Premelting and Postmelting in Clusters

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Caloric curves for sodium clusters with \( N = 139 \) and 147 atoms show a fine structure near the solid-to-liquid transition. Neither of the two sizes exhibit surface melting. For \( N = 139 \), diffusion of the surface vacancies is observed, which is not possible in the closed-shell \( N = 147 \) cluster. A few kelvin above the peak in the heat capacity, \( N = 139 \) is completely liquid. This is not the case for \( N = 147 \). Here the inner 13 atoms remain nearly fixed up to several tens of kelvin above the melting temperature of the outer two layers. A simple physical reason is suggested for this unexpected behavior.

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The solid-to-liquid transition of a large system is the prototype of a classical first-order phase transition and occurs for a given pressure at a fixed temperature \( T_{\text{m}}^{\text{bulk}} \). The transition is often simplified as occurring between a perfect crystal and a completely disordered liquid. Actually the story is much richer. Much is known about premonitory effects near the melting transition of macroscopic samples [1]. Examples are substantial changes in volume, compressibility, heat capacity, and electric conductivity long before \( T_{\text{m}}^{\text{bulk}} \) is reached. These effects are mainly due to anharmonic thermal motion and the slow beginning of diffusion. Also, a liquid layer usually forms on a surface before the crystal melts. We show here that related effects happen in clusters.

The calorimeter for free, mass-selected clusters has been discussed earlier [2–8]. Briefly, positively charged sodium clusters are thermalized in a heat bath of temperature \( T \), and mass selected. The clusters absorb several photons from a pulsed laser and the mass spectrum of the photofragments is measured. Its temperature dependence allows us to determine the internal energy \( E \), and to construct the caloric curve, \( E = E(T) \) [2–8]. Figure 1 shows an example measured with an improved setup [9]. The published melting temperatures [8] have been reproduced to better than 0.5 K. The absolute energy scale in Fig. 1 was obtained by extrapolating the experimental data to \( T = E = 0 \) using the bulk heat capacity [11].

The simulations were performed using orbital-free \textit{ab initio} isokinetic molecular dynamics [12], where density functional theory is used to calculate the forces acting on the nuclei, whose motion is treated classically. An approximate density functional for the electron kinetic energy leads to a substantial simplification over the Kohn-Sham method, enabling long simulations (up to nearly 2 ns for each temperature) of large samples [13,14]. The calculations were performed on neutral clusters, whereas the experiment has to use charged ones. It is known from previous studies that the number of electrons does not have a significant effect on the structure and melting of sodium clusters in this size range [2,12–16].

Figure 1 compares the experimental and simulated caloric curves for \( N = 147 \) sodium atoms. A nearly linear behavior is seen at low temperature, followed by a smooth rise near 260 K, which is due to the increase of phase space near the solid-to-liquid transition. Above the melting temperature \( T_{\text{m}} \) (defined here as the temperature corresponding to the maximum slope of the caloric curve) the curves show again a nearly linear increase, with a larger slope than below \( T_{\text{m}} \). Similar data have been published earlier, and

FIG. 1 (color online). Measured (circles) and simulated (solid red line) canonical caloric curves for a sodium cluster with 147 atoms [10]. The straight line indicates the thermal energy of an \( N = 147 \) atom cluster, whose atoms interact with classical, harmonic forces. The three curves have been normalized to each other at 185 K. The increase near \( T_{\text{m}} \) is due to the melting transition. The difference in measured (259.7 K) and simulated (254.4 K) melting temperatures is only 2%. The inset shows the icosahedral structure of the \( N = 147 \) cluster. There are 12 vertex atoms (red), 60 atoms are on the ridges (blue), while there is only one central atom on the 20 faces (black). The binding energies increase from vertex to ridge to central atoms.
a generally good agreement between experiment and simulation has been obtained [13,14].

Many publications have concentrated on the dominant feature of the caloric curves near $T_m$: the smooth rise giving the melting temperature and the latent heat of melting [2–8,12–14]. Instead, we will focus here on structures far from $T_m$ which are indicators of the premonitory effects of cluster melting. For an accurate calculation, the simulations had to be carried out for significantly longer times than previously reported [13,14]. The heat capacity is the derivative of the caloric curve, and it is a standard procedure to discuss its fine structure and its general effect also observed in simulations of Lennard-Jones (LJ) clusters [17] and (ii) the diffusion of surface vacancies; i.e., some of the 60 ridge atoms (blue in Fig. 1) become visible in the cluster energy. Results are collected in Table I.

The heat capacity is the derivative of the caloric curve, and it is a standard procedure to discuss its fine structure near the melting transition [1,2]. A better diagnostic tool for the experimental data can be obtained by subtracting $E^*$ from the caloric curve, where $E^* = (3N - 6)k_B T$ is the thermal energy of an $N$-atom cluster in the classical harmonic approximation, and $k_B$ is Boltzmann’s constant. The results are given in Figs. 2 and 3. They show an unexpectedly complex melting scenario. The value of $T_1$ is defined as the lowest temperature at which the average cluster energy departs (within the noise level of the simulations) from the harmonic limit $E^*$. The statistical error is about 0.1 meV/atom, or $\Delta T = \pm 2$ K.

Experiment and theory [8,13,16] agree that the ground state of Na$_{147}$ is an icosahedron (see Fig. 1). Similarly, Na$_{139}$ is an icosahedron with 8 of the 12 vertex atoms missing [14,16]; this difference will be the key for understanding the differences in the melting behavior.

For $N = 139$ one has $E = E^*$ below $T_1 < T_m - 60$ K, with $T_m$(expt) = 259.0 K, and $T_m$(sim) = 251.4 K. The simulations clearly show that the increase near $T_1$ is due to (i) an increasing importance of anharmonic motions (a general effect also observed in simulations of Lennard-Jones (LJ) clusters [17]) and (ii) the diffusion of surface vacancies; i.e., some of the 60 ridge atoms (blue in Fig. 1) and the four atoms in vertex positions visit free neighboring places, while the 20 central atoms (black) remain at their positions. This is far from a disordered liquid layer, so this isomerization stage can be called ridge melting, but not premelting [1,14,18].

The slow beginning of the ridge melting can be well seen in the calculated atomic equivalence indices (AEI) of Fig. 4 which are 5-ps averages of

$$\sigma_i(t) = \sum_j [\mathbf{R}_i(t) - \mathbf{R}_j(t)] \quad (i = 1, \ldots, N),$$  \hspace{1cm} (1)

where all distances from one atom ($i$) to all other atoms ($j$) are summed. If the AEI remain nearly constant, the atoms will not visit neighboring positions. Figure 4 shows that for $N = 139$ some atoms in the outer layer start to become mobile just 10 K above $T_1$, or 50 K below $T_m$.

About 20 K below $T_m$ (or 10 K below $T_m$ for Na$_{147}$), anharmonicities and thermal expansion increase strongly. The same behavior is observed for the bulk, and it can be considered a premonitory signal for the proximity of the melting point. Just below $T_m$ some subsurface atoms of the $N = 139$ cluster start to fill the surface vacancies, triggering the melting of the whole cluster until about 6 K above $T_m$ all atoms can freely interchange their positions and no apparent structural order remains.

The vacancy-free, icosahedral shape for $N = 139$ generates a different scenario. The isomerization stage is absent as there are no surface vacancies which could diffuse. From Fig. 4 one can deduce that even at 4 K below $T_m$ there is no interchange of atoms, and that no adatom-vacancy pairs are thermally generated. Thus Na$_{147}$ does not exhibit premelting.

Even more surprisingly, similar plots show that up to $T_2$ in Fig. 3 the central atom remains in its site and its first coordination layer of 12 atoms preserves on average an icosahedral symmetry. Here $T_2$ is defined as the lowest

![Fig. 2 (color online).](image1)

![Fig. 3 (color online).](image2)
TABLE I. Scenario of the melting transition as obtained from the simulations. Below a temperature of \( T_1 \) (see Figs. 2 and 3) one has mainly small amplitude harmonic motions. Above \( T_1 \) anharmonic effects become more and more important. Only \( \text{Na}_{139} \) shows ridge melting. Melting starts at \( T_m - \delta \), with \( \delta = 6 \pm 2 \) K. \( \text{Na}_{139} \) is completely liquid above \( T_m + \delta \), while for \( \text{Na}_{147} \) the central atom and its first coordination layer become mobile only at \( T_2 \).

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( T \leq T_1 )</th>
<th>( T_1 \leq T \leq T_m - \delta )</th>
<th>( \delta + T_m \leq T \leq T_2 )</th>
<th>( T_2 \leq T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N = 147 ) icosahedron</td>
<td>Mainly harmonic motion</td>
<td>Anharmonic motion</td>
<td>Only the outer two layers are molten</td>
<td>Liquid</td>
</tr>
<tr>
<td>( N = 139 ) icosahedron with 8 vertex atoms missing</td>
<td>As for ( N = 147 ), plus diffusion of the 8 vacancies of the missing vertex atoms</td>
<td></td>
<td></td>
<td>Liquid</td>
</tr>
</tbody>
</table>

FIG. 4 (color online). Calculated atomic equivalence indices in atomic units (a.u.). At left for \( N = 139 \) at \( T_m - 50 \) K, and at right for \( N = 147 \) at \( T_m - 4 \) K [see Eq. (1)]. The AEI lines are generally broader for \( N = 139 \), which indicates larger vibrational amplitudes; they also show motion of atoms in the outer shell. No interchange of atoms can be seen for \( N = 147 \); thus, there is no diffusion so close to \( T_m \) in this case. The numbers in parentheses give the total number of atoms up to the first, second, or third shell, respectively.

FIG. 5 (color online). The calculated atomic radial density is plotted against the normalized distance \( r/r_{\text{cluster}} \), where \( r \) is the distance from the cluster center of mass and \( r_{\text{cluster}} \) is defined here as the radius which contains 95% of the cluster mass. The two Na results are for a temperature of 270 K which is above \( T_m \) but below \( T_2 \); i.e., the inner core for \( N = 147 \) is still solid. The atomic layering can be clearly seen. Note that the first minimum for \( \text{Na}_{147} \) touches the \( r \) axis, indicating that the central atom does not diffuse at this temperature, a clear indicator of postmelting. A Lennard-Jones (LJ) cluster just above its \( T_m \) shows ridge melting. Melting starts at \( T_m - \delta \), with \( \delta = 6 \pm 2 \) K. \( \text{Na}_{139} \) is completely liquid above \( T_m + \delta \), while for \( \text{Na}_{147} \) the central atom and its first coordination layer become mobile only at \( T_2 \).
pressure-induced increase of $T_m$ by about 40–50 K according to the bulk Na phase diagram [23], correlating well with the $T_2$ given in Fig. 3.

Although the Laplace pressure is very similar in both clusters, postmelting is not observed for $N = 139$. At and above $T_m$, the less compact surface facilitates radial atomic diffusion, as seen in Fig. 5. The resulting strong fluctuations lead—via the Lindemann criterion [2]—to a melting of the inner core just above $T_m$. Some remnants of postmelting behavior can be seen very close to $T_m$ if one inspects the calculated trajectories: At $T_m + 3$ K it takes up to 400 ps on average for the innermost atom to exchange its position with another atom. But this happens so close to $T_m$ that its influence on the caloric curve is masked by the much larger contribution of the latent heat of melting.

We conjecture that postmelting should be quite general for metal clusters with a compact surface shell, as no sodium-specific properties have been used in the argument. Note also that layering is not observed in nonmetallic surfaces [21]; thus, postmelting is not expected to occur in these cases (see Fig. 5 for a LJ cluster). The postmelting scenario is presently only supported by the calculations. Some experimental data [9] seem to indicate a small change of slope in the predicted temperature range, but no clear statement can be made presently.

In summary, a joint experimental and theoretical study was done on the melting of sodium clusters containing 139 and 147 atoms, respectively. The simulations give a complete physical picture of the transition; in particular, the influence of anharmonic motion is seen several tens of kelvin below the melting temperature of the cluster. Neither of the clusters exhibit surface melting below $T_m$; the only disorder appearing here is a diffusion of the surface vacancies along the ridges in Na$_{139}$, which is not possible for $N = 147$ due to its closed-shell icosahedral shape. While Na$_{139}$ becomes completely liquid a few kelvin above the main transition temperature, Na$_{147}$ exhibits extended postmelting, with its central 13-atom icosahedral remaining solid up to 40 K above $T_m$.

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[10] The expensive first-principles simulation cannot be made completely ergodic very near to $T_m$, although each separate run was carried out for almost 2 ns. Even longer simulations can change the caloric curves near $T_m$ a bit but not several 10 K away, where the premonitory effects occur which are discussed here. A canonical evaluation was used for the experimental data [4]; therefore, the $S$-like shape (backbending) as observed earlier [7] for $N = 147$ is not seen in Fig. 1.
[18] Features in the heat capacity of Al clusters have been interpreted as being due to premelting; see G. A. Breaux, C. M. Neal, B. Cao, and M. F. Jarrold, Phys. Rev. Lett. 94, 173401 (2005).
[20] Premelting occurs below $T_m$ [1,18]. In analogy, the term postmelting is coined here, as it concerns a feature with a temperature higher than $T_m$.
[21] Several physical reasons are offered in the literature for surface layering. The one prevailing nowadays is that it is a general phenomenon for all materials having a wide liquid stability range, that is, a large difference between the melting and boiling temperatures. This happens for metals but not, e.g., for Lennard-Jones systems. E. Chacón et al., Phys. Rev. Lett. 87, 166101 (2001); O. G. Shpyrko et al., Science 313, 77 (2006).