Molecular Dynamics Simulations of Structural Changes for a Molten Ag$_{54}$Cu$_1$ Cluster during Cooling

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Abstract. Structural changes of an Ag$_{54}$Cu$_1$ cluster had been computationally studied by molecular dynamics approaches. Packing transition was demonstrated by analytical tools including potential energy, atomic density profiles, and shape factor as well as visually packing images. During the process of temperature decreasing, this cluster preferentially assumes icosahedral geometry. Copper atom usually has an atomic position inside a cluster. As temperature decreases, its position will change. Potential energy shows different temperature regimes in the structural transformation. Atomic density profile gives packing pattern in different region. Shape factor presents the morphology changes of this cluster.

1. Introduction
Nanometallic clusters can be used in many different fields such as optics, magnetism and catalysis [1]. This is because they have a lot of varieties in their morphologies, and this can directly leads to the result that they have a high degree of tunability. These are so interesting which made it attracts many researchers study on it. On the research of these nanometallic clusters, researchers had used different techniques in both theories and experiments for the structures of binary alloy clusters. Those researches show that as the size of those clusters changes, their structures and properties have significant differences [2, 3]. Especially when the atomic number included in one cluster is less than 100, because the ratio of surface/volume is large, their structures show greater diversities. In those small sized clusters, the clusters that included magic number are most attractive, for example, clusters made of 55 atoms. About those magic clusters, when they are doped with an element from other group, they will show some new properties. The problem of how to get small sized alloy clusters with specific structure is becoming a significant issue on producing new nanomaterials. Copper has the same d$^{10}$s$^1$ valence electron structure with silver, and because of that, copper is usually used as a doping element for silver cluster. Copper and silver alloy clusters can be used widely to improve the effectiveness of reaction, and the selectivity of catalyst [4-10]. The structural transformation in binary cluster of copper and silver containing magic number of 55 atoms is hard to be observed in laboratory. Computational approaches become the most efficient way to do the research on structural transformation during the process of cooling, where molecular dynamics (MD) is a way that suit the packing structure and atomic movements in those small sized clusters. The MD simulations have been used widely in phase transformation in metal and alloy [11-14].

In this work, MD simulations are used for studying structural transformation of a molten Ag$_{54}$Cu$_1$ cluster during cooling process. Potential energy, atomic density profile, shape factor and visualized packing structures describes the structure and morphology of this cluster at different temperature.
2. Model and Methods

The interaction among Ag and Cu atoms is described by the EAM form, which was proposed by Williams [15]. Potential energy $E_{\text{tot}}$ is being determined by the following equation

$$E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i,j} \phi_{ij}(r_{ij})$$  \hspace{1cm} (1)

where $\phi_{ij}(r_{ij})$ is a two-body central potential between atoms $i$ and $j$ with a separation of $r_{ij}$ in between, and $F_i(\rho_i)$ is the embedding energy of atom $i$ with the electron density $\rho_i$. The density value comes from the superposition and also the sum of the electron density from the nearest neighbor atoms of the atom $i$. $\rho_i$ is the electron density of the neighbor atom $j$ of the atom $i$. The simulations were done with the NVT ensemble using Andersen thermostat. Through the process of solving Newton’s motion equations, we were able to get the positions and velocities of each atom. Also, we used a predictor-corrector algorithm to integrate the equations of motion. Throughout the simulations, a time step of $1.6 \times 10^{-15}$ s is used. To accumulate statistics, before running, the system was first equilibrated in 485 000 time steps. Also the atomic trajectories and energy recorded in the subsequent 5 000 time steps were used to get the thermodynamic equilibrium values. Firstly, we constructed a 32.7×32.7×32.7 nm³ bulk faced center cubic (FCC) Ag crystal (the lattice constant $a_0$ is 4.09 Å), 55 atoms are extracted from this constructed Ag crystal. To make the box size of the simulated center cell large enough to avoid the interaction of the atoms in the central cell with the other atoms in its 26 neighbor imaging cells under periodic boundary conditions, the size of the MD simulation cell is 32.7×32.7×32.7 nm³. This cluster was subjected to structural relaxation at 1235K to obtain a molten state, and one silver atom was replaced with one copper atom. Then it decreased to 1000K, and decreased 50K each time until it reaches 300K. The following values were determined in the simulations.

$$\rho(r_i) = \langle N_i \rangle / N,$$ \hspace{1cm} (2)

where $\langle \rangle$ denotes the average over the entire trajectory, the atomic density profile $\rho(r_i)$ is calculated by dividing the system into some layers along the $r$ direction from the cluster center and accumulating a histogram of the number, $N_i$ of atoms in each layer, where $\langle N_i \rangle$ is the average number of atoms in layer $i$.

The moment of inertia can reflect atomic positions and mass distribution. As a tensor, it can be determined by:

$$I_{ij} = \sum_{i=1}^{N} m_{Cu/Ag}^i (x_{atom}^i - x_c) (x_{atom}^i - x_c) (i \neq j, i = 1, 2, 3)$$ \hspace{1cm} (3)

$$x_c = \frac{\sum_{i=1}^{N} m_{Cu/Ag}^i x_{atom}^i}{\sum_{i=1}^{N} m_{Cu/Ag}^i} \hspace{1cm} (i = 1, 2, 3)$$ \hspace{1cm} (4)

where $m_{Cu/Ag}$ is the mass of Cu or Ag atom, $x_c$ is the mass center, $x_i$ or $x_j$ is the coordinate of the $i_{\text{atom}}$. $i$ (or $j$) is 1, 2, 3 respectively corresponds to the x, y and z axes. $I^1$, $I^2$ and $I^3$ are three values of principle axes that are obtained by diagonalization of tensor component, where $I^1$ and $I^3$ stands for the maximum and minimum valued. The shape factor can be defined as:

$$F_{\text{shape}} = I^1 / I^3$$ \hspace{1cm} (5)

3. Results and Discussions
From the figure 1, it is clear that as temperature is decreased from 1235K to 300K, the potential energy has shown a pattern of decreasing. From 1235K to 1000K, although the potential energy decreased greatly, the atoms are packed disorderly at the two temperatures. The change of potential energy comes from the obvious change of cluster shape, where the ellipsoid shaped cluster becomes more round. After that, the decrease speed is slowed down until it reaches about 950K. From there, the energy is increased with a very small amplitude. Then there comes the sharp decline in the graph. If we look at the picture of this cluster, we can clearly see that at 850K, it becomes an almost perfect icosahedron. After that, the decreasing in potential energy begins to slow down, and there comes a short increase. In meanwhile, this cluster has changed a bit. Then, the potential energy begins to decrease slowly with only two short increases until the temperature finally reaches 300K.
Figure 2. Graph on the left shows the atomic densities of the cluster, to make things more clear, we divide the graph into four shells. The images on the right describe the amount of atoms and the structure in each shell.

As shown in figure 2, when the temperature is 900K, the graph has two broaden peaks, where the first shell in 900K is empty, with no atom there. In the second shell, there are 11 atoms there, which is included a copper atom in it, and the other atoms in the outer part of this cluster. At 850K, there are four distinct peaks, and the peaks become narrower. It can be noted there is a small peck in the center of this cluster, implying the first shell is not empty anymore, instead, one silver atom shift to the first shell. There’s also a change happens in the second shell compared with that at 900K, the copper left the second shell, and it shift to the third shell. Now, there are 12 atoms in the second shell and 30 atoms in the third shell. In the fourth shell, there are 12 atoms. As the temperature is decreased to 800K, although there are still 12 atoms in the four shell, one silver atom leaves the lattice position of icosahedron at 850K. In addition, the copper atom shifts back to the second shell. At 750K, compare to the graph above, the third and fourth peak seems to be closer together. The first shell still has 1
atom, 12 atoms in the second shell, 31 in the third shell, and 11 in the fourth shell. Correspondingly, there is a jump of potential energy as illustrated in figure 1. As the temperature decreases further, the peaks of the density profiles become higher and thinner, where the third and fourth peak seems more separate from one another. The atomic packing in the different shells shows that the first shell still has 1 atom, 12 atoms in the second shell, 30 in the third shell, and 12 in the fourth shell. Here, there atoms are at their icosahedral positions.

Figure 3. Graphs on the left show how potential energy changes as time step increases. Graphs on the left show shape factor changes as time step increases.

Figure 3 illustrates variations of the potential energy and shape factor with the time steps at 800K, 750K, and 700K. As illustrated in this graph, there is a significant change about 200 000 steps at 800K, suggesting that the structural transition occurs from molten state to icosahedral packing. In the meantime, the cluster turns into a shape that looks likely to a ball. Then the shape of this cluster stops to shift in a wide range. At 750K, the shape of this cluster shows significant changes. At first, this cluster presents ball shape, and then its shape is really different to a ball. After 300 000 time steps, its shape restores to the ball shape. At 700K, it is clear that the shape of the cluster is becoming more stable. Only at the beginning, the shape changes apparently. Correspondingly, potential energy fluctuates before 100 000 time steps.

4. Conclusion

In this paper, MD simulations were performed to study the structural changes during cooling the molten Ag$_{54}$Cu$_{1}$ cluster. Structural changes came from interchanging movements among the atoms,
which significantly affected potential energy to change accordingly. The present simulations visually showed the changes with the crystallization from the packing patterns in different shells obtained from atomic density profiles. The transformation of structure of this cluster happened within a temperature range. After transformed from molten state to icosahedron, there were still changes in positions of the atoms inside the cluster. At the same time, the shape of this cluster also had a significant change. This type of clusters’ structures usually significantly changed under high temperature. When the molten cluster was at high temperatures, the copper atom located inside the cluster. As the temperature decreased, the copper atom would begin to shift out the cluster. Keeping on the decrease of the temperature, the copper atom moved to the inside of this cluster.

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