

Simulations of Metal Cu in Heating Process

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Based on the Finnis-Sinclair (FS) many-body potential model, the melting process of a system, which consists of 500 Cu atoms, controlled by period boundary condition has been simulated. The means of pair correlation function, mean square displacement and Honeycutt-Anderson bonded pair have been used to characterize the melting behavior of Cu at different heating rates. The simulation indicates that melting point of metal Cu is 1444 K during a continuous heating process, and the calculated diffusion constant at the melting point is $4.31 \times 10^{-9} \text{ m}^2/\text{s}$. These results are better than those from the EAM method, showing that the FS potential model works well in some disordered systems.

Keywords FS potential, melting process, metal Cu

Introduction

In order to study the short-range order as well as thermodynamic properties, two distinct techniques of computer simulation, namely, the molecular dynamics and Monte Carlo methods, are most frequently employed. In both techniques, the interaction potential is the primary input for computation. Mitra and co-workers¹ have used a two-body model with Coulombic interactions and a power-law repulsion, fitted to the short-range structure and melting temperature of cristobalite. Three-body forces have been introduced mainly to bring the bond angle distributions into better agreement with the experimental data for the glass.² The effective pair potential was used to study the microstructure of amorphous Cr and Ga metals.³ Chen *et al.*⁴ used an EAM potential to study the structural features of the liquid and solid Al and Cu during rapid solidification. Stillinger and LaViolette⁵ reported local order in quenched states of simple atomic substances. Hsu and Rahman⁶ reported homogeneous nucleation and growth of a fcc crystalline phase with Lennard-Jones (LJ) 12-6 systems. Moutain and Brown⁷ reported an observation of the body-centered-cubic (bcc) structure within an LJ framework. Analyses were made on the size of critical nucleus,⁶ the structural feature of nucleation,⁸ the effects of types of potential used,⁷ the effects of boundary conditions⁶ *etc.* However, the simulated results mentioned above can only be used to demonstrate the temperature effects on the structure-dependent part of the energy. Transition from a liquid to a solid is investigated only by specific-heat or thermodynamics properties, and the process from a solid to a liquid is rather rarely mentioned. It is interesting to study how the local cluster changes when a transition occurs. However, results in

this research field have been insufficient till now. Moreover, a study of the transition from a solid to a liquid using many-body potential is scarcely reported.

In the present study, the computer simulation method and Finnis-Sinclair (FS) many-body potential have been adopted in the heating process of metal Cu. The means of pair correlation function, mean square displacement, and Honeycutt-Anderson bonded pair have been used to characterize the microstructure transfer behavior of Cu at different heating rates.

Interatomic potential and computer simulation

The FS potential⁹ is based on a second-moment approximation to the tight-binding theory¹⁰ incorporating charge conservation.^{11,12} For a pure metal the energy of an atom i can be written as

$$E_i = \frac{1}{2} \sum_j V(R_{ij}) - \left[\sum_j \Phi(R_{ij}) \right]^{1/2} \quad (1)$$

where the first term on the right side of Eq. (1) is the traditional part of pair potential. The second term on the right side is the contribution of the density of electron. i , j are the serial numbers of atom, R_{ij} denotes the distance between atoms. $V(R_{ij})$ expresses the pair potential contribution from j atom to i atom. $\Phi(R_{ij})$ shows the density of electron of j atom at the position of i atom. The function is fitted by Ackland *et al.*¹³ as

$$\Phi(R_{ij}) = \sum_{k=1}^6 A_k H(R_k - R_{ij})(R_k - R_{ij})^3 \quad (2)$$

$$V(R_{ij}) = \sum_{k=1}^6 \alpha_k H(r_k - R_{ij})(r_k - R_{ij})^3 \quad (3)$$

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The effective working range of the potential in Eqs. (2) and (3) is regulated by $H(x)$ function. When $x > 0$, $H(x) = 1$, otherwise $H(x) = 0$. R_k and r_k denote the cutting distance of the pairwise interaction potential and the density of electron respectively, and each parameter comes from Ref. 13.

The simulation in this paper is accomplished in a cubic box with 500 Cu atoms, which subjects to periodic boundary conditions to become pseudo infinite. We force the system to change uniformly by the Andersen constant pressure method.¹⁴ First these particles are put randomly into the box, whose velocities are initialized randomly according to the Maxwell-Boltzman velocity distribution at 300 K. Then a constant temperature process with a time step of 5×10^{-15} s is executed. At this temperature, the system is run for 8000 time steps to obtain a stable solid state. Then the damped force method is adopted to increase the temperature with heating rates of 4×10^{12} , 8×10^{11} and 4×10^{11} K/s respectively by forcing the bath temperature to increase linearly at every time step until 1900 K. The configurations are recorded at particular temperatures during the heating. For each of the recorded configurations, another run of 8000 time steps at the given temperature is performed in order to determine the thermodynamic quantities. During each of these runs, 20 configurations are saved, one at each 400 time steps.

Method of structural analysis

In this paper, the pair correlation function (PCF)¹⁵ is applied to detect the structural evolution in a melt. If some new structure occurs, the PCF shows relevant changes.

To analyze the local atomic structural changes accompanying melting, a common technique used in Ref. 16 was adopted. In this technique, two atoms are said to be near neighbors if they are within a specified cutoff distance of each other. A set of four indices is given under the following criterion: 1) The first index denotes which peak of the PCF belongs to the pair under consideration; 2) the second one counts the number of common nearest-neighbors of that pair; 3) the third one specifies the number of particles denoted by the second one; 4) a fourth one is sometimes necessary to distinguish configurations having the same first three indices, yet different topology. Different types of bond pairs are associated with different types of local order. It is necessary to point out that the number of 1551, 1541 and 1431 bonded pairs in a liquid is a direct measurement of the degree of icosahedral order. The 1421 bonded pair is the characteristic bonded pair for the fcc crystal structure. The 1661 and 1441 bonded pairs are the characteristic bonded pairs in the bcc crystal structure. The 1422 bonded pairs are the characteristic bonded pairs for the hcp crystal structure.

An additional strategy involves monitoring the mean square displacement (MSD) of atoms from their initial positions. The displacement MSD is given by¹⁷

$$\text{MSD} = \frac{1}{N} \left\langle \sum_{i=1}^N |\vec{r}_i(t) - \vec{r}_i(0)|^2 \right\rangle \quad (4)$$

where t is the physical time in the simulation; N is the number of particles; $\vec{r}_i(0)$ is the position vector of the i th particle for the system in its initial configuration and $\vec{r}_i(t)$ is the position vector of the i th particle at time t .

According to the Einstein diffusion law, MSD vs. time denotes the diffusion behaviour of metal atoms at liquid state. And it can be written as

$$\lim_{t \rightarrow \infty} \text{MSD} = c + 6Dt \quad (5)$$

where c is constant, D is diffusion constant. A nonzero value of D is suggestive of a liquid. It is a necessary but sufficient criterion for liquid like behavior.

Results and discussion

The $g(r)$ of Cu at a heating rate of 8×10^{11} K/s is shown in Figure 1. It is obvious that the first peak of $g(r)$ becomes lower and lower in magnitude accompanied by a gradually broadening in width with increasing temperature, which means that the number of first near neighbor of each atom is reduced and the probability of bonding between nearest atoms is also reduced. At the same time, the reduced and tardigrade trends of the second peaks of PCF are rather evident. All above denote that the long range order of metal Cu system is weakened and the short range disorder is strengthened with increasing temperature.

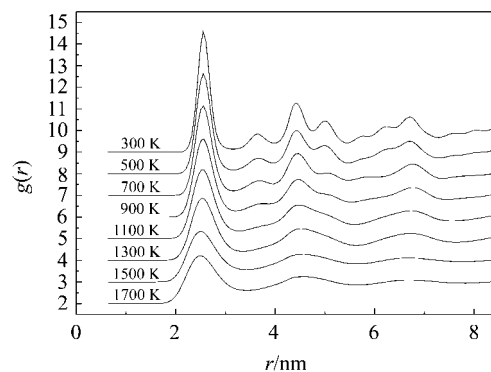


Figure 1 The pair correlation function at a heating rate of 8×10^{11} K/s.

Figure 2 shows the relationship between volume and temperature in the heating process. It can be seen that the variation of volume on temperature is rather weak below 1000 K, and the volume increases tardily in the range of 1000 to 1440 K. After this stage, the volume increases steeply with temperature.

The relationship between internal energy, volume and temperature at the heating rate of 8×10^{11} K/s is shown in Figure 3. From this graph, we can know that both the internal energy and volume increase rather

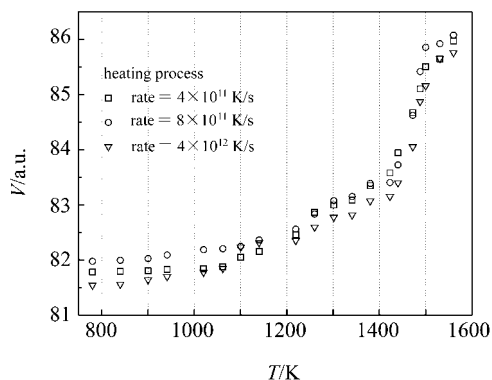


Figure 2 Volume vs. temperature in the heating process.

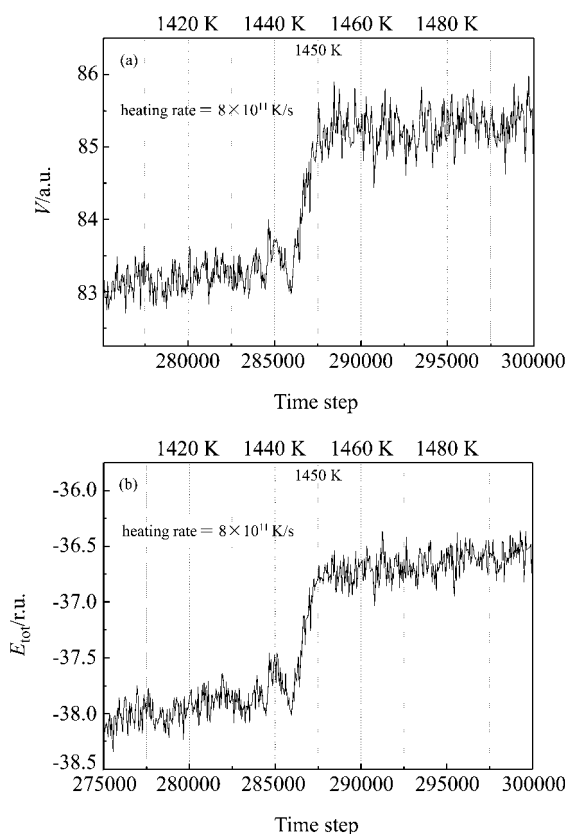


Figure 3 Volume vs. time (a) and energy vs. time step (b)

rapidly and steeply, which lasts about 1000 time steps, after undergoing about 1200 time steps from 1440 K. It can be seen from Figure 4(a) that the diffusion constant is almost zero in all conditions below 1300 K, but it increases rapidly in the range of 1300 to 1500 K. It means that the system is in solid state under 1300 K during heating, and a solid-liquid phase transfer occurs in the range of 1300 to 1500 K. The melting point is determined in Figure 4(b). We can easily know that the MSD is nearly zero before the 262500th time step ($T=1350$ K), which means there is no liquid phase in this system, and it is in its solid state. Although MSD increases from the 262500th to 286200th time step ($T=1350$ – 1444 K), it is still in solid state from the very small slope. MSD increases rapidly after the 286200th time step ($T=1444$ K). The diffusion constant estimated from the slope is $4.31 \times 10^{-9} \text{ m}^2/\text{s}$, and this value ap-

proaches to the experimental value ($3.97 \times 10^{-9} \text{ m}^2/\text{s}$)¹⁸ at the melting point of Cu, thus the melt temperature is determined to be 1444 K. We notice that this result approaches to the experimental value 1360 K. The relative error is merely 5.8%. Considering the limited particles number, an approximate interatomic potential used and so on, it is common that there is certain disagreement between simulation and experiment.^{19,20} However compared with the result²¹ from the simulation using the EAM potential (Table 1), the diffusion constant and melt temperature of this simulation is evidently better. It is suggested that some complicated disordered systems can be simulated by using the FS interatomic potential.

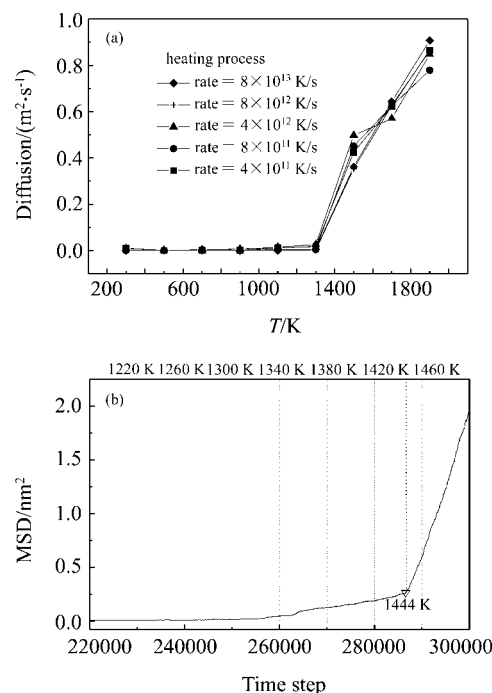
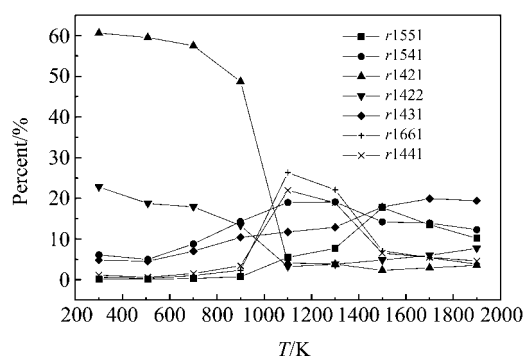


Figure 4 The fluidity of the simulation system in heating process. (a) The trend line of the diffusion constant; (b) the MSD at the heating rate of 8×10^{11} K/s.

Figure 5 illustrates the various types of bonded pairs for several temperatures at the heating rate of 8×10^{11} K/s. The results tell that the relative number of 1421 and 1422 bonded pairs relating to fcc and hcp structure respectively has the same characteristic in variation. First, they decrease slowly with temperature from the initial temperature, and then show a small numerical change after a rather rapid decrease stage from 900 to 1100 K. The numbers of 1551 and 1541 bonded pairs corresponding to icosahedral order increase standing as the temperature rises, moreover, a large number of 1431 clusters can be found in liquid. At a high temperature the three types of clusters amount to *ca.* 50% of all kinds of clusters. The 1551, 1541 and 1431 clusters are the main structure in liquid system. There is almost no change in relative number of 1661 and 1441 bonded pairs closely corresponding to bcc structure below 900 K, and then they have two absolute contrary changes

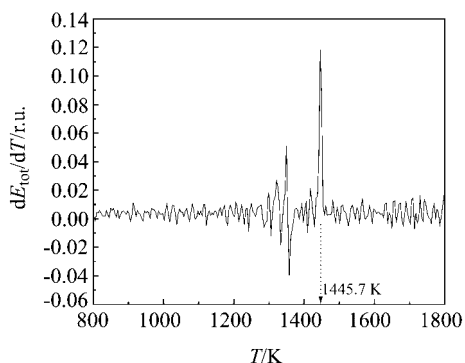
Table 1 The comparison among the experimental values and those from simulations using FS potential and EAM potential respectively

	Calculated value from FS potential (this paper)			Calculated value from EAM (Ref. 21)	Experimental value
	Heating rate as 4×10^{12} K/s	Heating rate as 8×10^{11} K/s	Heating rate as 4×10^{11} K/s		
Melt temperature T/K	1475	1444	1430	1520	1360
Diffusion constant $D/(m^2 \cdot s^{-1})$	4.55×10^{-9}	4.31×10^{-9}	4.3×10^{-9}	5×10^{-9}	3.97×10^{-9}

**Figure 5** The percent of the bonded pairs vs. temperature at the heating rate of 8×10^{11} K/s.

from 900 to 1500 K. They increase rather rapidly until 1100 K, and then decrease extraordinarily rapidly. After 1500 K, the rate of decreasing is slowed down, and the value approaches zero at the end of heating process. It is shown that there is the change trend to bcc structure near the melting point in the heating process of Cu. It is remarkable that there is an exchange in the numbers of bonded pairs in the range of 1300 to 1500 K. At this stage, icosahedral structure (1551, 1541 and 1431 clusters) occupies predominance rapidly. By contrast, the ratio of crystal (1661, 1441, 1421 and 1422 clusters) decreases quickly, and finally their values are almost zero at the end of this simulation. Thus the melting point is within the temperature range of 1300 to 1500 K.

Figure 3 also tells us that the system trends to stabilization at the melting stage after *ca.* 1000 time steps. Figure 6 shows the variation of the grade of the average

**Figure 6** The variation of the grade energy vs. temperature at the heating rate of 8×10^{11} K/s.

internal energy as a function of temperature for determining the most exquisite change point, which is at 1445.7 K.

Conclusions

The results of simulations show that the melting point of Cu is 1444 K, at which the corresponding diffusion constant is 4.31×10^{-9} m²/s. It is a better outcome compared with the results from the methods of other potentials. It is shown that FS potential can work well in some disordered systems like liquid Cu.

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