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Molecular dynamics simulation of thermodynamical properties of copper clusters

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The melting and freezing processes of Cu_N (N = 180, 256, 360, 408, 500, 628 and 736) nanoclusters are simulated by using micro-canonical molecular dynamics simulation technique. The potential energies and the heat capacities as a function of temperature are obtained. The results reveal that the melting and freezing points increase almost linearly with the atom number in the cluster increasing. All copper nanoclusters have negative heat capacity around the melting and freezing points, and hysteresis effect in the melting/freezing transition is derived in Cu_N nanoclusters for the first time.

Keywords: Copper Cluster, Thermodynamical Properties, Molecular Dynamics
PACC: 3640, 6740K, 6470D

1. Introduction

Nanoclusters, or nanoparticles, containing tens-to-thousands of atoms or molecules, play important roles in science and technology. Applications of clusters in innovative technology seem to be endless, as they range from industrial catalysis to the miniaturization of electron devices.[1] They have also been an attractive object for fundamental studies since they occupy a niche between isolated atoms or molecules at one extreme and bulk solids at another. This central role of clusters makes some specific areas of study particularly interesting, such as the evolutions of potential energy, melting point, freezing point and metallic behaviour with cluster size, finite-size effects due to the non-periodic nature of clusters, and the high proportion of atoms on the surface of a cluster leading to significant analogues of processes observed in surface science.[2] However, one difficulty in experiments is that by using most experimental techniques it is practically impossible to prepare a large ensemble of nanoclusters with a narrow size distribution. Furthermore, even for a given cluster size, a distribution of structural isomers inevitably takes place. Therefore, the interpretation of experimental data becomes very complicated,[3] and thus computer simulation is considered as not only a complementary but also an essential tool of cluster studies. By using empirical potential models, molecular dynamics (MD)[4−13] simulation is an ideal tool for investigating the physics of such clusters.

Several groups have been devoted to the study of the structural properties of copper clusters. An analytic expression for the melting temperature as a function of cluster size was deduced from earlier MD simulations.[14] Later, the structures and meltings of 13- and 14-atom copper clusters were studied in detail.[15] The results show that the 13-atom cluster has a high melting temperature, and a pre-melting phenomenon occurs in the 14-atom cluster with a single atom outside a very stable structural core. More recently, MD simulations on crystallizations of liquid copper clusters and meltings of free copper clusters (55-, 147- and 309-atom) were studied by Valkealahti and Manninen [16] and Lei[17] respectively. The former searched for the ground-state geometries of copper clusters, and the latter suggested that the dynamics coexistence (DC) process could extend to medium-size metallic clusters.

However, comparing with the full and accurate results of other noble metal clusters (gold and silver), a lot of the properties of copper clusters are still obscure.[18] Furthermore, there has been no systematic study of the free copper cluster containing 100 to 1000 atoms. Motivated by these facts, we study the melting and freezing processes of Cu_N (N = 180, 256,

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360, 408, 500, 628 and 736) clusters by using the MD technique and embedded-atom method (EAM)[19,20] in detail. Their thermodynamical properties are analysed and some useful conclusions are drawn.

2. Simulation method and potential function

In order to simulate clusters containing more than several hundred atoms, it is necessary to resort to an empirical description of the inter-atomic forces. Here, the EAM model is used, which is an n-body potential proven to be able to reproduce various static and dynamic properties of transition and noble metals, in either bulk or surface configurations. The model is "semi-empirical" in the sense that it approaches the total-energy from a local-electron-density viewpoint, but using a functional with parameters obtained from experiment (equilibrium lattice constant, bulk modulus, elastic constants, etc.).[21] Equations used in the EAM are as follows:

$$E_{\rm tot} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2}\sum_{i\neq j}\phi_{ij}(R_{ij}), \tag{1}$$

$$\rho_{h,i} = \sum_{j\neq i} f_j(R_{ij}), \tag{2}$$

where $E_{\rm tot}$ is the total energy, $\rho_{h,i}$ is the electron density at atom i due to all other atoms, f_j is the electronic density of atom j as a function of distance from its centre, R_{ij} is the separation between atoms i and j, $F_i(\rho)$ is the energy required to embed atom i into the background electronic density ρ, and $\phi_{ij}(R_{ij})$ is the core–core pair repulsion between atoms i and j. In this paper, the electronic density and two-body potential are cited from Ref.[20] as follows:

$$f(r) = f_{\rm e}\left(\frac{r_{1\rm e}}{r}\right)^{\beta}, \tag{3}$$

$$\phi(r) = \phi_{\rm e}\left(\frac{r_{1\rm e}}{r}\right)^{\gamma}, \tag{4}$$

Where

$$f_{\rm e} = \frac{E_{\rm C}}{S_\beta \Omega}, \quad S_\beta = \sum_{i=1}^{n}\frac{N_i}{k_i^\beta}, \tag{5}$$

$$\Phi_{\rm e} = 2\frac{E_{\rm C}}{S_\gamma}, \quad S_\gamma = \sum_{i=1}^{n}\frac{N_i}{k_i^\gamma}, \tag{6}$$

where $E_{\rm C}$ is the crystal binding energy, Ω is the atomic volume, the summation is performed over n neighbour shells, N_i is the number of atoms of the ith shell, and k_i is the ratio of the radius of the ith shell to the nearest-neighbour distance. All these parameters are cited from Ref.[22].

3. Computational details

The initial spherical copper clusters are obtained from a bulk crystal with a face-centred-cubic (fcc) structure by cutting off the atoms outside the sphere with a given radius R. Then, the clusters are annealed, which means heating the clusters from room temperature (300 K) up to the temperature near the melting point, and subsequently cooling them down to the room temperature slowly. After that, the obtained clusters are taken as initial structures to start the simulations.

In the simulation process, we change the total energy (or temperature) of a cluster by rescaling a random-velocity from Maxwell distribution for a given temperature to each atom. Because Maxwell distribution is a statistical distribution, the supposed initial temperature and the statistical temperature after relaxation may be different greatly. So it is very difficult to control the temperature accurately. To reduce computational cost, the time steps of thermalization are determined by the changing of the total energy (increasing or decreasing in the last simulation). The most important thing is to have enough simulation time to ensure that the system reaches its equilibrium after each thermalization. Because the bigger fluctuation in the smaller clusters cannot be avoided, the more simulation time is needed to solve this problem at present. In our calculations, simulation time step exceeds 4×10^6 in number each with a time step of 2 fs. Around the melting and freezing points, in order to attain the clusters' equilibrium state, more simulation time (with more than 4×10^7 steps) is used than at other positions.

In addition, it is also worth noting that the present study does not aim at the quantitative prediction of the physical and chemical behaviours of copper clusters, but rather at the qualitative exploration of the thermodynamical properties in connection with the occurrence of melting and freezing processes.

4. Results and discussion

The most common method of studying the phase transition is the calculation of the caloric, that is, the potential energy of the clusters as a function of T as

follows:[23]

$$U = U(T). \tag{7}$$

During phase transition, $U(T)$ will show a sharp jump, corresponding to a peak in the heat capacity curve $c(T)$; they are related by

$$c(T) = \partial U(T)/\partial T. \tag{8}$$

The melting and freezing points of the clusters are defined as the temperature corresponding to the extremum of the heat capacity.[24]

The calculated caloric for the Cu_{360} cluster in melting and freezing processes is shown as an example in Fig.1. (The curves for other Cu_N clusters are qualitatively similar.) Sharp jumps indicate a solid–liquid phase transition. It can be seen that the phase transition occurs in a range of temperatures, which means that the melting begins at the surface of the cluster and generally goes into the core until the whole clusters is totally melt and *vice versa*. In the inset, sharp drops of the heat capacities at the melting and freezing points, derived from the differentiation of the caloric data, are displayed.

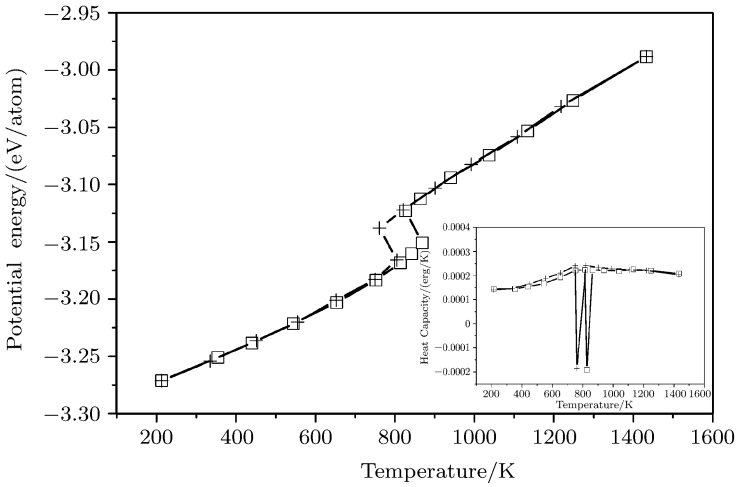


Fig.1. The caloric curves for Cu_{360} cluster in the melting (open squares) and freezing processes (pluses). Inset: the curves of heat capacity vs temperature for Cu_{360} cluster.

4.1. Size dependence of the melting and freezing points

The melting and freezing points of Cu_N clusters with different sizes are summarized in Table 1 and plotted in Fig.2. From Fig.2, one can find that firstly the melting and freezing points are both lower than 1375 K in bulk copper, which is consistent with the previous results,[3,18,24−28] while Shvartsburg and Jarrold [27] even found that tin cluster ions containing 10–30 atoms had a melting point at least 50 K above that of the bulk tin. Secondly, the melting and freezing points increase almost linearly with the atom number in the clusters increasing. This is not consistent with the previous results[25] where the phase transition temperature was proportional to the cube root of the clusters' atom number N. It should be noted that some studies have also shown the irregular behaviours of the melting point of cluster.[23,28] The reason why the melting and freezing points of copper cluster in our calculation are enhanced almost linearly with the increase of its atom number needs further studying.

Table 1. Melting and freezing points of various Cu clusters.

Atom Number	Melting Point/K	Freezing Point/K	Difference between Melting and Freezing Point/K
180	752	706	46
256	792	740	52
360	827	761	66
408	848	775	73
500	893	834	59
628	909	847	62
736	950	888	62

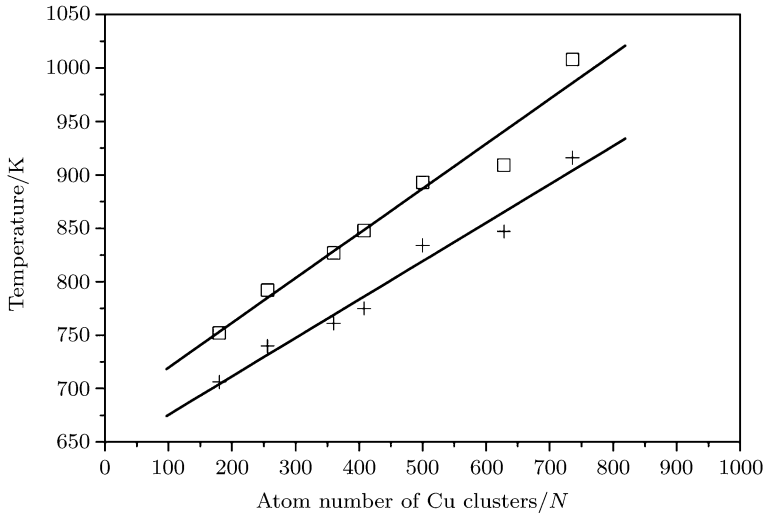


Fig.2. Melting (open squares) and freezing points (pluses) vs Cu cluster size, the solid line is a least square fit to the data.

4.2. Negative heat capacity

In our calculations, all the curves of potential energy vs temperature as shown in Fig.1 have knee points around melting and freezing temperatures. Around these points, as the energy increases (or decreases), the temperature decreases (or increases). The inset of Fig.1 shows that each curve of heat capacity vs temperature has a negative peak, their heat capacities are negative around the phase transition temperature.

It is well accepted that a system will become warmer if energy is added to it. However, negative heat capacities are well known in astrophysics,[29,30] where energy can be added to a star cluster, resulting in its cooling. A similar effect has been investigated for melting atomic clusters.[31,32] In fact, the negative micro-canonical heat capacity in Na_{147} was reported experimentally by Schmidt *et al*[33] near its solid-liquid transition temperature. More recently, negative heat capacities have also been found theoretically for Na_N (N = 135, 142, and 147) clusters around their melting-like transition by micro-canonical MD simulations.[34]

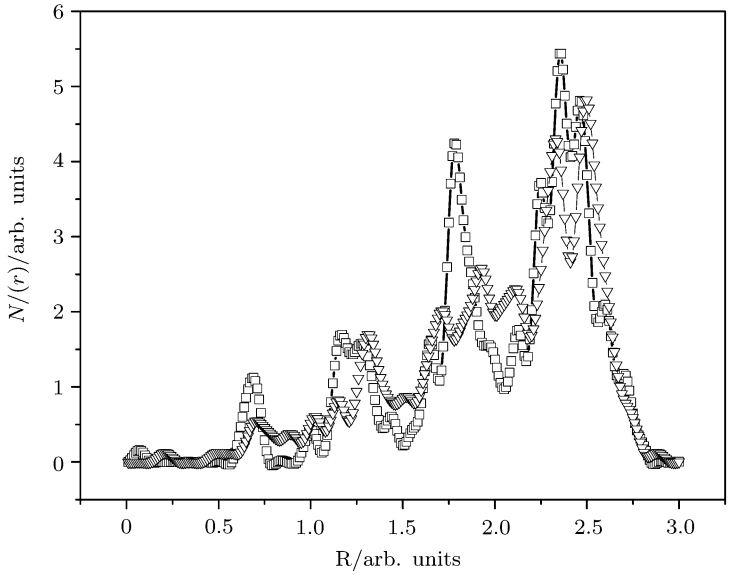


Fig.3. The radial distributions of atoms in the Cu_{360} clusters: open squares are for before-melting (910 K); open triangles for after-melting (827 K).

Schmidt *et al*[33] have considered a nanocluster as a small micro-canonical system, so as to avoid partly molten states. The system prefers to convert some of its kinetic energy into potential energy instead and the cluster probably becomes colder while its total energy gradually increases. To understand the micromechanism of negative heat capacity in our clusters and check Schmidt *et al*'s viewpoint, the atom distribution in the clusters has been studied. Figure 3 is the radial distribution of atoms in the Cu_{360} cluster before and after melting. Some pronounced peaks before melting represent the shell structure (order state) of solid state of the cluster. As the radius increases, the peaks become sharper due to the atom number in the shell increasing from inner to outer. However, the corresponding peaks after melting become lower and wider, some even have disappeared, which implies the disordered structure of liquid state appearing. This abrupt change of the cluster structure at the solid–liquid transition will lead to the potential energy jumping suddenly (or rather, increasing or decreasing). As the increase (or decrease in freezing processes) in total energy ($\pm E_{\rm tot} \sim 1.7023 \times 10^{-17}$ J for Cu_{360}) cannot balance the reduction (or increase in freezing processes) in potential energy ($\pm U \sim 2.9287 \times 10^{-17}$ J for Cu_{360}), the kinetic energy and potential energy are converted into each other, leading to a lower (in melting processes) or higher (in freezing processes) temperature. Consequentially, the negative heat capacity occurs in the clusters.

4.3. Hysteresis effect

As is well known, the melting point and freezing point are at the same temperature for the bulk crystal, but for cluster, it is another story. Hysteresis is observed in melting and freezing circles (in Fig.1). The freezing points are about a few tens of Kelvins lower than the melting points for the same cluster (Fig.2 and Table 1). Hysteresis effect indicates that transforming from ordered (solid phase) to disordered (liquid phase) is easier than from disordered to ordered, obeying the principle of entropy increase for the microcanonical ensemble. It also indicates that the melting point is probably much closer to the bulk thermodynamic transition point than the freezing point. To the best of our knowledge, the hysteresis effect in the melting and freezing circles is reported in a copper cluster system for the first time, while it has been expected theoretically[35] and observed experimentally in the case of lead cluster system.[36]

5. Conclusions

The melting and freezing processes of Cu_N ($N =$ 180, 256, 360, 408, 500, 628 and 736) nanoclusters have been investigated in detail by using the microcanonical molecular dynamics simulation technique. Our results show that the melting and freezing points increase almost linearly with the atom number of copper nanoclusters increasing. All the nanoclusters have negative heat capacities around melting and freezing phase transitions. It could be attributed to the potential energy jumping due to the abrupt change in cluster structure. Hysteresis effects are observed in all the Cu_N nanoclusters for the first time.

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