

Molecular dynamics study on the melting phase transition of aluminum clusters with around 55 atoms

Wei Zhang,^{1,2} Fengshou Zhang,^{1,2,*} and Zhiyuan Zhu³¹The Key Laboratory of Beam Technology and Material Modification of Ministry of Education, Institute of Low Energy Nuclear Physics, Beijing Normal University, 100875 Beijing, China²Beijing Radiation Center, 100875 Beijing, China³Shanghai Institute of Applied Physics, 201800 Shanghai, China

(Received 22 May 2006; revised manuscript received 9 June 2006; published 27 July 2006)

Heat capacities of aluminum clusters with around 55 atoms are investigated using extremely long constant-energy molecular dynamics simulations with an empirical many-body interaction potential. Different isomers are taken as the initial structures and found to anneal into the lowest-energy structure before melting during the temperature increase. The heat capacities of different isomers were found to be the same at low temperatures. Dips that emerged in the heat capacities in the previous experiment are not found.

DOI: [10.1103/PhysRevB.74.033412](https://doi.org/10.1103/PhysRevB.74.033412)

PACS number(s): 61.46.-w, 36.40.Ei

The melting transition of atomic clusters has attracted a lot of interest in recent decades due to their peculiar behaviors, different from their bulk counterparts. The investigation of this kind of phase transition leads to the understanding of thermodynamics of finite systems. Recent progress in experiments measuring thermodynamic properties of size-selected atomic clusters¹⁻⁸ has motivated the theoretical research interest in this area.⁹⁻¹⁷ 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 secondary role.⁶ 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 structure 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 the PES, with the number of isomers increasing after some threshold temperature. Usually, the most common procedure of theoretical methods is started with searching for the globally lowest-energy structure. Considerable effort has been spent in searching for this structure. However, in a recent experiment of Breaux *et al.*, the heat capacities of some aluminum clusters around 55 atoms showed an unusual temperature dependence behavior, that is, some dips were found in the heat capacities before the melting peak.⁵ This proved that not only the lowest-energy structure was 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 increasing temperature.

In the present work, in order to understand the experimental results, we investigate by constant-energy molecular dynamics (MD) simulations what process the cluster will experience in the case that the initial structure is not the lowest-energy structure. 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 increase if the simulation time at each temperature is long enough. At low temperatures, the heat capacities of different isomers are almost the same. We cannot find any sign of a dip in the heat capacities from our simulations. It has been shown that the effect of the positive charge on the thermodynamic properties of Na clusters is small.²¹ Although positively charged clusters are involved in the experiment, they are assumed to have the same thermodynamical properties as the neutral ones.

The many-body Gupta potential²² is used to model the interaction between the aluminum atoms of the cluster in this work, which is based on the second-moment approximation of a tight-binding Hamiltonian. Its analytical form is as follows:

$$V(r_{ij}) = \sum_i \left(\sum_{j \neq i}^N A e^{-p \bar{r}_{ij}} - \sqrt{\sum_{j \neq i}^N \xi^2 e^{-2q \bar{r}_{ij}}} \right); \quad (1)$$

here N is the number of atoms, $\bar{r}_{ij} = r_{ij}/r_0 - 1$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between atoms i and j . The parameters for aluminum have been determined by fitting the experimental bulk lattice parameters and elastic moduli²³ as $A = 0.1221$ eV, $\xi = 1.316$ eV, $p = 8.612$, and $q = 2.516$.

In the constant-energy MD simulations, the Newton equation is solved by the velocity Verlet algorithm.²⁴ Initial velocities of atoms are sampled according to the Maxwell distribution and the translational and rotational motion are eliminated. The temperature is increased by scaling up the velocities in a steplike manner. The time step of the MD run 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 algorithm²⁵ combined with a conjugate gradient minimization method. Using this method we can also get other structures corresponding to local minima in the PES. In the simulations, not only lowest-energy structures but also other isomers are used as the initial structure.

In Breaux *et al.*'s experiment, the clusters will have a higher temperature after the structural transition due to the

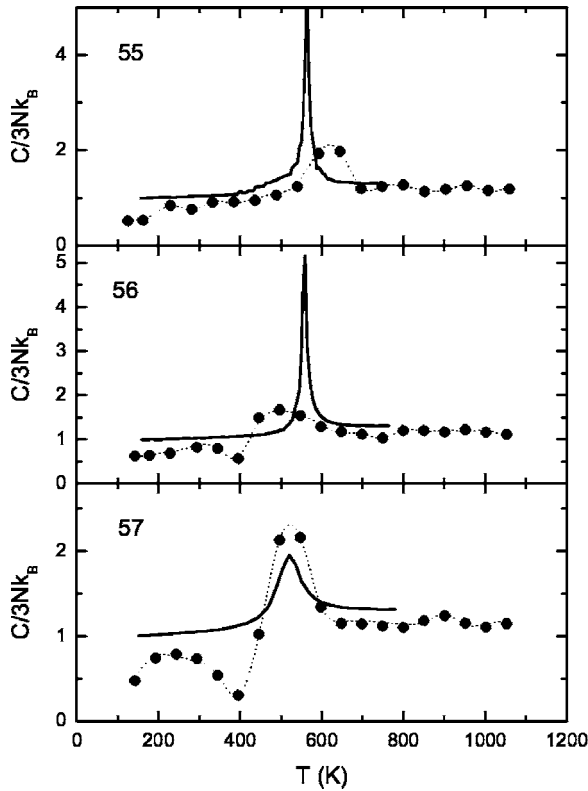


FIG. 1. Heat capacities of aluminum clusters Al_N , $N=55-57$, as a function of temperature. The solid lines are the results in this work. The points are experimental measurements in Ref. 5.

potential energy difference between the structures before and after the transition. Then they will be cooled down soon in a helium atmosphere in the extension of the cluster source. Thus this transition can be unidirectional and irreversible. In order to make the simulation quasiergodic, a very long simulation time is required. It is very interesting that in our extremely long time constant-energy MD simulations, irreversible transitions happen too. This is helpful in understanding the experiments.

The microscopic canonical specific heat capacity is calculated as^{26,27}

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

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

First, aluminum clusters with around 55 atoms are studied. The calculated results of heat capacities of Al_{55} , Al_{56} , and Al_{57} are shown in Fig. 1. From the figure it can be seen that the melting temperature corresponding to the peak is close to the experimental value. All clusters show well-defined peaks. The peak in the heat capacity is sharp pointed for clusters with 55 and 56 atoms.

Then for the clusters Al_{55} and Al_{56} , two different initial structures are tried in the simulation. Figure 2 shows a typical result of the heat capacity of two isomers of Al_{55} and Al_{56} respectively. The two structures of Al_{55} have I_h and C_s symmetry, corresponding to the potential energy -159.0475 and

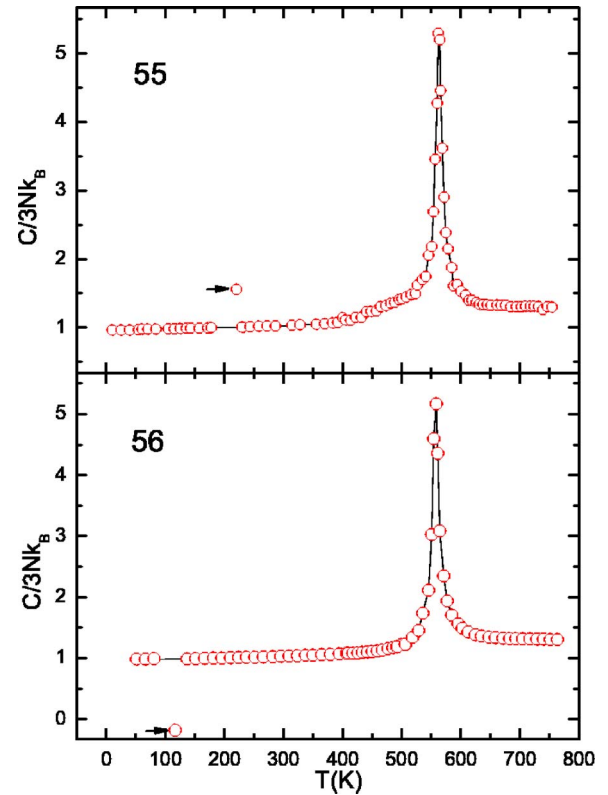


FIG. 2. (Color online) Plot of heat capacities of two isomers of Al_{55} (-159.0475 and -158.5483 eV) and Al_{56} (-161.7489 and -161.3523 eV). The solid lines are heat capacities of the lowest-energy structure and the open circles are those of the higher-energy isomers. The circles indicated by an arrow are unconverged values which indicate that a structural transition occurs.

-158.5483 eV, respectively. The first structure of Al_{56} has C_{3v} symmetry, with potential energy -161.7489 eV. The second has no symmetry and its potential energy is -161.3523 eV. For Al_{55} , at temperatures lower than 177 K, there is almost no difference between the heat capacities of the two isomers. At the point next to 177 K, the temperature jumps to 220 K and the heat capacity deviates very much from other values, which indicates that there is a structural transition. The same thing happens in Al_{56} , with the transition temperature lower and the deviated value negative. Because the process including this transition is not an equilibrium process, it becomes difficult to converge the heat capacity. As a consequence, these deviated values of heat capacity are not converged values. At the higher temperatures after this transition, the heat capacities of the two isomers become the same again.

Figure 3 shows the variation of potential and kinetic energies in the simulation runs during which the structural transition happens, corresponding to the two deviated points in Fig. 2. The steplike change of the potential energy is caused by a structural change. It is interesting to note that this change is irreversible in all these simulations. A series of this kind of simulations for several clusters shows that, whatever the initial structure is, it will transit into the lowest-energy structure before melting.

Since different isomers have almost the same heat capaci-

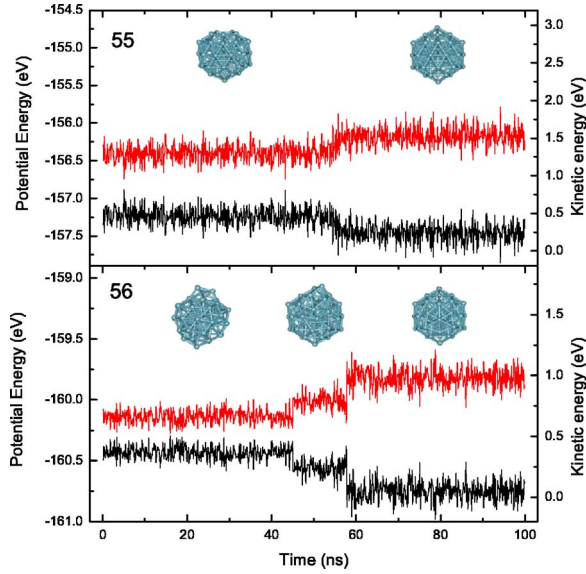


FIG. 3. (Color online) Variation of the potential energy (the lower line) and kinetic energy (the upper line) of Al_{55} and Al_{56} of the simulation runs during which structural transitions happen. The starting structures are higher-energy isomers. The temperature changes from 188 to 220 K after the transition for Al_{55} . For Al_{56} it changes from 95 to 113 K and 140 K.

ties at temperatures lower than the transition temperature, it is clear that the dip is not caused by the difference between the heat capacities of different structures. 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 capacity values of Al_{57} calculated in the simulation. First let us look back at Breaux *et al.*'s experiment. Assume that the clusters dissociate when their energy reaches E_m . The initial translational energy E_t needed to dissociate the clusters is related to the internal energy of the clusters U_i by

$$pE_t = E_m - U_i. \quad (3)$$

Here p is the proportional constant of the 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

$$C = \partial U_i / \partial T = -p \partial E_t / \partial T. \quad (4)$$

This is the starting point of the experiment.

Sparse data were taken from the numerical integration of the heat capacity curve as the translational energy required for 50% dissociation (TE50%D)⁵ values. Suppose there are two kind of isomers, 50% s_0 and 50% s_1 , involved in the experiment at low temperature T_1 . Since the internal energy of clusters is the only factor determining the TE50%D needed to dissociate them, we can substitute the clusters of structure s_0 by clusters of structure s_1 which have the same internal energy, when the temperature is below that at which structural transition happens. So those clusters are equal to 100% s_0 with temperature T_2 . Suppose the difference be-

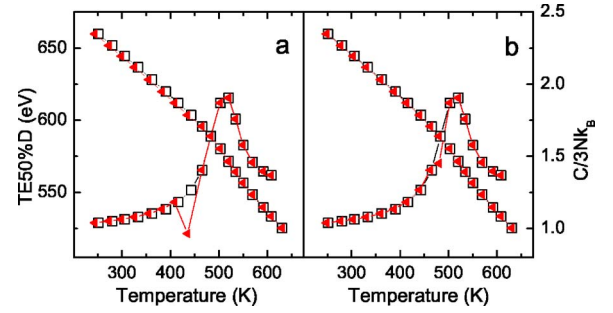


FIG. 4. (Color online) Plots of TE50%D and its derivative against temperature for Al_{57} . TE50%D values represented by open squares are converted from sparse data taken from integration of the heat capacities calculated from MD simulations. (a) Assume at about 443 K that all metastable structures are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

tween the potential energies of two structures is 0.1 eV, the temperature difference between two structures with the same internal energy is $\Delta T = 2\Delta(Ek)/(3N-6)k_B \approx 14$ K. So the difference between T_1 and T_2 is 50% $\Delta T = 7$ 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 Fig. 4(a). Considering that there may be several kinds of isomers generated by the cluster source, it is not hard to understand that in Breaux *et al.*'s results⁵ some slight decreases exist before the dip in heat capacities of Al_{57} . 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 in the same way as 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 needed to dissociate the cluster and this leads to shoulders, which is shown in Fig. 4(b).

In summary, we have investigated the heat capacity of aluminum clusters with around 55 atoms, using extremely long time MD simulations with the empirical Gupta potential.²² The melting points are in the same range as the experimental result. Using different structures as the initial structure for the simulation, we find that high-energy isomers transit into the lowest-energy structure before melting. Higher-energy isomers have the same heat capacity as the lowest-energy isomer at low temperatures. So the dips found in the experiment are not caused by the difference between the heat capacities between different structures before and after the structural transition.

This work was supported by the National Natural Science Foundation of China (Grants No. 10575012 and No. 10435020).

*Electronic address: fszhang@bnu.edu.cn

- ¹M. Schmidt, R. Kusche, W. Kronmüller, B. von Issendorff, and H. Haberland, *Phys. Rev. Lett.* **79**, 99 (1997).
- ²M. Schmidt, R. Kusche, B. Issendorff, and H. Haberland, *Nature (London)* **393**, 238 (1998).
- ³G. A. Breaux, R. C. Benirschke, T. Sugai, B. S. Kinnear, and M. F. Jarrold, *Phys. Rev. Lett.* **91**, 215508 (2003).
- ⁴G. A. Breaux, D. A. Hillman, C. M. Neal, R. C. Benirschke, and M. F. Jarrold, *J. Am. Chem. Soc.* **126**, 8628 (2004).
- ⁵G. A. Breaux, C. M. Neal, B. Cao, and M. F. Jarrold, *Phys. Rev. Lett.* **94**, 173401 (2005).
- ⁶H. Haberland, T. Hippler, J. Donges, O. Kostko, M. Schmidt, and B. von Issendorff, *Phys. Rev. Lett.* **94**, 035701 (2005).
- ⁷G. Bertsch, *Science* **277**, 1619 (1997).
- ⁸R. S. Berry, *Nature (London)* **393**, 212 (1998).
- ⁹F. Balletto and R. Ferrando, *Rev. Mod. Phys.* **77**, 371 (2005).
- ¹⁰H. L. Davis, J. Jellinek, and R. S. Berry, *J. Chem. Phys.* **86**, 6456 (1987).
- ¹¹A. Heidenreich, I. Oref, and J. Jortnor, *J. Phys. Chem.* **96**, 7517 (1992).
- ¹²J. Jellinek and A. Goldberg, *J. Chem. Phys.* **113**, 2570 (2000).
- ¹³F. Calvo and F. Spiegelmann, *J. Chem. Phys.* **120**, 9684 (2004).
- ¹⁴K. Manninen, A. Rytönen, and M. Manninen, *Eur. Phys. J. D* **29**, 39 (2004).
- ¹⁵D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A* **101**, 5111 (1997).
- ¹⁶D. J. Wales, *Science* **293**, 2067 (2001).
- ¹⁷Y. G. Chushak and L. S. Bartell, *J. Phys. Chem. B* **105**, 11605 (2001).
- ¹⁸A. Aguado and J. M. Lopez, *Phys. Rev. Lett.* **94**, 233401 (2005).
- ¹⁹M. Lee, S. Chacko, and D. G. Kanhere, *J. Chem. Phys.* **123**, 164310 (2005).
- ²⁰E. G. Noya, J. P. K. Doye, and F. Calvo, *Phys. Rev. B* **73**, 125407 (2006).
- ²¹F. Calvo and F. Spiegelmann, *J. Chem. Phys.* **112**, 2888 (2000).
- ²²R. P. Gupta, *Phys. Rev. B* **23**, 6265 (1981).
- ²³F. Cleri and V. Rosato, *Phys. Rev. B* **48**, 22 (1993).
- ²⁴L. Verlet, *Phys. Rev.* **159**, 98 (1967).
- ²⁵D. M. Deaven and K. M. Ho, *Phys. Rev. Lett.* **75**, 288 (1995).
- ²⁶E. M. Pearson, T. Halicioglu, and W. A. Tiller, *Phys. Rev. A* **32**, 3030 (1985).
- ²⁷S. Sawada and S. Sugano, *Z. Phys. D: At., Mol. Clusters* **14**, 247 (1989).