Size–sensitive melting characteristics of gallium clusters: Comparison of Experiment and Theory for Ga$_{17}^+$ and Ga$_{20}^+$

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Experiments and simulations have been performed to examine the finite-temperature behavior of Ga$_{17}^+$ and Ga$_{20}^+$ clusters. Specific heats and average collision cross sections have been measured as a function of temperature, and the results compared to simulations performed using first principles Density–Functional Molecular–Dynamics. The experimental results show that while Ga$_{17}^+$ apparently undergoes a solid–liquid transition without a significant peak in the specific–heat, Ga$_{20}^+$ melts with a relatively sharp peak. Our analysis of the computational results indicate a strong correlation between the ground–state geometry and the finite–temperature behavior of the cluster. If the ground–state geometry is symmetric and “ordered” the cluster is found to have a distinct peak in the specific–heat. However, if the ground–state geometry is amorphous or “disordered” the cluster melts without a peak in the specific–heat.

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I. INTRODUCTION

It is now well established that the melting points of particles with thousands of atoms decrease smoothly with decreasing particle size, due to the increase in the surface to volume ratio. However, unlike particles with thousands of atoms or the bulk material, probing the finite–temperature properties of small clusters (with < 500 atoms) is non–trivial and remains a challenging task. Experimental studies of the melting transitions of clusters in small size regime have only recently become possible. Several interesting phenomena have been observed, including melting temperatures that rise above the bulk values and strong size–dependent variations in the melting temperatures. These experimental findings have motivated many theoretical investigations on the finite–temperature behavior of clusters. Simulations based on first principles have been particularly successful in quantitatively explaining the factors behind the size–dependent variations in the melting behavior of clusters. Thus, a confluence of recent advances in experimental methods and theoretical studies using first principles methods have set the stage for a major increase in our understanding of phase transitions in these small systems.

Coming to the present work on gallium clusters, it is by now well known that gallium clusters not only melt at substantially higher temperatures than the bulk ($T_m$bulk = 303 K), but they also exhibit wide variations in the temperature dependences of their specific–heats, with some clusters showing strong peaks (due to the latent heat), while others (apparent “non-melters”) showing no peak. These features show a strong dependence on cluster size, where the addition of a single atom can change a cluster with no peak in the specific–heat into a “magic melter” with a very distinct peak. This behavior has been observed for gallium clusters, Ga$_n$, with $n$ = 30–55.

In the present work, we probe the melting behavior of small gallium cluster ions where we show that the “non-melting” and “melting” features in the specific–heats are observed in clusters as small as Ga$_{17}^+$ and Ga$_{20}^+$, respectively. Prior experimental results for Ga$_{17}^+$ over a limited temperature range showed no evidence for a melting transition. The experimental results in this case were specific–heat measurements performed using multi–collision induced dissociation, where a peak in the specific–heat due to the latent heat was the signature of melting. On the other hand, recent simulations for Ga$_{17}^+$ show a broad peak in the specific–heat centered around 600 K. The previous specific–heat measurements for Ga$_{17}^+$ extended only up to 700 K, so one possible explanation for this apparent discrepancy is that the melting transition occurred at a slightly higher temperature than examined in the experiments. Here, we report specific–heat measurements for Ga$_{17}^+$ over a more extended temperature range, along with specific–heat measurements for Ga$_{20}^+$. While no peak is observed in the heat–capacities for Ga$_{17}^+$, a peak is observed for Ga$_{20}^+$.

To further probe the melting transitions in these clusters, ion mobility measurements were performed for Ga$_{17}^+$ and Ga$_{20}^+$ as a function of temperature. The ion mobility measurements provide average collision cross sections which can reveal information about the shape and volume changes that occur on melting. For example, a cluster with a non–spherical geometry might be expected to adopt a spherical shape (a liquid droplet) on melting. If there is not a significant shape change, there may still be a volume change on melting. Most bulk materials expand when they melt (the liquid is less dense than the
across the collision cell by a small electric field and some
ions may be heated to the point where they dissociate.
initial kinetic energy is high enough some of the cluster
ions translational energy into internal energy. If the
cluster ions are generated by laser vaporization of a liquid
gallium target in a continuous flow of helium buffer gas.
Experimental and theoretical results on both clusters. We
the computational details. In Sec. III we discuss the ex-
accessible as the temperature is raised.
structure, and the isomer distribution that becomes
geometry, the bonding of the atoms within the ground–
state structure, and the isomer distribution that becomes
accessible as the temperature is raised.
In Sec. II we present the experimental methods and
the computational details. In Sec. III we discuss the ex-
perimental and theoretical results on both clusters. We
conclude our results in Sec. IV.

II. METHODOLOGY

Specific-heats were measured using the recently de-
veloped multi–collision induced dissociation approach. The
cluster ions are generated by laser vaporization of a liquid
gallium target in a continuous flow of helium buffer gas.
After exiting the laser vaporization region of the source
the clusters travel through a 10 cm long temperature vari-
able extension where their temperature is set. Cluster
ions that exit the extension are focused into a quadrupole
mass spectrometer where a particular cluster size is se-
lected. The size selected clusters are then focused into a
collision cell containing 1 Torr of helium. As the clusters
enter the collision cell they undergo numerous collisions
with the helium, each one converting a small fraction of
the ions translational energy into internal energy. If the
initial kinetic energy is high enough some of the cluster
ions may be heated to the point where they dissociate.
Dissociated and undissociated cluster ions are swept
across the collision cell by a small electric field and some
of them exit through a small aperture. The ions that exit
are analyzed in a second quadrupole mass spectrometer
and then detected by an off–axis collision dynode and
dual microchannel plates. The fraction of the ions that
dissociate is determined from the mass spectrum. Mea-
surements are performed as a function of the ions initial
kinetic energy, and the initial kinetic energy required for
50% dissociation (IKE50%D) is determined from a lin-
ear regression. IKE50%D is measured as a function of
the temperature of the temperature–variable extension on
the source. IKE50%D decreases as the temperature is
raised because hotter clusters have more internal en-
ergy, and hence less energy needs to be added in order
to cause dissociation. At the melting transition a sharp
decrease in IKE50%D is expected due to the latent heat.
The derivative of IKE50%D with respect to temperature
is approximately proportional to the specific–heat. The
proportionality constant is the fraction of the clusters ini-
tial kinetic energy that is converted into internal energy,
which is estimated from an impulsive collision model. A
drop in the IKE50%D values due to the latent heat of a
melting transition leads to a peak in the specific–heat.

Ion mobility measurements can provide information on
the shape and volume changes that occur when clusters
melt. For the ion mobility measurements, the collision
cell is replaced by a 7.6 cm long drift tube. 50 µs pulses
of cluster ions are injected into the drift tube and the drift
time distribution is obtained by recording the ions arrival
times at the detector with a multichannel scalar. Average
collision cross sections are obtained from the drift time
distributions using standard methods.21

All the simulations are performed using Born–
Oppenheimer molecular–dynamics based on Kohn–Sham
formulation of Density–Functional Theory (DFT).22
We have used Vanderbilt’s ultrasoft pseudopotentials23
within the GGA approximation, as implemented in the
VASP package24 for both clusters. For all calculations,
we use only 4s2 and 4p1–electrons as valence, taking the
5d–electrons25 as a part of the ionic core. An energy
cutoff of about ≈ 10 Ry is used for the plane–wave ex-
pansion of the wavefunction, with a convergence in the
total energy of the order of 0.0001 eV. Cubic supercells
of lengths 20 and 25 Å are used for Ga$_{17}^+$ and Ga$_{20}^+$,
respectively. For examining the finite–temperature behav-
ior, the ionic phase space of the clusters is sampled by
isokinetic MD where kinetic energy is held constant via
a velocity scaling method. For both the clusters, we split
the total temperature range from 100–1400 K into 15
different temperatures. We maintain the cluster at each
temperature for a period of at least 90 ps, leading to
total simulation times of the order of 1 ns. The result-
ing trajectory data were used to compute standard ther-
modynamic indicators as well as the ionic specific–heat,
via a multihistogram technique. Details can be found in
Ref. 20,21.
III. RESULTS AND DISCUSSION

Specific-heats measured for Ga\textsuperscript{+\textsubscript{17}} and Ga\textsuperscript{+\textsubscript{20}} as a function of temperature are shown in the lower half of Fig. 1. The points are the experimental values, while the dashed line is the prediction of a modified Debye model. In the case of Ga\textsuperscript{+\textsubscript{17}}, the specific-heats shown in Fig. 1 appear to gradually increase up to around 900 K. The sharp decrease in the specific-heats above 900 K is an artifact due to evaporative cooling, the spontaneous unimolecular dissociation of the cluster ions as they travel between the source extension and the collision cell. For Ga\textsuperscript{+\textsubscript{20}}, the specific-heats show a broad maximum, around 400 K wide, centered at around 725 K. The peak for Ga\textsuperscript{+\textsubscript{20}} is significantly broader than observed for larger clusters (like Ga\textsuperscript{+\textsubscript{39}} and Ga\textsuperscript{+\textsubscript{40}}) where the peak was attributed to a melting transition. However, it is well known that the melting transition, and the corresponding peak in the specific-heats, becomes broader with decreasing cluster size. Thus, even though the peak in the specific-heats for Ga\textsuperscript{+\textsubscript{20}} is around 400 K wide, it is appropriate to assign it to a finite-size analog of a bulk melting transition. The center of the peak is at around 725 K, this is well above the bulk melting point (303 K). This continues a trend reported for larger cluster sizes (\(n = 30–55\)) where the melting temperatures are also significantly above the bulk value. The unfilled red circles in Fig. 1 show the average collision cross sections determined for Ga\textsuperscript{+\textsubscript{17}} and Ga\textsuperscript{+\textsubscript{20}} as a function of the temperature. The cross sections are expected to systematically decrease with increasing temperature because the long range attractive interactions between the cluster ion and the buffer gas atoms becomes less important, and the collisions become harder as the temperature is raised. The thick dashed red line in the figures show the expected exponential decrease in the cross sections with increasing temperature. There is an inflection in the cross sections for Ga\textsuperscript{+\textsubscript{20}} that appears to slightly precede the peak in the specific-heat for this cluster. The inflection is consistent with a melting transition where the liquid cluster has a larger coefficient of thermal expansion than the solid. There is also an inflection in the cross sections for Ga\textsuperscript{+\textsubscript{17}}. This suggests that a solid–liquid transition also occurs for Ga\textsuperscript{+\textsubscript{17}}, but without a significant peak in the specific-heat.

To understand the reason behind the different behavior observed for Ga\textsuperscript{+\textsubscript{17}} and Ga\textsuperscript{+\textsubscript{20}}, we have carried out a detailed analysis of structure and bonding in both clusters. As will become apparent from the following discussion, that the ground-state geometry and the nature of bonding plays a crucial role in determining the finite-temperature behavior of the cluster. We begin with a discussion of the ground-state geometries of cationic Ga\textsubscript{17} and Ga\textsubscript{20} clusters. We have obtained more than 50 distinct equilibrium geometries by quenching more than 200 structures, selected from a few high temperature MD runs, for both sizes. In Fig. 2, we show the lowest energy structure along with some low lying excited state geometries of both clusters. The lowest energy geometry...
of the Ga$_{17}^{+}$ cluster (see Fig. 2(a(1))) is similar to that of Ga$_{17}$ reported in our earlier work. It has a distorted decahedral structure, which suggests the possibility of further cluster growth to a 19-atom double decahedron. In contrast, the ground–state geometry of Ga$_{20}^{+}$, shown in Fig. 2(b(1)), is more symmetric. It can be described as a double decahedral structure of 19 atoms, with the bottom capped atom merging into the pentagonal plane to form a hexagonal ring. In addition, an atom from the top pentagon and the upper capped atom rearrange to accommodate the 20th atom, leading to a dome–shaped hexagonal ring.

We now analyze the structural properties in detail to get an insight into the features that influence the melting characteristics. An analysis of the bond–length distribution shows that there are 12 bonds, for each cluster, having distances less than 2.55 Å. Interestingly, for Ga$_{17}^{+}$, these short bonds are spread all over the cluster, whereas for Ga$_{20}^{+}$, they form the upper and the lower hexagonal rings. The distribution of coordination numbers indicate that for Ga$_{20}^{+}$, almost all the atoms in the rings (about 16), have a coordination number of 4. The Ga$_{17}^{+}$ cluster, however, does not have such a uniform distribution of coordination numbers. Thus, the ground–state geometry of Ga$_{17}^{+}$ might be considered to be “disordered”, while that of Ga$_{20}^{+}$ exhibits a more–ordered structure.

Striking differences are also observed in the low energy isomers and their distribution on the potential–energy surface. As mentioned above, we have obtained more than 50 distinct isomers spanning an energy range of about 1.0 eV above the ground–states for each cluster. In Fig. 3 we plot the energies of these isomers relative to the ground–state structures of Ga$_{17}^{+}$ and Ga$_{20}^{+}$ with respect to their ground–states.

The most important difference between the two clusters is the nature of the bonding. We use the concept of an electron localization function (ELF) to describe the nature of bonding. This function is normalized to a value between zero and unity; a value of 1 represents a perfect localization of the valence charge while the value for the uniform electron gas is 1/2. The locations of maxima of an isosurface are essentially correct.

![Fig. 3: The energies of the isomeric structures of Ga$_{17}^{+}$ and Ga$_{20}^{+}$ with respect to their ground–states.](image)

| ELF value | Ga$_{17}^{+}$ | Ga$_{20}^{+}$ |
|-----------|--------------|--------------|
| 0.85      | 0            | 1 (2)        |
| 0.77      | 1 (2)        | 2 (5,7)      |
| 0.75      | 3 (2,2,2)    | 2 (5,7)      |
| 0.73      | 2 (3,4)      | 1 (14)       |

The table clearly shows a fragmented growth pattern of the basins for Ga$_{17}^{+}$, each containing very few atoms as compared to that of Ga$_{20}^{+}$. For instance, at an iso-value of 0.75, while Ga$_{17}^{+}$ has three basins containing more than one atom, Ga$_{20}^{+}$ contains 12 basins.

The ELF value of about 0.73 signifies a localized bond in the system. Typically, the existence of an isosurface around an ELF value of 0.73 is a good indication of a localized bond in the system.
basins each having 2 atoms, Ga$_{20}^+$ has just two basins each containing 5 and 7 atoms that corresponds to the two hexagonal rings. The ELF contours for the isovalue of 0.75 are shown in Fig. 4. The merged basins structures are shown by the black lines. It may be inferred that the bonds between atoms in the hexagonal rings of Ga$_{20}^+$ are strong and covalent in nature with similar strengths, while the fragmented basin growth pattern in Ga$_{17}^+$ indicates inhomogeneity of the bond strengths.

The calculated, normalized, canonical specific-heats are shown in Fig. 5 plotted against temperature. The plot for Ga$_{17}^+$ exhibits a broad feature (apparently consisting of three components) which extends from 300 K to 1400 K. For Ga$_{20}^+$, the calculated specific-heat remains nearly flat up to about 600 K, it then increases sharply and peaks at about 800 K, in excellent agreement with the experimental results described above. Thus, interesting size-sensitive features seen in the experimental heat-capacities are reproduced in our simulations. This behavior can be understood from our earlier discussion of the bond-length distributions, coordination numbers, isomer-distributions, and the nature of bonding in these clusters. While the Ga$_{17}^+$ cluster shows no real evidence for ordered behavior, the Ga$_{20}^+$ cluster has well-ordered ring-patterns. Thus, when Ga$_{17}^+$ is heated, the bonds soften gradually, and the cluster hops through all its isomers continuously. This is clearly demonstrated by the ionic motion as a function of temperature, which shows that this cluster evolves through all isomers smoothly from 300 K to 1400 K. On the other hand, the ionic motion for Ga$_{20}^+$ shows only minor rearrangements of the atoms until 600 K, and then the cluster visits all the isomers corresponding to the first group of isomers described above. At about 700 K, the upper hexagonal ring breaks, while at about 800 K, the lower ring breaks. Thus, melting of Ga$_{20}^+$ cluster is associated with the breaking of the well-ordered covalently bonded hexagonal units.

We have also analyzed the melting characteristics via traditional parameters such as, the root-mean-squared bond-length-fluctuations ($\delta_{\text{rms}}$) and the mean-squared ionic displacements (MSD). In Fig. 6 we show the $\delta_{\text{rms}}$ for Ga$_{17}^+$ and Ga$_{20}^+$ clusters. This plot correlates well with the specific-heat curve shown in Fig. 5. The $\delta_{\text{rms}}$ for Ga$_{17}^+$ rises gradually from 300 K, while for Ga$_{20}^+$, it rises sharply at about 700 K, and finally saturates to the same value for both clusters. It may be inferred from this observation that the behavior of both clusters at temperatures say, $T \geq 800$ K, are similar and that both clusters can be considered to be in liquidlike states. This conclusion is further substantiated by the MSD plots (figures not shown), which saturate at $\approx 21 \, \text{Å}^2$ at about 1200 K for both clusters.
IV. SUMMARY AND CONCLUSION

It is evident from the present study that the nature of the ground-state geometry and bonding strongly influences the finite-temperature characteristics of Ga$_{17}^+$ and Ga$_{20}^{20+}$. At high temperatures, $T \geq 800$ K, both Ga$_{17}^+$ and Ga$_{20}^{20+}$ have similar root-mean-squared bond-length-fluctuations and the mean-squared ionic displacements so that both of them can be considered to be in liquidlike states. The experimental results show that while Ga$_{17}^+$ apparently undergoes a solid–liquid transition without a significant peak in the specific–heat, Ga$_{20}^{20+}$ melts with a relatively sharp peak. The simulations show that if the cluster is “ordered” (i.e. a large fraction of the constituent atoms occur in a wide distribution of bonding environments) it will probably undergo a solid–liquid transition without a significant peak in the specific–heat. In the latter case, the number of isomers or conformations sampled by the cluster increases steadily as the temperature is raised, instead of the abrupt increase that occurs when a cluster undergoes a sharp melting transition.

These observations have interesting consequences for the finite-temperature behavior of small clusters as a function of cluster size. It is likely that as clusters grow in size their structures evolve from one well–ordered structure to another, passing on the way through some cluster sizes that have “disordered” structures. For instance, the 13–atom gallium cluster is predicted to have a highly symmetric decahedron structure with a bonding pattern that is similar to that found here for Ga$_{20}^{20+}$. So in the present case, cluster growth from Ga$_{13}$ (a decahedron) to (Ga$_{20}^{20+}$, a distorted double–decahedron) proceeds via a disordered Ga$_{17}^+$ structure. Such behavior is also observed for sodium clusters in 40 to 55 atom size range; the ground–state geometries of Na$_{40}$ and Na$_{55}$ are either icosahedron or close to icosahedron while that of Na$_{50}$ has no particular symmetry. In such cases, we expect that the specific–heats should change from showing a well–defined peak to a rather broad one, and back again to well–defined. We believe this behavior to be generic as it has not only been observed in case of gallium clusters but also in case of aluminum clusters, experimentally, and for sodium clusters in the simulations mentioned above.

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