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# Investigation of thermal behavior of graphite-supported Ag nanoclusters of different sizes using molecular dynamics simulations

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ABSTRACT

Thermal behaviors of Ag nanoclusters with 38, 108 and 256 atoms supported on static graphite bilayer substrate were investigated using molecular dynamics (MD) simulations. The many body quantum Sutton–Chen (QSC) potential was used to describe the Ag–Ag interactions, also, the Lennard–Jones (LJ) 12–6 potential was applied for Ag–graphite interactions. Nanoclusters were simulated for heating and cooling in the range of 100–1700 K in the canonical ensemble. The potential energy, specific heat capacity, density profile, deformation parameter and self-diffusion coefficient were calculated at different temperatures. Results show that melting temperatures are higher than that for free Ag nanoclusters of similar size and structure. Comparison of the potential curves in heating and cooling for three nanoclusters show that the hysteresis decreases when the cluster size decreases. Also, irreversibility of the structural changes relative to temperature, Flattening of nanocluster on the graphite surface and wetting were observed using the density profiles and deformation parameters.



## 1. Introduction

Metallic nanoclusters possess different physical, chemical and electronic properties from those of bulk metals and single atoms, owing to their great fraction of surface atoms [1]. This means that the surface atoms have a much greater effect on chemical and physical properties of nanoclusters. The low coordinated surface atoms are responsible for the remarkable properties of a nano-sized cluster, particularly the low melting temperature [2–4] and improved catalytic properties [5–7]. The catalytic properties of a metal cluster are modified substantially by anchoring it to support surfaces [8]. Ag nanoclusters possess many applications such as optical sensors, detection modes such as colorimetric, scattering, SERS (surface-enhanced Raman spectroscopy) and metal-enhanced fluorescence (MEF) techniques at extremely low detection limits, pharmaceutical diagnosis and therapy and antibacterial covering [9]. At recent years, researchers considered about the melting and thermodynamic properties of metal nanoclusters [10–16]. The melting temperature of metal nanoclusters is more dependent to their size, and usually it is much below the bulk melting point and decreases when the cluster size decreases.

Molecular dynamics (MD) simulation is a useful method to investigate properties of the nanoclusters. The melting point of free Ag nanoclusters at different sizes have been obtained using MD simulations, and shows that the melting point decreases with the cluster size [17–20]. Also, thermodynamic properties, diffusivity and structural changes of free Ag nanoclusters with temperature have been studied by MD simulation [21,22]. The thermal, structural and dynamic properties of metallic clusters (Pt, Cu, Pd-Pt, Ni and, etc.) supported on surfaces have also attracted much attention lately [23–29]. Ding et al. investigated the structural and dynamic changes during melting of free and supported iron clusters ranging from 150 to 10,000 atoms. Their results revealed a method for determining effective diameters of supported metal clusters, so that the melting point dependence on cluster size can be predicted in a physically meaningful way by the same analytic model used for free clusters [30]. Their results showed that the melting mechanisms of free and substrate-supported nanoparticles are similar. Kuo and Clancy's molecular dynamics simulations also verified that the melting temperature of the silica substrate-supported Au nanoparticles is higher than that of the free-standing Au nanoparticles [31]. By means of the thermodynamic model, Lee et al. [32] predicted that the slope of the melting point variation of nanoparticles with respect to the reciprocal of particle size was different depending upon the substrate–particle interaction. Recently, Safaei [33] pointed out that the normalized melting points of substrate-supported nanoparticles can be decomposed as the sum of that of its equally sized free-standing nanocrystals and the effect of the substrate–particle interaction, and the particle–substrate interface energy acts always like a driving force for lowering the melting

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point of a free-standing particle, meaning that the melting point of a substrate-supported particle should always be lower than that of a free-standing particle.

We have utilized MD simulation to investigate the melting behavior, thermodynamics and dynamics properties and structural evolution of Ag nanoclusters of different sizes supported on graphite surface in connection with temperature.

## 2. Computational methods

Cube-shaped Ag nanoclusters with $N = 38$, 108 and 256 atoms were supported with initial distance of 2.5 Å on a graphite substrate with two carbon layers and dimensions of 39.3 Å × 34 Å × 3.35 Å and 1024 carbon atoms. For frugality of the simulation time, the positions of graphite carbon atoms were fixed during the simulations.

The MD simulations were performed in *NVT* (the number of particles ($N$), the volume ($V$) and the temperature ($T$) of each system in the ensemble are constant) ensemble with periodic boundary conditions only in $x$ and $y$ directions. Temperatures were maintained constant using the Berendsen thermostat [34] with a relaxation time of 0.1 ps. The equations of motion were integrated using Verlet leapfrog algorithm [35] with a time step of 0.001 ps.

At the beginning, the heating was performed for all clusters in the range of 100–1700 K with increasing 100 K steps. Close to melting points, the temperature increments were reduced to 20 K. The simulations for each temperature were carried out for 800 ps of equilibration followed by production time of 2 ns for calculated properties. Similar simulations were performed in cooling in the range of 1700–100 K. The analysis of simulated trajectories and calculation of different properties were performed using the utilities of DL_POLY 2.18 program [36]. The interactions between metal atoms were modeled by quantum Sutton–Chen potential (QSC) [37,38].

The Sutton–Chen potential is:

$$U_{\mathrm{tot}} = \varepsilon \left[ \frac{1}{2} \sum_{i \neq j} \sum_{j} \left( \frac{a}{r_{ij}} \right)^{n} - c \sum_{i} \rho_i^{1/2} \right] \tag{1}$$

The first term is pair repulsion potential and the second term describes the cohesion associated with the local density $\rho_i$, which is given by:

$$\rho_i = \sum_{j \neq i} \left( \frac{a}{r_{ij}} \right)^{m} \tag{2}$$

In Eq. (2), $r_{ij}$ is the separation distance between atoms $i$ and $j$, $\varepsilon$ is a parameter with dimensions of energy, $a$ is a parameter with the dimensions of length, $c$ is a positive dimensionless parameter, and $m$ and $n$ are positive integer values with $n > m$. For Ag–Ag interactions, the QSC parameters are $\varepsilon = 0.033147$ eV, $a = 4.05$ Å, $n = 7$, $m = 6$ and $c = 16.399$. In these simulations, we considered two different force field models for the Ag–C interactions:

(1) The Lennard–Jones potential with $\varepsilon = 0.0301$ eV and $\sigma = 3.006$ Å, which was obtained from Ag–Ag to C–C Lennard–Jones parameters [39], utilizing the geometric mean for $\varepsilon$ and the arithmetic mean for $\sigma$.
(2) The Amft potential [40] was applied for Ag–C interactions. The parameters of the Amft potential can be found in Amft study [40]. Their results show that silver give no binding with graphite surface.

We compared the results obtained from the two models. There was no significant difference in results between the models.

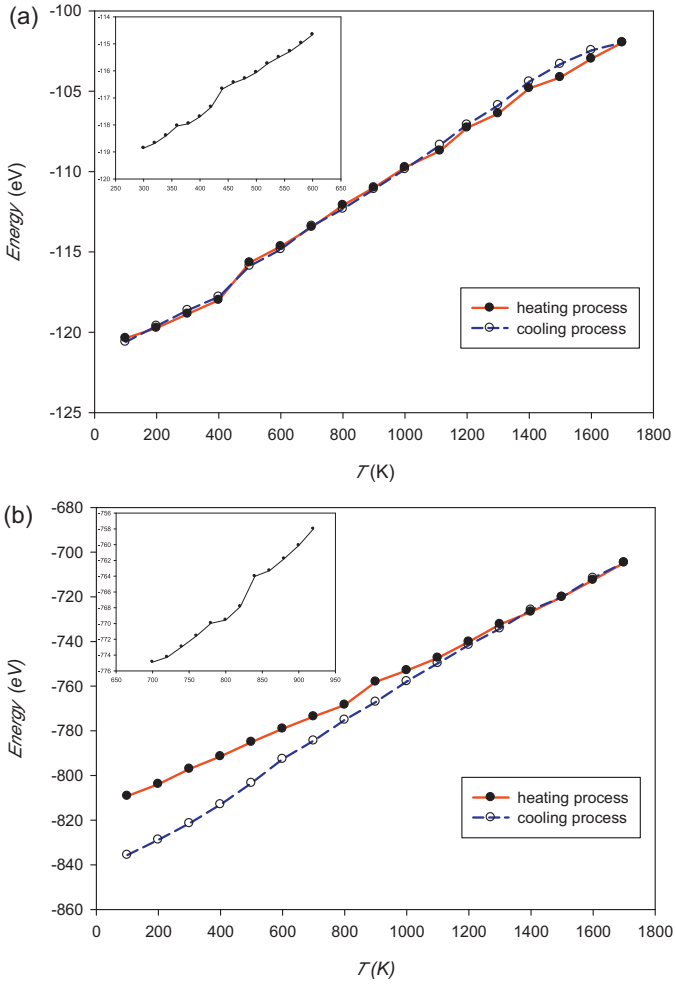


**Fig. 1.** The potential energy curves at different temperatures for heating and cooling for: $Ag_{38}$ (a), and $Ag_{256}$ (b). (Inset curves show the potential energy near the melting point with 20 K increments.)

Therefore, in this paper, we have reported the results obtained from the first model.

## 3. Results and discussion

### 3.1. Thermodynamic properties

The curves of total potential energy versus temperature of heating and cooling were obtained for $Ag_{38}$, $Ag_{108}$, $Ag_{256}$. Fig. 1 shows the temperature dependence of potential energy for the $Ag_{38}$ and $Ag_{256}$ atom clusters. Potential energy has included all the interactions between metal–metal and metal–carbon. The phase transition can be identified by a simple jump in the total potential energy curve. Paying attention to these curves the temperature range of the phase transition are 400–500, 600–700 and 800–900 K for $N = 38$, 108 and 256, respectively. Also, the heating was repeated near the phase transition temperature with 20 K increments, and curves were obtained for those. These curves are shown in the inset of Fig. 1. According to these curves the energy jump occurs in the range of 420–440, 620–640 and 820–840 K for $N = 38$, 108 and 256, respectively. Also, the melting and freezing process of free Ag nanoclusters with 38, 108 and 256 atoms were simulated [$T_m(Ag_{38free}) = 330$ K, $T_m(Ag_{108free}) = 570$ K and $T_m(Ag_{256free}) = 750$ K]. The melting temperatures for the free Ag nanoclusters are lower than that for the supported Ag nanoclusters with similar size and structure.