Effect of the Energy Characteristics on the Structure and Shape of Nanoparticles

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Abstract—The potential energy of the equilibrium conformations of metallic nanoparticles has been calculated by the molecular dynamics method. A comparative analysis of methods for obtaining equilibrium nanoparticle shapes has been carried out. It has been found that a minor potential energy variation leads to a noticeable change in the nanoparticle shape.

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The problems of calculating the equilibrium nanoparticle conformations are highly relevant, since the knowledge about the structural, energy, and mechanical properties of nanoparticles is important for the development of nanotechnologies [1]. The experimental determination of these characteristics of nanoparticles is a labor-intensive, technically complex, and expensive task because of small sizes of these objects. Therefore, computer modeling is currently the main way to study the equilibrium nanoparticle shapes and the only way to evaluate the dynamics of a nanoparticle atomic system over time [2]. In addition, it should be noted that the methods for identification of the mechanical properties of nanoparticles include both measurements of the parameters of a nanoparticle under loading and calculations of the parameters of a nanoparticle by the molecular dynamics method [3].

The aim of this study was to analyze the effect of the energy characteristics of nanoparticles on their shape and structure.

FORMULATION OF THE PROBLEM AND SOLUTION METHODS

To estimate the energy parameters of a nanoparticle, it is necessary to obtain its equilibrium shape. The problem of obtaining equilibrium nanoparticle configurations is solved by the molecular dynamics method in two stages. At the initial modeling stage, it is necessary to "warm up" the system. To do that, we use a system of Langevin differential equations [4]. At the second stage of obtaining the optimum equilibrium shape of a nanoelement, we use Newton's system of differential equations [2] or the potential energy minimization by the gradient descent method [5]. We specify the initial arrangement of atoms in a nanoparticle in the form of a cube (Fig. 1) with distance σ between neighboring atoms. In the problem solved, we use free boundary conditions.

The interaction between atoms is governed by the van der Waals forces [6], the distribution of which, depending on the distance between atoms, is presented in the Lennard–Jones potential

$$V_{ij}(\mathbf{r}_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{\mathbf{r}_{ij}} \right)^{12} - \left(\frac{\sigma}{\mathbf{r}_{ij}} \right)^{6} \right].$$
(1)



Fig. 1. Initial arrangement of atoms.

Here, ε is the potential well depth, r_{ij} is the distance between atoms *i* and *j*, and σ is the r_{ij} value at which $V_{ij}(r_{ij})$ is zero. The distance at which the Lennard–Jones potential reaches its minimum value ε (the potential well depth) is

$$r_{\min} = 2^{1/6} \sigma. \tag{2}$$

When using the system of Langevin equations, an important issue is setting temperature T of an atomic system, which is maintained throughout the entire specified modeling stage. The use of the Langevin dynamics is necessary to prevent a collapse of the initial cubic structure of atoms at the specified free boundary conditions. However, setting of a too high temperature can lead to the breakdown of the system. The temperature is selected experimentally. A criterion for the correct choice of temperature is the lowest potential energy of the system obtained after the second modeling stage. Instead of temperature, initial velocities v_i of atoms can be set. The atomic velocity distribution density is described by the Maxwell distribution

$$f_{V}(v_{x}, v_{y}, v_{z}) = \sqrt{\left(\frac{m}{2\pi kT}\right)^{3}} \exp\left[\frac{-m\left(v_{x}^{2} + v_{y}^{2} + v_{z}^{2}\right)}{2kT}\right], (3)$$

where m is the atomic mass and k is the Boltzmann constant.

The equilibrium structure is found under the condition that the derivatives of potential energy V are zero along all coordinates x_i :

$$\frac{\partial V}{\partial x_i} = 0. \tag{4}$$

It should be noted that the method for minimizing the potential energy is inapplicable at the initial stage of the nanoparticle relaxation process, since it allows one to find only the nearest local minimum of the potential energy.

At the second modeling stage, we use Newton's system of differential equations of motion. Periodically, after a specified number of iterations, the velocities of all atoms in the investigated system are reset, which leads to a gradual energy dissipation occurring in real experimental systems. At this stage, we use the potential energy minimization method.

RESULTS OF THE CALCULATION

Most of the calculations were carried out on an MVS 1000M supercomputer of the Joint Supercomputer Center of the Russian Academy of Sciences using the NAMD program [7].

The properties of nanoparticles consisting of a relatively small number (up to ten thousand) of atoms were examined. The equilibrium spherical configura-



Fig. 2. Dependence of minimum potential energy V(J) on number N of atoms in (1) zinc, (2) cesium, (3) calcium, and (4) magnesium nanoparticles.

tions of metal (zinc, cesium, magnesium, calcium, and copper) nanoparticles were obtained.

Figure 2 shows the dependence of minimum potential energy V of zinc, cesium, magnesium, and calcium nanoparticles on number of atoms N. It can be seen that, at the same number of atoms, the potential energy of zinc particles is higher than the potential energy of cesium particles, which, in turn, is higher than the potential energy of magnesium particles. This nature of the dependence is caused by a decrease in the potential well depth parameter ε of metals.

It should be noted that, for particles with a number of atoms greater than 4000, the equilibrium shape resembles a melted crystal. Finer particles have a spherical shape. When the number of atoms in a particle is small, its size is comparable to the distance of action of the Lennard–Jones potential; therefore, the energy of the central atoms in a particle will be significantly greater than the energy of the surface atoms. As a result, the surface atoms will shift towards the nanoparticle center with the formation of an equilibrium spherical shape. If the size of a nanoparticle prepared for the relaxation is sufficiently large (i.e., the minimum distance from the center of the cube to its face is several times greater than the distance of action of the Lennard–Jones potential), only the atoms located in the cube corners will move towards the center, since they have the lowest potential energy.

The average potential energy of an atom in nanoparticles with a number of atoms greater than 4000 tends to the horizontal asymptote and barely changes (Fig. 3). This explains why particles with a number of atoms less than 4000 have a spherical shape, while the equilibrium shape of coarse nanoparticles resembles a melted crystal.

Figure 4 presents the dependence of potential energy V (J) on number n of iterations for a cesium nanoparticle consisting of 4913 atoms. At the first stage of modeling of an equilibrium nanoparticle (T = 70 K), the potential energy can increase (1 in Fig. 4).

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Fig. 3. Dependence of average potential energy $\langle V_i \rangle$ (J) of an atom in a nanoparticle on number *N* of atoms in copper nanoparticles.



Fig. 5. Dependence of potential energy V(J) on number n of iterations for a cesium cluster consisting of 4913 atoms; the first modeling stage.

At the second modeling stage, the potential energy gradually decreases to its minimum value (2 in Fig. 4).

A sharp change in the potential energy at the second modeling stage corresponds to a stop in the computation. In this case, the velocities of atoms are zeroed, which leads to the kinetic energy dissipation in the investigated molecular ensemble.

Figure 5 shows, in the enlarged form, the first stage of modeling of an ensemble of 4913 cesium atoms. One can see a sharp decrease and, then, a smooth increase in the potential energy. No jumps in the nanoparticle potential energy are observed.

Figure 6 presents a small part of the second stage of modeling a nanoparticle of 4913 cesium atoms. One can see a smooth decrease and, then, a smooth rise in the potential energy. This potential energy change is dictated by the energy conservation law. At some point in time, the potential energy stops dropping, after



Fig. 4. Dependence of potential energy V(J) on number *n* of iterations for a cesium nanoparticle consisting of 4913 atoms at (1) the first and (2) second modeling stages.



Fig. 6. Dependence of potential energy V(J) on number n of iterations for a cesium nanoparticle consisting of 4913 atoms; a small part of the second modeling stage.

which we restart the computation (reset the atomic velocities), which leads to the sharp dissipation of the kinetic energy of the system. The kinetic energy of the system can be smoothly dissipated and the temperature of the entire system can be reduced by lowering it by 5-10% at each start of a computer.

The values of the potential energy of the equilibrium shape of a cesium nanoparticle consisting of 4913 atoms optimized using Newton's system of equations of motion and the minimization method coincide. The potential energy minimization by the gradient descent method multiply reduces the computation time.

The drawback of many molecular dynamics simulation programs is that the initial data must be the coordinates of atoms located at the crystal lattice sites and displaced in space by a random value. Otherwise,



Fig. 7. Equilibrium shapes of silver nanoparticles consisting of 365 atoms.

the optimization algorithm ends accidentally, since the correct crystal structure is an equilibrium form.

The investigations of silver nanoparticles consisting of 365 atoms yield slightly different results. The initial

positions of atoms were specified at the sites of the crystal lattice with a fcc structure.

After minimizing the potential energy, the newly obtained state of the system has the potential energy



Fig. 8. Dependence of potential energy V(J) of equilibrium configurations of silver nanoparticles consisting of 365 atoms on configuration number N: spherical particles (circles), crystal lattice (triangles), and crystal lattice (rectangles) after minimizing atoms.

lower than that of the crystal lattice. This is explained by the fact that the Lennard–Jones pair potential does not accurately describe the structure of atoms, as well as by the error in determining the distance between atoms in the lattice. The potential energy of the initial silver crystal lattice consisting of 365 atoms is $V_0 = 1.2653 \times 10^{-16}$ J, while in the final state of the system it is $V_0 = 1.2679 \times 10^{-16}$ J. Let us conduct the following computer experiment. We set the initial positions of atoms of a silver nanoparticle consisting of 365 atoms in the form of a ball with distance σ between atoms. Using the Langevin dynamics equations, we "shake up" the system and, to obtain equilibrium nanoparticle shapes, perform the minimization.

Figure 7 shows the equilibrium shapes of the investigated nanoparticle for ten implementations of the experiment. Each equilibrium shape corresponds to a local minimum around the global minimum of the potential energy of the system. For the same number of atoms, many such configurations and the corresponding potential energies can be calculated. This is explained by the fact that, when the temperature of the entire system is set, the distribution of atomic velocities obeys Maxwell distribution (3) implemented using a random number generator.

As can be seen in Fig. 8, the potential energy of a nanoparticle for different conformations smoothly decreases according to the second-degree polynomial law. Note that the nanoparticle with the lowest potential energy will not meet the condition of the global minimum of the potential energy, but will undoubtedly be close to it.

Figure 9 shows that a small, in some cases, change in the potential energy of a nanoparticle of only 0.2%leads to a noticeable change in its shape.



Fig. 9. Equilibrium shapes of silver nanoparticles consisting of 365 atoms. (a) Crystal lattice corresponding to the point N = 9 in Fig. 8 and (b) conformation corresponding to the point N = 10 in Fig. 9.

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CONCLUSIONS

The potential energy of the equilibrium conformations of metallic (zinc, cesium, magnesium, calcium, and copper) nanoparticles was calculated. We carried out a comparative analysis of the methods for obtaining equilibrium nanoparticle shapes: the molecular dynamics method and the potential energy minimization using the gradient descent method. The effect of the average potential energy of a nanoelement atom on its shape was studied. It was shown that the dependence of the average potential energy of an atom on the number of atoms in metallic nanoparticles tends to a horizontal asymptote. It was found that a small potential energy change leads to a noticeable change in the nanoparticle shape.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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