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# Molecular dynamical simulation of the structural and melting properties of $Al_{196}$ cluster

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**Abstract.** Based on the Gupta-type semi-empirical inter-atomic many-body potential, the melting behaviors of the $Al_{196}$ cluster are systematically studied by using the molecular dynamics method combined with the annealing and quenching techniques. Our simulation results show that from different initial structures one can observe quite different melting behaviors. From a relatively low-energy stable geometry, two peaks occur clearly in the heat capacity curve; But only one peak dominates the heat capacity curve if starting from the ground-state or its closer low energy structures. Reasons of the different melting properties of the $Al_{196}$ cluster are explored by analyzing the energy distributions of the simulated quenching structures of $Al_{196}$ at different temperatures.

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**Key words**: Gupta potential, cluster, molecular dynamics, melting

## 1 Introduction

Clusters are aggregates composed of several to thousands of atoms (molecules) bonding in certain physical or chemical forces, that exist stably in microscopic state [1]. It has been aroused a great interest, just because of its unique physical and chemical properties and potential applications in many fields such as the new material physics, the nano-electronics and the nano-catalyst [2-14]. It has already become a new and significantly important field to study the formation, structures, properties and evolution behaviors of clusters. The melting behaviors of clusters are completely different from that of the bulk materials, and the melting points of clusters usually decrease with decreasing the cluster size, and moreover, there are apparent premelting temperature intervals of clusters. For the small clusters their melting behaviors are accompanied by obvious size effects.

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For example, the experimental study of the melting behaviors of simple monovalent Na clusters [11] show that the melting points of clusters change nonmonotonously (oscillatorily) of the clusters containing less than 200 atoms, and the negative heat capacity has been observed for $Na_{147}$ cluster [12]. Some exotic behaviors are also observed, for example, for the simple trivalent Ga clusters in a small size regime, the melting temperatures are observed to be higher than the bulk melting point [13-14]. The preeminent heat conductivity and malleability of trivalent aluminum crystal have brought extensive applications in social practice, and the study of aluminum clusters has also revealed a series of singular behaviors. For example, the ferromagnetic properties of extremely small aluminum cluster [15], and the super-stability of $Al_{13}^{-}$ cluster which can provide a great potential as being cluster-assembled materials [16], and the good performance in catalyst [17]. Recently, Jarrold and co-workers have conducted plenty of experiments on the melting properties of small and medium-sized $Al_n$ ($n<200$) cluster and observed generally irregular phenomenon on the heat capacity curves of small-sized $Al_n$ ($n<100$) clusters [18] (if the heat capacity curve has no clear peak, then considered irregular). Moreover, a double-peak feature in heat capacity has been clearly observed for some larger-sized $Al_n$ ($n>100$) clusters, and the authors also conjectured the reason of the double-peak [19], but still lack of specific dynamic description at atomic level (like molecular dynamics simulation study).

In this paper, by using the molecular dynamics method based on the semi-empirical Gupta interatomic potential combined with the molecular dynamics simulated annealing and quenching techniques, the melting behaviors of $Al_n$ cluster are systematically studied, and the origin and reason of different melting behaviors of $Al_n$ cluster are also analyzed in detail by the potential energy distributions at different temperatures.

## 2 Computational methods

### 2.1 Potential function

The interaction between atoms, which is depicted by the potential function, is the fundamental to determine the dynamic behaviors of clusters. In this letter, the interaction between atoms of Al clusters are described by using the semi-empirical many body Gupta potential based on the embedded-atom potential and tight-binding model of the second moment approximation, in which the potential parameters are obtained from fitting the relevant physical parameters of crystal (cohesive energy, lattice constant and elastic moduli, etc ). Moreover, this kind of many body potential has been extensively used to study the geometries [20-21] and dynamic behaviors [22] of the metal and alloy clusters. Gupta potential can be written as the sum of a Born-Mayer type repulsive part and a many-body attractive part, as shown below:

$$V=\sum_i\Big(\sum_{j(\neq i)} A\exp[-p(\frac{r_{ij}}{r_0}-1)]-\sqrt{\sum_{j(\neq i)} B^2\exp[-2q(\frac{r_{ij}}{r_0}-1)]}\Big) \tag{1}$$

where $r_0$ is the nearest-neighbor distance of crystal, and $r_{ij}$ is the distance between the $i$th and $j$th atoms. $A$ is the index to measure the interatomic repulsive strength, and $B$ is a effective jump integral only related to the category of atoms. In this paper, the parameters of Gupta potential of Al clusters are $A$=0.1221 eV, $B$=1.316 eV, $p$=8.612, $q$=2.516 and $r_0$=2.86Å, respectively [23].

## 2.2 Molecular dynamics

In this paper, we applied the constant temperature molecular dynamics (MD) method. The Berendsen thermostat is used to control the temperature[24]. The velocity Verlet algorithm is used to integrate Newtonian equation of motion, and the time step of integration is 1fs. Started from different stable structures (Such stable structures can be obtained from either the MD annealing or the MD quenching method) several simulations of the melting processes of $Al_{196}$ cluster are performed. The specific procedures are as follows:

(1) (a) The initial stable structure of a Al cluster is obtained by applying the molecular dynamics simulated annealing method with specific steps as follows: Firstly, for any chosen initial stable structure (for example, this can be achieved by using the stochastic method combined with the steepest descent method), it is heated directly to 1200K (ensure the cluster is in liquid-state). Secondly, the temperature of the cluster is decreased slowly through applying molecular dynamics simulated annealing method, and the final temperature is 200K (ensure the cluster is in the solid-state). The temperature interval is taken to be 20K in the cooling process. Total of $1\times10^6$ MD steps are propagated at each temperature point. For the final structure at 200 K, it is relaxed to a stable structure by using the steepest descent method. (b) Started from the initial stable structure obtained above by MD annealing method, the cluster is heated from 200 K to 1200 K by carrying out the MD simulation with the temperature interval of 20 K, and $5\times10^6$ MD steps are propagated at each temperature point. (c) With accompanying the MD heating process the MD simulated quenching process is carried out with concrete steps as follows: One Al cluster geometry is preserved every $5\times10^5$ MD steps at each temperature (so 10 cluster structures obtained at each temperature point), and then quenching all structures obtained at each temperature to the stable states (that means each original structure will be relaxed to its near stable state on the potential energy surface). Finally, keep all simulated quenching structures and their energies (Thus, the potential energy distributions of all simulated quenching structures can be obtained) and mark the lowest energy one of them.

(2) Starting from the (above) lowest-energy quenching structure, a heating-up process is carried out by MD simulation. Along with the MD warming process the MD simulated quenching process is performed with same steps as the above (1) process, and also identify and mark the lowest-energy quenching structure during this quenching process.

(3) Compare the energy of the initial structure (the lowest-energy quenching structure in the process before the last quenching one) of the above process with that of the lowest-energy quenching structure obtained in the same process, if the two values are

different (that means the latter is lower than the former), then a new MD heating-up and quenching process will be carried out until same values are obtained.

### 2.3 Calculation of physical quantity

As to every molecular dynamics simulation, the heat capacity of cluster will be calculated at each temperature, and the energies of all quenching structures will be recorded at different temperatures. The heat capacity per atom of a cluster can be calculated from the equation:

$$C_v = \frac{< E_t^2 >_T - < E_t >_T^2}{2NK_bT^2} \tag{2}$$

Where $E_t$ is total energy of the cluster, $K_b$ is the Boltzmann constant, $T$ is the temperature, and $<>_T$ denotes ensemble average.

## 3 Results and discussion

### 3.1 Low-energy geometries of $Al_{196}$ cluster

Three different MD processes are performed to investigate the melting properties of $Al_{196}$ cluster. The initial stable structures of the three different MD processes are given in Fig. 1(a), (b) and (c), respectively, where the above figures are top-views and the below ones are side-views. Fig. 1(a) gives the initial stable structure of $Al_{196}$ cluster obtained by using the simulated annealing method in the first MD simulation process. This is a structure in disorder overall (partially in order); Fig. 1(b) is the lowest-energy one of all those quenching structures in the first MD process, and it is also the initial structure of the second MD process. Fig. 1(b) gives an ordered structure totally, and if neglecting the deep-colored (black) atoms in Fig. 1(b), the residual structure will be a high-ordered pentagonal prism containing 147 atoms (with the $D_{5h}$ symmetry). Started from the structure shown in Fig. 1(b), with carrying out the process of MD heating-up and quenching, the lowest-energy quenching structure can be obtained as shown in Fig. 1(c) (it is also the initial structure of the third MD process). The two structures shown in Fig. 1(b) and (c) are quite similar, with the only difference of one atomic position (the only one different black atom shown in Fig. 1(b) and (c) ). As compared with the geometry shown in Fig. 1(b), the structure in Fig. 1(c) is in higher order.

### 3.2 Melting behavior of $Al_{196}$ cluster

By applying the MD simulated quenching method stated above, the potential energy distributions of the quenching structures of $Al_{196}$ cluster at different temperature can be obtained, and we can describe the structural evolution behaviors in potential energy surface of $Al_{196}$ cluster in further, and so as to explore the characteristics of the structural evolution at different temperatures in the process of cluster melting.

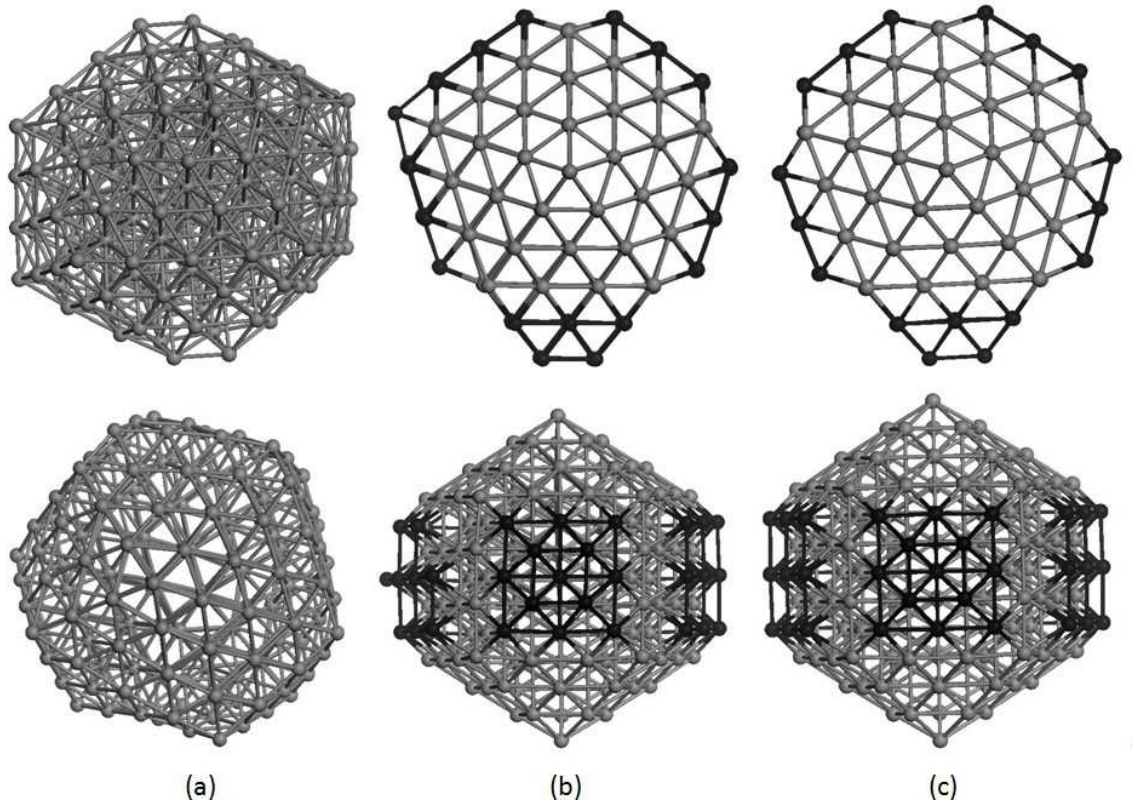


Figure 1: Low energy structures of $Al_{196}$ clusters, correspond to the initial geometries in different MD processes

Fig. 2(a), (b) and (c) give the heat capacity curves ($C_v$) and the potential energy distributions of the quenching structures at different temperatures in the three MD processes started from different initial structures stated above (as shown in Fig. 1(a)∼(c)). The initial stable structure of the first MD heating-up process (corresponding to Fig. 2(a)) is obtained by the MD annealing simulation (as shown in Fig. 1(a) with the potential energy of -595.89 eV), and the heat capacity curve shows a double-peak phenomenon clearly (there is a sharp decrease at about 540 K in the heat capacity curve) in this MD process, and from the potential energy distributions of the quenching structures one can also find that the quenching structures change abruptly at near 540 K, from a relatively high-energy overall-disorder quenching structure (shown in Fig. 1(a)) to an overall-ordered low-energy quenching structure (as shown in Fig. 1(b) with the potential energy of -596.42 eV). That means at that temperature structures of $Al_{196}$ cluster change clearly in the potential energy surface, and correspondingly the total energy of the system also changes clearly, and that is just the main reason of the abrupt decrease (the double-peak) in heat capacity curve at 540K. Fig. 2(b) shows the heat capacity curve and the potential energy distributions of the quenching structures in the MD heating-up processes started from the

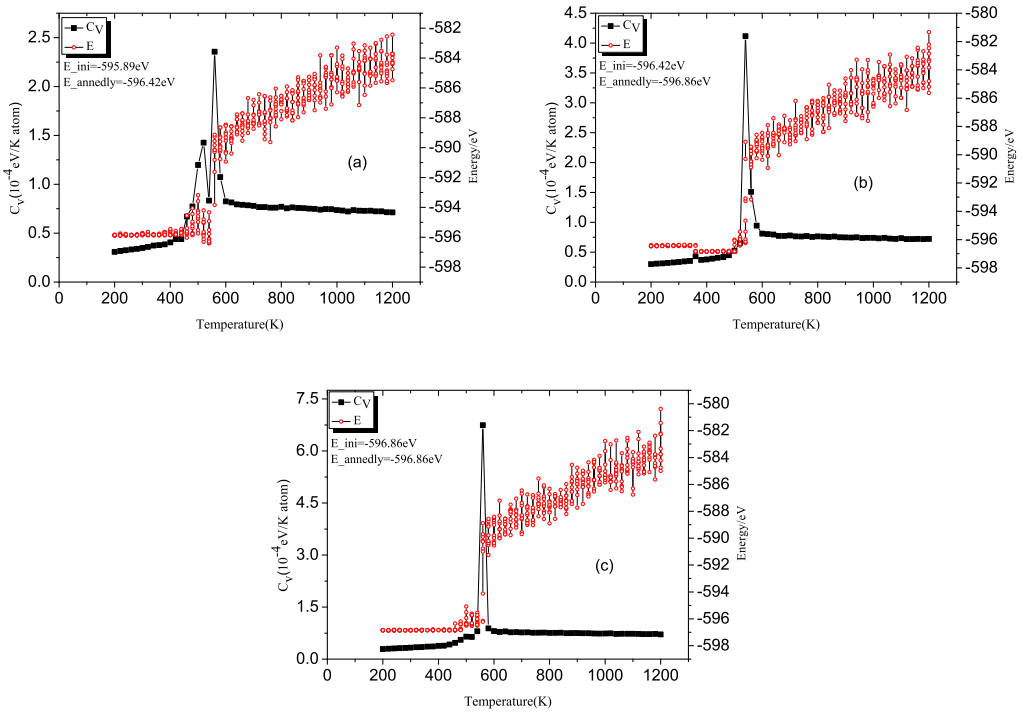


Figure 2: The heat capacity curves and the potential energy distributions of the quenching structures of $Al_{196}$ cluster at different temperatures.

initial structure shown in Fig. 1(b). The heat capacity curve in this process shows a well-defined single peak (no double-peak) and its maximum corresponds to the temperature of 540 K, and that is the melting point of $Al_{196}$ cluster. From analyzing the heat capacity curve in Fig.2 (b) one can also find there is a small jump at the temperature of 360K which is far below the melting point, and the potential energy of the cluster quenching structure just shows a clear decrease at that temperature, from a relatively low-energy quenching structure (shown in Fig. 1(b)) to a structure (as shown in Fig. 1(c) with the potential energy of -596.86 eV) with much lower energy. That means at that temperature the structure (energy) of $Al_{196}$ cluster also changes clearly, and as a result there is a small jump emerged in the heat capacity curve.

Fig. 2(c) shows the heat capacity curve and the potential energy distributions of the quenching structures in the MD heating-up processes started from the initial structure shown in Fig. 1(c). The main features of this process are similar to that of Fig. 2(b), and the heat capacity curve in this process also shows a well-defined single peak (as compared with that in Fig. 2(b), the heat capacity peak in Fig. 2(c) is much sharper, narrower and higher), from which the melting point is determined as 560 K. The main difference between Fig. 2(b) and (c) is that the lowest-energy quenching structure obtained from the

melting process shown in Fig. 2(c) is completely the same as the initial structure in this process, and this structure can be regarded as the ground-state geometry of $Al_{196}$ cluster.

The peak value of the heat capacity in Fig. 2(a) is $2.36\times10^{-4}$eV/K atom, and the corresponding values in Fig. 2(b) and (c) are $4.12\times10^{-4}$eV/K atom and $6.74\times10^{-4}$ eV/K atom, respectively. This reflects the correlation between the heat capacity and initial structure. That means, the lower energy the initial structure holds, the sharper the corresponding heat capacity curve should be.

As previously mentioned, if started from the ground-state structure or a low energy stable structure near the ground-state, there will be a sharp single peak in the capacity curve. But if started from a relatively low-energy stable structure far from the ground-state, the heat capacity will be characterized by a double-peak curve. Such phenomena (whether a single-peak or a double-peak emerges) in the heat capacity curve are highly correlated with the structural evolution in the melting process. In addition, from the potential energy distributions of the quenching structures shown in Fig. 2(a)∼(c) one can also find that the cluster structures all change from ordered to disorder at the temperature between 540 K and 560 K (the melting point of $Al_{196}$), and this is just the typical characteristics of melting of materials. It should be noted that the MD quenching process as shown in Fig. 2(a)∼(c) can also be quite effective in searching the ground-state geometries of clusters (for example, the structure shown in Fig. 1(c) is just the ground-state geometry of $Al_{196}$). We have found the ground-state geometries of all those aluminum clusters containing less than 200 atoms (that will be published elsewhere) by using the MD quenching method, and we find that the MD quenching method has high efficiency (especially for large-sized clusters) in searching the ground-states of clusters with comparing the traditional methods such as the annealing method and the genetic algorithm.

## 4 Conclusion

In this paper, the melting behaviors of $Al_{196}$ cluster are systematically studied by using the constant temperature molecular dynamics simulation method and the Gupta-type semi-empirical interatomic potential, and the low-energy structures as well as the structural evolution on potential energy surface during the cluster melting process are analyzed through the molecular dynamics simulated annealing and quenching methods. The main conclusions are summarized as follows: Different melting behaviors can be observed from different initial structures. From the ground-state or a state near the ground one peak emerges in the heat capacity curve, but two peaks occur clearly in the heat capacity curve if started from a structure far from the ground-state; Reasons of the different melting properties of the $Al_{196}$ cluster are explored by analyzing the energy distributions of the simulated quenching structures of $Al_{196}$ at different temperatures.

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