

Caloric Curve across the Liquid-to-Gas Change for Sodium Clusters

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The caloric curve for Na_{139}^+ has been measured from 100 K up to the temperature where the clusters are boiling hot and spontaneously emit atoms. In this limit the clusters form an evaporative ensemble, the temperature and energy of which have been determined. As the caloric curve of an atomic gas with a finite number of atoms is known, one can construct the caloric curve for this finite system below and above the boiling point. A conjecture is made on how to link the evaporative ensemble temperature of the free cluster in vacuum to the boiling temperature of a finite system at a given pressure. This allows one to determine the enthalpy of vaporization at the phase transition of the finite system.

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Conventional statistical mechanics studies systems containing infinitely many particles in an infinitely large volume. It is common opinion that phase transitions occur only in this limit of an infinite number of particles. This is certainly so if one defines phase changes as singularities of the thermodynamic functions, since these cannot occur in finite systems. Yet real systems are necessarily finite, even if the number of particles is on the order of 10^{23} ; nevertheless, they do show phase transitions. Indeed even for very small systems, phenomena which will evolve into a phase transition for large systems have been observed both in simulations [1–4] and in experiments [5–7]. Actually many of these effects were predicted a long time ago [8–10].

If the temperature of a cluster exceeds a certain limit, it will start to evaporate atoms, or fragment as it is colloquially called in cluster science. Cluster fragmentation has been investigated intensively both experimentally [11,12] and theoretically, where it was described within fragmentation theory [13] or the concept of the evaporative ensemble [14,15]. The closely related transition from the liquid to the gaseous state has received much less attention. The size scaling of the boiling temperature has been estimated [16]. Also, boiling [17] and sublimation [18] processes have been studied theoretically.

We propose here a way to construct the caloric curve of a cluster across the liquid-to-gas transition in three steps: (i) We measure the caloric curve of a cluster between 100 and 380 K, where the transition occurs. (ii) We calculate the caloric curve of a gas of atoms caged in a closed box using standard thermodynamics. (iii) We relate the fragmentation rate of the free cluster to a vapor pressure of the enclosed atoms. This allows us to tie together the two caloric curves from steps (i) and (ii).

Our experiment to measure thermal properties of free, mass selected clusters has been described earlier [5–7,19–22]. Briefly, photofragmentation is used to measure the internal energy of clusters with known tem-

perature. In more detail, one can divide the experimental procedure into two steps: (i) Cluster ions are produced in a gas aggregation source and thermalized in helium gas of controlled temperature T , which represents an ideal heat bath. A mass spectrometer is used to select a single cluster size. This prepares clusters of known size and known temperature T . (ii) These clusters are irradiated by a laser beam. A second mass spectrometer measures the distribution of the charged fragments produced. The number of evaporated atoms is related to the original internal energy of the cluster. As discussed earlier [5–7,19,22], it is possible to extract the caloric curve from the temperature dependence of the photofragmentation pattern. In summary, step 1 prepares clusters of known size and temperature T , and step 2 measures their energy $E(T)$. Note that the laser irradiation in step 2 is just an experimental trick used to measure the internal energy $E(T)$ before the photons were absorbed.

Figure 1 shows the result for Na_{139}^+ . The caloric curve is roughly linear between 100 and 260 K, where a smoothed out step is observed, the height of which is the latent heat of the melting process. Below 100 K the caloric curve was extrapolated using bulk data. Above the melting region, the curve is again roughly linear, with a higher slope due to the increased anharmonicities of the molten state.

Above 380 K the curve in Fig. 1 is flattened out. The reason for this behavior is evaporative cooling. At those temperatures, the clusters start to emit atoms between the heat bath and the mass spectrometer. This evaporation cools the clusters, which thus no longer have the temperature of the heat bath when their energy is measured. Since the temperatures of clusters and heat bath differ from each other, the data above 380 K in Fig. 1 do not represent the caloric curve anymore. At sufficiently high bath temperatures the clusters reach a saturation energy instead, which no longer depends on the temperature of the heat bath. The energy distribution of the cluster ensemble is no longer canonical. It is now governed by the fragmentation

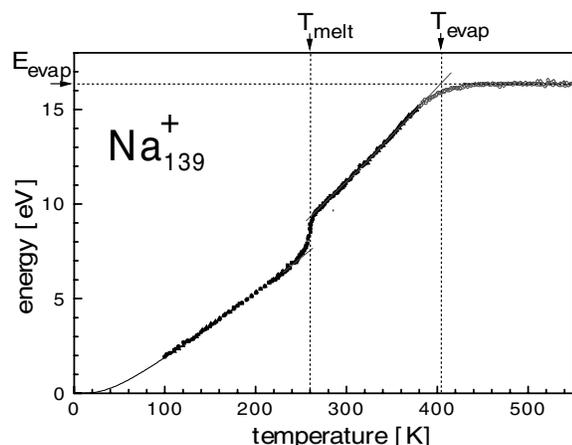


FIG. 1. Experimental caloric curve for Na_{139}^+ : internal energy of the cluster as a function of the heat bath temperature. Below 100 K the curve is extrapolated using bulk data. The step at T_{melt} indicates the melting. At high heat bath temperatures the cluster energy approaches a saturation value, as the cluster cools by evaporation of atoms in the time between thermalization and mass selection. In this region the data points do not represent the clusters caloric curve anymore. Temperature T_{evap} and energy E_{evap} of the evaporative ensemble can be deduced from the high temperature part of the data.

process. Clusters with energies above a certain limit decay before they reach the first mass spectrometer. This leads to an upper limit of the energy distribution. If the clusters evaporate atoms, they cool down. The cooling stops when the evaporation rate gets too low for further evaporations on the way between heat bath and spectrometer. This leads to a lower energy limit. The resulting energy distribution of this so-called evaporative ensemble [14,15] is sharper than the canonical one. It does not depend on the temperature of the heat bath, but only on the cluster drift time between heat bath and mass spectrometer.

The mean energy of the ensemble $E_{\text{evap}} = 16.4$ eV can be deduced from Fig. 1. The ensemble temperature $T_{\text{evap}} = 403 \pm 2$ K is obtained from a linear extrapolation of the caloric curve up to E_{evap} . This is the first time that energy and temperature of an evaporative ensemble are determined directly by experiment without using the complex models of fragmentation theory [13–15].

There are some similarities between the evaporative ensemble temperature T_{evap} of a cluster and the boiling temperature of bulk matter: Continuous energy input increases the temperature of both the free cluster and the condensed macroscopic system. The temperature increase stops when the bulk system reaches the boiling temperature. The same happens to the cluster at T_{evap} . Both systems now use the energy input to evaporate atoms. Only after each system has been transformed to gas, the temperature increases again on further energy input. The close analogy has motivated this attempt to connect the cluster concept of the evaporative ensemble to the macroscopic boiling phase transition.

The phase transitions of simple macroscopic systems are governed by two control parameters: temperature and pres-

sure. For the melting transition the latter is not very important; the heat capacities at constant volume and constant pressure are nearly the same [23]. For a boiling system, on the other hand, there is a big difference between a process at constant volume V , which does not show a phase transition, and a process at constant pressure p , which shows a phase transition and a huge increase in volume. The appropriate thermodynamical potential is thus the enthalpy $H = E + pV$ which includes the work pV that has to be done during the expansion.

The definition of pressure is a problem when dealing with clusters in vacuum, as there is neither volume nor applied pressure [24]. Furthermore, the free cluster is not in an equilibrium, the number of evaporated atoms depends on the experimental observation period. Thus equilibrium thermodynamics cannot be applied to such a system. We will discuss instead a different system consisting of a finite number of N atoms being caged in a closed box at constant pressure. The container has to be idealized in a way that the atoms do not stick to the walls. Additionally, the piston that provides for constant pressure should be mechanically inert to prevent big fluctuations of the volume. When these conditions are fulfilled, many aspects of the thermodynamics of such a system are known.

At sufficiently high temperature the atoms will form a gas. If additionally the pressure is small it will be an ideal gas. Its caloric curve at constant pressure is not pressure dependent and simply given by $H_{\text{gas}}(T) = (5/2)Nk_B T$ (see Fig. 2), where k_B is Boltzmann's constant.

At low temperatures, on the other hand, the atoms in the box will form a cluster. It will bounce around in the box, push the piston, and thus provide for an appropriate volume of the box which is orders of magnitude bigger than the volume of the cluster itself. The work connected to the small thermal expansion of this "one atomic gas" against any not too huge pressure is very small compared to the internal energy of the cluster. Therefore there is only a negligible difference between the systems enthalpy $H_{\text{cl}}(T)$ and the internal energy of the free cluster $E(T)$. One can thus replace the energy scale of Fig. 1 by an enthalpy scale, as was done in Fig. 2.

Both parts of the caloric curve (solid/liquid and gas) have been plotted on the same enthalpy scale in Fig. 2. The energetic difference between the cold cluster $H_{\text{cl}}(T = 0) = 0$ and the cold gas $H_{\text{gas}}(T = 0)$ is by definition the cohesive energy E_{coh} . One obtains $E_{\text{coh}} = \sum_{n=2}^{139} D_n = 128$ eV from the data given in Refs. [25,26].

Neither the curve for the condensed nor for the gaseous N -atom systems are significantly pressure dependent as long as the pressure is not huge [24]. This is analogous to the situation in the bulk. Thus Fig. 2 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 point. Where does the curve step from liquid to gas? In a macroscopic system this of course depends on the external pressure.

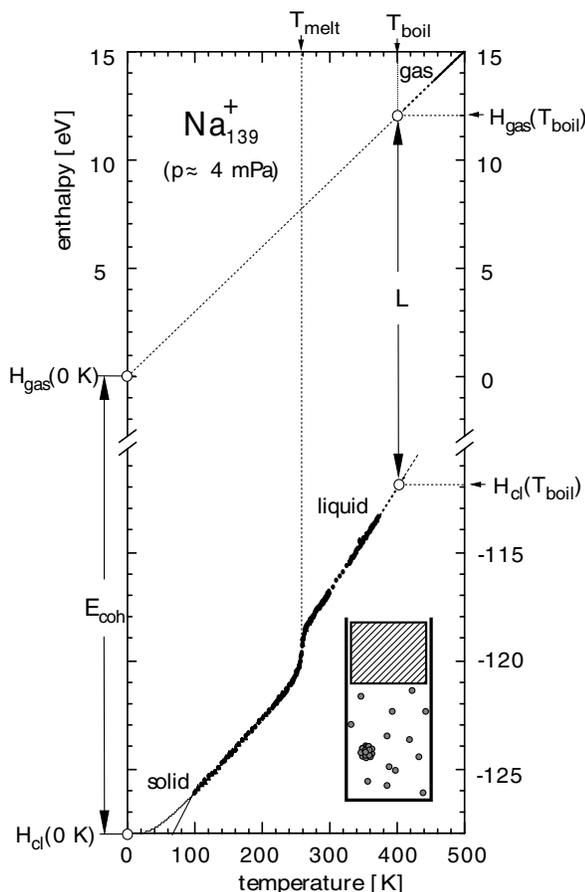


FIG. 2. Caloric curve for 139 sodium atoms and one positive charge in a container at constant pressure showing the solid/liquid and the liquid/gas transition. The solid/liquid part of the data is from Fig. 1. The progression of the upper part is that of an ideal gas. Both parts are pressure-independent at the experimental pressure analog of 4 mPa, which can be calculated from Eq. (4). The boiling temperature T_{boil} corresponds to this pressure. The enthalpy of vaporization [see Eq. (5)] can be estimated by using the cohesive energy E_{coh} . 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.

We will show now that the evaporative ensemble temperature of the free cluster can be understood as being the boiling temperature of the system of atoms caged in the box. The corresponding external pressure can be deduced from the cluster's evaporation rate at the evaporative ensemble temperature.

Let us start with a condensed bulk system in thermodynamic equilibrium whose surface of area A is in contact with a gas of density n . Equilibrium implies that the rate of evaporation $k_e(T)$ is exactly compensated by the rate of sticking $k_s(T)$. This latter quantity is equal to the product of the sticking probability per collision $\pi_s(v)$ times the rate of collision with the surface. Thus we have from kinetic gas theory:

$$k_e(T) = k_s(T) = An\langle\pi_s(v)v\rangle/4, \quad (1)$$

where v is the velocity of the gas particles and $\langle\rangle$ means an ensemble average. Since the density n is proportional

to the pressure, one sees that there is a direct link between pressure and evaporation rate.

Let us now come back to the free cluster. The evaporative ensemble is not in equilibrium in the sense of statistical thermodynamics, but nevertheless the evaporation rate k_e of the cluster at the evaporative ensemble temperature can be deduced by

$$k_e(T_{\text{evap}}) \approx 1/t_s \approx 2 \times 10^3 \text{ s}^{-1}, \quad (2)$$

where t_s is the time the clusters need to drift from the thermalizer to the mass selector. It can be estimated to be about 500 μs using the velocities given in Ref. [27]. Note that T_{evap} and E_{evap} are slowly decreasing with increasing t_s .

For a system with a finite number of caged atoms there is an equilibrium between a cluster and a surrounding gas at the boiling temperature. As in the bulk this implies that the evaporation rate $k_e(T)$ of the cluster has to compensate the condensation or sticking rate $k_s(p, T)$, which is related to the sticking cross section $\sigma_s(v)$:

$$k_s(p, T) = n\langle v\sigma_s(v)\rangle, \quad (3)$$

where n is the density of the gas. The sticking cross section can be measured or computed (see [28], for example), and all the other quantities are known from kinetic theory. For macroscopic sizes, σ_s is just the sticking probability π_s times the geometric cross section of the sphere, which is 1/4 the total surface, so that Eq. (3) is equivalent to Eq. (1) when $N \rightarrow \infty$.

Using the ideal gas law $p = nk_B T$ and Eq. (3) this gives the vapor pressure of the cluster:

$$p(T) = \frac{k_e(T)k_B T}{\langle\sigma_s v\rangle}. \quad (4)$$

One obtains the wanted vapor pressure at T_{evap} by replacing $k_e(T)$ by Eq. (2). When the atoms are caged at this external pressure $p(T_{\text{evap}})$ the system's boiling point will just be at the free cluster's evaporative ensemble temperature. Of course the cluster passes through all the smaller cluster sizes during its transition from liquid to gas. This will also change the equilibrium temperature since T_{evap} and σ_s and thus $p(T_{\text{evap}})$ depend on cluster size. In consequence the liquid-to-gas transition of a finite system will not occur steplike at a boiling point. Furthermore, the cluster can break up into several big fragments during its transition to gas. This multifragmentation [4] is used as an indicator for the phase transition in nuclear physics and has been found very recently for clusters [29]. It additionally influences the progression of the caloric curve at the transition. As in the case of melting [7] the transition will thus be spread out in a complicated way over a finite temperature range.

To estimate the pressure by Eq. (4) we use a mean evaporative ensemble temperature of about 400 K as deduced in this work for Na_{139}^+ and also found for clusters smaller than Na_{41}^+ [11]. A typical cross section can be evaluated by taking the Langevin cross section for a polarization potential $V(r) = -\alpha/2r^4$ with $\alpha = 24 \text{ \AA}^3$

the polarizability of the sodium atom [30]. This cross section is roughly 3 nm^2 , while the geometrical cross section is rather 4 nm^2 for a 139 atom cluster.

Inserting these values into Eq. (4), one obtains a vapor pressure of $4 \pm 3 \text{ mPa}$ at $T_{\text{evap}} (\approx 400 \text{ K})$. Consequently, this experimental evaporative ensemble temperature can be seen as the boiling temperature of a system of 139 sodium atoms caged in a container at a pressure of about 4 mPa . In the bulk, the same vapor pressure is reached at a temperature of about 445 K , which compares favorably with our measured finite-size boiling temperature.

At atmospheric pressure, the bulk boiling temperature is 1156 K . This large difference to T_{evap} is not a finite-size effect. It is simply given by the pressure dependence which becomes a time-of-flight dependence in our experiment.

Once the boiling temperature is known, the enthalpy of vaporization L can be deduced from a Born-Haber cycle as indicated in Fig. 2. One obtains

$$L(T_{\text{boil}}) = E_{\text{coh}} + H_{\text{gas}}(T_{\text{boil}}) - H_{\text{cl}}(T_{\text{boil}}) \approx 124 \text{ eV}. \quad (5)$$

The enthalpy of vaporization is enormously larger than the latent heat of melting (1.85 eV) [5,6,19,22,], a phenomenon well known from bulk data. The value of L corresponds to the pressure $p = 4 \text{ mPa}$. L is a function of p , since T_{boil} depends on p , and the slope of $H_{\text{gas}}(T)$ is smaller than that of $H_{\text{cl}}(T)$. As in the bulk, the enthalpy of vaporization depends on the pressure and finally vanishes at the critical point.

In summary, the evaporative ensemble temperature and energy have been measured accurately for Na_{139}^+ . Then the caloric curve for 139 sodium atoms in a box at a small pressure of 4 mPa was constructed. The construction relies only on measurable quantities (cohesive energy and caloric curve) of the cluster and perfect gas theory. It is stressed that there is a close connection between pressure and evaporation rate for a bulk system and for a cluster, both of them in equilibrium with their vapor. This allows one to relate the temperature of the evaporative ensemble to an equilibrium boiling temperature at a given pressure. From this the enthalpy of vaporization has been determined.

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