

## AGRÉGATS COMME PRÉCURSEURS DES NANO-OBJETS *CLUSTERS AS PRECURSORS OF NANO-OBJECTS*

### Phase transitions in clusters

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**Abstract** The solid to liquid transition of clusters is discussed, mainly from an experimental point of view. An experiment is sketched which allows to measure the caloric curve of size selected sodium clusters. Melting temperatures, latent heats, and entropies of melting are determined in the size range between 55 and 357 atoms per cluster. The melting temperatures are about 30% less than the bulk value and fluctuate strongly, one additional atom can change it by  $\pm 10$  K. Latent heats and entropies show a similar behaviour. From the change in entropy one can deduce the increase of phase space upon melting, which is about twelve orders of magnitude already for  $\text{Na}_{55}^+$  and increases exponentially for larger clusters. The theoretical prediction that a finite particle can have a negative heat capacity is verified experimentally, showing that there are differences between a canonical and a microcanonical description. Finally the analogue of the boiling phase transition is shown for a finite system. *To cite this article: M. Schmidt, H. Haberland, C. R. Physique 3 (2002) 327–340.* © 2002 Publié par Éditions scientifiques et médicales Elsevier SAS

phase transition in clusters / solid–liquid transition

### Transitions de phase dans les agrégats

**Résumé** La fusion et l'ébullition des petites particules sont discutées comme exemple d'un changement de phase du premier ordre dans un système fini. Un bref résumé de travaux antérieurs est présenté, ainsi qu'une expérience permettant la mesure des courbes de chaleur spécifiques pour de petits agrégats de sodium, sélectionnés en taille et se propageant dans le vide. Températures de fusion, chaleurs latentes et entropies de fusion sont déterminées pour des agrégats comportant de 55 à 357 atomes. On examine le cas d'agrégats présentant une capacité calorifique négative ainsi que la possibilité d'étudier une transition liquide–gaz pour des systèmes finis et isolés. *Pour citer cet article: M. Schmidt, H. Haberland, C. R. Physique 3 (2002) 327–340.* © 2002 Publié par Éditions scientifiques et médicales Elsevier SAS

changement de phase pour agrégats / transition solide–liquide

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## 1. Introduction

All properties change with the size of a cluster. The transition from the atom or molecule to the bulk is often quite smooth and the asymptotic behaviour well understood [1–6]. This is not the case for some thermal properties. Large and irregular fluctuations are observed e.g. in the melting temperature, even for clusters containing several hundred atoms.

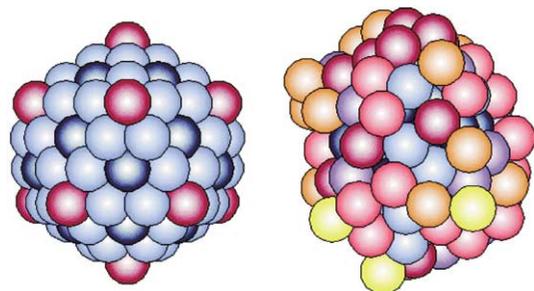
Concepts like temperature, phase etc. had originally been defined for infinitely large systems only. However, one has learned how to generalize these concepts to finite sizes [2,7–9]. For the solid to liquid transition of finite systems, one finds four main differences with respect to the bulk counterpart: (1) the melting temperature is generally reduced; (2) the latent heat is smaller; (3) the transition does not occur at one definite temperature but is spread out over a finite temperature range; and (4) the heat capacity can become negative.

Many computer simulations have shown that the bulk concepts of *solid* or *liquid* can be transferred to small systems. At low temperatures the atoms in a cluster or in a large piece of matter make only small amplitude vibrations around a fixed position. It is very improbable that one atom accumulates by chance enough energy to be able to leave its position. When the temperature increases, atoms in the cluster can visit neighbouring places and start a diffusive motion. There exists very little resistance to external deformation forces and the cluster is now liquid. This is demonstrated in Fig. 1 which shows simulations for a cold, rigid and a hot, liquid cluster. The simulations were performed using a Lennard–Jones potential which is not adequate for metals. But the main features of small harmonic oscillations at low and more diffusive motion at high temperatures are independent of the force field assumed.

From the experimental results discussed in Section 3.1 one can deduce that between 100 K and nearly the melting temperature, the thermal properties of sodium clusters can be well described by a classical collection of harmonic oscillators. At the melting temperature, where the cluster starts to explore an extremely larger phase space, the motion becomes quite anharmonic. The atom will make many oscillations and then diffuse to the next position. An instructive graphical example of the different types of trajectories in the solid, liquid, and gaseous state is given in Ref. [10].

### 1.1. A short history of cluster melting studies

The reduction of the melting temperature of micron sized particles of an organic solid has been observed experimentally as early as 1908 by Pawlow [11,12]. This was confirmed 45 years later by Takagi [13] by electron diffraction. With the same experimental method, Buffat and Borel [14] made the first thorough study of the melting temperatures of deposited gold clusters. These and many later studies using several different techniques found that the melting temperatures reduce linearly as a function of the inverse cluster radius  $R$ :



**Figure 1.** A simulation of a cluster of 147 atoms at  $T = 0$  K (left figure) and at a high temperature. The darker the colour, the more strongly an atom is bound. The calculation was made using a Lennard–Jones potential, which is not adequate for the sodium clusters discussed here. So one does not know whether the low temperature structure of  $\text{Na}_{147}^+$  really looks like an icosahedron whose regular, five fold symmetry can be well seen on the left. The general features of the solid to liquid transition however, should be independent of the force field assumed. (Calculation by Michael Moseler/Freiburg.)

$$T_{\text{melt}}(R) = T_{\text{bulk}}(1 - \sigma/R) \quad (1)$$

where  $\sigma$  is a positive constant, which does not vary too much from one metal to the next [15–20].

In principle, a diffraction or scattering experiment would be the preferred one for deducing melting temperatures. But so far, such an experiment has not been performed for free, mass selected clusters in vacuum. The density of mass selected clusters is so small that it is near to impossible to collect a diffraction signal. However, there is hope for the future; an experiment on electron diffraction on stored cluster ions has recently been published [21], which opens the possibility of making such an experiment on stored, thermalized ions.

The early theoretical treatments introduced phenomenological size corrections to the standard thermodynamical treatment of melting [11–16,19,20]. More physical insight was obtained from many computer simulations on the cluster melting process [2,7–9,22–27]. These were instrumental in our understanding of how bulk concepts such as temperature and melting can be generalized to finite systems. Nearly all simulations have been performed for free clusters of known size, while most earlier experiments have been performed with particles on surfaces having a very broad size distribution.

There is quite a history of experiments trying to measure the melting behaviour of free cluster. The groups of Leutwyler [28], Whetten [29], Even and Jortner [30], Buck [31], and also our group [32,33] looked for evidence of cluster melting by optical spectroscopy. Electron diffraction from a supersonic expansion gives Debye–Scherrer like diffraction rings, the intensity of which is a measure of cluster temperature. This was pioneered by the Farges and Torchet group [34] and later intensively studied by Bartell et al. [35].

The T.P. Martin group [36] was the first to publish a size dependence of the melting temperatures of free clusters. They showed that the structure on mass spectra of large sodium clusters depends sensitively on temperature if the photon energy is chosen appropriately. The disappearance of the structure was interpreted as being due to melting. The heat capacity of neutral clusters composed of Ni, Co and Fe was studied by de Heer and collaborators. The clusters were crudely mass selected to  $\pm 20$  atoms and their temperature was measured by magnetic deflection. The energy was increased stepwise by photons, similar to our experiment discussed below. For nickel clusters a sure sign of a magnetic phase transition was found, while Co and Fe showed a more complex behaviour [37].

Shvartsburg and Jarrold [38] have studied small tin clusters with the surprising result that their melting temperature is higher than the bulk one. They injected cluster ions into a helium gas, pulled the ions by an electric field through the gas, and measured their velocity. This allows them to determine the collision cross-section. Small Sn-clusters have a rather elongated structure which should change to near spherical upon melting. A change in collision cross-section can thus be expected upon melting. No signature of melting is observed, so that the authors conclude that tin cluster ions containing 10 to 30 atoms have a melting temperature which is at least 50 K above the bulk one [38,39].

In all the experiments discussed above, some physical property (optical or mass spectrum, diffusion cross-section, ...) is studied as a function of temperature. A change (or not) is observed in the data and conjectured to correlate with the melting process. A more direct way is to measure the caloric curve, i.e. the energy of a cluster as a function of its temperature. Two such experiments have been published for free clusters: the experiment of our group on mass selected sodium clusters as discussed below, and an experiment on tin clusters [40]. These were produced by a laser ablation source using a pulsed nozzle whose temperature is variable. The authors estimate that nozzle and cluster temperature deviate from one another by only 10 to 20 K. Neutral clusters are studied so that no mass selector can be used. The distribution of cluster sizes is not given, but similar experiments give a  $\delta m/m$  not smaller than 60%. The energy is measured using a sensitive pyroelectric foil whose temperature increase leads to a measurable voltage jump. The measured caloric curve looks very similar to the one given in Fig. 3. Only the solid/liquid transition region is broader due to the broader cluster size distribution. The interpretation of the experiment has been questioned, however [41].

## 2. Cluster calorimetry

One of the goals of cluster science is to understand the transition from the atom or molecule to the bulk. It is often extremely useful to look at these asymptotic limits before one embarks on the study of the clusters themselves. The bulk melting transition is – of course – well documented. But atoms and small molecules cannot melt. This is an interesting situation, a bulk property ceases to exist for sufficiently small particles. It seems that at least seven atoms are needed before something like a liquid behaviour is seen in numerical simulations [24].

### 2.1. The bulk limit

It is in principle easy to measure the caloric curve for bulk materials. One puts the material into a thermally isolated container (see Fig. 2), adds energy  $E$  and measures the temperature  $T$ . After compensation for the influence of the container, one can construct the caloric curve  $E = E(T)$ .

For a large system, the caloric curve exhibits a step at the melting temperature  $T_{\text{melt}}$ . The height of the step is the latent heat  $q$ . Energy can be added to the system at  $T_{\text{melt}}$  without an increase of temperature; all the energy is used to destroy the regular solid structure and thus increase the entropy. This fact is widely used when drinks are cooled by ice cubes. The large latent heat of ice makes it an efficient coolant. Only when the system has become completely liquid, the temperature will rise again upon addition of energy. Note, that one has phase separation for a large sample, i.e. water and ice coexist together at  $T_{\text{melt}}$  which is not possible for a sufficiently small system [42,43]. The derivative of the caloric curve is called the heat capacity  $C(T)$  or also the specific heat:

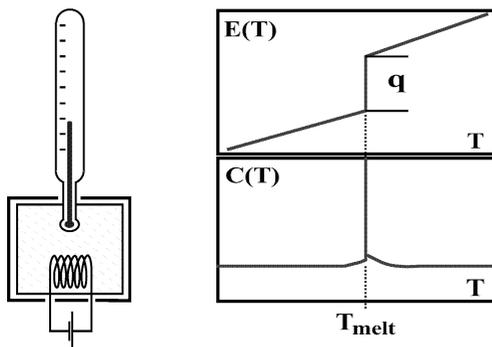
$$C(T) = \frac{\partial E(T)}{\partial T}. \quad (2)$$

For a bulk system,  $C(T)$  has a delta function-like peak at the melting temperature. In our early work on cluster melting, a finite difference approximation was used [45–47] instead of Eq. (2), while recently a more refined method was used to determine the caloric curve  $E(T)$  directly from the temperature dependence of the photo fragment mass spectra [48]. It is not necessary to differentiate between heat capacity of constant volume or pressure in Eq. (2), as these are very nearly the same for a solid or liquid [44].

### 2.2. Calorimetry for free clusters

The experiments on free, mass selected clusters have only been performed so far with charged sodium clusters, because of several reasons:

1. It was the aim of this experiment to work with mass selected clusters, i.e. the number of atoms in the cluster is exactly known. In this case one has to use a mass spectrometer which forces one to work with ions.



**Figure 2.** Calorimeter (left), caloric curve  $E = E(T)$  and heat capacity  $C(T)$  for a macroscopic sample. The caloric curve increases abruptly at the sharp melting temperature ( $T_{\text{melt}}$ ). The height of the jump is given by the latent heat  $q$  of melting. The heat capacity has a delta function-like peak at  $T_{\text{melt}}$  (see Eq. (2)).

2. For non-metallic elements, there can be quite a difference between the electronic and geometric structure of a neutral and a positively charged cluster [49,50]. Due to the delocalized nature of the chemical bond this is not the case in metals.
3. From all the metals available, sodium is the easiest to treat theoretically, as it is the best physical realization of the Nearly Free Electron Gas model [44].

The cluster calorimetry [45–47,51–53] method developed in our group does the inverse of the bulk method shown in Fig. 2. Size selected clusters of known temperature are prepared and their energy (more exactly their energy distribution averaged over an experimental broadening) is measured [48]. The method consists essentially of two steps:

**Step 1:** *preparation of size selected clusters of known temperature.*

Cluster ions are produced in a gas aggregation cell [54] and thermalized in a heat bath. This is a helium gas at about 70 Pa and variable temperature  $T$ . Here the clusters make enough collisions to be thermalized. In other words, if one averages over many atom–cluster collisions shortly before the cluster leaves the heat bath, there will be no energy exchange between the cluster and the helium gas. The clusters leave the heat bath, are transferred into high vacuum, and mass selected. Experimental details are given in [48]. This prepares clusters of known size and known temperature  $T$ . The temperature has a sharp value (that of the thermalization cell) and the energy has a distribution of finite width [48], as given by Eq. (3).

**Step 2:** *determination of the cluster energy.*

The energy is measured by irradiating the clusters prepared in step 1 with photons and measuring the mass distribution of the photo fragments. From these data one can extract the cluster energy as explained in [48,51]. Note that this is energy of the cluster *before* it had absorbed the photons.

### 2.3. Canonical or microcanonical experiment?

The small clusters are thermalized in a macroscopic heat bath. Standard thermodynamics tell us that in this case the small system has a *canonical* distribution of energies  $P_T(E)$  which is given by the number of states of energy  $E$  of the cluster  $\Omega(E) = \exp\{S(E)/k_B\}$  times the Boltzmann factor [55]:

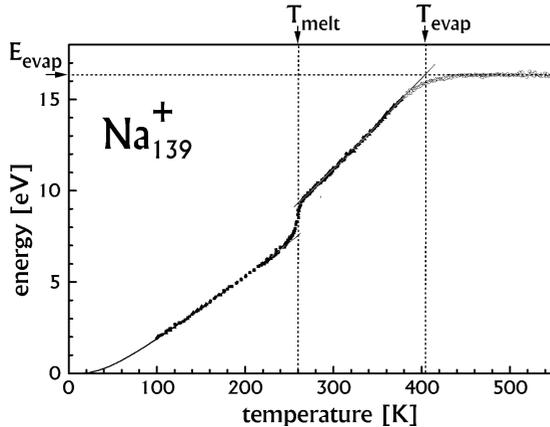
$$P_T(E) \propto \Omega(E) \exp\{-E/k_B T\} = \exp\{S(E)/k_B - E/k_B T\}, \quad (3)$$

where  $S(E) = k_B \ln \Omega(E)$  is the entropy, and  $k_B$  is Boltzmann's constant. The implications of Eq. (3) and the unusual shape of  $P_T(E)$  near a phase transition are discussed in more detail in chapter 5 of [48].

High vacuum is needed to operate a mass spectrometer, so that the clusters have to be transferred from the heat bath (about 70 Pa) to a pressure below  $10^{-5}$  Pa necessary for mass selection. Provided that there are no collisions of the cluster with background molecules and/or nets of the ion optics, the energy of each *single* cluster stays effectively constant after it has left the heat bath. Thus each isolated cluster has a fixed energy and thus corresponds to a *microcanonical* ensemble. Averaging over many clusters, one regains  $P_T(E)$  of Eq. (3). The energy of a single cluster is just a sample of this distribution.

## 3. Results

The experiment consists of measuring the mass spectra of the photofragments as a function of the temperature  $T$  of the heat bath. The mass spectra show an oscillatory structure, which allows to extract the cluster energy  $E$  and to plot the caloric curve  $E = E(T)$ . Intensive tests have been made, in order to show that this method gives reliable and robust results. The data treatment is explained in [48].



**Figure 3.** Caloric curve: the total energy of  $\text{Na}_{139}^+$  is plotted as a function of the temperature of the cluster heat bath. Below 100 K the curve has been extrapolated using the bulk result. The sudden increase near 260 K is due to the melting process; the temperature of the steepest slope is taken as the melting temperature  $T_{\text{melt}}$ . The latent heat is obtained by extrapolating the linear portions of the caloric curves (thin solid lines) and taking their energy difference at  $T_{\text{melt}}$ . Above 400 K the data deviate from the caloric curve as the cluster can no longer be thermalized. Energy and temperature of the evaporative ensemble [56] can be obtained, as indicated.

### 3.1. Caloric curves

A typical caloric curve is shown in Fig. 3. Above about 100 K the caloric curve increases roughly linearly. Just below the increase near 260 K, the slope of the caloric curves is nearly  $3k_B$  per atom where  $k_B$  is Boltzmann's constant, a result expected from the classical Dulong–Petit law [44]. Near the melting temperature there is a strong change in slope, a relative large amount of energy is needed for a small increase of temperature. This is the cluster analogue of bulk melting; the sudden jump of bulk systems is smoothed to a finite width, as expected for a small system [22,42,43]. The melting temperature is indicated in Fig. 3. The latent heat  $q$  is equal to the increase in the caloric curve near  $T_{\text{melt}}$ . For higher temperatures, a nearly linear increase is again observed. The following data can be read off Fig. 3: (1) the melting temperature  $T_{\text{melt}}$ ; (2) the latent heat  $q$ ; and (3) more generally, the specific heat as a function of temperature. In the temperature range studied, the heat capacity (the derivative of the caloric curve with respect to the temperature) is nearly constant below and above  $T_{\text{melt}}$ . It is higher above  $T_{\text{melt}}$  due to the anharmonicities of the interaction potential probed in the liquid state.

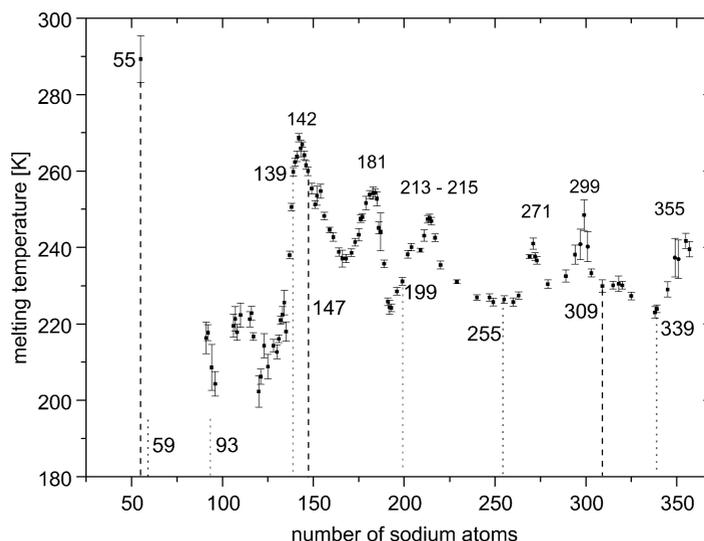
At a temperature above 400 K, the clusters are so hot that they can evaporate atoms without having absorbed a photon. Thus they are no longer thermalized when they arrive in the laser interaction zone. Therefore the very high temperature part of the curve does not belong to the caloric curve, but describes an evaporative ensemble [56], whose temperature and energy can be read off Fig. 3, as discussed in more detail in Ref. [57].

It has been discussed in [48] that Fig. 3 does show for temperatures below 400 K a microcanonical caloric curve, but averaged over the canonical energy distribution and an unavoidable broadening due to the photofragmentation process. Therefore a possible backbending (see Section 3.5) cannot be seen [22,42,43, 58], and the curve looks like a canonical one. Outside  $T_{\text{melt}} \pm 20$  K canonical and microcanonical curves agree within experimental error.

### 3.2. Melting temperatures

The temperature corresponding to largest slope of the caloric curve is identified as the melting temperature. The data available so far are shown in Fig. 4. The melting temperatures show surprisingly large variations: one additional atom can change  $T_{\text{melt}}$  by more than 10 K. Several points can be observed: (1) the melting temperatures are about one third lower than in the bulk, and (2) they fluctuate by  $\pm 50$  K. From less complete data it had earlier been conjectured [46] that the melting temperatures are high, if electronic and geometric shell closings are close to each other. This is no longer supported by the new data presented here covering a wider mass range. (3) There is no indication of the  $R^{-1}$  law expected from

**Figure 4.** The melting temperatures of  $\text{Na}_n^+$  are plotted against the number of atoms. Large fluctuations are seen whose systematics is not understood. They do not correlate with electronic (dotted line) or geometric (dashed) shell closings, which are indicated in the figure. Note, that one additional atom in the size range of about 150 atoms can change the melting temperature by more than  $\pm 10$  K. The highest melting temperature belongs to the smallest cluster studied,  $\text{Na}_{55}^+$ , which is known to have an icosahedral shape. The bulk melting temperature is 371 K.



Eq. (1). Even the data from the Martin group [36] do not show this behaviour, although they extend to clusters containing 10 000 atoms.

Several calculations [26,59–63] have been performed on melting of sodium clusters, but the overall structure of the data in Fig. 4 has not been reproduced so far. The maxima and minima in Fig. 4 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 [25].

The smallest cluster which could be studied,  $\text{Na}_{55}^+$ , has the highest melting point. A cluster containing 55 atoms – and displaying an unusual behaviour – can be expected to be of icosahedral shape. Indeed theoretical [64,65] as well as experimental [66] results show clearly that  $\text{Na}_{55}^+$  is icosahedral below the melting point. Only upon melting it transforms into the oblate shape, as expected from the jellium model [3–5]. Icosahedra have very close packed, stable structures, and for Lennard Jones clusters also a high melting temperature [67]. The icosahedral structure is thus also favored for a sodium cluster with 55 atoms. Contrary to what is calculated for Lennard–Jones clusters, the higher icosahedra, with  $n = 147, 309, \dots$  atoms, do not have an exceptional melting temperature. The  $\text{Na}_{55}^+$  latent heat and entropy of melting are also high, as discussed below. From the discussion in Section 3.4 it follows that the phase space of  $\text{Na}_{55}^+$  enlarges by about 12 orders of magnitude upon melting.

Many simulations have found indications of pre-melting, i.e. the outer layer of the cluster melts at a lower temperature than the inner layers. This would lead to a second step in the caloric curve which has not been observed so far for sodium clusters. Pre-melting is a common behaviour for macroscopic surfaces where it occurs only just below the melting point.

Many calculated melting temperatures for a variety of cluster sizes with less than 30 atoms show a surprisingly simple scaling with the parameter  $\bar{E}_{\text{int}}/\bar{E}_{\text{sur}}$  where  $\bar{E}_{\text{int}}$  and  $\bar{E}_{\text{sur}}$  are the mean potential energies of the internal atoms and the surface atoms, respectively [68]. It would be interesting to see if the larger clusters studied here behave similarly.

Fig. 4 shows something unusual in cluster science. Normally one observes that for small clusters – say below 20 to 50 atoms – there are pronounced oscillations in some physical property (ionization energy, dissociation energy, etc.) followed by a rather smooth behaviour to the bulk [2,4,6]. In the small cluster region, where each atom counts, the geometric and electronic structure of the clusters can vary strongly by adding just one atom. For the melting temperatures, on the other hand, these large fluctuations persist up to several hundred atoms.

### 3.3. Latent heats

For large systems, the latent heat is the energy to destroy the rigid crystalline lattice at the sharp melting temperature. This remains true for small systems, only the melting occurs over a finite temperature range. The latent heat is extracted from the caloric curves as indicated in Figs. 2 and 3. It is given by the height of the increase of the caloric curve near  $T_{\text{melt}}$ . The vertical scale in Fig. 3 is energy calibrated, so that the latent heats are obtained absolutely. Data are presented in Fig. 5. They are more noisy than those in Fig. 4, as they are taken as a difference of two larger numbers. Also there can be a systematic uncertainty on how to extrapolate the linear portions of the caloric curves below and above  $T_{\text{melt}}$ . Note the exceptionally high values of the latent heat and of the melting temperature for the  $n = 55$  atom cluster, which indicates again an icosahedral shape for this cluster.

### 3.4. Entropies of melting

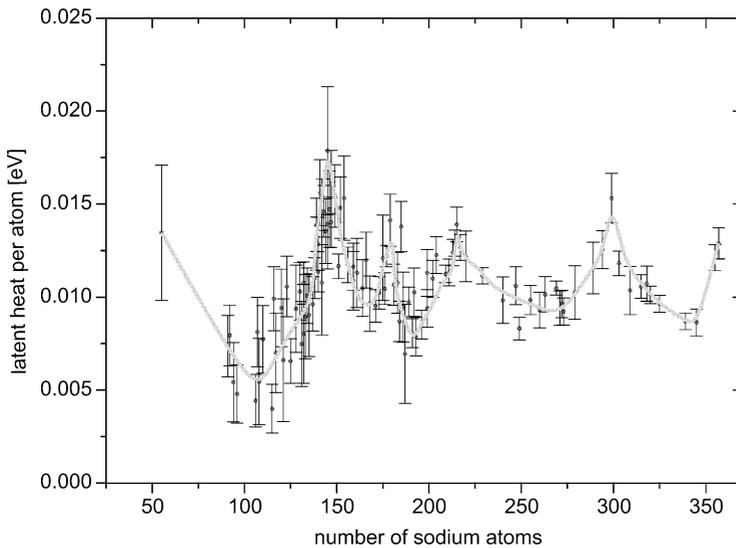
The bulk entropy change upon melting is defined as:

$$\Delta S = \frac{n \cdot q}{T_{\text{melt}}} \quad (4)$$

where  $n$  is the number of particles and the latent heat  $q$  per atom is given in Fig. 5. The same equation can be used for clusters [27]. As the latent heats  $q$  and melting temperatures  $T_{\text{melt}}$  are known, the entropy change upon melting can be calculated from the experimental data. The resulting relative entropies ( $\Delta S/n$ ) are shown in Fig. 6. This allows us to estimate the change of the phase space  $\Omega$  upon melting. Entropy is defined [55] as  $S = k_B \ln(\Omega)$ , and the entropy change upon melting becomes

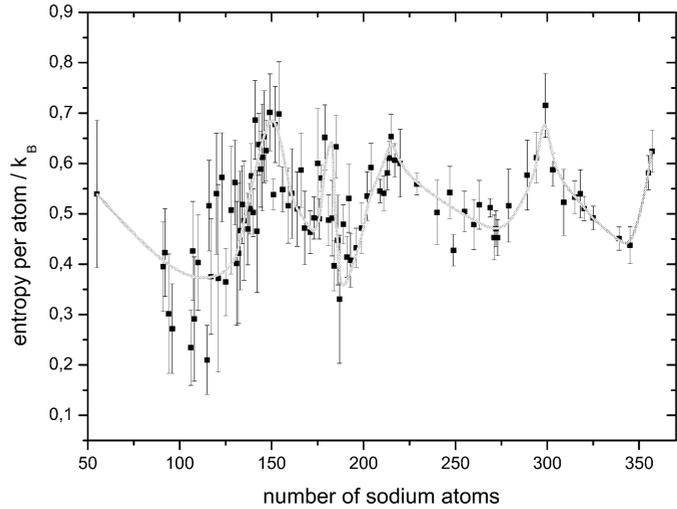
$$\Delta S = S_l - S_s = k_B \ln\left(\frac{\Omega_l}{\Omega_s}\right) \quad (5)$$

where the subscripts  $l$  and  $s$  stand for liquid and solid, respectively. From Fig. 6 one obtains that the mean value of the total entropy change is about  $nk_B/2$ . Inserting this value into Eq. (5) one obtains the result that the phase space enlarges by a factor of about  $\exp(n/2)$  upon melting, i.e. by about 12 or 43 orders of magnitude for  $n = 55$  and 200, respectively. Already for these medium sized clusters, there is a tremendous increase in phase space upon melting.



**Figure 5.** The latent heat per atom is plotted against the number of atoms in the cluster. Large fluctuations are visible which correlate with those of the melting temperature. The line through the data is only drawn to guide the eye. The bulk value is 27.5 meV. There seems to be an increase in the latent heat around 150 atoms, where a next geometric shell starts. This is more evident if the total latent heat is plotted. Note the high value for  $n = 55$ , which correlates well with the high melting temperature.

**Figure 6.** The relative entropy of melting is plotted against the cluster size. Above about 120 atoms the entropy is oscillating between 0.4 and  $0.7 k_B$  with maxima near 150, 180, 220, and 300 atoms, similar to the latent heat as given in Fig. 5. The bulk value of the change of entropy upon melting is  $0.85k_B$  per atom.



The melting of bulk metals is well studied. The entropy change upon melting of most elements follows Richards rule [69], which states that  $\Delta S \approx nk_B$  with a fluctuation margin of  $\pm 30\%$ . The only exception are elements whose geometric and electronic structure changes dramatically upon melting, like, e.g., silicon. For the bulk alkalis the value of  $\Delta S$  is reduced by about 15% compared to Richards rule.

### 3.5. Systems with negative heat capacity

There exists a surprising theoretical prediction for a small system at a phase transition of first order: its heat capacity can become negative; an increase of energy leads to a decrease of temperature. Every day experience tells us the contrary, if energy is added to a system it will get warmer. But negative heat capacities have since long been known in astrophysics [70,71], where energy can be added to a star or star cluster which then cools down. A similar effect has been calculated for melting atomic clusters [22,58] and fragmenting nuclei [42,43,72,73].

The common feature of these very different systems is that their energy is non-additive, in other words, the thermodynamics is *non-extensive*. The energy of such a system of  $N$  particles is *not* proportional to  $N$ . This can occur for the following reasons:

1. Small systems if the interaction decays faster than the inverse distance, and if the range of the force is not negligible compared to the diameter of the system. Examples are cluster and atomic nuclei.
2. Systems of any size with long range interaction; e.g. astronomic systems with their infinite range gravitational force.

If such systems are divided into arbitrary subsystems, the total energy is not simply the sum over the subsystems. The interaction between the subsystems has to be taken into account [55,70,71,74]. For example, in stars it is impossible to neglect the gravity between parts of the system [70,71]. Similarly in clusters and nuclei the interaction between subsystems is not negligible due to their small size.

The entropy  $S(E)$  of a small system can exhibit a curious structure near a phase transition, a dent with an inverted curvature, also known as a ‘convex intruder’. This structure has been predicted by theory and has been observed in many numerical simulations [22,25,26,42,43,58]. The inverted curvature of the entropy has two interesting consequences: (1) the microcanonical caloric curve  $T_\mu(E)$  gets a negative slope (colloquially called backbending), which means that the corresponding heat capacity becomes negative; (2) the canonical energy distribution  $P_T(E)$  shows a bimodal structure [22,25,26,42,43,58]. A macroscopic system avoids the inverted curvature by phase separation, i.e. being partly liquid, partly solid, as described

by the well-known van Hove construction [42,43,70,71,74]. This is not advantageous for a small system, due to the large percentage of atoms at a liquid/solid interface.

One can indeed show that  $\text{Na}_{147}^+$  has a bimodal energy distribution and consequently a negative heat capacity in the energy range near a phase transition [75]. At the melting temperature an increase of the internal energy of  $\text{Na}_{147}^+$  by 1 eV leads to a concomitant decrease in temperature by about 10 K. One can expect that other clusters have a also negative heat capacity, but this has not been verified experimentally so far.

How can this negative heat capacity be interpreted? Upon melting, a large system converts added energy completely into potential energy, reducing continuously the fraction of its solid phase. The mean kinetic energy and thus the temperature remain constant. A small system, on the other hand, tries to avoid partly molten states and prefers to convert some of its kinetic into potential energy instead. Therefore the cluster can become colder, while its total energy increases.

### 3.6. The cluster analogue of boiling

The cluster liquid to gas transition has received much less attention compared to the solid to liquid one. The volume change is nearly negligible for the latter, but amounts to a factor of about thousand under standard conditions for the boiling transition. This leads to problems, both experimentally and in the simulations, which have impeded progress in this area. Only, the size scaling of the boiling temperature has been estimated [76], and boiling [77] and sublimation[78] processes have been simulated. For the kindred nuclear case, the groups of Chomaz [72], Dorso [73], and Gross [42,43] have performed simulations using extreme excitation conditions, which occur in heavy ion collisions at extremely high kinetic energies.

For a bulk system, the boiling phase transition occurs only under constant pressure conditions. To study the bulk liquid to gas transition is again easy, in principle. The closed container of Fig. 2 is replaced with one where a piston ensures constant pressure conditions. However, no experiment is known with which one could study the analogous transition for clusters. Two papers have recently been published which attack this problem from different angles [57,79].

Our group has proposed the Gedankenexperiment sketched in Fig. 7. A sodium cluster of known size is enclosed under a small constant pressure in a container. Under sufficiently low pressure, the ideal gas law is a good approximation and one has thus for the caloric curve in the gaseous state:

$$H = E + pV = 5/2k_B T \quad (6)$$

where  $H$ ,  $E$ ,  $p$ ,  $V$  and  $T$  are enthalpy, energy, pressure, volume and temperature, respectively. This defines for zero temperature also the zero of the enthalpy scale. For the solid/liquid part, the pressure is very small and the volume change negligible, thus energy and enthalpy are nearly the same. One can thus use the caloric curve obtained experimentally as described earlier (see Fig. 3). The energetic difference between the cold cluster  $H_{\text{cl}}(0) = 0$  and the cold gas  $H_{\text{gas}}(0)$  is by definition the cohesive energy  $E_{\text{coh}}$ . One obtains  $E_{\text{coh}} = \sum_{n=2}^{139} D_n = 128$  eV from the data given in Refs. [80,81].

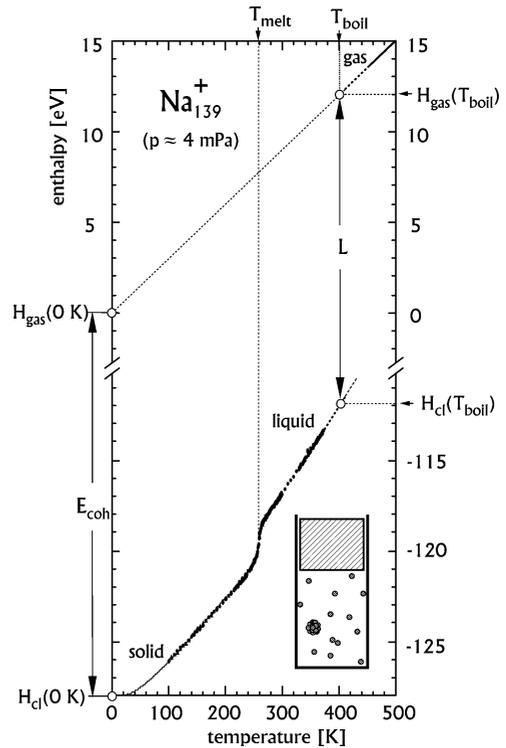
Neither the curve for the condensed nor for the gaseous  $n$ -atom system are significantly pressure dependent as long as the pressure is not huge. This is analogous to the situation in the bulk. Thus Fig. 7 shows the caloric curve of the system of 139 caged atoms (and one positive charge) at any small pressure. The only remaining question concerns the boiling temperature. Where does the curve step from liquid to gas? In a macroscopic system this of course depends on the external pressure.

It is discussed in [57] that the evaporative ensemble temperature [56] of the free cluster can be understood as being the boiling temperature of the same cluster caged in a box. The corresponding external pressure can be deduced from the cluster's evaporation rate at the evaporative ensemble temperature.

The experimental approach of the Lyon and Innsbruck groups [79] uses a method from nuclear physics. If two heavy nuclei, say Au on Au, are collided at energies of several hundred MeV/amu one can determine the temperature and the excitation energy of the hot decaying compound nucleus [42,43,72,73,79]. A

**Figure 7.** Caloric curve for 139 sodium atoms and one positive charge in a container at a constant low pressure showing the solid/liquid and the liquid/gas transition.

The solid/liquid part of the data is from Fig. 3. The progression of the upper part is that of an ideal gas as given by Eq. (6). Both parts are pressure-independent at the experimental pressure analogue of 4 mPa, which can be calculated from Eq. (4) of [57]. The boiling temperature  $T_{\text{boil}}$  corresponds to this pressure. The enthalpy of vaporization can be estimated by using a Born–Haber cycle as  $L(0.004 \text{ Pa}) = 124 \text{ eV}$ . Note that the enthalpy of vaporization  $L(T_{\text{boil}})$  is only slightly pressure-dependent and about a factor of 70 higher than that of melting.



plot of the two quantities gives a characteristic plateau expected for a phase transition. The method was adapted to the study of small hydrogen clusters. Mass selected  $\text{H}_3^+(\text{H}_2)_m$ , with  $m \leq 14$  were accelerated to 60 keV/amu, collided with a helium gas target and all the fragments (neutral and charged) measured. A caloric curve could be extracted as discussed in [79]. Not only neutral but also charged particles are produced under these violent collision conditions. So the transition studied is not really the liquid/gas transition discussed above; rather a transition to a high temperature gaseous plasma is probed.

#### 4. Summary

The melting of a small finite system in vacuum has been discussed. The experiments have been carried out with positively charged sodium clusters, but many results should be independent of the chemical nature of the element under study and thus be quite general in nature. The main results can be summarized as follows:

1. The caloric curve of free, mass selected clusters in vacuum has been measured. The measuring process can be divided into two parts:

**Step 1:** Sodium cluster ions,  $\text{Na}_n^+$ , are thermalized, and one cluster size is selected. This prepares a cluster of known temperature  $T$ , containing an exactly known number of constituents, having a canonical distribution of internal energies.

**Step 2:** The selected cluster is irradiated with a laser, and the distribution of photofragments is measured as a function of the cluster temperature. From this the total internal energy  $E$  of the cluster – before it had absorbed a photon – can be determined.

Knowing  $E$  and  $T$ , one can construct the microcanonical caloric curve  $E = E(T)$ .

2. The melting temperature, and the latent heat of fusion can be directly read off the caloric curve.
3. The melting temperatures of  $\text{Na}_n^+$ ,  $55 \leq n \leq 357$

- are about one third lower than in the bulk;
  - they fluctuate by about  $\pm 50$  K;
  - the systematics behind the fluctuations are not understood.
4. The latent heat of fusion shows similar fluctuations as the melting temperature.
  5. The entropy of melting is calculated from the data. It shows 20% oscillations around one half Boltzmann constant per particle. From this one can calculate that the increase of phase space is about 12 orders of magnitude already for  $\text{Na}_{55}^+$ .
  6. The smallest cluster studied,  $\text{Na}_{55}^+$ , has the highest melting temperature and also a high value for the latent heat per particle. This is due to its known icosahedral structure.
  7. The microcanonical heat capacity is negative near  $T_{\text{melt}}$  for  $\text{Na}_{147}^+$ . Theory indicates that this should be not an uncommon behaviour for other clusters.
  8. Boiling of clusters has been discussed and a suggestion on how to connect the caloric curves of the liquid to that of the gas.

There are several other fields of science where similar phenomena are observed or applied. The atomic *nucleus* is a finite system for which phase transitions have been studied intensively. Due to its large zero point motion, the nucleus does not become solid. However, it shows a (Fermi) liquid to gas transition, which has interesting similarities to the cluster case [42,43,72,73,79], i.e. it can have also a negative heat capacity. The determination of energy and temperature are more involved in the nuclear case.

Finally, are there any applications of the size dependence of the melting temperature of small particles? This plays an important role in the softening and melting of polymers [82]. Even a medical application has recently been proposed [83]. A drug could be encapsulated in or bound to a tiny particle, whose melting temperature is adjusted via its size to be just above the body temperature. By an external warming of a specific part of the body the particles could be forced to release the medicine exactly there. One can thus have a high drug concentration in some part and a very small one in another part of the body. As all drugs have unwanted side effects, the potential of such a technique would be great.

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