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On the melting phase transition of aluminum clusters around 55 atoms

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Abstract. Melting phase transition of atomic clusters has attracted a lot of interest in the last several decades due to their peculiar behaviors different from their bulk counterpart. Investigation of this kind of phase transition leads to the understanding of thermodynamics of finite systems. Recent progress in the experiments measuring thermodynamic properties of sized-selected atomic clusters has motivated the theoretical research interest in this area. In this report, heat capacities of aluminum clusters with around 55 atoms are investigated using extremely long constant energy molecular dynamics simulation with empirical many-body interaction potential. Some features of the heat capacity can be interpreted by the energy spectra obtained from quenches along the trajectories. Dips that emerged in the heat capacities in the previous experiment are not found. Different isomers are taken as the initial structures and found to anneal into the lowest energy structure before melting during the temperature increasing process.

PACS. 36.40.-c Atomic and molecular clusters

1 Introduction

The melting transition of bulk materials is a paradigm of a first order phase transition. For finite systems like atomic clusters, it appears as a first order transition rounded by size effect. There are some features in the melting transition of clusters that are difficult to understand, such as irregular size dependence of melting temperature and different temperature dependences of heat capacities [1]. Melting of atomic clusters has attracted a lot of interest in the last decades because recent progress in the experiments measuring thermodynamic properties of sized-selected atomic clusters [2–9] has motivated the theoretical research interest in this area [1,10–17]. Through the analysis of the irregular variation of melting points of sodium clusters with respect to their sizes, it has been shown that the geometric structure seems to govern the thermodynamic properties near the melting temperature, while electronic effects may play a second role [7]. Recent simulations of sodium and aluminum atomic clusters also support this point [18–20].

As is known, the potential energy surface (PES) determines the structure, dynamics and thermodynamics of any system in a particular electronic state [16]. At low temperatures, the most favored structures of a cluster is believed to be the structure corresponding to the global minimum in the PES. In a temperature-increasing process, the cluster explores the local minima in PES, with the number of isomers increasing after some threshold temperature. Usually, the most common procedure of theoretical methods is started with the searching of globally lowest energy structure. Considerable effort has been spent in searching this structure. However, in a recent experiment of Breaux et al., the heat capacities of some aluminum clusters around 55 atoms show an unusual temperature dependence behavior, that is, some dips were found in the heat capacities before the melting peak [6]. This proved that not only the lowest-energy structure involved in the initial stage of the measurement. There is also a considerable proportion of higher-energy structures at the low temperature, which anneal into the ground-state structure with temperature increasing.

In this report, in order to understand the experimental results, we investigated the melting of aluminum clusters with the size from 49 to 62 by constant energy molecular dynamics simulation. Especially, we studied what a process the clusters will experience in the case that the initial structure is not the lowest energy structure. Particular attention is paid to the physical meaning of the dips. By using different isomers as the initial structures in the simulations, it is found that these clusters will anneal into the lowest energy structure before melting during the temperature increasing process in case the simulation time is

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long enough. At low temperatures, heat capacities of different isomers are almost the same. We cannot find any sign of dip in the heat capacities from our simulations.

2 Method

The many-body Gupta potential [21] is used in this work, which is based on the second moment approximation of a tight-binding Hamiltonian. This potential correctly describe the surface contraction observed in metals. Its analytical form is as follows:

$$V(r_{\{ij\}}) = \sum_{i}^{N}\left[\sum_{j\neq i}^{N} A e^{-p\overline{r}_{ij}} - \sqrt{\sum_{j\neq i}^{N} \xi^2 e^{-2q\overline{r}_{ij}}}\right], \qquad (1)$$

here N is the number of atoms, $\overline{r}_{ij} = r_{ij}/r_0 - 1$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between atom i and j. The parameters for aluminum have been determined by fitting the experimental bulk lattice parameters and elastic moduli [22] as $A = 0.1221$ eV, $\xi = 1.316$ eV, $p = 8.612$ and $q = 2.516$.

Constant energy MD simulations are conducted to study the melting transition of aluminum clusters. The initial velocities of atoms are sampled according to Maxwell distribution and the translational and rotational motion are eliminated. The temperature is increased by scaling the velocities step by step. The time step is taken as 2 fs. For each temperature, the cluster is equilibrated during the initial 10^5 steps. Then a run with 5×10^7 steps is used to converge the specific heat capacity. During this run the total energy can be conserved within 0.001%. We get the lowest energy structure using an evolutive algorithm [23] combined with a conjugate gradient minimization method. Using this method we also can get other structures corresponding to local minima in PES. In the simulations, not only lowest energy structures but also other isomers are used as the initial structure.

3 Results and discussion

In Breaux et al.'s experiment, the clusters will have a higher temperature after the structural transition due to the potential energy difference between the structures before and after the transition. They will be cooled down soon in the helium air in the extension to the cluster source, which is used to thermalize the clusters [4]. Thus this transition can be unidirectional and irreversible. In order to make the simulation quasi-ergodic, very long simulation time is required. It's very interesting that in our extremely long time constant energy MD simulation, irreversible transition happens too. This is helpful in understanding the experiments.

The microscopic canonical specific heat capacity is calculated as [12]

$$\frac{C}{k_B} = \left[N - N\left(1 - \frac{2}{3N-6}\right)\langle E_k\rangle\langle E_k^{-1}\rangle\right]^{-1}, \qquad (2)$$

where k_B is the Boltzmann constant. $\langle E_k\rangle$ is the average kinetic energy of the cluster.

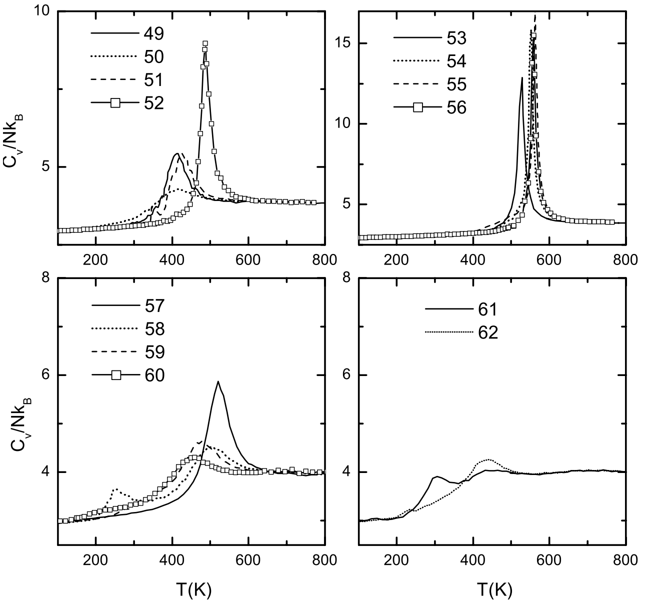

Fig. 1. Heat capacities of aluminum clusters Al_N (N = 49–62) as a function of temperature.

First, aluminum clusters with around 55 atoms are studied, the calculated results of heat capacities of Al_N (N = 49–62) are shown in Figure 1. The results shown here are almost the same as the results in reference [20], except that the peaks of several clusters in the middle are much higher. This should be attributed to the difference between the microcanonical and canonical ensembles. Most clusters show well-defined peaks except that Al_{58} and Al_{61} have some premelting features. As is known, premelting is usually caused by surface melting and partial melting [1]. Al_{55} has the highest peak and with the size being further away from 55, the peak of heat capacity becomes lower. This is in agreement with the experiment. However, apparently, there is no such kind of dips as those emerged in the experimental results. The peak of Al_{50} is much lower than those of the clusters with neighboring size. In order to understand this, we performed a series of quenches from the instantaneous configurations extracted from the MD simulations. The energy spectra are shown in Figure 2. This energy spectra reflect the isomerizations that happen during the temperature increase process. It can be seen that the shape of energy spectra of Al_{50} is different from those of Al_{49} and Al_{51}. For Al_{50}, the melting starts at a relatively lower temperature with a few isomers involved at the initial stage. With the temperature increases, the number of isomers involved increases gradually. While for Al_{49} and Al_{51}, the number of isomers increase abruptly at a temperature close to the melting temperature. This gradual exploration of potential energy surface results in the relatively lower peak of Al_{50}. We also took Al_{55}, Al_{58} and Al_{61} as examples to make further investigation. In Figure 2, Al_{55} shows a quite big gap between the energies of the first isomer and the lowest-energy

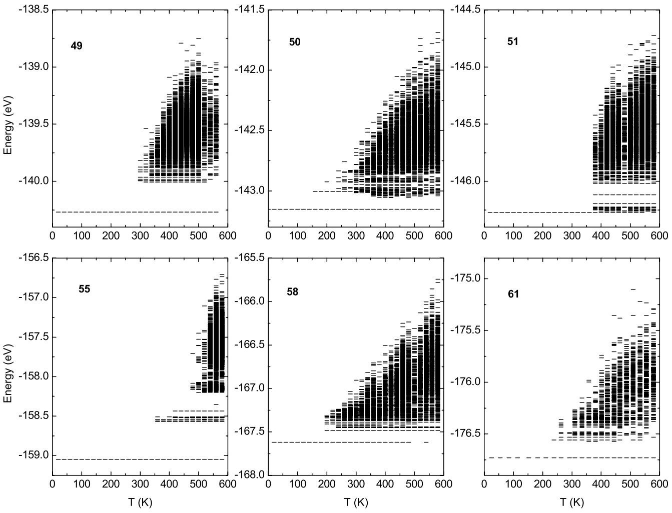

Fig. 2. Energy spectra of aluminum clusters Al_N ($N = 49$–51, 55, 58, 61) calculated by quenching trajectories.

isomer. The exploration of a large amount of isomers happens only close to the melting temperature. So Al_{55} has a high peak in heat capacity. The same case happens for other clusters that have a high peak. For Al_{58} and Al_{61}, the gradual exploration of potential energy surface also causes them to have a low peak. Because the number of our quenches is relatively limited, it's not possible to explain the details of the behavior of heat capacity as in Calvo and Spiegelmann's work [13].

Then for some clusters, different initial structures are tried in the temperature increasing simulation. Figure 3a shows a typical result of the heat capacity of Al_{55}. The two initial structures of Al_{55} have I_h and C_s symmetry, corresponding to the potential energy –159.0475 eV and –158.5483 eV respectively. At temperatures lower than 177 K, there is almost no difference in their heat capacities. At the point next to 177 K, the temperature jumps to 220 K and the heat capacity become much deviated from other values, which indicate that there is a structural transition. Because the process including this transition isn't an equilibrium process, the heat capacity calculated by equation (2) becomes difficult to converge. As a consequence, these deviated value of heat capacity are not converged values. At the higher temperatures after this transition, the heat capacities of two isomers becomes the same.

Figure 3b shows the variation of potential and kinetic energy in the simulation run during which the structural transition happens, corresponding to the two deviated points in Figure 3a. The step-like change of the potential energy is caused by the structural change. It's interesting to note that this change is irreversible in all these simulations. A series of this kind of simulations for several clusters show, whatever the initial structure is, it will transit into the lowest-energy structure before melting.

Since different isomers have almost the same heat capacities at temperatures lower than the transition temperature, now it is clear that the dip is not caused by the difference between the heat capacity of different structure. Now from another standpoint of the temperature variation caused by the structural transition, it can be shown how the dip came into being in the experiment, using the heat capacities of Al_{57} calculated in the simulation. First let's look back at Breaux et al.'s experiment. Assume that the clusters dissociate when their energy reaches E_m. Initial translational energy E_t needed to dissociate the clusters is related to the internal energy of the clusters U_i by

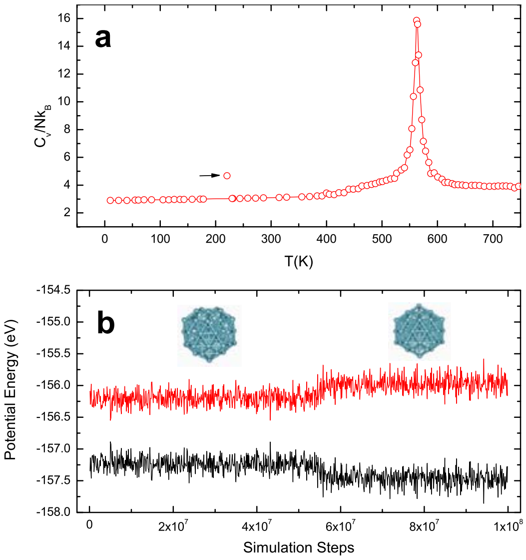

Fig. 3. (Color online) Plot of heat capacities calculated in simulations starting from two isomers of Al_{55}, with the potential energy –159.0475 eV (solid line) and –158.5483 eV (open circles). The circle pointed by an arrow indicates structural transition occurs which causes the heat capacity unconverged. Variation of the potential energy (black) and kinetic energy (red) of Al_{55} of the simulation runs during which structural transitions happen. The starting structures are higher energy isomer. The temperature changes from 188 K to 220 K after the transition.

$$pE_t = E_m - U_i. \tag{3}$$

Here p is the proportional constant of fraction of the clusters' translational energy that is converted into internal energy in the collision cell. So according to the laws of thermodynamics of equilibrium systems, the heat capacity is given as

$$C = \partial U_i/\partial T = -p\partial E_t/\partial T. \tag{4}$$

This is the starting point of the experiment.

Sparse data were taken from the numerical integration of the heat capacity curve to simulate the translational energy required for 50% dissociation (TE50%D)[6] values in the experiment. Suppose there are two kind of isomers, 50% s_0 and 50% s_1 generated by the source in the experiment at low temperature. Since the internal energy of clusters is the only factor determining the TE50%D value that is needed to dissociate them, we can substitute the s_0 by the s_1 that has the same internal energy, when the temperature is below that at which structural transition

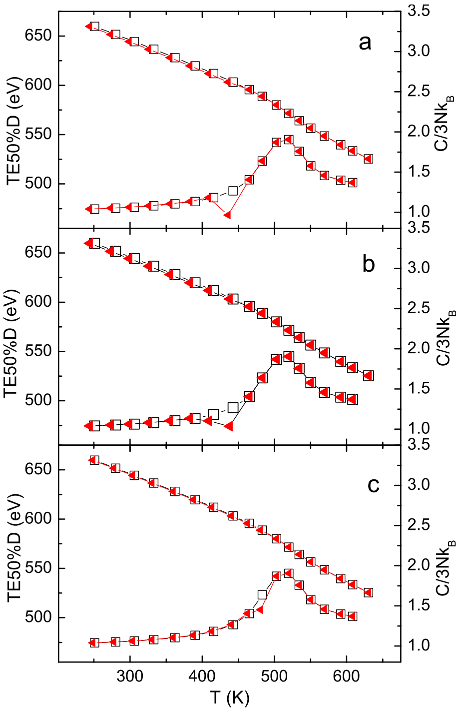

Fig. 4. Plots of TE50%D and its numerical derivative against temperature for Al_{57}. TE50%D values represented by open squares are simulated by sparse data taken from the numerical integral of the heat capacities calculated from MD simulations. (a) Assume at about 443 K, all metastable structures are annealed into the lowest energy structure. Suppose the corresponding temperature of TE50%D lower than 443 K is underestimated by 7 K. Take the TE50%D points left by 7 K, a dip in the derivative appears. (b) Assume at about 409 K, all metastable structures are annealed into a lower energy structure. Then at about 443 K, they are annealed into the lowest energy structure. (c) Assume at about 483 K, the metastable structures are annealed into the lowest energy structure. Take the TE50%D left by 1.5 K, a shoulder is obtained.

happens. Suppose the difference between the potential energies of two structures is 0.1 eV, the temperature difference between two structures with the same internal energy is $\Delta T = 2\Delta\langle E_k\rangle/(3N-6)k_B \approx 14$ K. So the difference between T_1 and T_2 is 50%D × 14 K = 7 K. We move the points of TE50%D left by 7 K in the figure at low temperatures and calculate the derivative of TE50%D with respect to temperature numerically. A dip is obtained in the heat capacity, which is just the same as the experimental result, as shown in Figure 4a. Considering there may be several kinds of isomers generated by the cluster source, it is not hard to understand that in Breaux et al.'s results [6] some slight decreases before the dip exist in heat capacities of Al_{57}. An example is shown in Figure 4b. No premelting shoulder is found in the heat capacity of Al_{51} and Al_{52} calculated in simulations. In the experiment, the shoulder may be caused by the same reason for the dips. That is, when the solid-solid structural transition happens at a temperature very near to the melting temperature corresponding to the peak in the heat capacity, there will be a small increase in the initial translational energy need to dissociate the cluster and this leads to the shoulders, which is shown in Figure 4c.

In summary, we have investigated the heat capacity of aluminum clusters with around 55 atoms, using extremely long time MD simulation with empirical many-body interaction model. Dips emerged in the experiment are not found in the simulation results. Using different structures as the initial structure for the simulation, it is found that high energy isomers transit into the lowest energy structure before melting. The dips found in the experiment are not caused by the difference between the heat capacities of different structures before and after the solid-solid transition.

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