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On the effect of relative stabilities of FCC-like and HCP-like atoms on structure of FCC silver nanoclusters

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ABSTRACT

Freezing simulations of silver nanoclusters were carried out using molecular dynamics for two types of interatomic potentials - embedded atom method (EAM) potential and Gupta potential. In total, three interatomic potentials were used: two EAM potentials and one Gupta potential which differ in parameterization. The percentage of hcp-like atoms observed in the crystallized fcc nanoclusters and its correlation w.r.t the energy differences between fcc-like and hcp-like atoms were analysed. The results reveal that the percentage of hcp-like atoms is dependent not only on the magnitude of the energy difference but also on its local variation around the equilibrium interatomic distance.

1. Introduction

Metallic nanoclusters are an important class of materials that exhibit properties which are different from their bulk counterparts. For nanoclusters, surface-to-volume ratio increases with decrease in size and surface energy becomes significant compared to volumetric internal energy at small sizes. It is favourable to minimize surface energy at smaller sizes and hence non-crystalline structures such as icosahedra and decahedra become energetically favourable [1]. Surface energy in these non-crystalline structures is optimized by having close-packed {1 1 1}-like facets at the expense of internal strain. With increase in size, the energy contribution due to the volume of the structure becomes more significant and crystalline face centered cubic (fcc) structures such as octahedra are energetically favourable. Unlike icosahedron which is quasi-spherical, decahedron is far from being spherical leading to low stability. Ino [2] and Marks [3] proposed truncation schemes that expose {1 0 0}-like and {1 1 1}-like facets resulting in relatively stable structures compared to regular decahedra.

Metallic nanoclusters are commonly synthesized from gas-phase [4–7] or in solution using wet chemical route [8–11]. Along with the aforementioned structures, nanoclusters with defects such as twinned octahedra [5,8] and decahedra with twinning planes [12,13] are also observed experimentally. The non-crystalline structures without defects are shown in Fig. 1. Icosahedron and decahedron have strained fcc-like tetrahedral units. In an icosahedron, there are 20 tetrahedral units which share a common twinning plane with neighbouring tetrahedral units. In a decahedron, there are five tetrahedral units placed around a 5-fold axis and tetrahedral units share a twinning plane similar to icosahedron. The coordination environment for each atom in a given structure can be calculated using an adaptive common neighbour analysis (a-CNA) method [14] as implemented in OVITO [15]. The atoms in these structures have either fcc-like or hcp-like coordination. Excluding the atoms that do not have a well-defined coordination environment, the atoms lying on the twinning plane have hcp-like coordination and remaining atoms have fcc-like coordination environment (Fig. 1).

To understand the stability and structure of nanoclusters, molecular dynamics (MD) simulations have been used. The interaction between atoms is usually modelled with different interatomic potentials such as embedded-atom method (EAM) [16] potential, Gupta [17] potential, Sutton-Chen [18] potential among others. Studies have been performed to identify the optimal nanocluster structures mainly through growth simulations starting from a small seed [19–22], freezing simulations of a liquid droplet

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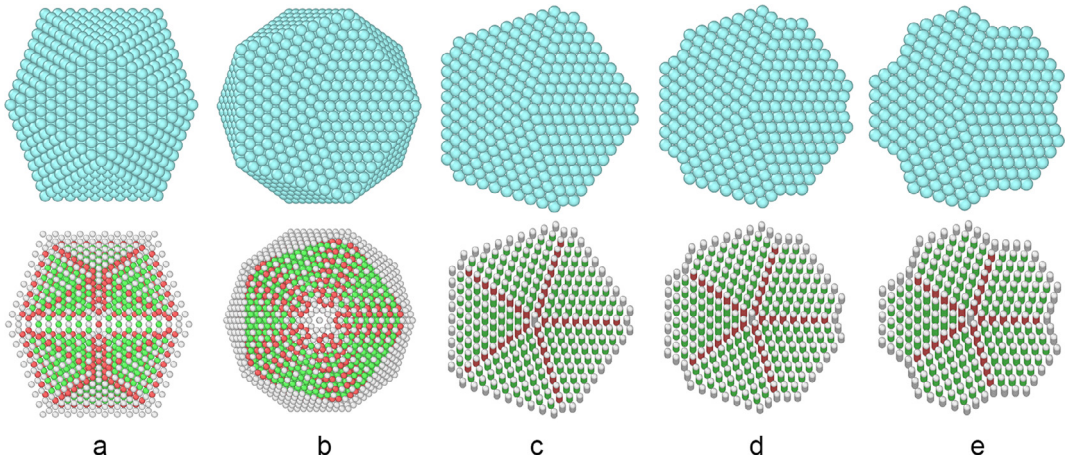

Fig. 1. Projection of icosahedron shown along (a) 2-fold axis and (b) 5-fold axis. (c), (d) and (e) projection of Marks' decahedral structures with different groove depths shown along 5-fold axis. The second row indicates the coordination type of an atom as fcc-like (green), hcp-like (pink) and neither fcc-like nor hcp-like (white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[23–27] or growth simulations of nanoclusters in solution phase [28,29]. These studies result in the same structures as observed experimentally. Atypical structures such as decahedron with more than one decahedral axis [30], capped decahedron [31] have also been predicted. The lack of experimental observation of such structures could be due to the difficulty in acquiring and interpreting high resolution transmission electron images. Due to the kinetic effects [1], it is not trivial to draw comparisons between theoretically predicted structures and the experimentally obtained structures.

In metallic nanoclusters that have low stacking fault energy such as Ag [32–34], twins and hcp-like stacking planes in fcc structures are observed [35–37]. The presence of hcp-like coordinated atoms along with fcc-like coordinated atoms in the non-crystalline structures and in fcc structures suggests that relative energies of the two types of atoms might have an influence on the final structures obtained. This raises an important question: what is the effect of relative energy of hcp-like atoms compared to fcc-like atoms for a given interatomic potential on the energetics and optimal structures obtained from MD simulations? To the best of our knowledge, this aspect is not addressed explicitly for any of the inter-atomic potentials used for MD studies of metallic nanoclusters and the conclusions drawn from these simulations do not factor in this effect. The main objective of the current work is to understand the effect of energy difference between hcp-like and fcc-like coordinated atoms on the structure of silver nanoclusters obtained from freezing. Silver was chosen as a model system since the energy difference between hcp, fcc phases [38,39] and the stacking fault energy is small.

In the current work, freezing simulations were carried out using two different interatomic potentials – embedded-atom method (EAM) potential and Gupta potential. The nanoclusters obtained from these freezing simulations were used to assess the effect of difference in energy of hcp-like and fcc-like coordinated atoms. These nanoclusters form as icosahedron, decahedron with re-entrant grooves or fcc structures. Among the fcc structures, the number of pure fcc structures in our freezing simulations was very small and the fcc structures commonly exhibited either twins or hcp-like stacking planes. The atoms in the twins or hcp-like stacking planes have hcp-like coordination. Such fcc structures consist of three types of atoms based on their coordination environment: hcp-like, fcc-like or neither. The percentage of hcp-like atoms in the fcc structures in these nanoclusters was compared for the potentials considered.

2. Simulation methodology

All the MD simulations were carried out using LAMMPS [38] package. The structure visualization and analysis were done in OVITO [15]. Ag was modelled using two different interatomic potentials – embedded atom method (EAM) potential and Gupta potential. The two EAM potentials used were developed by Sheng et al. [39] and Williams et al. [40] and referred to as EAM-hi and EAM-lo respectively. The naming is made such that they indicate the cohesive energy difference of Ag in bulk hcp and fcc phases. EAM-hi has higher cohesive energy difference between hcp, fcc in the bulk phase compared to EAM-lo. The parameters of Gupta potentials used in the current work for Ag were taken from the work by Cleri and Rosato [41]. The difference in cohesive energy between bulk hcp, fcc phases for Ag with Gupta potential is lower than the corresponding values for EAM-hi and EAM-lo potentials. The values of cohesive energy difference between bulk hcp, fcc phases for all the three potentials used in the current work are given in Table 1. The cutoff distance for all the potentials is ~6 Å which includes four nearest neighbours.

2.1. Freezing of Ag nanoclusters

Silver nanoclusters consisting of 231, 309, 489, 561, 891, 1469, 2255 and 2869 atoms were used for freezing simulations. The initial structure of nanoclusters with 309, 561 and 2869 atoms was cuboctahedron and for the other sizes, it was octahedron. Freezing simulations were carried out in an NVT ensemble with a time step of 5 fs. The temperature control was achieved with Nose-Hoover thermostat. Each nanocluster was heated to 1200 K (where all the cluster sizes are in liquid state) and held at that temperature for 5 ns. Subsequently, the temperature was decreased in steps of 100 K up to a final temperature of 100 K. The dwell time at each temperature was 20 ns. For each nanocluster size, 5 simulations

Table 1
Values of bulk cohesive energy difference between hcp and fcc phases for all the three potentials.

Potential	$E_{hcp} - E_{fcc}$ (meV)
EAM-hi	6.0
EAM-lo	4.2
Gupta	0.2