Melting Behaviour of Shell-symmetric Aluminum Nanoparticles: Molecular Dynamics Simulation

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Molecular dynamics simulations with embedded atom method potential were carried out for Al nanoparticles of 561 atoms in three structures: icosahedron, decahedron, and truncated octahedron. The total potential energy and specific heat capacity were calculated to estimate the melting temperatures. The melting point is $540 \pm 10\ K$ for the icosahedral structure, $500 \pm 10\ K$ for the decahedral structure, and $520 \pm 10\ K$ for the truncated octahedral structure. With the results of mean square displacement, the bond order parameters and radius of gyration are consistent with the variation of total potential energy and specific heat capacity. The relaxation time and stretching parameters in the Kohlraush-William-Watts relaxation law were obtained by fitting the mean square displacement. The results show that the relationship between the relaxation time and the temperatures is in agreement with standard Arrhenius relation in the high temperature range.

Key words: Al nanoparticle, Shell-symmetric structure, Molecular dynamics simulation

I. INTRODUCTION

Metal nanoparticles have attracted much attention in the last few decades. Due to the small size and the large surface to volume ratio, they have different physical, chemical, and electrical properties in comparison with the bulk liquid or solid. Many nanoparticles have been applied to catalysts [1], electronic devices [2], biosensor [3], nanoenergetic materials [4], and so on. General introduction to the structural properties and development trend of single metal nanoclusters (Au, Ag, Pt, and Al) and nanocomposites (based on Au, Ag, and Cu) can be seen in Ref.[5,6]. As technologically important metal, the aluminum (Al) nanoparticles are currently attracting considerable interest for their special characteristics and applications.

The basic problems for studying the nanoparticles are how they are formed by atoms, and the change of structures related to size, structure, and composition. Mostly, the shape of nanoparticles formed by experiments is spherical. However, Weigle et al. has investigated the formation of Al nanoparticles by passing an aerosol of micrometer-scale particles in argon [7]. Their results indicated the size and shape of Al nanoparticles depend on the operating conditions. Tadpole-structured gold nanoparticles were also synthesized in a large quantity by a simple aqueous-phase chemical method [8]. As finite objects, nanoparticle or cluster never have a fixed size or composition. As sizes increase, the icosahedral, the truncated octahedral and decahedral structures are respectively the most possible structures. The icosahedral and decahedral structures are the best known noncrystalline structures, and the truncated octahedra structures are the familiar face centered cubic (fcc) cluster [5].

For further applications of the metal nanoparticles, the knowledge of the thermodynamics behavior and the kinetic properties are particularly important. Since melting temperature has a significant impact on thermodynamic properties. The melting process has been investigated by abundant experiments [9-15] and simulations [16-27]. An Al oxide passivation layer was examined in the melting behavior of aluminum nanoparticles by using a differential scanning calorimetry (DSC) [15]. The oxide layer resulted in a compressive pressure on the aluminum core. With decreasing particle size, the melting response moved towards lower temperatures and the heat of fusion decreased. The size dependence on the melting point was consistent with the results of molecular dynamics (MD) simulations [16,17].

During the heating and cooling processes, nanoparticles will have a structural transformation. For example, free gold nanoparticles have been found to undergo a structural change from the initial fcc configuration to an icosahedral structure around the melting point [18-20].

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The reason for the formation of icosahedral structures may be that thermodynamics dominated over kinetic processes. As pointed out by Doye and Calvo [21], the entropy effects should be considered. The equilibrium structure of a nanoparticle corresponds to its lowest free energy, rather than the potential energy.

In this work, MD simulation was used to investigate the thermal behavior and dynamic properties of Al nanoparticles based on embedded atom method potentials. Recently, the structures of small Al$_n$ ($n<65$) clusters have been studied [28]. The stable Al$_n$ clusters mostly have atoms of the magic number. The nanoparticles with three structures, such as truncated octahedral, icosahedral and decahedral structures, of the same atom magic number 561, were adopted to study the effect of surface reconstruction in the melting process. The relationships between total potential and heat capacity and the temperature were obtained to define the melting point. For further describing the melting behaviors, the atomic diffusion coefficient and relaxation times in the Kohlraush-William-Watts relaxation law were calculated. Finally, the bond order parameters was also considered.

II. SIMULATION METHODS

A. Molecular dynamics simulation procedure

Al nanoparticles consisting of 561 atoms were placed in a cubic box (100 Å × 100 Å × 100 Å) without periodic boundary conditions in the molecular dynamics simulation. The initial configurations have three structures, including truncated octahedral, decahedral, and icosahedral structures. They, derived from Turner et al. [29], are shell-symmetric structures with five layers of atoms. The atom numbers of every layer from inner to surface are 1, 12, 42, 92, 162, and 252. The number of surface atoms is so large that it reaches nearly 45% of all atoms. All the atoms are treated as a point masses, and the atomic motion is based on Newton’s equations. Thermodynamic and dynamical properties are obtained by time averaging of the atoms.

Energy minimization optimizations for these initial configurations were performed by using conjugate gradient algorithms before the MD simulation. The velocities were sampled from a Maxwell-Boltzmann distribution matching the start temperature 200 K. Then, we run the MD simulation at 200 K in the constant-NVT (number, volume, and temperature are fixed) ensemble with zero initial total angular momentum. The temperature was controlled by using the Nosé-Hoover thermostat [30,31]. The time step was 1.0 fs. Before collecting the thermodynamic data, the simulation was carried through an equilibration period of 5 ns. It is necessary to simulate a long time to compensate for the poor statistics caused by the small systems. Moreover, we simulated the three types of Al nanoparticles at 50 K intervals from 200 K to 1000 K. Specially, around the melting point the simulations were done in intervals of 10 K.

B. The potential

In the MD simulations, interactions between atoms are so important that we need to use an exact force field to describe them. The choice of appropriate potential model depends on the size of research system and the simulation time scales. Various many-body potential functions have been developed based on the embedding atom idea, such as the effective medium theory (EMT) [32], the embedded atom method (EAM) [33,34], Finnis-Sinclair (FS) potential [35], the Glue potential [36], the Sutton-Chen (SC) potential [37], and the tight-binding (TB) potential [38].

The EAM is based on density-functional theory and the concept of a quasi-atom or effective-medium approach [33]. In simulation of metallic systems, EAM potential model can provide good results of physical properties compared with the first principles calculations and experiments. For example, the thermal properties [39], diffusion coefficients [40], and size-dependent spontaneous alloying for Au and Ag were close to the experimental values [26]. In particular, for the Al metal, many researchers reported using the EAM potential model to define the atom interactions. The shear viscosity and the self-diffusion coefficient were investigated in detail by Cherne and Deymier [41]. The vacancy and migration energies and the vacancy migration volume were studied by Mendelev and Bokstein [42]. A good review of embedded atom method was given by Voter [43].

The EAM potential with the version of Voter-Chen (VC) [44] was adopted in the MD simulation. The total internal energy of a system in the EAM potential is expressed as:

\[ E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i,j} \sum_{j \neq i} \Phi(r_{ij}) \]  

\[ \rho_i = \sum_{j \neq i} f_j(r_{ij}) \]

where, $E_{\text{tot}}$ is the total energy of Al nanoparticles. $\rho_i$ is atomic electron densities depending on $r_{ij}$, which is the distance between atoms $i$ and $j$. $F_i$ is an embedding functional that approximates the energy required to embed a positively-charged core ion $i$ into a linear superposition of spherically averaged given by $\rho_i$. The pairwise portion of the potential, $\Phi(r_{ij})$, is a primarily repulsive interaction between atoms $i$ and $j$. The effective cutoff distance, $r_{\text{cut}}$, is the distance at which the values of $f(r)$ and $\phi(r)$ drop to zero for all atoms present in the simulation.

C. Bond order parameters

The bond order parameters (bop) introduced by Steinhardt et al. to study the liquid crystal, quasycrystals.
tals, metallic glass, and supercooled liquids, are used to illustrate the internal structure in the liquid and solid states [45]. A bond is defined as the vector joining a pair of neighboring atoms. The idea of the bond order parameters is to capture the symmetry of bond orientations regardless of the bond lengths. The first peak in the radial distribution function is defined as the cutoff distance. The bond with a bond \( r \) can be expressed as,

\[
Q_{lm} \equiv Y_{lm}(\theta, \phi(r))
\]

(3)

where \( Y_{lm} \) are the spherical harmonics, \( \theta \) and \( \phi \) are the polar angles of the bond measured with respect to an arbitrary coordination system. By averaging \( Q_{lm}(r) \),

\[
\bar{Q}_{lm} = \langle Q_{lm}(r) \rangle = \frac{1}{N_b} \sum_{\text{bonds}} Q_{lm}(r)
\]

(4)

where \( N_b \) is the number of bonds. The second-order invariants are defined as,

\[
Q_l \equiv \sqrt{\frac{4\pi}{2l+1}} \sum_{m=-l}^{l} |Q_{lm}|^2
\]

(5)

and the third-order invariants are defined as,

\[
W_l \equiv \sum_{m_1,m_2,m_3} \left( \begin{array}{ccc} l & l & l \\ m_1 & m_2 & m_3 \end{array} \right) Q_{lm_1} Q_{lm_2} Q_{lm_3}
\]

(6)

where coefficients \( \left( \begin{array}{ccc} l & l & l \\ m_1 & m_2 & m_3 \end{array} \right) \) are the Wigner 3j symbols. Thus a normalized quantity is defined as,

\[
\hat{W}_l \equiv \frac{W_l}{\left( \sum_m |Q_{lm}|^2 \right)^{3/2}}
\]

(7)

The bond order parameter depends on the value of \( l \). However, the four bond order parameters \( Q_4, Q_6, W_4, W_6 \) are generally sufficient to identify different internal structures.

### III. RESULTS AND DISCUSSION

#### A. Thermodynamic properties

The total potential energy \( (E_p) \) and the specific heat capacity \( (C_v) \) at constant volume are very important thermodynamic properties. They are usually used to identify the melting temperature [22-25]. The \( C_v \) is calculated as given:

\[
C_v = \frac{k_B \langle \delta E_p^2 \rangle}{(k_B T)^2} = \frac{\langle E_p^2 \rangle - \langle E_p \rangle^2}{k_B T^2}
\]

(8)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature.

To avoid the influence of the number of atoms \( N \), we deal with the \( E_p \) and \( C_v \) as \( E_p/N \) and \( C_v/N \). The variations in the \( E_p/N \) and \( C_v/N \) at constant volume of the \( \text{Al}_{561} \) nanoparticles with three structures as the function of the temperature are shown in Fig.1. At low temperature, the atoms of solid state always make small amplitude vibration around their equilibrium position. It is seen in Fig.1 that the average total energy for three nanoparticles increases monotonically with temperature in the early stage. Then, a distinguishable sudden increase in the total energy occurs, corresponding to the melting transition of the nanoparticles. There is a distinguishable energy jump between the temperatures from 540 K to 550 K in the \( E_p \) curve in the Fig.1(a), due to the melting transition from the solid state to the liquid state. The maximum of \( C_v \) curve also appears in the range. The specific heat capacity \( C_v \) at constant volume of the \( \text{Al}_{561} \) nanoparticles in Fig.1 are a strong indication of the melting, which

![FIG. 1 Potential energy and heat capacity of three \( \text{Al}_{561} \) nanoparticles during the heating process from 200 K to 1000 K.](image-url)
is consistent with the variation of total $E_p$. Thus we can unambiguously establish the melting temperature $T_m=540\pm10$ K for the icosahedral structure, 500\pm10 K for the decahedral structure, and 520\pm10 K for the truncated octahedral structure. The melting temperature is much lower than the bulk Al ($T_m=933.4$ K) because of the nanoparticles with the larger proportion of surface atoms. Comparison with three type structures of nanoparticle, the nanoparticle with icosahedral structure has a little higher melting temperature than the others.

There are some small peaks in the $C_v$ curves below the melting temperatures. These behaviors are results from the surface melting [22,25,27], or surface reconstruction [46]. For different structures, these small peaks appear at the different temperature, e.g. at 460 K for a nanoparticle of icosahedral structure. The particular structural properties and the surface reconstruction will be discussed below.

B. Structure properties

1. Pair distribution function

Pair distribution function (PDF) is the relation function of instant number density of atoms. PDF is the probability of finding another atom from the place of one atom. Because it can describe the relative position and the array of atom in the material, PDF can give the information of local structure and average structure. PDF is calculated as:

$$g(r) = \frac{1}{\rho N} \left[ \sum_i \sum_{j \neq i} \delta (r - r_{ij}) \right]$$

(9)

here, $\rho$ is the density of the system, $N$ is number of nanoparticles, and $r_{ij}$ is the distance between atom $i$ and atom $j$.

We show the nanoparticles with icosahedral structure as an example in Fig.2 to describe the change of total $g(r)$. The peaks are the total contributions of the atoms from the inner to the surface. At 200 K, the total $g(r)$ presents solid-like well-segregated sharp peaks. The main five peaks are due to the five shells $g(r)$ [47]. From 300 K to 500 K, the total $g(r)$ maintains solid-like features. However, the main five peaks in the curve become lower and wider and many other small peaks disappear. This result illustrates that the atoms begin to move and become out-of-order in shells. Above 600 K, the total $g(r)$ shows similar features of the liquid-like state.

We also show the $g(r)$ of the other structures in Fig.3. At 450 K, there are obvious differences among the three structures, but the differences disappear at 500 K. That is due to the decahedral and truncated octahedral structures undergoing reconstruction between 450 and 500 K.

The detailed melting snapshots are listed in the Fig.4. At 200 K, the Al$_{561}$ nanoparticles take on clear structures as icosahedron, decahedron, and cuboctahedron. When temperature is 500 K, below the melting temperature, the nanoparticles with decahedral and cuboctahedral structure have obvious reconstruction changes. Both structures show local five-fold symmetry in Fig.4. Therefore, we can deduce that atoms in those nanoparticles have clear reconstruction to make their structure similar to the icosahedron structure close to melting point. Surface atoms move from their location to form a new structure of lower energy. The average potential energy of three nanoparticles approaches the line of $E_p\approx1.6966$ keV at 500 K. All of the three structures become approximately spheroid above the melting
FIG. 4 Nanoparticles snapshots are taken at different temperatures.

2. Radius of gyration

The radius of gyration of Al nanoparticles is calculated as follows:

\[ R_g = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (R_i - R_{cm})^2} \quad (10) \]

here, \( R_g \) is the radius of gyration. The distance from every atomic center to the coordination point is expressed by \( R_i - R_{cm} \). The \( R_{cm} \) is the nanoparticle center of mass.

Figure 5 shows the radius of gyration of the three types of structures at different temperatures. The \( R_g \) of icosahedral structure is increasing in the simulation process, and shows a jump from 500 K to 550 K range consistent with the variation of the total potential and specific heat capacity. The \( R_g \) for the other structures shows special changes before melting. The value of \( R_g \) falls from 1.025 nm (decahedral structure) and 1.022 nm (truncated octahedral structure) to 1.021 nm, which is close to the value of the icosahedral structure (1.020 nm). The characteristic of \( R_g \) also illustrates that the structure and shape changes approach the icosahedral structure due to the structural reconstruction.

3. Bond order parameters

The bond order parameters are taken on average over all bonds, and used to monitor global structural changes. For a nanoparticle with cubic and decahedral symmetry, the bond order parameter at \( l=4 \) is nonzero, but it is nonzero for icosahedral atomic arrangement at \( l=6 \). For amorphous and liquid nanoparticles, the bond order parameters should be near zero. Due to this property, the bond order parameters are used to distinguish different structures of nanoparticles. As Fig.5 shows, the bond order parameters are observed to have obvious changes with temperature. For the icosahedral structure in Fig.6(a), the \( Q_4 \) and \( W_4 \) are always nearly zero with very little change during the simulation. The \( Q_6 \) and \( W_6 \) have much larger absolute value than \( Q_4 \) and \( W_4 \) at 200 K, which indicates that the nanoparticle structure is appropriate like the Mackay icosahedron.

As the temperature is close to the melting point, the \( Q_6 \) decreases quickly to near zero while the \( W_6 \) increases to near zero at the same time. The jump changes illustrate that the nanoparticle undergoes a phase transition from the solid state to liquid state, which is similar to the result of the \( E_p \) and \( C_v \) curves.

However, we can see some differences in the other structures as shown in Fig.6 (b) and (c). The \( Q_4 \) and \( W_4 \) of the truncated octahedral structure has a nonzero value at 200 K (\( Q_4=0.19, W_4=-0.15 \)). Then the \( Q_4 \) decreases (and \( W_4 \) increases) to near zero at 500 K, which indicates rapid structural rearrangement in the nanoparticles with truncated octahedral structure. The \( Q_6 \) have an approximate decrease close to zero above the melting point, whereas the \( W_6 \) is almost equal to zero except at the 500 K, where it abruptly reduces to \(-0.11\) in Fig.6(b). Above 550 K, the bond order four parameters are nearly unchanged. The more complicated changes of the four bond order parameters are found in the decahedral structure, shown in Fig.6(c). The \( Q_6 \) and \( W_6 \) have a fluctuation below the melting temperature, which is attributed to the structure reconstruction of nanoparticles.

As a result, the \( Q_6 \) and \( Q_4 \) are very appropriate to identify the local atomic arrangement. The \( Q_6 \) values of cuboctahedron structure and decahedral struc-
Variation of bond orientation order parameters (bop) with temperature for Al\(_{561}\) nanoparticle. (a) Icosahedral structure; (b) truncated octahedral structure; (c) decahedral structure.

Mean square displacement (MSD) as function of simulation time for nanoparticles with icosahedral structure.

Diffusion coefficients as functions of temperature.

Dynamic properties

1. Self-diffusion coefficient

The method of using the MD simulation to study the diffusion is universal. At first, it requires computing the movement equation of all atoms in the nanoparticle.

\[
\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} ||r_i(t) - r_i(0)||^2
\]

where \(r_i(t)\) is the atomic position of atom \(i\) at time \(t\) and \(\langle r^2(t) \rangle\) is the thermal average. The atomic self-diffusion coefficient \((D)\) can be expressed as:

\[
D = \lim_{t \to \infty} \frac{1}{6t} \langle r^2(t) \rangle
\]

The changes of mean square displacement for nanoparticles with icosahedral structure are shown in Fig. 7 as a function of simulation time.
2. Kohlraush-William-Watts relaxation law

The relaxation time calculations used the Kohlraush-William-Watts (KWW) relaxation law [26] as follows:

\[
\langle \tau^2 (t) \rangle \approx \frac{6R}{5}[1 - e^{-(t/\tau)^\beta}] \quad (13)
\]

\[R = R_g \sqrt{\frac{5}{3}} + R_{Al} \quad (14)\]

here, \(\tau\) is the relaxation time, and \(\beta\) is the stretching parameter. \(R\) is the radius of the \(Al_{561}\) nanoparticles. \(R_g\) is obtained by Eq.(10). \(R_{Al}\) is the half the atomic distance in the Al bulk, and the numerical value is 1.18 Å.

In low temperatures \((T<500\ K)\), the relaxation times are very large as a result of the small displacement and low energy. Generally speaking, the lower the temperatures, the larger the relaxation times. In high temperatures, the relaxation time can be displayed in a standard Arrhenius relation, which shows that the relaxation time can be described this way. From these plots, we can also obtain the activation energy \(E\). The activation energy is 146.0 meV for nanoparticles with icosahedral structure, 143.1 meV for decahedral structure, and 145.9 meV for truncated octahedral structure. The stretching parameters \(\beta\) as the function of temperature are shown in Fig. 9. After melting, \(\beta\) have a decreasing trend following the increase of the temperatures. This characteristic means the motion of atoms is easy at high temperature.

IV. CONCLUSION

The melting characteristics of aluminum nanoparticles were carried out using molecular dynamics simulations based on the embedded atom method potentials. The initial structures of nanoparticles, including icosahedron, decahedron, and truncated octahedron, were simulated in the heating process from 200 K to 1000 K. At 200 K, the \(Al_{561}\) nanoparticles take on clear initial structures in stable solid phase. When the temperature becomes close to the melting temperature, the surface reconstructions are observed due to the movement of the surface atoms. The total potential energy and the specific heat capacity also have other particular changes used to identify the melting temperature. The melting point \(T_m\) of \(Al_{561}\) is 540±10 K for icosahedral structure, 500±10 K for the decahedral structure, and 520±10 K for the truncated octahedral structure. At high temperatures, all three structures become an approximate spheroid in stable liquid state. The diffusion coefficients also show a large jump in this range indicating the nanoparticles undergo phase transitions from the solid state to the liquid state. From the changes of bond order parameters and radius of gyration, it is observed that the nanoparticles with decahedral and cuboctahedral structures undergo an obvious structural rearrangement, and their structures have five-fold symmetry before the melting.

The Kohlraush-William-Watts relaxation law is used to study the relaxation time and stretching parameter. In the solid phase, the relaxation times are very large as a result of the small displacement and low energy. Above the melting temperature, there is a good standard Arrhenius plot between relaxation time and temperature. The activation energy can also be obtained.

FIG. 9 The stretching parameters \(\beta\) with temperature for Al nanoparticles.

V. ACKNOWLEDGMENTS

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