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Melting and Boiling of Clusters

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All properties change with the size of a cluster. The transition from the atom/molecule to the bulk is often quite smooth and the asymptotic behaviour well understood[1]. This is not the case for cluster melting, where large and irregular fluctuations are found even for clusters containing more than hundred atoms.

We have recently developed a method to measure caloric curves for size selected cluster ions[2, 3, 4, 5]. The caloric curve is a plot of the cluster energy as a function of cluster temperature, and contains all its basic thermodynamic properties. Our method can be divided into two steps. In step 1, sodium cluster

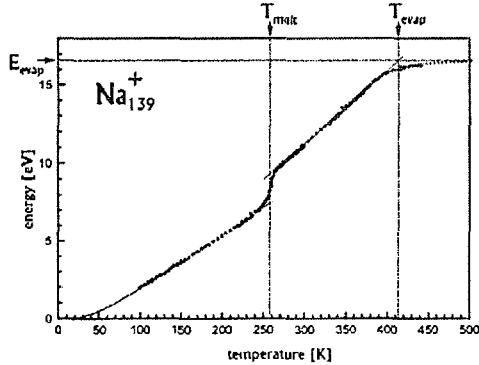


Figure 1: Caloric curve for Na_{139}^+ . The cluster energy is plotted against the temperature of the heat bath of the clusters. Below 100 K the curve has been extrapolated using the bulk result. The increase near 260 K is due to the melting process. Melting temperature and latent heat can be easily read off the curve. Above 400 K the data deviate from the caloric curve as the cluster can no longer be thermalized. They are so hot that they evaporate already in the heat bath. This situation corresponds to an evaporative ensemble, whose temperature and energy can be so determined. It has been argued in ref.[6] that the evaporative ensemble corresponds to cluster boiling at a low pressure.

ions are produced and thermalized. The heat bath is a helium gas of known temperature T , where the clusters make so many collisions that they reach thermal equilibrium. The thermalized clusters are extracted, transferred to high vacuum, and mass analyzed. One has thus prepared a cluster of known mass and known temperature T .

In step 2 the internal, dominantly vibrational energy E of the cluster is measured by a photofragmentation technique explained earlier[2, 4, 7, 8]. If one knows E and T one can plot the caloric curve $E = E(T)$. Fig. 1 shows an example. Below the melting temperature, the caloric curve has about the slope expected by the classical Dulong-Petit law of $3k_B$, where k_B is Boltzmann's constant. Near the melting point, there is a stronger increase of energy over a small temperature interval. For an arbitrarily large system, this increase would be abrupt. We take as melting temperature (T_{melt}) the position of the largest slope of the caloric curve. The latent heat is given by the step height of the smoothed-out step.

The melting temperatures are given in Fig. 2. They show surprisingly large variations: one additional atom can change T_{melt} by up to 10 K. This result is very far from the expected $(\text{radius})^{-1}$ behaviour often deduced for supported, non-mass selected clusters. Two main points can be observed: 1) the melting

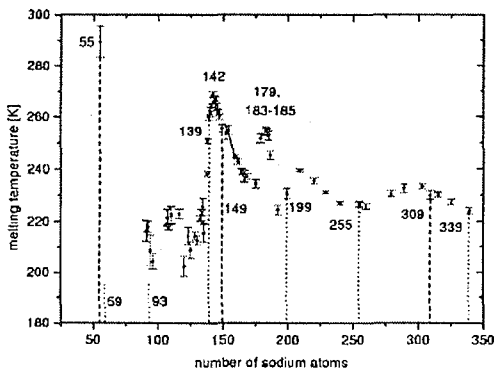


Figure 2: The melting temperatures of Na_n^+ are plotted against the number of atoms. Large fluctuations are seen whose origin is not well understood. They do not correlate with electronic (dotted line) or geometric (dashed) shell closings, which are indicated in the figure. The bulk melting temperature is 371 K. Note, that the zero is suppressed.

temperatures are about one third lower than in the bulk, and 2) they fluctuate by ± 50 K. From less complete data it had earlier been conjectured that the melting points are high, if electronic and geometric shell closings are close to each other[4]. This is no longer supported by the new data covering a wider mass range.

Several calculations have been performed on melting of sodium clusters, but the overall structure of the data in Fig. 2 has not been reproduced so far. The number of atoms for the maxima and minima in Fig. 2 do not generally correspond to any known shell closings, be they electronic or atomic in origin. Also, it might be that the cluster changes its geometry near the melting temperature, as has been observed in a simulation on gold clusters by Landman[9] et al.

There are several features that make cluster melting – or more generally phase transitions in finite systems – an interesting physical problem[3, 5, 10]: One can develop a thermodynamics of finite systems[10] and observe how the standard Boltzmann-Gibbs statistical mechanics (where always infinitely large systems are considered) is emerging as a limiting case. The most important difference between bulk and finite systems is, that the energy in the latter can be non-additive, i.e. the sum of the energies of N particles is not proportional to N . This property is also called *nonextensive*. Nonextensivity occurs if the range of interactions is not negligible compared to the diameter of the system. This has far reaching consequences[10]: e.g. the heat capacity can become negative. Near a phase transition, a small system can become cooler upon heating, as was predicted long ago[10, 11] but only very recently observed experimentally[12, 13].

The liquid to gas transition of finite systems has received much less attention. It has been linked to the evaporative ensemble in a Gedankenexperiment[6]. A first measurement was reported[13] by a Lyon/Innsbruck group, which has used a method adapted from Nuclear Physics to study this phase transition in hydrogen clusters.

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