Molecular Dynamics Investigation of Differences in Melting Behaviors of \( \text{Cu}_{57} \) and \( \text{Cu}_{58} \) Clusters

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(Dated: Received on August 27, 2008; Accepted on November 14, 2008)

Within the framework of the embedded-atom method, we performed molecular-dynamics calculations to investigate the structural transformation during melting of two copper clusters containing 57 and 58 atoms. The simulation results reveal how their different structural changes can strongly influence internal energy and radial distribution functions. The local structural patterns of different regions during the temperature increase, determined by atom density profiles, are identified for the melting of each cluster. The simulations show sensitivity of the structural changes for these two small size clusters with different structures.

Key words: Molecular dynamics, Cluster, Surface, Melting

I. INTRODUCTION

In low-dimension materials, the investigation of metallic clusters has aroused the interest in both physics and chemistry due to their key roles in novel nanocatalysis and nanotechnology [1,2]. In these clusters, optical, magnetic, and electronic properties, as well as their thermodynamic properties, are greatly dependent on their geometrical structures. Unlike their bulk counterparts, the metal clusters exhibit various structural motifs. In most accepted models, icosahedra are expected to be favorable at small cluster sizes, and crystalline clusters with fcc local order are usually found at the macroscopic limit. In past decades, melting behavior studies of the metal clusters with different structures have provided a deep understanding of thermal stabilities in such low-dimension systems. The melting behaviors of different types, as well as compositions and sizes of particles, are similar in some aspects but do have their own unique thermodynamic properties. Owing to the high surface-to-volume ratio of these metal nanoparticles, the reduction in the melting temperature of these clusters increases with the decrease of their size, there exist broadened melting transition regions, structural isomerizations occur prior to melting, surface premelting and solid-melt phase coexistence may occur in sufficiently large clusters, and the melting process is found to be punctuated by solid-solid structural transformations to icosahedral structures upon heating [3-8]. These kinds of phase transformation maps are important because they allow us to understand the critical role of temperature in cluster growth. Therefore, the ideal growth condition would be obtained by choosing an annealing temperature that is high enough to transform a performed cluster into a desired structure. For instance, nanoclusters with three-dimensional symmetry, which are used in nonvolatile memory cells, can provide the best charge confinement and physical stability [8].

Although considerable progress has been made in determining structural changes of these clusters by utilizing many experimental and theoretical studies, issues pertaining to structural change differences in small size clusters containing tens of atoms in their melting processes continue to be a subject of current interest. In these small systems, the most important chemical and physical properties have a dramatic dependence on their geometrical structures [9-19]. When the detailed structure changes of these isolated small metal clusters are difficult to be observed due to the lacking of sensitive experimental methods, theoretical calculations on density function \textit{ab initio} methods and empirical potentials, give some insight into the cluster structures. Because of limitations from the prohibitive computational expense, none of the \textit{ab initio} approaches can be implemented on clusters containing more than tens of atoms. Many researchers have used molecular dynamics (MD) simulations on the empirical potentials determined by embedded atom method (EAM) to study the melting behaviors of the coinage metal clusters [20-26]. For example, the structural changes of the small Cu clusters containing 54, 55, and 56 atoms described by Mei et al. using the EAM potential have been studied, where the optimized structures of the three clusters at 300 K are in agreement with the lowest energy structures by employing the other potentials [10]. The three cases present a picture of removing or adding one atom to...
a perfect icosahedron cluster causing different change patterns during their melting processes. However, for some small-sized clusters containing tens of atoms with deformed icosahedron-based geometries, how the structural changes are sensitive to the atom number is still less understood.

As a complement of our previous study on the melting of the Cu$_{54}$-Cu$_{56}$ clusters, we investigated the structural change differences between Cu$_{57}$ and Cu$_{58}$ clusters in terms of their melting behaviors by molecular dynamics simulations. The melting process is traced from the atomic energy and radial distribution functions (RDFs). In the simulations, the structural changes of the two clusters are presented by the atomic packing in different shells, where the shells in multilayer structures of these clusters are determined by atom density profile calculations.

II. COMPUTATIONAL DETAILS

The atomic calculations reported in this work were carried out with the EAM potential of Cu described by Mei et al. The following formula for the total energy of a system containing $N$ atoms is given [27],

$$E_{\text{tot}} = \sum_i F_i(\rho_e) + \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij})$$

(1)

where $\phi_{ij}(r_{ij})$ is a two-body central potential between atom $i$ and $j$ with the separation distance $r_{ij}$, and $F_i(\rho_e)$ is the embedding energy of the atom $i$ with the electron density $\rho_e$. The forms of the two-body potential, the electronic density, and the embedded energy are from Ref.[27]. The atom trajectories of these Cu clusters are recorded in canonical ensemble MD simulations. In calculating the structural changes of these clusters, the following values are determined,

$$g(R) = \frac{V}{N} \left( \sum_{i \in L_g} \sum_{j \neq i \in L_g} \delta(\vec{R} - \vec{R}_{ij}) \right)$$

(2)

$$\rho(r_i) = \frac{\langle N_i \rangle}{N}$$

(3)

where $\langle \rangle$ is the average calculated over the entire trajectory, $g(R)$ is the radial distribution function, $V$ the volume of the simulated MD cell, and $N$ is the number of atoms in this cell, and where the sum of $\delta(\vec{R} - \vec{R}_{ij})$ is processed by recording all the pairs of atoms within the shell volume interval $(R, R + \delta R)$. The density profile $\rho(r_i)$ is calculated by dividing the system into some layers 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 the layer $i$, and $r_i$ is taken as the center of this layer [28].

The simulations for the two studied clusters are performed by starting with the optimal structures at 300 K, then increasing gradually the temperature to 1000 K at an increment of 50 K corresponding to the process at the same heating rate of $6.25 \times 10^{10}$ K/s, where the heating rate is calculated from the temperature interval divided by the simulation time. At each temperature, the initial runs take about $48 \times 10^4$ time steps to reach equilibration, and subsequently $2 \times 10^4$ time steps to record the atomic trajectories that are used to study structural properties of the simulated system. A time step of $1.6 \times 10^{-15}$ second is used in the calculations. The temperature is kept constant by rescaling the atomic velocities every time step.

Figure 1 shows the stable structures and corresponding atomic density profiles of the clusters containing 57 and 58 atoms at 300 K. In this figure, the lattice constant $a_0$ of Cu is 3.615 Å. The most characteristic features of these density profiles are intensity peaks.
corresponding to different shells labeled as s1-s6 for the Cu$_{57}$ cluster and s1-s5 for the Cu$_{58}$ cluster. The widths of these intensity peaks result from thermal movements of the atoms around their equilibrium positions.

III. RESULTS AND DISCUSSION

Figure 2 illustrates the temperature variation of the system total internal energy per atom from 300 K to 1000 K to check the structural arrest against thermal agitation. It should be noted that because the kinetic energy per atom is given by the temperature, the difference value of the total internal energy at each temperature equals that of the potential energy for the two clusters. Internal energy curves of these two clusters exhibit different change behaviors upon heating, as shown in Fig. 2. For the Cu$_{57}$ cluster, internal energies rise linearly within relative low temperature regions including 300-400 and 400-500 K, where the slope at 400-500 K is higher than that at 300-400 K. Then followed a fluctuating increase region of the internal energy, which is an indication of the occurrence of dramatic structural changes. Above 700 K, the internal energy rises in a nearly linear fashion as a function of temperature with a higher slope than those at the low temperature regions, implying that the cluster has become wholly disordered. Although the energy change of the Cu$_{58}$ cluster also can be divided into several stages with different slopes, it does not present the abrupt increase stage as illustrated in the energy curve of the Cu$_{57}$ cluster. As a general change measure of the energy, from 300 K to 500 K, the energy per atom of the Cu$_{57}$ cluster has a lower value compared to the Cu$_{58}$ cluster. Above 700 K the energy of the Cu$_{58}$ cluster is lower than that of the Cu$_{57}$ cluster. The differences of the energy changes between the two clusters indicate the structural change differences, and the following MD observations will be used to interpret the differences.

Figure 3 respectively presents the RDFs of the simulated Cu$_{57}$ and Cu$_{58}$ clusters at elevated temperatures. As shown in these figures, at the position of 0.75$a_0$, the first peaks of these RDFs are far higher than the other peaks, which implies that most of the atom pairs are populated in the first peaks. For the Cu$_{57}$ cluster, besides the first big peak, there are three peaks within the range of 1.5$a_0$ as well as other small peaks occurring out of that range below 500 K, and these peaks decrease in height with increasing temperature, suggesting that structural changes have occurred. A notable phenomenon in Fig.3(a) is that the fifth peak becomes small at 300-400 K and at 500 K it has almost disappeared, where the lower energy slope of this cluster at 300-400 K compared to that at 400-500 K as shown in Fig.2 can be attributed to the structural changes. When the temperature is increased to 550 K, the second peak disappears and the fourth peak becomes small, but meanwhile the third peak is broadened. At 600-650 K, the fourth peak disappears. As the temperature is increased further, the RDF of the Cu$_{57}$ cluster gradually shows disordered behavior. When the cluster is heated up to above 750 K, the RDFs show liquid-like patterns including the disappearance of the second and fourth peaks as well as the broadening of the third peak, which is different from that at 300 K. Above 500 K, the RDF changes for the Cu$_{58}$ cluster have similarities to those for the Cu$_{57}$ cluster with increasing the temperature; for example, the second and fourth peaks disappear while the third peak broadens, and in the high temperature range, it becomes liquid. Nevertheless, at 300-500 K,
the RDF changes of the Cu$_{58}$ cluster are different from its counterpart. Compared to the RDFs at 400 and 450 K, the second and fourth peaks of this Cu$_{58}$ cluster at 300 and 350 K are quite small in the range of 1.5a$_0$. These suggest that the structures at 400 and 450 K may be more ordered than those at 300 and 350 K. When the temperature is increased from 450 K to 500 K, the second peak disappears, and the fourth peak again becomes small. These RDFs indicate that the structural changes of the two clusters are different, but information has not been obtained about the position evolution information of the atoms in the two clusters corresponding to their structure changes. The following study of atom density profiles and local atom packing will be used to provide such information.

Figure 4 shows the atom density profiles of the two clusters upon heating. As shown in Fig.4(a), at 400 K, although the atom density profile of the Cu$_{57}$ cluster is composed of some shells corresponding to the intensity peaks, the peak heights are decreased greatly as well as broadened compared to that at 300 K. With increasing of the temperature, some peaks disappear or are combined into one peak. At 550 K, the density profile exhibits a feature that there exist three broadened peaks and their heights are also decreased compared with those at low temperatures. When the temperature reaches 600 K, the peak heights of the density profile are increased. Then in the following temperature range of 650-700 K, the changes of the density profile are similar to those at 550-600 K. Further increased temperature results in the lowering and broadening of peaks of the atomic density profiles above 750 K, which is a proof that the atom packing becomes disordered at these temperatures. At 350 K, the characteristic features of the Cu$_{58}$ cluster are similar to that at 300 K, where its density profile includes some peaks corresponding to different shells. When the temperature is increased, owing to the more dramatic atom movements, the peak heights of the density profiles above 400 K are lower, the widths become wider, and some peaks combine into one peak. A noted phenomenon occurs in the curve at 500 K, where the second peak height is noticeably higher than that at 400 K, implying that more atoms are located in this shell. Then, the peak again becomes broad resulting from the dramatic thermal movements of the atoms at the elevated temperature. When the temperature is above 850 K, the density profiles show liquid-like behaviors similar to those of the Cu$_{57}$ cluster.

Figure 5 and 6 presents the detailed atom packing of the Cu$_{57}$ and Cu$_{58}$ clusters at different temperatures in their melting processes. As seen in Fig.5, below 400 K the Cu$_{57}$ cluster is composed of six shells as labeled in Fig.1, where there is one atom in the first shell and in the third shell, the atomic configurations in the second and fifth shells respectively contain 12 atoms in two
pentagonal bipyramids, the configuration in the fourth shell is constructed by 12 pentagons and 20 triangles with one vacancy formed by 29 atoms, and there are two atoms in the sixth shell. As the temperature is increased to 500 K, two atoms in the sixth shell move into the fifth and fourth shells. Correspondingly, the thirty atoms in the fourth shell pack together in the configuration including 12 pentagons and 20 triangles, and the atomic configuration in the fifth shell is the two pentagonal bipyramids with one additional atom. Hence, the structural changes from the atom movement result in the higher slope of the energy at 400-500 K than that at 300-400 K, as illustrated in Fig.2. The elevated temperature increases the atom movements. At 500-550 K, owing to the atom movements of two atoms in the fifth shell into the fourth shell and one atom into the second shell, the cluster forms a four-shell structure. In the meantime, the atom configurations in the second and third shells become greatly disordered. When the temperature is increased to 650 K, six atoms in the fourth shell move into the third shell accompanied by the movement of one atom in the second shell into the third shell. At 650-850 K, the atoms continue to move in the different shells. Above 850 K, a three-shell structure occurs in this Cu$_{58}$ cluster, where some atoms in the outermost shell move into the inner shell, resulting in the higher slope of the energy as illustrated in Fig.2 and liquid-like RDF curve shown in Fig.3. The number of atoms in the second shell at 1200 K reaches thirty-three because of the movement of the fourteen atoms in the third shell to the inner part of this cluster.

**IV. CONCLUSION**

MD simulations were performed to determine the structural change differences upon heating between two copper clusters respectively containing 57 and 58 atoms, which have deformed icosahedral geometries as described by the Mei 	extit{et al}. version of the EAM potential. Although the two clusters have similar volume shrink-
age because of the atom movements from the outer shells into the inner shells in their melting processes, the atom packing changes present different patterns. The initial structural changes of both the Cu$_{57}$ and Cu$_{58}$ clusters result from the atom movements from the outermost shells into the inner shells. However, owing to the continuous interchange positions of the atoms in the different shells, an apparent fluctuating energy increase region of the Cu$_{57}$ cluster occurs. Although the two clusters have nearly the same beginning temperature for the structural changes, the temperature of the Cu$_{58}$ cluster forming the stable three-shell structure is larger than that of the Cu$_{57}$ cluster forming the four-shell structure. The scenario of the two simulated clusters with the icosahedron-based geometries reveals that a minor change in the number of atoms can result in the large differences of the optimized structures, and further cause different change patterns during their melting processes.

V. ACKNOWLEDGMENT

This work was supported by the National Basic Research Program of China (No.G2006CB605103).


DOI:10.1088/1674-0068/22/01/69-74 ©2009 Chinese Physical Society