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Melting of free copper clusters

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Abstract

Extensive molecular-dynamics simulations of melting processes of copper clusters, Cu_{55} , Cu_{147} and Cu_{309} with closed-shell icosahedral structure, were performed using an environment-dependent classical tight-binding potential. The results reveal that the cluster may transit completely from pure solid to pure liquid phase with temperature via a dynamics-coexistence (DC) process, depending upon the latent heat and vibrational entropy. In the DC regime, no other than the first-order solid–liquid phase transition with time is related to the specific structure of the cluster.

1. Introduction

A detailed knowledge of the melting process of the clusters is essential to understand their special properties and applications. Various investigations in the past decades experimentally and theoretically have revealed that a few very different processes are responsible for the melting of the clusters [1–8]. Generally, the melting temperature decreases with the reduction of the cluster size (Borel [1]) while recent experiments have displayed that this temperature for a small tin cluster is pronouncedly above that for bulk (Shvartsburg and Jarrold [1]). Other main findings include, for example, broadening of the melting transition [2], the so-called premelting stage [3] and a solid-to-solid structural transformation precursor to the melting transition [4]. For larger clusters, a ‘conventional’ equilibrium phase may be established, i.e. the equilibrium states of the cluster consist of coexisting solid and liquid fractions at all times [6]. In particular, Berry has investigated theoretically the melting of some rare-gas clusters and found the ‘dynamics coexistence’ (DC) states in the vicinity of melting, where the cluster fluctuates in time between solid and liquid phases [5]. However, it is not clear to what extent the DC process dominates the melting of the cluster.

Several groups have been devoted to the structural properties of copper clusters. An analytic expression for the melting temperature as a function of cluster size was deduced from earlier molecular dynamics simulations [7]. Later the structures and melting of 13- and 14-atom Cu (Garcia-Rodeja *et al* [3]) and Cu–Au bimetallic clusters (Lopez *et al* [3]) were studied carefully and it was found that the Cu–Au bimetallic clusters melt respectively in the same way as the corresponding pure Cu clusters. The melting scenario described here for copper nanoclusters suggests that the dynamics coexistence (DC) process cannot be limited only to

small rare-gas clusters, but extends to medium-size metal clusters, depending on the latent heat and vibrational entropy. The solid–liquid phase transition with time at the DC regime is very sharp and may thus be identified as a first-order one while the transition from pure solid to pure liquid phase with temperature is broadened pronouncedly.

2. Model

The realistic interaction potential is essential to simulate accurately the motions of atoms in the materials. In the past decades classical many-body interaction potentials (e.g. embedded-atom potential (EAM), effective-medium theory (EMT) and the second moment approximation of the tight-binding scheme (TB-SMA)) have been playing an important role and achieving vast success in the studies of materials, but they suffer from one drawback: that their parameters are generally obtained from bulk properties of materials and do not incorporate the charge transfer effect, which is important for clusters and surfaces. Some investigations have shown that these empirical potentials usually underestimate surface energy [9] and may not be able to accurately predict the binding properties of the clusters [10]. In the present MD simulations we modified empirically TB-SMA [10] to make it dependent on local environment and the atomic interaction range is extended up to the fifth neighbours. The parameters were obtained by fitting the $T = 0$ lattice constant, the cohesive energy, the elastic constant of bulk copper crystal, the binding energy and the bond length of the copper dimer. It reproduces well the vacancy formation energy, surface energy, surface relaxation and temperature-dependent mean squared displacement as well as the melting temperature of bulk copper crystal compared with experiments, as detailed elsewhere¹. Similar to [12], the environment-dependent TB-SMA potential predicts that icosahedral structure dominates the small clusters and the closed-shell ones are Cu₁₃, Cu₅₅, Cu₁₄₇, Cu₃₀₉ and so on at 0 K.

In this paper, we report the results of extensive simulations of the melting processes of three clusters: Cu₅₅, Cu₁₄₇ and Cu₃₀₉. The simulations were performed by starting with the optimal structure: a closed-shell icosahedron at $T = 0$ K, then incrementing gradually the temperature, and running the cluster at each temperature for long periods (about 20 ns; the integration time step is 2×10^{-15} s). At each temperature, the linear and angular momenta were eliminated. A damping force μv , where v is the velocity of an atom and the factor μ is determined by the electron–phonon characteristic coupling time and temperature, was imposed on the Newton motion equation so as to model an isothermal system [13]. In calculation of the properties of the cluster, the first 2 ns of the simulations at each temperature was excluded.

The atomic diffusion coefficient D is calculated by

$$D = \left\langle \frac{[R_i(t + \Delta t) - R_i(t)]^2}{6\Delta t} \right\rangle$$

where R_i is the vector position of atom i from the cluster centre of mass; $\langle \quad \rangle$ means averaging over time and atoms.

3. Results and discussions

In this section, we focus mainly on Cu₁₄₇ to explore in detail the melting processes of the clusters. We present first the temperature evolution of the cluster and then turn to a careful

¹ H Lei unpublished. Simply, after modification, the cohesive energy E_c of an atom is a function of the distance r between it and another atom and of the number of the L th neighbours $Z(L, r)$. The influence of $Z(L, r)$ on E_c depends further on r and L . In our present case, the interaction distance is extended up to the fifth neighbour and L thus ranges from 1 to 5. Especially, the melting temperature of bulk copper crystal from the modified potential (1385 K) is in good agreement with the experimental one (1356 K).

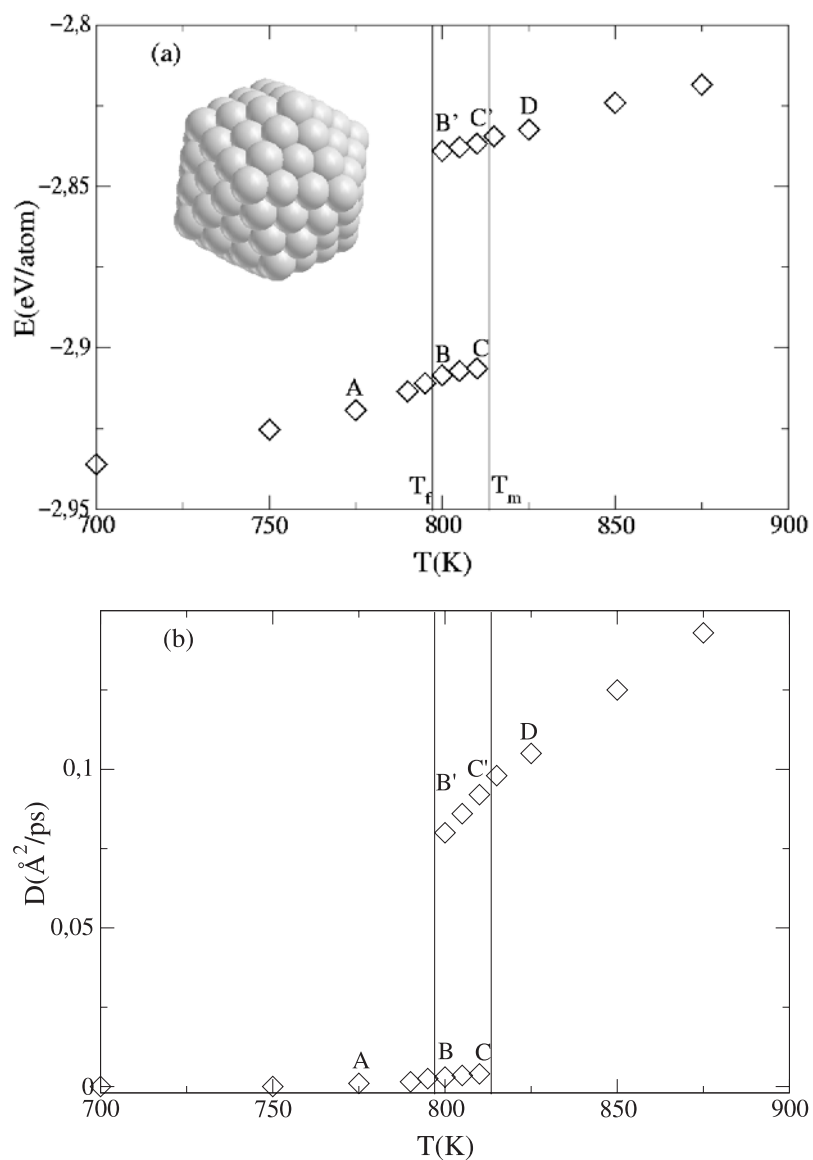


Figure 1. (a) The internal energy E and (b) diffusion coefficient D as a function of temperature. Inset of (a): the atomic configuration of the closed-shell icosahedral Cu₁₄₇ at 0 K, in which one atom locates at the centre of mass and the shells from the centre to outside are the first shell with 12 atoms, the second one with 42 atoms and third shell with 92 atoms ($T_f \approx 795$ K and $T_m \approx 815$ K).

analysis of the cluster structures during melting.

The caloric curve, as shown in figure 1(a), exhibits that (i) internal energy rises linearly with temperature at $T < T_f$; (ii) there are two very different internal energies observed at each temperature of $T_f < T < T_m$, which implies a drastic structural change may be likely to occur; (iii) at $T > T_m$, internal energy rises monotonically with temperature with higher slope than at $T < T_f$, i.e. an increase of heat capacity $C = \partial E / \partial T$, resulting from structural relaxation driven by vibrational and configurational entropy [14]. The characteristics of the

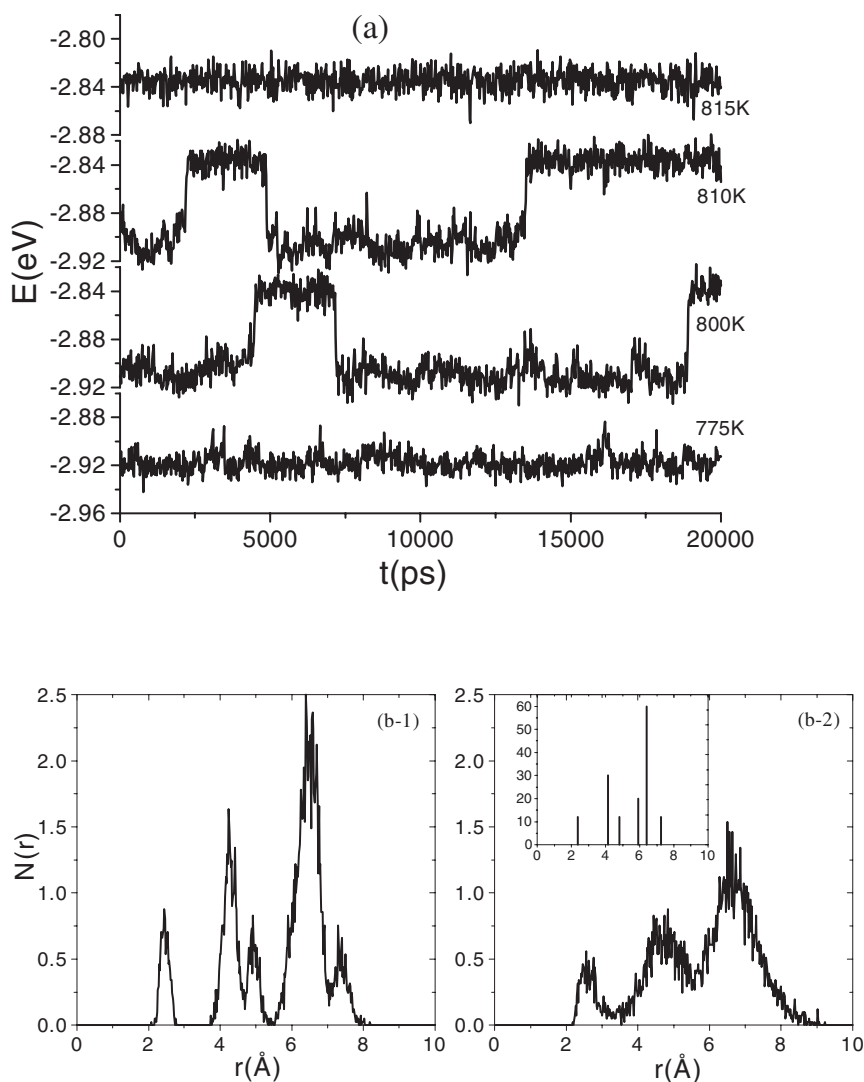


Figure 2. (a) The internal energy evolves with time at four typical temperatures, starting from the same initial configurations. (b) One example: radial distribution function (RDF), plotted as the number of atoms ($N(r)$) versus distance from the cluster centre of mass, in the time range with low energy (-2.906 eV/atom) (b-1) and with high energy (-2.840 eV/atom) (b-2) at 800 K. (b-1) shows that Cu_{147} is in the solid state and (b-2) signifies it is in the liquid state. In the inset of (b-2) we show the RDF of Cu_{147} at 0 K, where from left to right the first peak corresponds to the first shell, the second and third peaks to the second shell, and the fourth to sixth peaks to the third shell.

caloric curve correlate with one of the calculated diffusion coefficients (figure 1(b)). It can be observed that the diffusion coefficients are rather small from the points marked A–C relative to those from B'–D. Additional examinations of shell-by-shell diffusion coefficients and radial distribution functions (RDFs) signify that Cu_{147} is completely in the solid phase at $T < T_f$ and completely in the liquid phase at $T > T_m$.

To further explore the melting of Cu_{147} , the internal energy of Cu_{147} as a function of

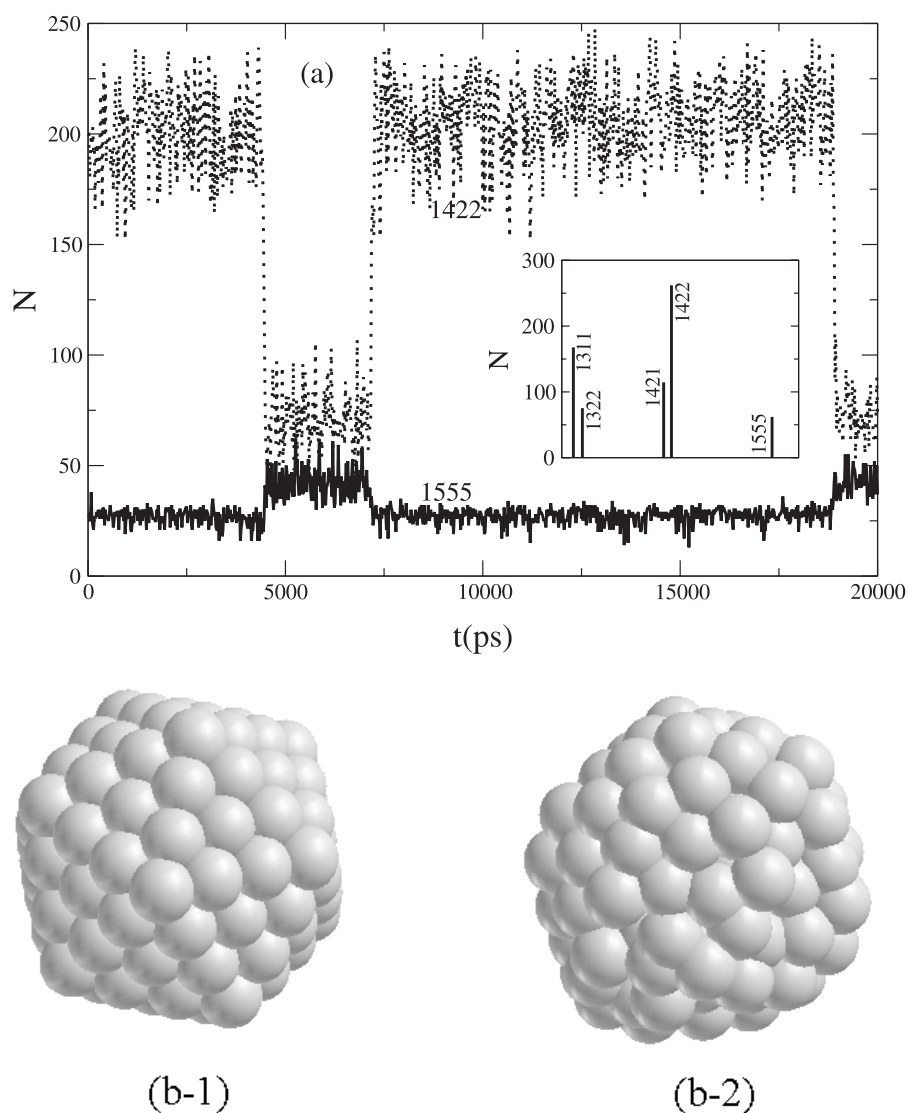


Figure 3. (a) Time evolution of the two typical CNA signatures of Cu_{147} at 800 K. For comparison, the CNA signatures at 0K are shown in the inset. (b) The configurations of Cu_{147} at the stage of low-energy solid (b-1) and of high-energy liquid phases (b-2) at 800 K.

evolution time at four typical temperatures is displayed in figure 2(a). At 775 K (Cu_{147} is completely of the solid phase) or 815 K (Cu_{147} is completely of the liquid phase), internal energy fluctuates only around some value (-2.92 eV/atom at 775 K and -2.84 eV/atom at 815 K) with time. However, at 800 K or 810 K, it is two very different internal energies which can transform into each other in time. RDF in figure 2(b-1), corresponding to the low-energy state, shows an elaborate series of well defined peaks to suggest that the cluster be in the solid phase with rather low atomic diffusion in the cluster while these typical peaks merge into a continuum, which is characteristic of liquid (figure 2(b-2)) to result in a large diffusion coefficient (figure 1(b)) during the time with high internal energy. Based on the facts, we

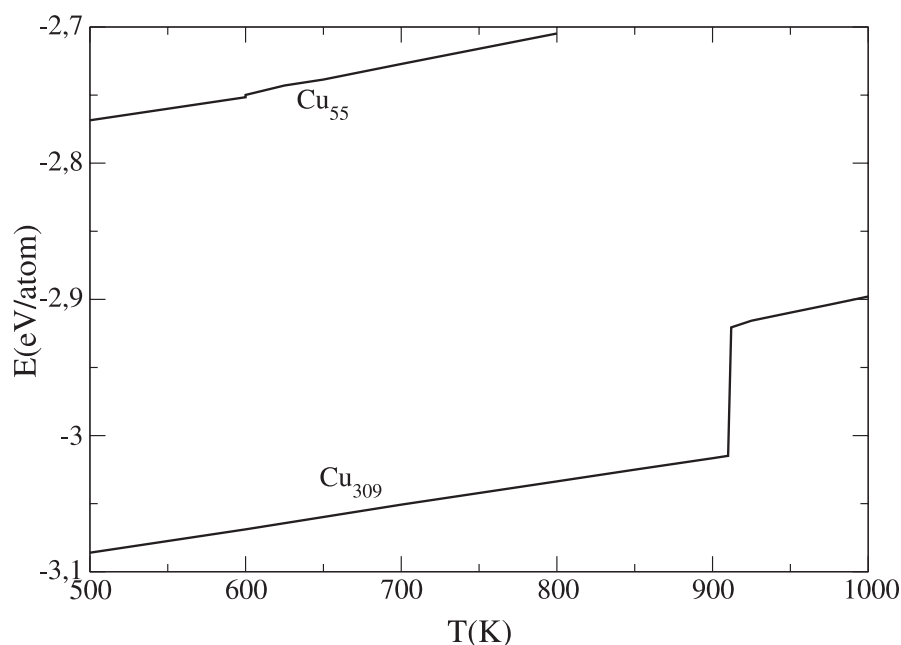


Figure 4. The caloric curve of Cu_{55} and Cu_{309} . Apparently, there is no energy fluctuation at any temperature and the latent heat is close to zero for Cu_{55} and 85 meV for Cu_{309} .

can now be sure that at $T_f < T < T_m$ the cluster fluctuates in time between solid and liquid phases, i.e. DC. It can be determined from figure 2(b-2) that the liquid phase is enhanced with increasing temperature, for the state with high internal energy at 810 K lasts a longer time than at 800 K within the simulation time. Apparently, at the DC regime low internal energy E (or high E) changes sharply to high E (or low E) to imply the first-order solid–liquid phase transition with time at each temperature.

In order to facilitate the analysis of the structures of Cu_{147} during melting, the local atomic order is examined by common neighbour analysis (CNA) [4]. A closed-shell icosahedral cluster always contains five CNA signatures: 1311, 1322, 1421, 1422 and 1555 (see the inset in figure 3(a)). The signatures as a function of time were recorded at each temperature, of which two, 1422 and 1555, are displayed in figure 3(a). The time is consistent with figure 2(a). It may be found that the signatures, when the cluster is in the low-energy solid phase, have no significant vibration and almost the same weight as at 0 K, indicating that no structural transformation occurs at this stage. This can be confirmed by figure 2(b-1), where the three-shell sequence can still be well formed while the characteristic peaks are broadened and even partially obliterated (compare with the inset in figure 2(b-2)) which originates from enhanced thermal vibration since we note that atomic diffusion in each shell is rather low. However, when the cluster transits from solid to liquid phases, the significant changes of the amplitudes of the signatures state that the originally structural order could be obliterated. After some time when the cluster transits from liquid to solid phases, the amplitudes of the signatures and thus the cluster reverts to its original icosahedral form.

The single first-order solid–liquid phase transition with time at the DC regime is related to the specific structure of Cu_{147} , a closed-shell icosahedron, where only (111) facets are present. Previous investigations elucidated that (111) has a lower surface free energy than the

liquid surface [15]. As a result, the clusters with non-icosahedral structures such as truncated octahedra tend to transform to icosahedra prior to melting [4]; and the surface premelting for the closed-shell icosahedral cluster is impossible to observe, as in the present case. Indeed, detailed analysis of configurations of the cluster (figure 3(b)) and of shell-by-shell diffusion coefficients indicates that at the stage of the low-energy solid phase Cu_{147} always contains well defined surfaces as at 0K while the optimized structure would be thoroughly lost in the high-energy liquid phase (see figure 2(b) and compare figure 3(b) with the inset in figure 1(a)). Our result cannot hence support the existence of a surface-melting phase [5].

In the same way, the melting processes of the other two closed-shell icosahedral clusters, Cu_{55} and Cu_{309} have been simulated and the caloric curves are presented in figure 4. In contrast to Cu_{147} , the internal energies of the two clusters do not fluctuate at any temperature and the latent heat of Cu_{55} is close to zero and of Cu_{309} is 85 meV. Examinations of the evolution of the structural characteristics of the cluster with temperature and time explore that the two clusters can transit sharply from solid to liquid phases with temperature showing no indication of dynamic coexistence fluctuations. The melting temperature is 600 K for Cu_{55} and 910 K for Cu_{309} . Whether the DC process occurs or not relies on the two sufficient conditions. As conventional-coexistence phases, the solid and liquid phases should have almost the same minimum free energy in the cluster $F = E - TS$ at the DC regime. Higher internal energy (negative) must thus be balanced by larger vibrational entropy (positive). Generally, atoms in the liquid phase take on higher disorder than in the solid phase and thus larger vibrational entropy. Therefore, if the latent heat or the internal energy difference between solid and liquid phases at melting temperature is zero as Cu_{55} or too large as Cu_{309} to be compensated by vibrational entropy, the DC process would not take place. The other sufficient condition for the DC process is that the free energy must not vary monotonically, but smoothly and spinodally with solid-liquid phase ratio, as was suggested in [5].

4. Summary

In this paper, we have applied an environment-dependent TB-SMA potential to investigate the melting of the three clusters, Cu_{55} , Cu_{147} and Cu_{309} , with specific structures, closed-shell icosahedra. The results show that the medium-size metal cluster, Cu_{147} , undergoes a dynamics-coexistence (DC) phase before it transits completely from pure solid to pure liquid phase. At the DC regime, there is no other structural transformation than the first-order solid-liquid transition with time. The DC process does not always dominate melting of icosahedral clusters, depending on such conditions as the latent heat and vibrational entropy.

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