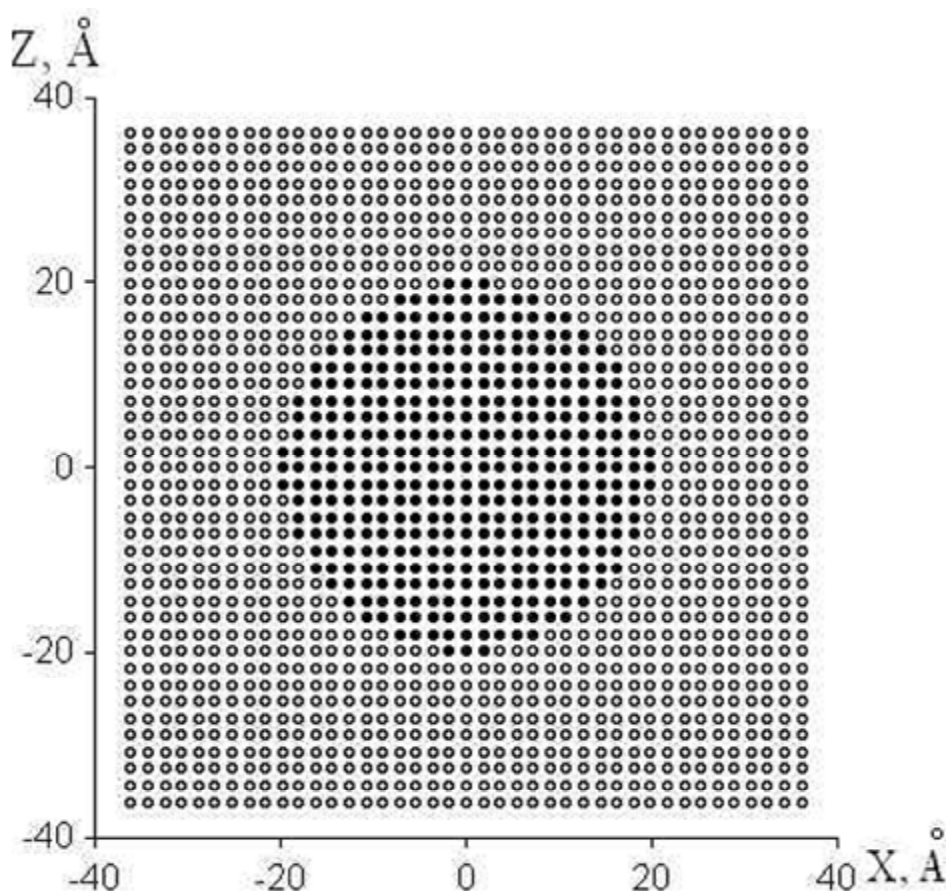


Fig. 1. Projection of the system for initial data detection in the XZ plane. Empty circles – the initial ideal crystal. Black circles – selected atoms with the radius below the assigned one (20 Å in this case).

To find out the TLC, the known expression $\Delta\tilde{R} = (R - R_0)/R_0 = \alpha\Delta T$ was used. Hence the dependence of the thermal expansion coefficient on the initial size of the nanostructure was detected and respective interpolation polynoms were plotted. The calculation results are shown in Fig. 4-c. For convenience, the same graphs show the experimental values of the thermal expansion coefficient for copper macroscopic samples.

As is seen, the cluster size highly influences the thermal expansion process. For the spherical clusters we observe the decrease of the thermal expansion coefficient as the size increases, and the calculated magnitude of the thermal expansion linear coefficient approaches to experimental values.

Moreover, the variation of the nanosphere volume with the temperature during the heating was calculated. Fig. 5-a shows the dependence of the relative variations of the volumes $\Delta\tilde{V} = (V - V_0)/V_0$ on the temperature for various initial cluster sizes. Note that in the spherical clusters case,

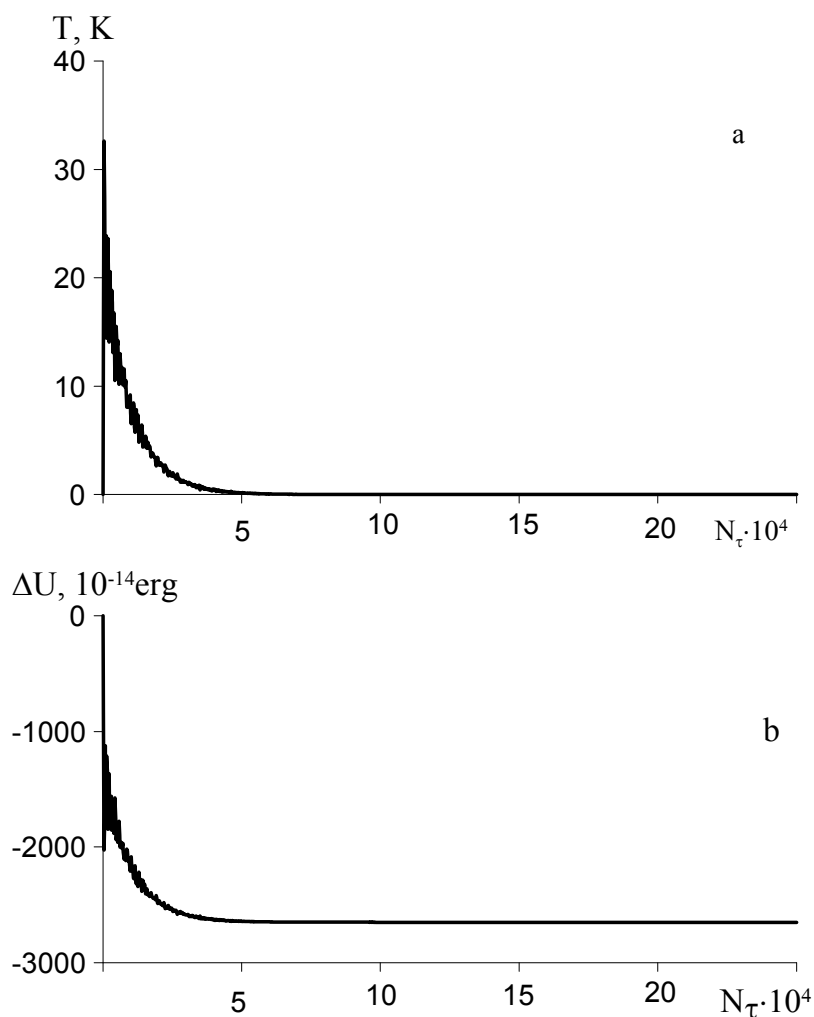


Fig.2 a – Temperature dependence on time pitch number. b – the dependence of variation of the system potential energy.

the inclination angle tangent highly depends on the initial structure size up to $80 \text{ \AA}$, as well as for the dependence $\Delta \tilde{R} = (R - R_0)/R_0$ on the temperature. The inclination angle decreases as the radius increases. Thus the conclusion similar to the above one can be derived that with further increase of the radii the dependencies will end up with the asymptote which corresponds to the similar characteristic for macrobodies.

The following calculation stage included the linear temperature interpolation for every specified initial value of the cluster linear size. Hence the dependence of the thermal expansion volume coefficient on the initial nanoclusters size was found. The calculation results are shown in Fig. 5-b. For convenience, the experimental value of the thermal expansion volume coefficient for copper macroscopic samples is presented in the same axes.

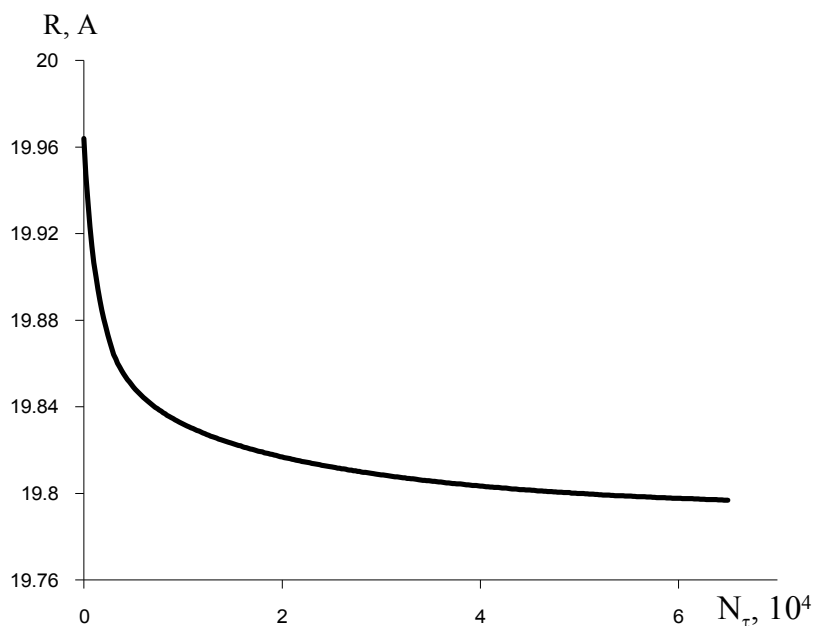


Fig.3 Cluster radius dependence on time pitches number during the system cooling ($R=20 \text{ Å}$).

It is known from the solid-state physics that for anisotropic bodies with cubic symmetry, the thermal expansion linear coefficients coincide in each direction and make approximately one third of the thermal expansion volume coefficient. The results of our molecular-dynamic calculations show this ratio as is seen from Fig. 5-c. This graph gives the calculation value of the thermal expansion volume coefficient as well as the tripled thermal expansion linear coefficient. These characteristics are given with due regard to the nanoclusters radius.

5. CONCLUSION

The obtained results enabled to conclude that both linear and volume coefficients of thermal expansion of metal nanoclusters depend on the size of the studied system. As the nanocluster size increases, the values of the thermal expansion coefficient approach to the experimental values obtained for macrobodies (copper in this case). At the next stage, it will be necessary to compare the influence of the nanoclusters shape on the results. A cubic nanocluster will be used for this purpose. The developed procedure can be used for the calculation of the thermal expansion coefficients for other metals.

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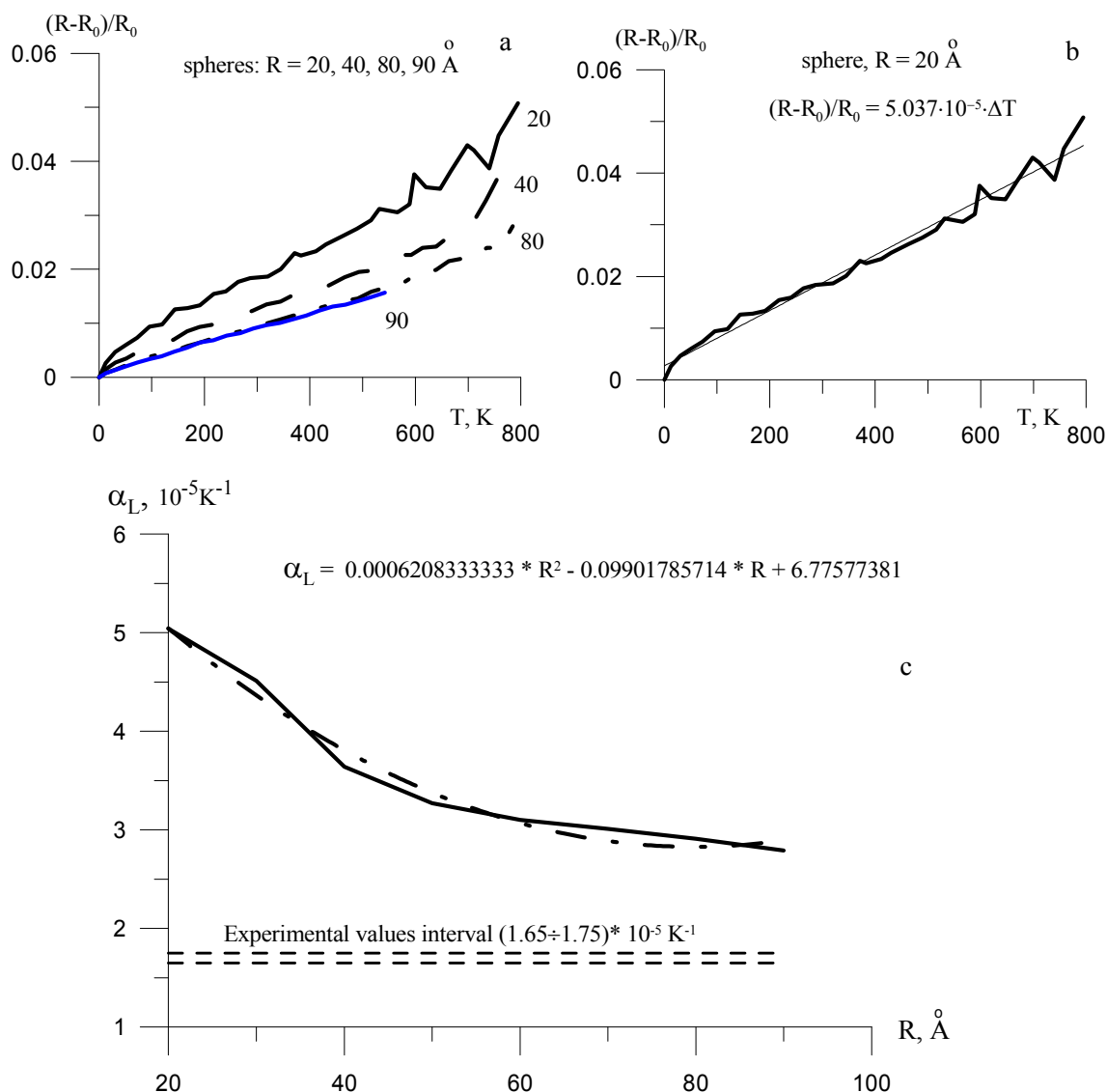


Fig.4 a – relative variation of nanoclusters radius vs the temperature for various radii. b – relative variation of nanoclusters radius vs the temperature for the radius $20 \text{ \AA}$, heavy line – the results of the molecular-dynamic modeling, thin line – approximation straight line, the formula is presented on the graph. c – α_L vs the cluster size (nanosphere radius), solid line – the result of the molecular-dynamic calculation, chain line – quadratic polynom approximation, the formula is on the graph, experimental values are shown with the dashed line.

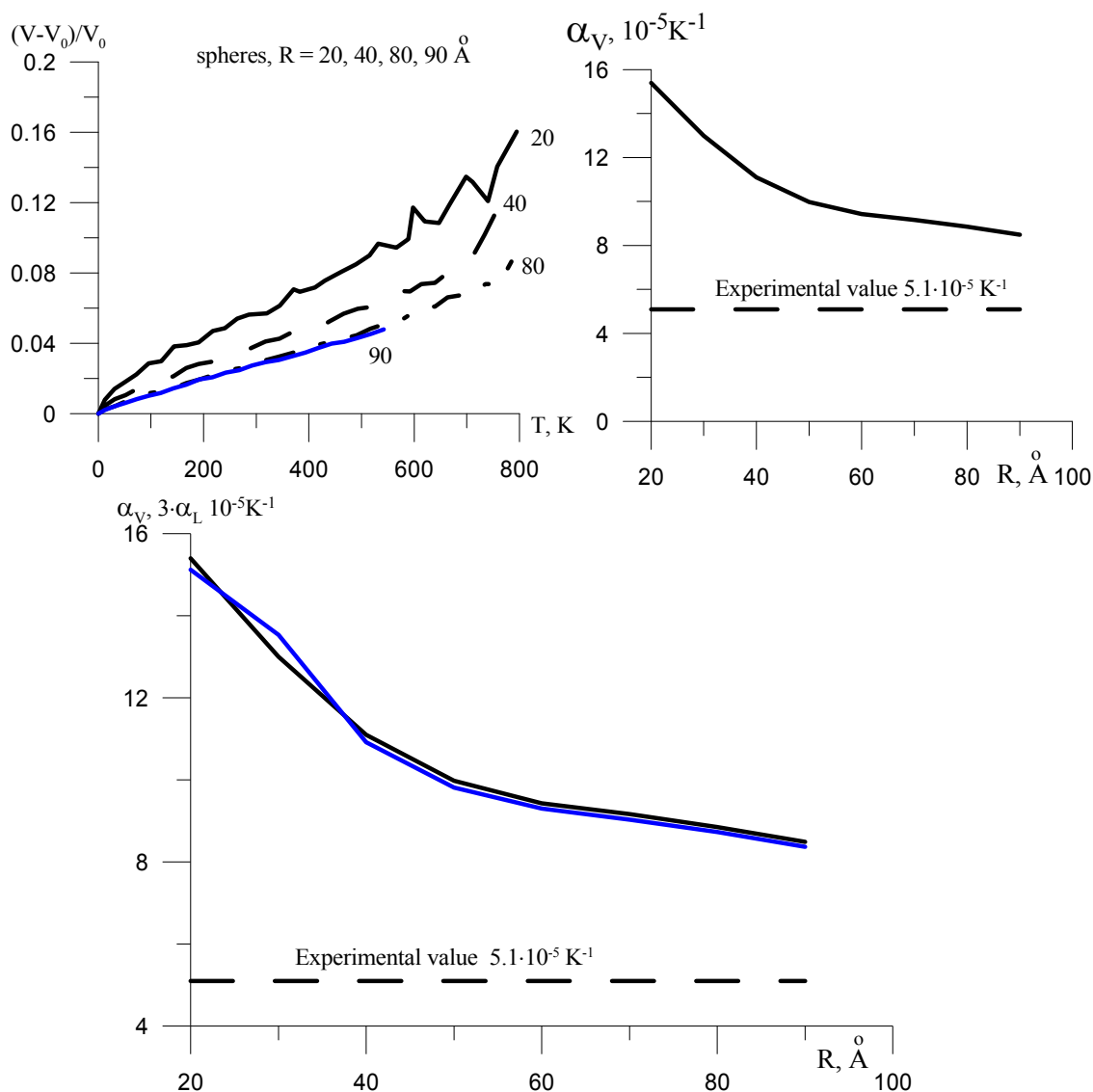


Fig.5 a – relative variation of the nanoclusters volume on the temperature for various sphere radii. b – dependence of the thermal expansion volume coefficient on the cluster size (nanosphere radius), solid line – the result of the molecular-dynamic calculation, chain line – quadratic polynom approximation. C – dependence of the thermal expansion volume coefficient (black solid line) and tripled thermal expansion linear coefficient (blue line) on the cluster size, experimental values for the thermal expansion volume coefficient for copper are shown with the dashed line.

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