Vol 16 No 1, January 2007
1009-1963/2007/16(01)/0077-06
Chinese Physics
© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Local structure changes of Cu_{55} cluster during heating*

Zhang Lin(张 林), Zhang Cai-Bei(张彩碚)†, and Qi Yang(祁 阳)

College of Science, Northeastern University, Shenyang 110004, *China*

(Received 31 March 2006; revised manuscript received 24 July 2006)

The structural relaxation of a cluster containing 55 atoms at elevated temperatures is simulated by molecular dynamics. The interatomic interactions are given by using the embedded atom method (EAM) potential. By decomposing the peaks of the radial distribution functions (RDFs) according to the pair analysis technique, the local structural patterns are identified for this cluster. During increasing temperature, structural changes of different shells determined by atom density profiles result in an abrupt increase in internal energy. The simulations show how local structural changes can strongly cause internal energy to change accordingly.

Keywords: cluster, molecular dynamics, computer simulation, surface
PACC: 3640B, 6120J, 6185, 6800

1. Introduction

Clusters have attracted much attention of researchers in the fields of physics, chemistry and materials science because they play an important role in bridging the gap between isolated atoms and bulk material.[1,2] In the study of clusters, the structures of face-centred cubic (FCC) metallic clusters are hotspots in research due to their importance in catalysis and surface nanotechnology. It has been recognized that the most important chemical and physical properties of these clusters are dramatically dependent on their geometrical structures.[3−8] And researches have demonstrated that cluster surface atoms possess much higher energy than interior atoms and surface can be premelting.[5,7] Nevertheless, the mechanism of structural changes of these clusters during their heating is still poorly understood. One main cause is that it is difficult to experimentally observe the details of atomic packing in samples. In the case where appropriate experimental techniques on these systems are lacking, computer simulations can be used to investigate the equilibrium cluster structures.

Although the sophisticated density function *ab initio* methods predict both the stable geometries and energetics at a very high degree of accuracy,[9−12] none of the approaches is available to very small clusters owing to prohibitive computational expense; in addition these approaches cannot give the direct information about cluster structural stability at finite temperatures. What is needed, therefore, is a simulation technique for studying the structural changes in a fully dynamic medium. Molecular dynamics (MD) is a well-established technique for studying the microscopic details of liquids and solids.[13−17] In MD simulations, the empirical potentials based on the embedded atom method (EAM) are adequate to the characterizing of these metallic systems, and some EAM versions have been employed to describe the properties of free clusters and clusters supported on surfaces of the same kind of material for FCC transition metals, such as Cu systems.[18−21] In ÖzÇelik and Güvenç's simulations on Voter's EAM, the melting temperature of a Cu_{55} cluster is near 950 K(about 677 C°).[19]

The purpose of this paper is to make an MD investigation of structural changes at elevated temperatures in a copper cluster containing 55 atoms. How the local structural changes accompanying with the atom packing affect the internal energy with increasing temperatures is demonstrated by decomposing the radial distribution function (RDF) according to the local environment of the pairs of EAM atoms. Here, the shells with multilayer structures of the cluster studied are determined by atom density profile calculations.

2. Model and simulation

All the atoms in the simulation are assumed to interact via an EAM potential of Cu constructed by

*Project supported by the National Natural Science Foundation of China (Grant No 50572013) and the National Basic Research Program of China (Grant No 2006CB605103).
†Corresponding author. E-mail: gsj-cn@tom.com

Mei *et al*,[22] and atomic trajectories are generated in the canonical ensemble MD at elevated temperatures. In calculating the structural changes of this cluster, the following values are determined:

$$g_{L_g}(r) = \frac{V}{N}\left\langle \sum_{i\in L_g} \sum_{j\neq i\in L_g} \delta(\boldsymbol{r} - \boldsymbol{r}_{ij}) \right\rangle, \qquad (1)$$

$$\rho(r_i) = \langle N_i \rangle, \qquad (2)$$

where $\langle\ \rangle$ denotes the average over the entire trajectory, $g_{L_g}(r)$ is the pair distribution function in the layer L_g, V the volume of the simulated MD cell, and N the atom number in this cell. 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 layer i, and r_i is taken as the centre of this layer. The structural change analyses of the cluster are performed by using the pair analysis technique.[23,24]

3. Results and discussion

Figure 1 shows the temperature variation of the system internal energy from 350 to 1400 K, indicating the stability of the cluster structure against thermal agitation. In this figure, there exist one energy peak at the temperature of about 650 K, and two abrupt increases in internal energy occurring at the temperatures of about 550 K and 700 K. With temperature further increasing the energy increases linearly. These can be interpreted as the changes of local structures in this cluster with increasing temperature, and the following MD observations related to the structural changes will support this interpretation. Figure 2 presents the RDFs of the simulated cluster at the temperatures 350 K, 550 K, 700 K, and 1100 K. As shown in this figure, at the position of $0.75a_0$, where the lattice constant a_0 of Cu is 3.615 Å, the first peaks of these RDFs are far higher than the other peaks, which implies that most of atom pairs are populated in the first peaks. Besides the first big peak, there are other three peaks occurring at the temperatures 350 K and 550 K, their first peaks decrease in height with temperature increasing, which implies that the structural changes have occurred in the range of 550 K, though the cluster structures at these temperatures are very similar. At the temperature 700 K, the second and the fourth peaks become small, and the third peaks are broadened. When the cluster is heated up to 1100 K, the RDF shows a disordered behaviour, where the second and the fourth peaks disappear and the third peak is also broadened.

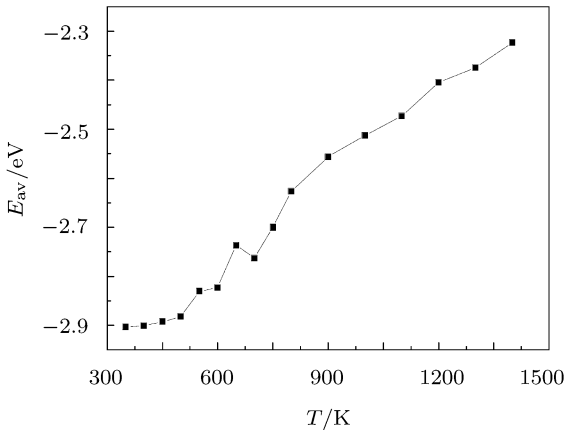


Fig.1. Variation of internal energy per atom in the cluster with temperature.

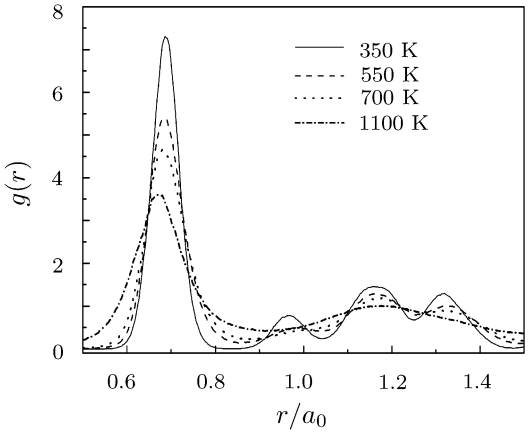


Fig.2. The RDFs of the cluster at the temperatures 350 K, 550 K, 700 K and 1100 K.

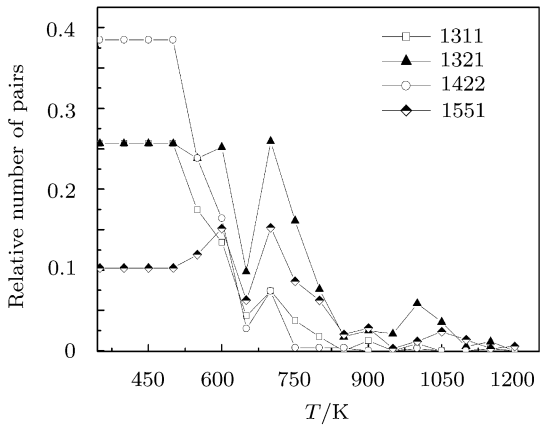


Fig.3. The relative number of bonded atom pairs versus temperature.

To investigate the differences in local structure among these temperatures, Fig.3 illustrates the relative numbers of different kinds of bonded atom pairs as a function of temperature during heating the clusters corresponding to the first peaks of RDFs as shown in Fig.2. In Fig.3 the relative number is the ratio of the number of atomic pairs of one kind to the sum of atomic pairs and it can be used to determine the ordered degree for this cluster at elevated temperatures. From this figure, it can be found that as the temperature varies in the range of 500 K, the cluster is mainly composed of four types of pairs: 1311, 1321, 1422 and 1551, and none of these pairs shows any significant change. Here, these pairs represent the positions of atomic pairs in this cluster, for example the 1551 pairs correspond to two neighbouring atoms with five common neighbours that form a pentagon of near-neighbour contacts, and it is characteristic of icosahedral ordering. In the case of 550 K, there is an increase in the number of 1551 pairs, and the numbers of 1311, the 1321 and the 1422 pairs decrease apparently at the same time. A similar change occurs at the temperature 600 K, where the numbers of 1311 and 1422 pairs decrease while the number of 1551 pairs increases. At the temperature 650 K, all of the four types of pairs abruptly decrease to low values in number, and their relative numbers again reach top values at the temperature 700 K. When the temperatures are higher than 700 K, the numbers of these pairs again decrease. The changes in the relative number of pairs are coincidentally corresponding to the changes in internal energy as shown in Fig.1, indicating that the atomic local structural changes result in the energy changes during heating.

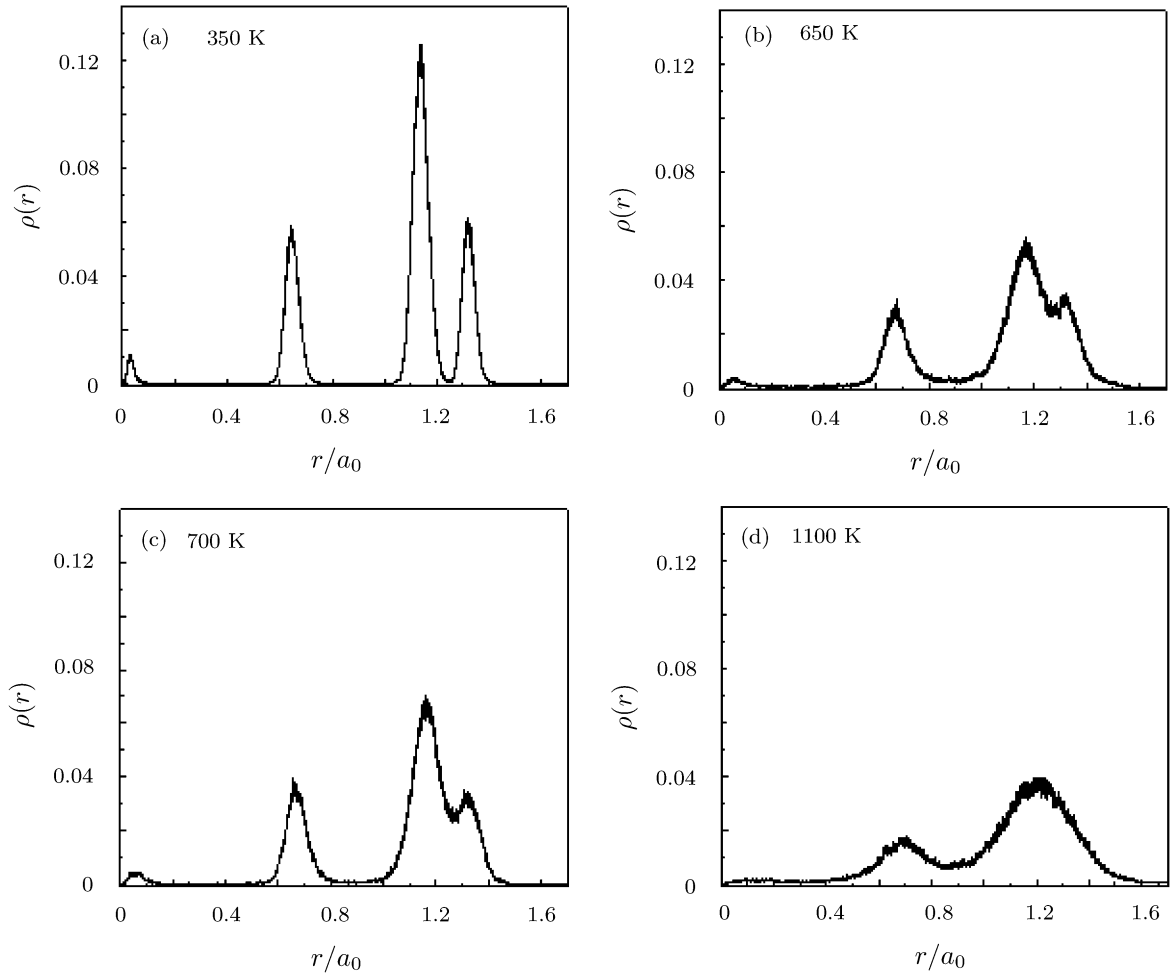


Fig.4. The atomic density profiles of the cluster at different temperatures.

Figure 4 shows the atomic profiles of the cluster at temperatures 350 K, 650 K, 700 K, and 1100 K. The profiles in the temperatures ranging from 350 K to 700 K have some similarities including that they can be regarded as being composed of four shells corresponding to four intensity peaks, and the first and the second shells are separated from the other shells. However except for the temperature 350 K, the third peaks are connected with the fourth peaks at the other temperatures, where the third and the fourth peaks almost are combined into one peak. In addition, the second peak of the profile at 650 K is apparently broadened more than at 700 K, which implies that the atom packing in this shell at this temperature may be different from that at other temperatures. When the temperature increases up to 1100 K, the density profile at this temperature exhibits a feature that there exist only two broadened peaks and their heights are also decreased compared with those at low temperatures, which is a proof that the atom packing has become disordered at the temperatures as shown in Fig.2.

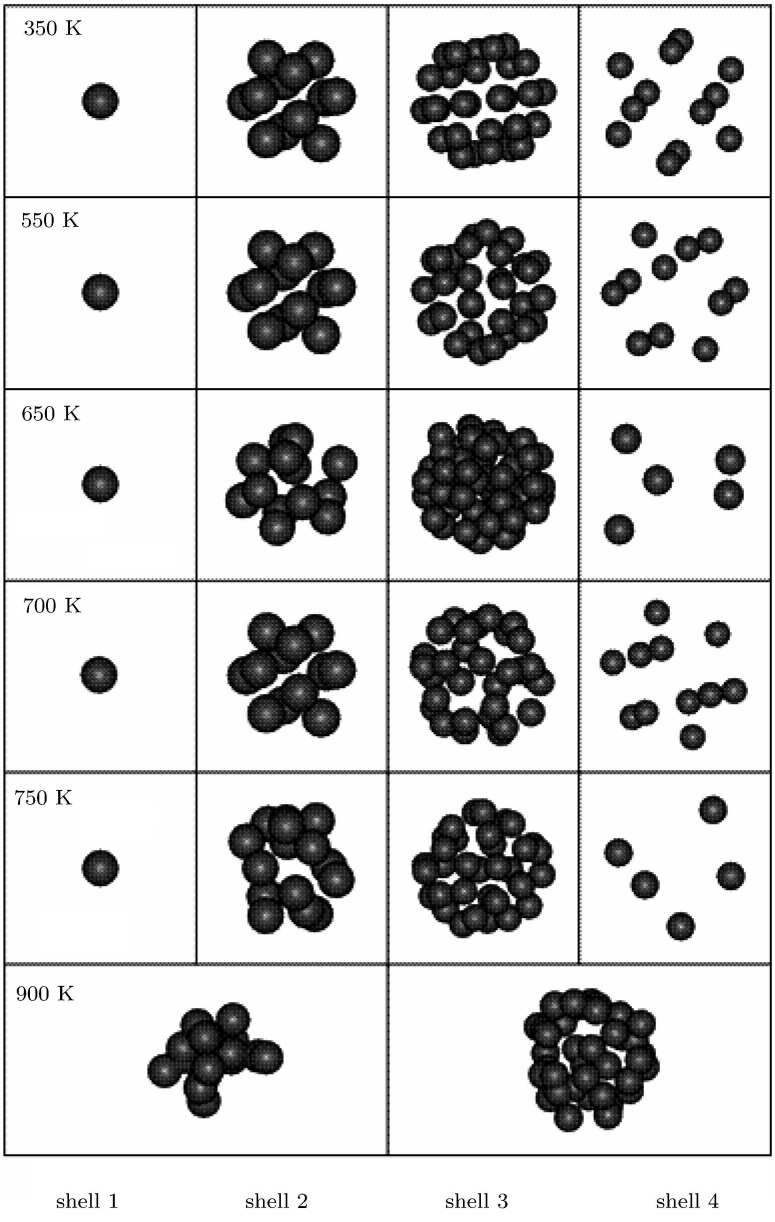


Fig.5. The atomic configurations of the cluster at different temperatures.

Figure 5 respectively shows the geometrical structures of atoms in the first, the second, the third, and the fourth shells at temperatures 350 K, 550 K, 650 K, 700 K, 750 K and 900 K. When the temperatures are below 700 K, the atomic configuration in the second shell is constructed by two pentagonal bipyramids except for the temperature 650 K. If one atom in the first shell is added into the second shell, the structure of these 13 atoms is of icosahedron: unexposed copper atom and the remaining 12 atoms form a spherical shell with a central atom. Additionally, the atomic positions in the third and the fourth shells have some similarities at these temperatures. In the case of 350 K, atomic configuration presents a perfect icosahedron, where the configuration in the fourth shell can also be constructed by two pentagonal bipyramids, and the configuration in the third shell by twelve pentagons and thirty triangles, and this type of structural rigidity is maintained up to 500 K. When the temperature is 550 K, there are 11 atoms in the fourth shell and 31 atoms in the third shell. Owing to the one added atom at the temperature, which is very well localized in the third shell, the numbers of the 1311, 1321, and 1422 pairs decrease while the number of the 1551 pairs increases as illustrated in Fig.3. To a 1311 pair of this type, its two bonded atoms are in the third shell, the three common neighbouring atoms respectively lie in the second, third and fourth shells, and the two neighbouring atoms in the second and the fourth shells form a bond. One atom in the third shell and one in the fourth shell form a 1321 pair with two neighbouring atoms in the third shell and one neighbouring atom in the second shell, while the neighbouring atom in the second shell is separately bonded with the two neighbouring atoms in the third shell. The bonded atoms of some 1422 pairs are in the second shell, and the others are from the bonded atoms in the third and the second shells. To the first type of the 1422 pairs, one neighbouring atom in the first shell forms two bonds with the two neighbouring atoms in the second shell, and the fourth neighbouring atom is in the third shell. In their four neighbouring atoms for the second type of the 1422 pairs, one is in the second shell, two in the third shell and one in the fourth shell, and the atom in the fourth shell bonded with the two neighbouring atoms in the third shell. The changes of local environments of atoms result in the abrupt increase in internal energy at the temperature 550 K as shown in Fig.1. At the temperature 650 K, there exist 13 atoms in the second shell. As a result, the second peak of the atom density profile becomes wide, and its height decreases as shown in Fig.4. Meanwhile, there exist only five atoms in the fourth shell, and 36 atoms in the third shell. Hence, the numbers of the 1311, 1321, 1422 and 1551 pairs are small as illustrated in Fig.3, and an abrupt increase in internal energy occurs at this temperature as shown in Fig.2. In the case of 700 K, it is noted that since the atomic number in the third shell again becomes 31 and the number in the fourth shell 11, the atomic configuration is different from that at the temperature 550 K. Therefore, there is an abrupt decrease in number of pairs at this temperature, but the energy is apparently higher than that at the temperature 600 K. At the temperature 750 K, the numbers of these four types of pairs become decreased, implying that the structure of the cluster begins to become disordered. When the temperature is raised up to 900 K, the atoms are mainly located in two shells: sixteen atoms are in the first shell and thirty-nine atoms in the second shell. Hence, at this high temperature, atomic positions in this cluster are greatly changed as shown in this figure, and correspondingly, the relative number is also low in the four types of pairs as illustrated in Fig.3.

4. Conclusions

In this work, MD simulations show the structural changes of the cluster during heating in quite a simple picture, and also reveal the local structure changes according to the local environment of atom pairs at elevated temperatures: the local structural changes can strongly cause the internal energy to change. In the high-temperatures ranging from 900 K to 1400 K, the system suffers a large distribution of energy, but its structure is independent of temperature. By calculating the atomic density profiles at these temperatures, it can be found that the atoms are populated in two shells, and most of atoms are in the outer shell. As the temperature decreases, the system starts to become localized, and prefers to be populated in a minimal region that represents denser packing. In the computer simulations, the processes, in which one atom moves from the fourth shell into the third shell and the local structure changes take place in the third shell, contribute to a sudden increase in internal energy at the temperature 550 K. The atomic configurations, which are changed in the second, the third and fourth shells at the temperatures 650 K and 750 K, result in two abrupt increases at the two temperatures. Thus, it

can be concluded that surface premelting occurs at the temperature 550 K, and this cluster is melting at the temperature 900 K.

References

[1] Eberhardt W 2002 *Surf. Sci.* **500** 242
[2] Baletto F and Ferrando R 2005 *Rev. Mod. Phys.* **77** 371
[3] Kunz R E, Blaudeck P and Hoffmann K H 1998 *J. Chem. Phys.* **108** 2576
[4] Gotwald D, Kahl G and Likos C N 2005 *J. Chem. Phys.* **122** 204503
[5] Howe James M 1997 *Interfaces in Materials* (New York: John Wiley & Sons) p116
[6] Kabir M, Mookerjee A and Bhattacharya A K 2004 *Phys. Rev.* A **69** 043203
[7] Jin Z H, Shen H W and Lu K 1999 *Phys. Rev.* B **60** 141
[8] Grigoryan V G and Springborg M 2004 *Phys. Rev.* B **70** 205415
[9] Jug K, Zimmermann B, Calaminici P and Köster A M 2002 *J. Chem. Phys.* **116** 4497
[10] Fernandez E M, Soler J M, Garzon I L and Balbas L C 2004 *Phys. Rev.* B **70** 165403
[11] Bauschlicher C W, Jr, Langhoff S R and Partridge H 1989 *J. Chem. Phys.* **91** 2412
[12] Liu H T and Li J M 2005 *Chin. Phys.* **14** 1974
[13] Zhang J M, Wei X M and Xing H 2005 *Chin. Phys.* **14** 1015
[14] Zhang L, Wang S Q and Ye H Q 2006 *Chin. Phys.* **15** 610
[15] Yang Q W and Zhu R Z 2005 *Acta Phys. Sin.* **54** 4245 (in Chinese)
[16] Liu Z J, Cheng X L, Zhang H and Cai L C 2004 *Chin. Phys.* **13** 384
[17] Yang Q W, Zhu R Z and Wen Y H 2005 *Acta Phys. Sin.* **54** 89 (in Chinese)
[18] Dai Y B, Shen H S, Zhang Z M, He X X, Hu X J and Shun F H 2001 *Acta Phys. Sin.* **50** 244 (in Chinese)
[19] ÖzÇelik S and Güvenç Z B 2003 *Surf. Sci.* **532-535** 312
[20] Shin Z P, Zhang Z, Swan A K and Wendelken J F 1996 *Phys. Rev. Lett.* **76** 4927
[21] Longo R C, Rey C and Gallego L J 2000 *Surf. Sci. Lett.* **457** L441
[22] Mei J, Davenport J W and Fernado G W 1991 *Phys. Rev.* B **43** 4653
[23] Dana J and Andersen H C 1987 *J. Phys. Chem.* **91** 4950
[24] Clarke A S and Jonsson H 1993 *Phys. Rev.* E **47** 3975