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Molecular Dynamics Simulation of Melting and Freezing of Gold Nanoclusters

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Melting and freezing of nanometer-size gold clusters were simulated using the isothermal molecular dynamics. The results obtained confirm the results of other authors demonstrating, at the same time, the best agreement with the results of direct (laboratory) experiments.

Keywords: Gold nanoclusters, Melting and freezing, Molecular dynamics, Tight-binding potential.

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1. INTRODUTION

Nanometer-size particles have being intensively studied in view of many possible applications in nanotechnology. We focus on gold (Au) nanoclusters which have provoked many investigations in both fundamental and applied directions. Possible applications of gold nanoclusters in electronics, catalysis and optics were reviewed in [1]. Besides, individual Au nanoparticles have ferromagnetic spins and their ensembles are described by the superparamagnetic model [2] in spite of the diamagnetism of the bulk Au. Quite recently a new way of the silicon semiconductor nanocrystal growth involving just Au nanoclusters was also reported [3].

All the available experimental data [4-6] demonstrate the reduction of the nanocluster melting temperature T_m in comparison with the bulk value $T_m^{(\infty)}$ that agrees Thomson's formula

$$\lambda_\infty \frac{T_m^{(\infty)} - T_m}{T_m^{(\infty)}} = \frac{2\gamma_{sl}}{R}\upsilon_s , \qquad (1)$$

where λ_∞ is the specific (per atom or per unit mass) bulk value of the melting heat, υ_s is the specific volume and γ_{sl} is the interfacial tension, i.e. the specific (per unit area) excess free energy of the solid-liquid boundary.

Up to the present time, freezing of metallic nanoparticles, i.e. the inverse transition from a liquid-like cluster to the crystal-like one has been much less studied. So, the most of scientists have avoided using the term "crystallization" to nanoparticles. The term "freezing" was also used by Lewis et al. [7] in their early but interesting work on MD simulation of melting and freezing of Au nanoparticles.

In this work we are using our own computer program developed involving the tight-binding potential (TBP) which was proposed and justified taking into account some results of quantum mechanics [8]. Earlier [9] we used another computer program involving, however, the same many-body potential to investigate the size dependence of the specific heat capacity of metallic nanoclusters.

2. PREPARATION OF THE INITIAL CONFIGURATION AND SIMULATION RESULTS

The initial spherical, to some extent, configuration used to begin the melting and freezing simulation cycles is carved out of the bulk face-centered cubic (fcc) Au crystal. After setting the initial cluster configuration into the center of the simulation cell and its equilibrating (relaxing) at a chosen low temperature, the cluster is gradually and uniformly heated and cooled, i.e. subjected to the chosen number of the melting and crystallization cycles in order to identify the melting and freezing transitions. It is clear enough that the lowest temperature $T_{\min}$ should be noticeably less than the macroscopic melting temperature $T_m^{(\infty)}$ and the highest $T_{\max}$ noticeably higher than $T_m^{(\infty)}$. At the same time, $T_{\max}$ should not be so high to provoke the thermal instability of the cluster.

In our program Verlet's MD algorithm of velocities and Berendsen's thermostat are used. A small (at nanoscale distances) time run step 0.01 fs is chosen in order to provide the thermal relaxation under gradual increasing and decreasing the temperature.

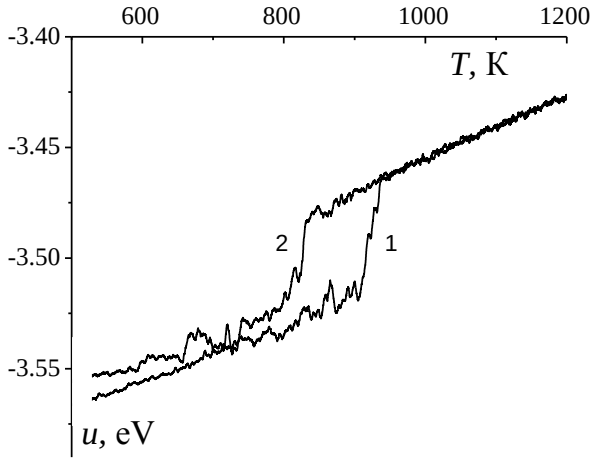

Fig. 1 – Melting (line 1) and freezing (line 2) curves for Au nanocluster containing 1000 atoms

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In Fig. 1 the dependences of the specific (per atom) potential part u of the cluster total, i.e. internal, by thermodynamic terminology, energy are presented corresponding to heating (curve 1) and cooling (curve 2) the particle. In what follows these curves will be referred to as the melting and freezing curves, respectively. The noticeable upward jump in the potential energy u seen in Fig. 1 (curve 1) should be accompanied by the absorption of the heat. Respectively, the upward jump can be interpreted as the cluster melting and the temperature of about 950 K as the melting temperature. Upon cooling from $T_{\max}$, the cluster undergoes the liquid-solid transition, i.e. to freezing which can be identified by the sharp downward jump in curve 2. As the freezing temperature $T_f < T_m$, we observe the melting-freezing cycle, i.e. a hysteresis loop.

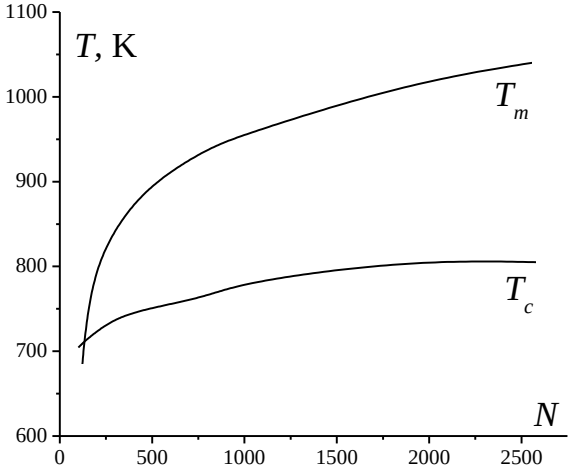

Fig. 2 – Size dependences of the melting T_m and freezing T_f temperatures obtained using results of our molecular dynamics experiments

The size dependences of T_m and T_f (Fig. 2) may be presented both as dependences of these quantities on N and on the particle diameter D or its radius R. To recalculate the $T_m(N)$ and $T_f(N)$ curves into the $T_m(D)$ and $T_m(D)$ dependences, one should know the *N(D)* function. For this purpose the relationship $N = n_s \pi D^3 / 6$ may be used as a first approximation where $n_s = \upsilon_s^{-1}$ is the bulk value of the cluster density (in m^{-3}). For Au nanoclusters formula $D^3_{(nm)} = 0.0342N$ may be also used [10].

In Fig. 3 the size dependence $T_m(N)$ obtained using the results of our MD experiments (curve 1) is compared to MD results of other authors (curves 2 and 3) as well as with the available results of direct experiments (curves 4, 5, and 6). In Fig. 4 the dependences of T_m on R^{-1} are presented to compare the same experimental and MD results with dotted lines 7 and 8 obtained using Thomson's formula (1). Experimental values of λ_∞ and υ_s are presented and referred by Castro et al. [5]. However, contrary to λ_∞ and υ_s parameters, experimental data on γ_{sl} are rather scanty and not quite reliable. So, our calculations using Thomson's formula (1) were carried out for two noticeably differing values of the interfacial tension: 190 mJ/m^2 [11] and 270 mJ/m^2 [11, 12].

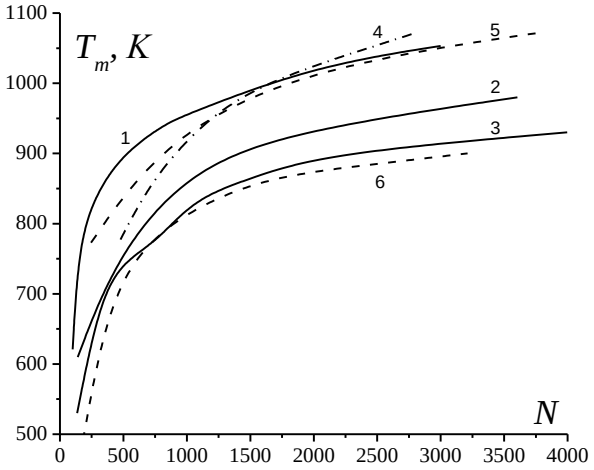

Fig. 3 – Comparison of size dependences of the Au nanocluster melting temperature obtained in available molecular dynamics and laboratory experiments. Solid line 1 presents the results of our molecular dynamics experiments, lines 2 and 3 molecular dynamics results by Zhang Yan-Ning et al. [13] and Lewis et al. [7], respectively. Dashed lines 4, 5 and 6 display experimental results by Buffat and Borel [4], Dick et al. [6] and Castro et al. [5], correspondingly

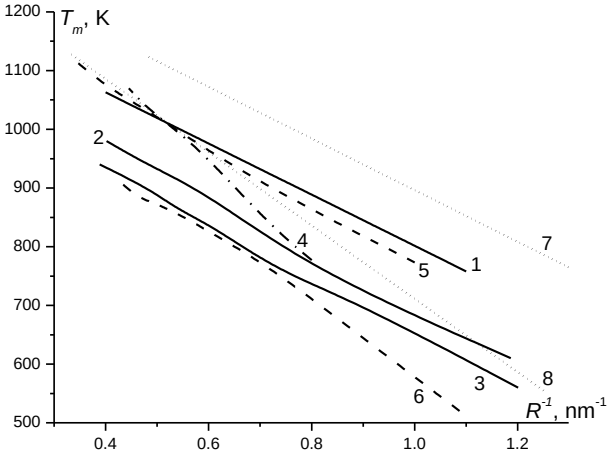

Fig. 4 – The dependence of T_m on R^{-1}. Line 1 presents our molecular dynamics result. Lines 2-6 correspond to the same references as in the caption to Fig. 5; the straight dotted line 7 was obtained using Thomson's formula (1) and the value $\gamma_{sl} = 190$ mJ/m^2, straight dotted line 8 was calculated proposing that $\gamma_{sl} = 270$mJ/m^2

3. DISCUSSION

Though, as was mentioned above, the relaxation of nanoclusters in the course of their heating and cooling was specially controlled, the existence of the hysteresis itself shows that current states of nanoclusters during their remelting and refreezing cycles can not be treated as quite equilibrium. In other words, we agree, in general, with the opinion of Lewis et al. [7] that the melting and freezing hysteresis occurs as it is much easier for the cluster to go from an ordered, i.e. the crystalline state, to the disordered, i.e. to liquid state than the

opposite. Really, the cluster freezing has never given the initial configuration with the perfect fcc-structure. To investigate structural transformations in Au clusters in the course of their heating and cooling we have also studied the probability p of different coordination polyhedra. A detailed analysis on this topic is beyond frames of this paper. Let us only note that for the initial relaxed configuration cubo-octahedra corresponding to fcc local structure are typical with $p = 100$ %. After melting any definite polyhedra can not be found around 65 % of atoms, and with low enough probabilities cubo-octahedra ($p = 5$ % as well as icosahedra ($p = 30$ %) were observed. After refreezing, i.e. at $T = T_{\min}$, cubo-octahedra (60 %), anti-cubo-octahedra (20 %) and icosahedra (5 %) can be built up. All the above polyhedra correspond to the close packed structures, i.e. to the first coordination number $z_1 = 12$. However, as no coordination polyhedra could be constructed around 15 % of atoms, the average value $\overline{z_1}$ of the first coordination number z_1 is less than the maximal value $z_1^{(\max)} = 12$.

The size dependence of the melting temperature obtained in our work and shown in Fig. 2 demonstrates the best agreement with the results of two independent direct experiments in comparison with MD results of other authors also presented in this figure. Obviously, experimental results of Castro et al. [5] are underestimated though they used an interesting method proposing that the melting temperature was fixed when the shape of Au nanoclusters on the solid surface suddenly changed. In our computer experiments, not presented here, we also used an analogous method and nanoparticles demonstrated some fluidity at temperatures $T < T_m$ proposing that T_m had been prior found via the calorimetric method descried above. Early experimental data [4] based on the electron diffraction technic seem to be more reliable from this point of view as well as resent enough experimental data [6] obtained using DTA, i.e. a calorimetric method similar to that used in our computer experiments. Just the size dependence of the melting temperature obtained in [6] demonstrates the best agreement with our MD results.

To prove whether the linear dependence of T_m on the reciprocal particle radius R^{-1} is fulfilled, as Thomson's formula (1) predicts, all the $T_m(N)$ dependences have been also recalculated and shown in Fig. 3 as functions of T_m on R^{-1}. One can see that, except experimental data by Castro et al. [5], the linear dependence of T_m on R^{-1} is fairly good fulfilled for all the data corresponding to direct and computer experiments. The slope of the straight line 7 obtained using Thomson's formula (1) and providing that $\gamma_{sl} = 190\text{mJ/m}^2$, coincides in general with the slopes of lines 1 and 5 describing our MD results and experimental results by Dick et al. [6]. The value $\gamma_{sl} = 270\text{mJ/m}^2$ [11] gives another slope which does not agree with our MD results.

4. CONCLUSION

Very good agreement of our MD results for the size dependence of the melting temperature with the available experimental data demonstrates that computer simulation methods, including MD, may be really competitive in nanoscience with direct (laboratory) experiments. Besides, our MD results confirm the reliability of the available experimental data on melting and freezing of Au nanoparticles as well as former MD results of other authors. At the same time, some specific structural features of Au nanoclusters as well as of the melting temperature behaviour have been revealed in our MD experiments. Some of them have no satisfactory explanations yet. These experiments have also confirmed the applicability of thermodynamics and, in particular, of original Thomson's formula (1) to small nanoparticles of 1-5 nm in radius.

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