

# Calculations of the heat capacity of Cu clusters synthesized by condensation from the gas phase

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## Abstract.

On the basis of our former simulations, we conclude that the heat capacity in the case of isolated free clusters can exceed that of a bulk material. It was found that at  $T=200\text{K}$  the increase in the Cu nanocluster heat capacity ( $D = 6\text{nm}$ ) was only 10%, decreasing with growing nanoparticle proportionally to the reduction in the fraction of surface atoms. Thus, the considerably larger heat capacities of copper nanostructures observed in the experimental works cannot be related to the characteristics of free clusters. In our view, these properties of a nanomaterial can be associated with the degree of agglomeration of its constituent particles, i.e., the interphase boundaries and the increase in the root-mean-square displacements of atoms on the combined surface of the interconnected nanoclusters can have a strong effect. To test the above hypothesis, we took copper clusters of various sizes (4071–15149 atoms) that we produced when simulating the synthesis of Cu nanoparticles. Thus, in our molecular-dynamics experiments using a tight-binding potential at high temperatures, we failed to properly assess the role of the interphase boundaries in calculating the heat capacity of nanoparticles. The reason was the mass diffusion of Cu atoms to impart an energetically more favorable shape and structure to the cluster. At low temperatures, the heat capacity of the clusters exceeded that of the bulk same by a value from 10% to 17%. Consequently, the Cu clusters produced in direct experiments cannot be immediately applied in devices using the thermal energy of such clusters, because their external shape and internal structure are nonideal.

## Introduction

Current, advances in new constructional and functional materials are associated, first of all, with the development of compactificated nanomaterials. In particular, the practical application of nanocrystalline metals and their various compounds has caused intensive studies of their mechanical, thermal, electrical, magnetic and other properties. For theoretical interpretation of experimental data obtained on compactificated nanomaterials it is, first of all, necessary to separate surface effects and those relating to small volume of particles the nanomaterial consist of. The problem is far of its solution as studying compactificated nanomaterials is yet at its prior stage of the result collection [1].

Thus, according to [2], the heat capacity of coarse-grained copper clusters of about 50 nm in size is higher than the normal heat capacity of the bulk copper in 1.2-2.0 times at temperatures from 200 K to 450 K. In [3] similar results were obtained for nickel nanoparticles of 22 nm in diameter: their heat capacity was twice higher than that of the bulk nickel at temperatures 300-800 K. A study of the heat capacity of nanostructures consisting of nickel clusters with of the diameter 10 nm by the fast neutron scattering method [4] also demonstrated the increase in the heat capacity in 1.5-2.0 times compared to that for conventional materials. However, according to [5], for nanocrystalline palladium ( $D = 6\text{nm}$ )



and copper ( $D = 8$  nm) in the temperature range 150-300 K the heat capacity increasing effect should be much smaller (29-53% and 9-11%, respectively, compared to conventional polycrystalline values for Pd and Cu).

To sum up, obvious discrepancies take place in experimental data on the heat capacity of the compactified metallic nanomaterials. All works show an excess of the heat capacity for a nanostructured material compared to a bulk body, but the values of this difference vary greatly. In fact, not individual nanoclusters but a nanostructured material composed of particles with a diameter of at least 6 nm was studied in these works. In this case, the sample under consideration is similar to colloidal crystals, because the developed surface and its fraction in determining the atomic mobility of the nanostructure are the main factor of an increase in heat capacity. Therefore, to fill in the existing gap, we undertook computer simulations of the heat capacity for copper nanoclusters produced through the simulation of condensation from the gas phase. This chemical element is typical representatives of the transition metals and the data obtained for him can also be largely extended to nanoparticles of other transition metals.

### **The computer model**

The study of clusters plays a very important role in understanding the transition from a microscopic to a macroscopic structure; however, it is difficult to determine many physical properties for clusters experimentally [6]. Computer experiments may be considered as another way to investigate thermal properties of nanoparticles. In the molecular dynamics (MD) simulations presented here, Newton's equations of motion are solved numerically for each atom in the force field of the remaining ones by using a particular interatomic potential.

After analysis of different forms of the functional presentation of the potential energy, we have chosen the modified tight-binding potential TB-SMA [7] with the fixed cut-off radius corresponding to the 5-th coordination sphere, inclusively for following calculations of interatomic forces. This method is based on the fact that a significant group of transition metals can be fully described from the density of states of outer-shell d electrons. Despite a simple functional form, the tight-binding model well describes the elastic properties, the characteristics of defects, and the melting of a wide range of fcc and hcp metals.

As a test, this scheme of potential energy is tested using various thermodynamic characteristics of copper clusters, such as the melting and solidification temperatures, the hysteresis width, the convergence of a potential in the range of small clusters, and the binding energy. On the whole, when analyzing the results of various authors, we conclude that the Cleri–Rosato TB-SMA potentials [7] satisfactorily describe the behavior of a number of thermodynamic quantities of metallic fcc clusters on qualitative and quantitative levels. The differences between the simulation results and the data obtained by other collective potentials do not exceed 3–5%.

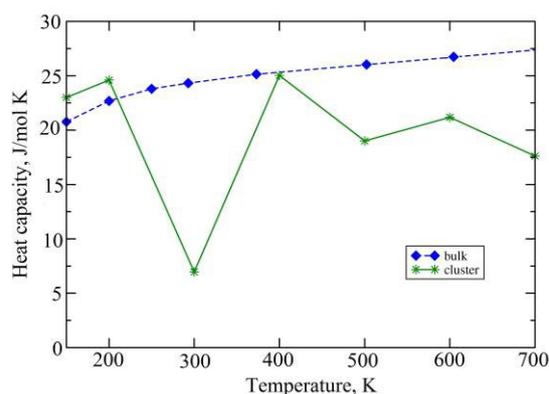
By computer simulations with molecular dynamics method, we used the MDNTP computer code developed by Dr. Ralf Meyer (Universität Duisburg, Germany). During simulation, the temperature was determined by the average kinetic energy of atoms calculated with the rapid Verlet algorithm at a time step  $h = 2$  fs [8]. Modeling occurred in frameworks a canonical ensemble for which the number of particles  $N$ , volume  $V$ , and temperature  $T$  are constant (NVT ensemble) and total momentum  $p$  of the system is zero, we placed the system in a thermal reservoir (Nose thermostat [9]) by introducing a random force to simulate collisions with virtual particles. The advantage of this technique is a very good stabilization of a fixed temperature: the deviations from this value are at most one percent.

### **Results and discussion**

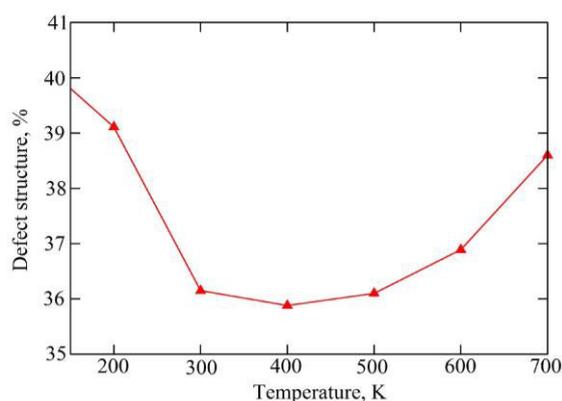
Taking into account the mentioned above significant scatter in values of the heat capacity of nanoclusters and nanostructured materials, the heat capacity of ideal separate Ni and Cu nanoparticles was investigated in our former work [10] in the temperature range 200-800K. It was found that at  $T = 200$ K the increase in the Cu nanocluster heat capacity ( $D = 6$ nm) was only 10%, and 13% for Ni

nanoclusters of the same diameter.

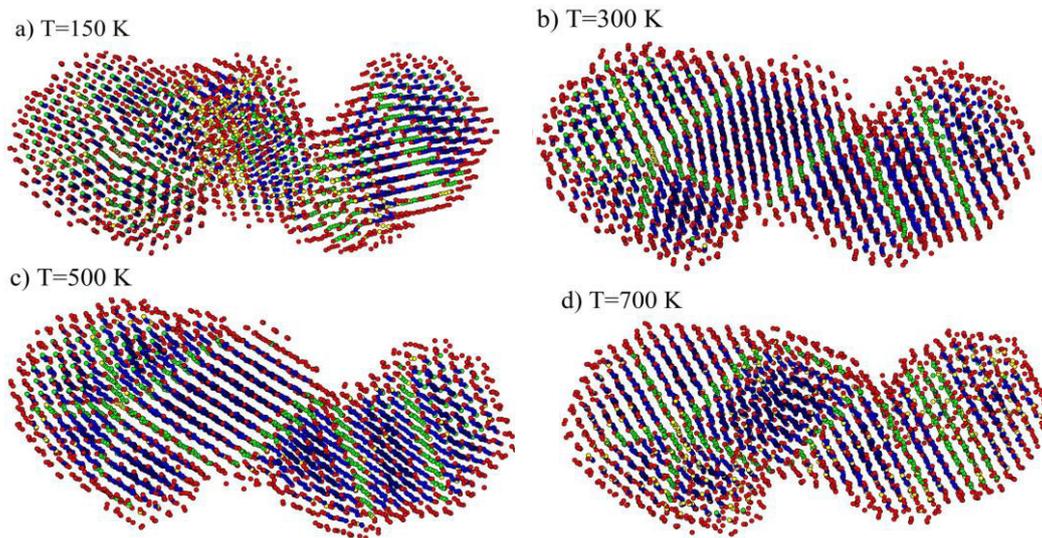
Having analyzed the results of our former simulations using a modified tight-binding potential, we conclude that the heat capacity in the case of isolated free clusters can exceed that of a bulk material, decreasing with growing nanoparticle proportionally to the reduction in the fraction of surface atoms. Thus, the considerably larger heat capacities of copper and nickel nanostructures observed in the experimental works [2–4] cannot be related to the characteristics of free clusters but are determined by different factors that are yet to be studied.



**Figure 1a.** Temperature dependence of the heat capacity for the bulk copper and  $\text{Cu}_{4071}$  cluster produced by condensation from the gas phase.



**Figure 1b.** Temperature dependence of the percent of atoms with coordination number less than 12 (defective structures) in  $\text{Cu}_{4071}$  cluster.



**Figure 2.** Evolution of the  $\text{Cu}_{4071}$  cluster as a function of the heating temperature: a)  $T = 150$  K, b)  $T = 300$  K, c)  $T = 500$  K, d)  $T = 700$  K.

In our view, these properties of a nanomaterial can be associated with the degree of agglomeration of its constituent particles, i.e., the interphase boundaries and the increase in the root-mean-square displacements of atoms on the combined surface of the interconnected nanoclusters can have a strong effect. Thus, the increase in the heat capacity of nanostructures can be affected significantly by the

appearance of low-frequency atomic vibrations with increasing amplitudes attributable to the increased surface of the agglomerated clusters and the interphase boundaries in the nanostructures.

To test the above hypothesis, we took copper clusters of various sizes (4071–15149 atoms) that we produced when simulating the synthesis of Cu nanoparticles. Therefore, at the first (preliminary) stage, we simulated the condensation of copper nanoparticles from a high-temperature gas phase for a physically and technologically proper representation of the computer sample of synthesized nanoparticles. At the second (main) stage of our studies, we calculated the heat capacity of the copper clusters with an already real shape and internal structure obtained from the gas phase to find the main patterns of the accumulation of thermal energy by them.

As example, consider a copper cluster of 4071 atoms. This cluster was ultimately formed when the  $\text{Cu}_{1385}$  particle collided with the  $\text{Cu}_{2686}$  particle. The latter turned out to be the result of the agglomeration of two particles containing 1856 and 830 atoms, respectively. In the long run, the cluster of 4071 atoms turned out to be the result of the agglomeration of more than 20 individual primary particles with typical sizes from 1.0 to 2.0 nm. However, most of these particles subsequently combined between themselves, so that only four particles separated by well-defined interphase boundaries remained distinguishable in the internal structure of the  $\text{Cu}_{4071}$  cluster at the final stage. One of the clusters with  $N = 2686$  had a seed of the icosahedral phase. The second part of the  $\text{Cu}_{4071}$  cluster corresponded to the primary  $\text{Cu}_{1385}$  particle with a fairly regular fcc arrangement of atoms.

To properly estimate the heat capacity of the  $\text{Cu}_{4071}$  cluster, we compared it with the data obtained for a bulk copper. In Figure. 1a, we see a significant difference in the results for the bulk copper and the cluster that we produced through the simulation of real synthesis. The heat capacity of the cluster turned out to be comparable to that of the bulk sample only at low temperatures. For example, at  $T = 150$  K it exceeded the heat capacity for the bulk copper approximately by 10.26%, but the heat capacity of the cluster was  $\sim 30\%$  of its value when the temperature rose to 300 K. To find the cause of these discrepancies, let us examine Figure. 2 that shows the external view and internal structure of the  $\text{Cu}_{4071}$  cluster at various temperatures.

A characteristic feature of the condensation of a dispersed material is known to be a steep temperature gradient. At cooling rates of  $105\text{--}108\text{ K s}^{-1}$ , Al, Ni, and Cu powders with particle sizes of 0.5–50 nm and specific surface areas of  $(70\text{--}30)\cdot 10^3\text{ m}^2\text{ kg}^{-1}$  can be produced [11]. Because of such a high cooling rate, the diffusion processes turn out to be essentially blocked at the final synthesis stages ( $T = 77\text{ K}$ ). As a result, the synthesized nanoparticles clearly have no time to optimize their internal structure, as is clearly seen from Figure. 2a.

To minimize the energy-consuming diffusion processes at higher temperatures and to separate only the contribution from the interphase boundaries to the heat capacity, the clusters were heated at chosen temperatures for only 0.02 ns. As we see from Figure. 2, even this short time turns out to be quite sufficient for a partial rearrangement of the structure of the cluster. Thus, the heat supplied to the  $\text{Cu}_{4071}$  cluster is often expended not in increasing the store of internal energy but on the massive diffusion of atoms to impart an optimal shape and structure to the cluster. In massive reorganization of structure specifies also decrease in percent of defective structures in  $\text{Cu}_{4071}$  cluster with rising temperature to 300K (Figure. 1b).

The assumption that the cluster with the greatest difference in heat capacity with respect to the ideal nanoparticle was simultaneously also the spatially most extended one appears more plausible. The large linear length of the cluster probably allows the low-frequency part of its photonic spectrum to manifest itself by reducing the mean vibration frequency, which can lead to an increase in the cluster heat capacity.

Consequently, the Cu clusters produced in direct experiments cannot be immediately applied in devices using the thermal energy of such clusters, because their external shape and internal structure are nonideal. First of all, a preliminary stage of optimization, for example, by the thermal relaxation method, will be necessary here, which, in some cases, allows clusters with an ideal spherical shape and a single internal structure to be produced [12], or it is necessary to make changes to the cluster synthesis procedure itself to produce such ideal clusters [13].

## 1. Conclusions

Development of contemporary science has resulted in the necessity to use new devices comparable in size with the atomic scale. Then, up to the present time, it becomes clear that properties of nanomaterials the devices in question consist of do significantly depend on specific features of their constituents. In this connection, intensive studies have been beginning of small particles (clusters) in the size range from 10 to several thousand atoms. However, experimental study of nanoclusters faces definite difficulties relating, first of all, to their small size. For this reason, one of possible approaches to study nanosized objects may be the treatment of their computer models. Most promising for studying physical-chemical properties of metallic clusters is, in our sight, molecular dynamics method which makes it possible to understand effects of different factors on properties of particles at the atomic level.

When nanotechnologies are introduced into industry the main up-to-date problem is rather not the production of new materials itself but the investigation of thermal effects and force fields (radiational, deformational and others) in the course the usage of nanomaterials. All the above factors should affect physical-chemical properties and, as a consequence, maintenance resources of nanomaterials. The thermal properties of nanoparticles and, in particular, the capability of a cluster to accumulate the thermal energy are among the important peculiarities of their behavior. At present, active works are being performed to solve a number of problems for a more efficient use of such energy in various fields of science and engineering. Given the already revealed experimental and theoretical facts, our analysis of the heat capacity for Cu nanoparticles allows us to generalize the previously reached conclusions and to determine the direction of further research on revealing all of the mechanisms responsible for the growth of the heat capacity in nanostructured copper.

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