

Peculiar features of heat capacity for Cu and Ni nanoclusters

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Received: 1 February 2011 / Accepted: 22 April 2011 / Published online: 11 May 2011
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Abstract The heat capacity of copper and nickel clusters (from 2 to 6 nm in diameter) was investigated in the temperature range 200–800 K using molecular dynamics method and a modified tight-binding potential. The simulation results demonstrate a very good agreement with the available experimental data at $T = 200$ K and a fairly good agreement at higher temperatures. A number of regular trends are revealed in computer experiments which agree with the corresponding theoretical predictions. A conclusion is made that in the case of single free clusters the heat capacity may exceed the capacity of the corresponding bulk material. It is found that at 200 K, the copper nanocluster ($D = 6$ nm) heat capacity is higher by 10% and for nickel cluster by 13%. The difference diminishes with increasing the nanoparticles size proportionally to the relative number of surface atoms. A conclusion is made that very high values of the nanostructure heat capacity observed in laboratory experiments should not be attributed to free clusters, i.e., the effect in question is caused by other reasons.

Keywords Molecular dynamics · Heat capacity · Copper and nickel clusters · Modeling and simulation

Introduction

At present, the research of single nanoparticles and nanostructures is the most developing brunch of investigations in physics, chemistry, and engineering. Great scientific and applied interest to these investigations is caused by unique properties of nanoparticles which are to be applied in the nearest future for producing microelectronic devices, obtaining new materials and surface processing. Metallic and composite clusters are beginning to attract growing interest in connection with their potential application as new high-temperature superconductors (Makarov 2010). However, the application of clusters and nanoparticles in different branches of nanotechnologies is possible under the exact definition of their physical, chemical and thermodynamic properties.

Thermodynamic and other physical properties are characterized by size-dependencies to be revealed at diminishing of the linear extension of the body. Such properties of the substance as the heat capacity, the heat conductivity, the Debay temperature, the melting temperature and the melting heat depend on the lattice dynamics which may be principally different in the case of the nanostate of matter (Sun 2007).

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Experimental measurements of these quantities for clusters face many difficulties in spite of the technical progress and the development of a number of original methods described (Makarov 2010; Kusche et al. 1999). Computer experiments may be considered as alternative way to investigate thermal properties of nanoparticles. Up to the present time there exist a number of numerical methods which can be used to study these properties. Computer simulation makes it possible to observe the structure and dynamics of complex systems before direct experiments are possible. Simulation can successfully describe the behavior of a nanosystem under an external action and determine the values of physical quantities with a good accuracy.

During last 20–30 years, a great number of direct and computer experiments were performed to determine the melting temperature and the melting heat of metallic nanoparticles. However, thermal properties of clusters have not been completely evaluated. For example, the heat capacity is a very important and, at the same time, poorly studied physical property of nanoparticles. At the same time, the heat capacity is a parameter characterizing the cluster ability to stock and keep the thermal energy at variations of the temperature. This ability should not be overlooked by specialists in nanotechnologies to be used in the future designing new nanodevices.

Our analysis of the available scientific literature has demonstrated that there are very few papers on this topic and up to the present the calculation and experimental determination of the heat capacity are carried out in very special cases only. First of all, these estimations have been made in the following cases:

- (i) at low temperatures ($T < 100$ K) (Zemlyanov et al. 2006; Nonnenmacher 1975; Goll and Lohn-ey 1995; Comsa et al. 1976; Chen et al. 1995a; Morokhov et al. 1981);
- (ii) for very small clusters ($N < 100$ where N is the number of atoms) (Salian, 1998; Cheng et al. 1992; Lai et al. 2004);
- (iii) to determine the cluster melting temperature (Cheng et al. 1992; Lai et al. 2004; Schmidt et al. 1997; Qi et al. 2001).

Some experimental works on this topic (Rupp and Birringer 1987; Trampenau et al. 1995; Chen et al. 1995b; Yao et al. 1995) were performed long ago. In

these papers, the temperature dependences of the heat capacity were investigated for nanostructures consisting of strongly interacting clusters. These nanostructures can be obtained, for example, by the condensation from gases phase. In other words, in these works single nanoclusters have not been studied but a nanostructural materials consisting of particles of the diameter not less than 6 nm. The objects in question are similar to colloidal crystals, and the main factor of the heat capacity growth is a developed surface and its term into the atomic mobility in nanostructures (Suzdalev 2006).

To bridge the above gap in the heat capacity investigations, we have carried out a computer simulation research of thermal properties of copper and nickel clusters. These chemical elements are typical transitional metals, and data obtained for them can be, to a less or greater extent, attributed to nanoparticles of other transitional metals. The problem we want to solve in the present paper is the evaluation of the heat capacity of single metallic nanoclusters in the region of high temperatures at which nanodevices of the new generation should be really applies.

Method of simulation

Following to other authors (Lai et al. 2004), we believe that molecular dynamics (MD) can be treated as the most promising numerical method for analysis of the heat capacity of clusters of diameter from 2 to 6 nm in the temperature range from 200 to 800 K. In the case of the ab initio treatment, calculations of interaction forces take too much time. These methods make it possible to carry out very exact calculation for clusters but in the picosecond range only and for sizes which, as a rule, do not exceed 100 atoms.

In the MD simulations presented here, Newtonian equations of motion are solved numerically for each atom in the force field of the remaining ones by using an interatomic potential. The existing approximations differ in terms of mathematical complexity and accuracy of representation. The choice of the interaction potential depends on the problem formulation, the properties to be examined, the available computing resources, and the desired accuracy of results. The time scale available for simulation and the reliability of its results depend on the choice of the potential.

After analysis of different expressions for the energy to be used for calculations of forces acting between atoms, we have chosen the modified tight-binding potential (Cleri and Rosato 1993) with a fixed cut-off radius corresponding to the 5th coordination sphere.

The potentials proposed by Cleri and Rosato (1993) have already worked very well in the simulation of systems in the crystalline state and have been thoroughly verified for many parameters (Cleri and Rosato 1993). In particular, the results of the simulation of a number of parameters of structural point defects (vacancies, interstices, and their small complexes), thermodynamic properties of metals (melting and other transitions temperatures, transition temperatures, heat capacity, thermal expansion coefficient, Grüneisen parameter, etc.), and phonon spectra were compared with experimental data. It should be noted that the calculated phonon spectrum of face-centered cubic copper at $T = 80$ K (Cleri and Rosato 1993) differs from the experimental spectrum by no more than 5%.

In order to check the applicability of this algorithm for constructing the potential energy function in the high-temperature range, Liu et al. (2001) investigated a sample containing 500 copper atoms distributed in a cubic cell with the use of periodic boundary conditions. The analysis of the radial distribution function $g(r)$ (which is also termed the pair correlation function) obtained in (Liu et al. 2001) has clearly demonstrated that the calculated data are in good agreement with the results of direct experiments in the high-temperature range up to at least $T = 1300$ K.

The interaction between the system under investigation and the thermal reservoir (thermostat) is another important topic of the simulation. For molecular dynamics method, the microcanonical ensemble is the most natural (adiabatic molecular dynamics). For this ensemble, the energy keeps a constant value. However, in most cases, thermodynamic properties calculated under conditions of the microcanonical ensemble do not correspond to real systems. The simulated system with the fixed value of the temperature T , i.e., the canonical ensemble, is of much greater interest than the system with a constant value of the total energy E . In the case of the canonical ensemble the system is not isolated and should be interpreted as that in a contact with a thermal reservoir. For these purposes, a number of special simulation methods were proposed and

developed, in particular, the Hoover thermostat (Hoover 1985) which can be interpreted as a modified Nosé one (Nosé 1984a, b). This approach makes it possible to fix the value of the temperature with the exactness of 1 K that can be very important, particularly when the cluster melting temperature is defined (Gafner et al. 2009).

To simulate the thermal actions on nickel and copper clusters we used the MDNTP software developed by Dr. Ralf Meyer, Universität Duisburg, Germany. The computations were performed on a Dell PowerEdge SC1420 workstation, with two 64-bit Intel Xeon processors (dual-core, 3.2 GHz) and 2 Gb RAM, running under the SUSE Linux 10.0 operating system.

Results and discussion

Up till now, the investigation of size effects on thermodynamic properties of nanocrystals is of special interest as a restriction of the long-range order and greater degree of the free surface result in developing new physical properties in comparison with bulk materials. For this reason, spherical FCC nickel and copper clusters of 2, 4, and 6 nm in diameter obtained cutting out spheres of the ideal FCC-lattice were chosen as initial objects to carry out the computer analysis of the heat capacity.

In order to investigate accurately thermodynamic parameters, it is necessary first of all to minimize the interaction between the particle and its environment. In this respect, we considered so-called “free” (or isolated) clusters that were placed in a thermal reservoir filled with virtual particles (the N ose thermostat) and did not interact with the substrate. Analogous laboratory experiments correspond to the synthesis of nanoparticles from gases medium. In this case, metallic clusters produced in the gaseous phase are involved into the continuous Brownian motion in the synthesis camera because of the smallness of their size and mass. The camera is blown by a weak flow of a noble gas, heated up to the desired temperature that ensures the thermal regime corresponding to experimental conditions.

As the low temperature region seems to be the most studied, we have carried out calculations of the heat capacity of metallic nanoparticles (Ni, Cu) at temperatures exceeding 200 K. The choice of this

temperature region can be justified by an obvious point that real nanodevices should operate just at temperatures in question. It is also noteworthy that there are extremely few works on the investigation of the cluster heat capacity at these temperatures and the available results have very noticeable divergences: the values of the heat capacity of the metals in question distinguish in several times.

The aim of the first stage of our simulation is their thermal relaxation, i.e., the optimization of the particle structure and form. For this purpose, clusters were kept for a long time (of order of 2 ns) at the temperature $T = 200$ K. In the simulation, the temperature was determined via the averaged kinetic energy of atoms calculated, in turn, according to the Verlet algorithm (Pang 2006) with the time step $h = 2$ fs. When the thermal relaxation had completed, copper and nickel nanoclusters were heated in the temperature range from 200 to 800 K. In the process of the heating imitation, the temperature of the system was changing step by step (with a step of ~ 50 K), and the clusters at each fixed temperature were kept for 0.5 ns. The heat capacity of particles was determined as the derivative of the internal energy with respect to the temperature.

The results of simulations are presented in Fig. 1. It is distinguishably seen that the heat capacity of Ni and Cu nanoparticles is gradually increasing with the increasing of the temperature, and the increasing of the heat capacity follows in an approximation, to the linear law. To compare with the data of laboratory experiments, the heat capacity dependences for copper nanoclusters and bulk materials (Rupp and Birringer 1987) are presented in Fig. 2. The nanostructured copper was obtained by the consolidation of nanoclusters of the average size 8 nm, and the measurements showed that the nanostructured copper heat capacity is by 9–11% higher than the heat capacity of the corresponding bulk polycrystalline material.

Our computer simulation data for copper nanoparticles of 8 nm in diameter at 200 K exceed experimental values (Rupp and Birringer 1987) by $\sim 1.8\%$ that, no doubt, confirms the adequate choice of the interatomic interaction potential. However, at higher temperatures the divergence with (Rupp and Birringer 1987) is growing. Thus, at 300 K, experimental values exceed ours by 3% and as one can conclude comparing forms of the $C(T)$ dependence obtained in

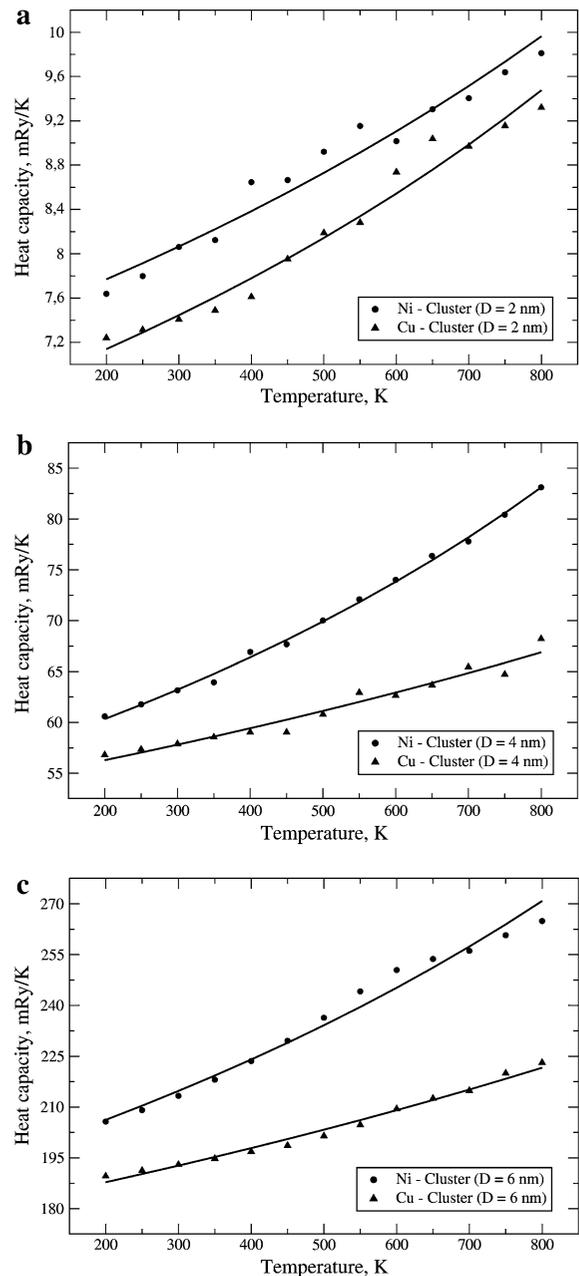


Fig. 1 **a** Temperature dependence of the heat capacity for copper and nickel nanoclusters of diameter $D = 2$ nm. **b** Temperature dependence of the heat capacity for copper and nickel nanoclusters for $D = 4$ nm. **c** Temperature dependence of the heat capacity for copper and nickel nanoclusters of $D = 6$ nm in diameter

(Rupp and Birringer 1987) and from analysis of our data. This divergence increases with the increasing of the temperature.

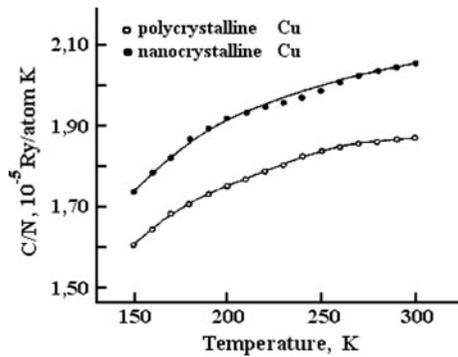


Fig. 2 Temperature dependence of the heat capacity for bulk and nanostructured copper (Rupp and Birringer 1987)

We shall try to understand the nature of this divergence. Obviously, the reason is that the heat capacity was in fact determined (Rupp and Birringer 1987) not for single (free) clusters but for a nanostructured material consisting of binding, by some way, particles. High divergences in values of the heat capacity can be observed on samples produced using a deformation which effects on $C_v(r)$ in connection with significant structural disturbances. Besides, the main factor determining an increased value of the nanostructured material heat capacity may be attributed to the degree of binding (agglomeration) in nanoparticles. For example, in the case of nanostructured palladium (Rupp and Birringer 1987), the difference in the heat capacity relative to a bulk sample becomes much higher (29–33%) than for copper (9–11%) because of lower values of the measured structure density. In other words, the structure was more unconsolidated, i.e., with lower degree of binding between particles. The degree of the particle agglomeration in the nanomaterial changes significantly and results in an alteration of the internal structure of the material under consideration. So, these structural rearrangements should be, in our sight, the main reason of the heat capacity increasing (relative to our results) observed in (Rupp and Birringer 1987).

Our conclusion can be confirmed using the results of other experimental works. In (Chen et al. 1995b) the heat capacity of the coarse-grained Cu nanoclusters of order of 50 nm in size was investigated in the temperature range 300–800 K. In this temperature interval, the bulk copper had the lowest heat capacity, lower in comparison with copper nanoparticles by 1.2–2.0 times up to 450 K. The further temperature

increasing resulted in an intensive nanopowder growing and, respectively, in the diminishing of the heat capacity up to the values typical for the bulk copper. Analogous results were obtained for Ni nanoparticles of 22 nm in diameter: their heat capacity was twice higher than that for the bulk nickel at 300–800 K (Yao et al. 1995). Investigation of the heat capacity of a consolidated nanostructure consisting of nickel clusters of 10 nm in diameter by the fast-neutron scattering method (Trampenau et al. 1995) demonstrated an increase of the heat capacity of this material by 1.5–2.0 times in comparison with the bulk material. In other words, there exists an apparent discrepancy in experimental data on copper and nickel. Really, all the mentioned above works demonstrate an exceeding of the nanostructured material heat capacity in comparison with the bulk body but estimations of the corresponding difference vary in a wide range of values. In Rupp and Birringer (1987) the copper nanostructure heat capacity was by 9–11% higher than that of bulk samples whereas other authors had obtained even twice higher values in spite on high enough values of the nanoparticle size.

Below our simulation results for the heat capacity of single nickel and copper nanoclusters of different sizes are presented. Particularly, the specific (per an atom) heat capacity of nickel clusters at $T = 200$ K in dependence on their diameter is shown in Fig. 3. One can see that the heat capacity diminishes tending asymptotically to the bulk value (the dashed line). The difference in the heat capacities is about 17% at $D = 2$ nm and 13% at $D = 6$ nm. The diminishing in

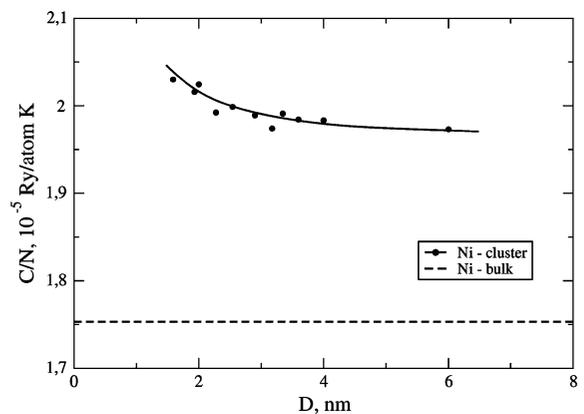


Fig. 3 Size dependence of the nickel cluster heat capacity at $T = 200$ K. The bulk value is presenter by the dashed line

question correlates well enough with the diminishing of the percentage of surface atoms at the increasing of the nanoparticles size. Really, the relative diminishing of ΔC with the increasing of the particle diameter from 2 to 6 nm is about 23%, and the diminishing of the portion of surface atoms in this case is about 28%. We have also observed an analogous trend for copper nanoclusters. In Gu et al. (2007), on the basis of computer simulation, size effects of the Al nanoparticles heat capacity were investigated, and it was shown that the heat capacity tends to its bulk value with the growth of the nanoparticle diameter.

Conclusion

Higher than usual interest of the industry to the creation of new technical devices yields the necessity of detailed investigations of small metallic particles. This interest is based on the principal distinction of the nanoparticle properties in comparison with bulk materials. For example, nanoparticles are more chemically active that makes them very attractive for applications in catalysis and sensors of different types. Development of electronic devices also requires the miniaturization of basic elements up to the nanoscale range. However, the determination of conditions of the normal operation of nanodevices is possible under an accurate study of properties of particles the devices in question consist of. The thermal properties belong to such peculiar features of the cluster behavior.

The analysis of the heat capacity of Ni and Cu nanoparticles carried out in our paper with respect of available experimental data makes it possible to generalize former conclusions and to determine directions of future investigations on the mechanism of the heat capacity growth in the nanostructured copper and nickel. Thus, on the basis of the above analysis of our simulation results obtained using the tight binding potential, a conclusion can be made that in the case of single free clusters, the heat capacity can be higher than that for the bulk material and diminishes at the increasing of nanoparticles proportionally to the diminishing of the portion of surface atoms. At $T = 200$ K, the excess of the heat capacity is equal to 10% for copper nanoclusters of $D = 6$ nm and to 13% for nickel clusters. Respectively, much higher values of the heat capacity for nickel and

copper nanostructures can not be attributed to properties of free clusters and are caused by other reasons to be studied in the future. We believe that the properties of nanomaterials may be related to the degree of the agglomeration of the particles the material consists of, i.e., noticeable effects can be caused by free surfaces, interfacial boundaries and the increasing of square-mean displacements of atoms of a general surface of united nanoclusters.

Acknowledgments This article was prepared under the financial support of Russian Foundation for Basic Research (grant No. 10-02-98-001-r_Siberia_a), grant of President of Russian Federation (No. MK-2207.2009.2) and in frames of the research program “Scientific and pedagogical stuffs of the innovation Russia 2009–2013”.

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