Size dependent melting mechanisms of iron nanoclusters

Haiming Duan a,*, Feng Ding b, Arne Rosén a, Avetik R. Harutyunyan c, Stefano Curtarolo d, Kim Bolton a,e

a Physics Department, Göteborg University, SE-412 96 Göteborg, Sweden
b ME&MS Department, Rice University, Houston, TX 77005, USA
c Honda Research Institute USA Inc., Columbus, OH 43212, USA
d ME&MS, Duke University, Durham, NC 27708, USA
e School of Engineering, University College of Borås, SE-501 90, Borås, Sweden

Received 1 September 2006; accepted 3 January 2007
Available online 9 January 2007

Abstract

Molecular dynamics simulations were used to study the change in the mechanism of iron cluster melting with increasing cluster size. Melting of smaller clusters (e.g., Fe_{55} and Fe_{100}) occurs over a large temperature interval where the phase of the cluster repeatedly oscillates between liquid and solid. In contrast, larger clusters (e.g., Fe_{300}) have sharper melting points with surface melting preceding bulk melting. The importance of the simulation time, the force field and the definition of cluster melting is also discussed.

Keywords: Iron cluster; Molecular dynamics; Melting mechanism

1. Introduction

Nanoscale clusters are becoming increasingly important in many technological applications, such as the use of pure metal or alloy nanocatalysts for carbon nanotube production. For example, pure iron catalysts are used in the carbon vapour deposition (CVD) production of single-walled carbon nanotubes (SWNTs) [1]. These particles are believed to act as catalysts for the decomposition of carbon feedstock as well as templates for the nucleation and growth of the SWNTs [2]. An important step that links these two roles is the diffusion of carbon from the decomposition site to the growing nanotube structure, which is expected to be affected by the liquid or solid phase of the nanocluster [1,3]. It is therefore important to know how the melting point of these clusters depends on, for example, cluster size and carbon content, and to understand cluster dynamics of solid, molten and melting clusters that may affect carbon diffusion.

There have been numerous experimental [4–10] and theoretical [11–13] studies of cluster melting. These have lead to the development and application of various models of melting, such as the homogeneous melting model with a liquid layer [5], the liquid-layer melting model [14,15], the liquid nucleation and growth model with an unstable liquid layer [16,17], the liquid drop model [18] and the surface phonon instability model [19]. All of these models, which generally fit well to experimental measurements, yield a (near) linear decrease in melting point with decreasing cluster diameter. Other studies have focused on phase coexistence in finite systems [20], the pre-melting transitions between two stable solid structures [21–23], the formation of ‘liquid-like’ surface layers on solid particles that precedes bulk melting [24–26], the bistability between liquid and solid phases at temperatures below complete melting [27,28] and high cluster melting temperatures for very small clusters [29] and magic number geometries [30].

* Corresponding author. Tel.: +46 31 7723296; fax: +46 31 7723496.
E-mail address: Haiming.Duan@physics.gu.se (H. Duan).
The molecular dynamics (MD) results presented here, for iron clusters containing 55, 100 and 300 atoms, extend our understanding of the melting mechanism as a function of cluster size. For the initial geometries at the low temperature, the 55 atom cluster has the Mackay icosahedral magic number structure, and the 100 and 300 atoms clusters are spherical.

Similarly to previous studies using microcanonical simulations and critical droplet theory [31], this work covers the range from small clusters that show oscillations between liquid and solid phases during melting, to larger clusters that show surface melting. In addition, we evaluate the atomic motion during the melting process, at the same time as analysing parameters such as the Lindemann indices and cluster energies that are traditionally used for studying cluster melting. This allows us to explicitly correlate changes in these parameters with the atomic motion, giving a deeper insight of the melting mechanism, and how this mechanism changes with cluster size.

2. Method

The force field and simulation method used in this work is discussed in detail elsewhere [2]. Briefly, a many-body interaction potential, which is based on the second moment approximation of the tight binding model [32,33], is used for the Fe–Fe interactions, with parameters from Ref. [34]. The simulated melting point of bulk iron, obtained by extrapolating the cluster melting points to infinitely large size, is 1640 K which is lower than the experimental value of 1809 K. This difference, which may be due to the inclusion of free cluster surfaces in the simulations or inaccuracies in the force field, does not affect the results reported here, which focus on trends of cluster melting. Melting of $N_{atom}$ (where $N_{atom} = 55, 100$ and $300$) clusters was studied by constant temperature MD using the Berendsen scaling method [35] and an integration time step of 1 fs. Initial cluster geometries were obtained by randomly placing the atoms in a sphere before steepest decent optimisation to a local energy minimum. The cluster was then heated to 2000 K, which is well above the melting point, before using simulated annealing (SA) to search for the global minimum structure [36]. This was done by decreasing the temperature from 2000 K to less than 200 K, which is lower than the melting point of any cluster studied here. 50000 MD steps were propagated at each temperature, which was decreased by 5% between successive temperatures. Varying the number of MD steps or the cooling rate did not affect the melting temperatures reported here.

Simulation of cluster melting began with the annealed structure about 400 K below the melting point, and the temperature was increased in steps of 20 K (Fe$_{55}$ and Fe$_{100}$) or 25 K (Fe$_{300}$) until melting occurred. To test the effect of simulation time on the results, two set of simulations were performed. In the first, called 1 ns simulation below, $10^6$ MD steps were propagated at each temperature, and in the second, termed 10 ns below, $10^7$ MD steps were propagated at each temperature. The average total cluster energy, $E_{tot}$, was determined at each temperature and used to plot caloric curves. In addition, the Lindemann index [37] of each atom

$$\delta_i = \frac{1}{N-1} \sum_{j\neq i} \sqrt{\langle r_{ij}^2 \rangle_T - \langle r_{ij} \rangle_T^2}$$

was calculated at each temperature, where $\delta_i$ is the Lindemann index of the $i$th atom, $\langle \cdots \rangle_T$ denotes the thermal average at temperature $T$ and $r_{ij}$ is the distance between the $i$th and $j$th atoms. The cluster Lindemann index, $\delta_c$, is the average over all $\delta_i$.

To explicitly correlate the change in cluster energy and Lindemann indices with the atomic motion (i.e., the melting mechanism), we also analysed the change in atomic positions over time at each temperature. This was done by monitoring the spherical coordinates, i.e., the distance of each atom from the cluster centre of mass, $r$, and the motion in the two directions perpendicular to the vector $r$ and that are tangential to the sphere with radius $r$. The latter two coordinates are denoted $\theta$ and $\phi$ which have values between $0^\circ$ and $180^\circ$ and $0^\circ$ and $360^\circ$, respectively.

3. Results and discussion

Fig. 1a shows the caloric curve and cluster Lindemann indices, $\delta_c$, obtained for Fe$_{55}$ from a 1 ns simulation. It is clear that there are fluctuations in the caloric curve (and in the Lindemann indices) which, as described previously [26], is a result of coexistence of liquid and solid phases during melting. That is, there is a temperature interval...
(≈860–940 K seen by the vertical lines in the figure) where the cluster repeatedly oscillates between being completely liquid and completely solid. However, as discussed below, the oscillations are also a result of the short simulation time, and the solid–liquid coexistence does not lead to oscillations in the caloric curve when one obtains statistically converged results.

The details of the solid–liquid coexistence are revealed by monitoring the dynamics of the individual cluster atoms. Fig. 2 shows the variation in centre of mass distance, \( r \), and angle \( \theta \) that is typical for atoms that are initially the core, middle and surface cluster atoms (the Fe\(_{55}\) cluster has approximately two atomic shells surrounding a core atom). The change in \( \phi \) is similar to that in \( \theta \) and is thus not shown. Panels a and b show changes in \( r \) and \( \theta \) at 780 K, Panels c and d at 860 K and Panels e and f at 920 K. It is evident that the movement of the atoms in the cluster is highly correlated. That is, atoms do not move independently of one another, but the movement of any atom is accompanied by the movement of all, or most, of the other atoms. For example, at 780 K there is very little change in \( r \) for any of the atoms until 0.5 ns, at which stage all atoms show a change in \( r \). After this time there is, once again, very little change for any of the atoms. Similarly, there is very little change in \( \theta \) for any of the atoms at this temperature until 0.35 ns, when both the outer and middle atoms show change in this coordinate. At 0.5 ns all atoms show large changes in \( \theta \), as they did in \( r \) at this time, and after this none of the atoms display any further changes. Similar correlations are seen at the other temperatures. The cluster can be considered as ‘liquid’ during the periods when all atoms move, and solid when all atoms remain in their lattice positions. It is clear that the time when the cluster is liquid increases with increasing temperature, leading to the increase in the caloric curve and cluster Lindemann indices.

Fig. 2 also shows the reason for the fluctuations in the caloric curve in Fig. 1a. The average energy at each temperature depends on the relative times that the cluster is in the liquid versus solid phase. At 780 K there are less than five liquid–solid transitions during the 1 ns trajectory, and at 860 K there are less than 15 transitions. To compare the average cluster energy at different temperatures, the simulation time must be sufficiently long to obtain statistically converged results at each temperature. That is, the short simulation times used for Fig. 2 do not allow for valid sampling of liquid–solid transitions, and this leads to fluctuations in the caloric curve in Fig. 1a. Increasing the simulation time to 10 ns at each temperature results in the smoother caloric curve shown in Fig. 1b. Hence, the liquid–solid phase coexistence seen in Fig. 2 does not necessarily result in fluctuations in the caloric curve, and these fluctuations are also a result of too short simulation times that do not yield statistically converged results.

A second issue made evident by Fig. 2 is the difficulty in defining the onset of cluster melting. From Fig. 2a and b it is clear that the Fe\(_{55}\) cluster has two solid–liquid–solid transitions (≈0.4 and 0.55 ns) at 780 K, which is far below the melting temperature of ≈860–940 K that one obtains from the caloric curves in Fig. 1a or b. That is, these two transitions in the 1 ns simulation do not make a significant change to the average energy. However, the Lindemann index is sensitive to these transitions, as seen by the large fluctuation in Fig. 1a at 780 K. We have also observed that, due to its sensitivity, the Lindemann index can show fluctuations even when some cluster atoms have large amplitude vibrations around their lattice positions, which may not be associated with melting. For example, Fig. 3a shows the Lindemann index of each atom as a function of its average distance from the cluster centre of mass at 760 K for Fe\(_{55}\) and the 1 ns simulation (this corresponds to the first large increase in the cluster Lindemann index seen at 760 K in Fig. 1a). The Lindemann indices for the same cluster at 600 K and 980 K are shown for comparison. It is clear that the increase in the cluster Lindemann index at 760 K is primarily due to the increase in the indices of the surface atoms and that, since these increases are only due to vibrations, they are far lower than those for the melted cluster at 980 K. This, together with the fact that there are distinct core, middle and surface atoms (seen by the grouping of the atoms at ≈0, 2.5, 4.3 and 5 Å at 760 K but not at 980 K), indicates that the cluster is not melted at 760 K. This is confirmed by the change in position of the atoms over time and, as exemplified by \( r \) and \( \theta \) in Fig. 3b and c, the change in Lindemann index at 760 K is due to vibrations of the atoms and not by changes in their location. That is, there is almost no change in \( r \) for any of the atoms shown in Fig. 3b, and the change in \( \theta \) is also very small for all atoms (note that very small changes in position of the atoms would affect the change in \( \theta \)).
core atom can yield large changes in $\theta$ for this atom). For these reasons, and since there are significant fluctuations in the Lindemann indices even for the longer 10 ns trajectories (Fig. 1b), we use the caloric curves to determine the melting temperatures in this work. This is consistent with experimentally measured melting points which are usually determined from latent heats. However, the choice of the parameter (Lindemann index or cluster energy) depends on how one identifies the onset of melting, and it is important to clearly state which parameter one uses to obtain the simulated melting point.

The melting mechanism of the Fe$_{100}$ cluster is very similar to that of the Fe$_{55}$ cluster, showing that the mechanism is not specific for magic number clusters. Similarly to the discussion above, there are fluctuations in the caloric curve for the shorter 1 ns trajectory, making it difficult to identify a melting interval. However, the caloric curve obtained from the 10$^7$ step simulation was smooth (similar to that of Fig. 1b) and yielded a melting interval of 760 to 800 K. The melting interval is thus narrower than that of Fe$_{55}$, as is expected for larger clusters. It is noteworthy that the Fe$_{100}$ cluster melts at a lower temperature than Fe$_{55}$, which is due to the increased stability of the magic number cluster as previously seen for Ga clusters [30]. Preliminary results of studies based on other iron clusters show that clusters that have similar sizes to Fe$_{55}$ but that are not magic number clusters (e.g., Fe$_{50}$ and Fe$_{60}$) have melting points ($\approx$640–780 K) that are lower than that of Fe$_{55}$.

Very different melting is seen for larger clusters. Fig. 4 shows the caloric curve and Lindemann indices for Fe$_{300}$ obtained from the 10 ns simulation (similar results are observed for the 1 ns simulation). The melting point at $\approx$1100 K is sharp, which is consistent with the trend that larger clusters have narrower melting intervals. Also, in contrast to the results obtained from the smaller clusters, the change in Lindemann indices is in fairly good agreement with the change in total energy, although it still occurs at slightly lower temperatures.

The melting mechanism is also very different for these larger clusters. Fig. 5a and b show the change in $r$ and $\theta$ for inner and surface atoms of Fe$_{300}$ at 1075 K obtained from the 10 ns simulation. It is clear that the movement of inner and surface atoms is not strongly correlated (as they were in Fig. 2 for Fe$_{55}$) and that the surface atom is more mobile. For example, the surface atom exhibits two changes in $r$ and $\theta$ between 1 and 2 ns, and a very large change in these variables at 10 ns. This is not accompanied by similarly large changes in the inner atom coordinates, where $r$ remains almost constant over the entire trajectory and the fluctuations in $\theta$ (which are rather large since this is the inner atom) are not pronounced at the times when the outer atom showed large amplitude motion. This large amplitude motion of the outer atoms that is not accompanied by similar motion of the inner atoms is associated with ‘surface melting’ or a ‘liquid-like layer’, and is also evident in Fig. 5c, which shows the atomic Lindemann indices for Fe$_{300}$ obtained from the 10 ns simulation at 900, 1075 and 1100 K. Similarly to the small clusters, one can identify inner and ‘surface’ atoms at temperatures below melting. However, in contrast to the smaller clusters, the surface atoms just below melting (1075 K) have Lindemann indices.
of similar magnitude to the atoms in the molten cluster, and there is a clear clustering of the average centre of mass positions of these atoms (around 8 Å in the figure).

It is important to note that this paper focuses on qualitative results, i.e., trends in the melting intervals and mechanisms with changes in cluster size. This is partly due to the difficulty in defining the onset of the melting (using the Lindemann indices would yield different melting points but the same trends), but also because of possible inaccuracies in the force field used for these calculations. We have thus not focussed on quantitative results such as the specific cluster size(s) where the change from ‘solid–liquid coexistence’ to ‘surface melting’ mechanism occurs. However, of significance here is that other force fields, including those for gold [22] and aluminium [26] clusters, show similar trends as those seen here, which indicates that the results reported here are not an artefact of the force field.

4. Conclusion

The molecular dynamics studies presented here show that small and large iron clusters have different melting mechanisms. Melting of smaller clusters (e.g., Fe\textsubscript{55} and Fe\textsubscript{100}) occurs over a large temperature range, where there are repeated transitions between the liquid and solid phases. That is, at any particular instant the cluster is entirely liquid (seen by the simultaneous motion of all, or most, cluster atoms) or entirely solid. In contrast, larger clusters have sharper melting points, and ‘liquid-like’ surface regions simultaneously coexist with solid cluster cores at temperatures below melting. Hence, although both mechanisms can be described as liquid–solid phase coexistence, the coexistence for the small clusters is over time and for the large clusters over space.

The work presented here focuses on qualitative trends in the change in melting points and mechanisms with cluster size, which are not sensitive to the simulation time, force field, or if the Lindemann index or caloric curve is used in the analysis.

Acknowledgements

The authors are grateful for time allocated on the Swedish National Supercomputing facilities. Financial support was obtained from the Swedish Research Council, the Swedish Foundation for Strategic Research (CARAMEL consortium) and The Honda Research Institute, Inc.

References
