

Caloric Curves of Small Fragmenting Clusters

C. Bréchnignac, Ph Cahuzac, B. Concina, and J. Leygnier

Laboratoire Aimé Cotton CNRS, Université Paris-Sud, Bâtiment 505, F-91405 Orsay, Cedex, France

(Received 26 October 2001; published 29 October 2002)

The kinetic energy release distribution of neutral atoms emitted from photoexcited clusters Sr_n^+ with $n = 4\text{--}15$, has been obtained by time-of-flight velocity dispersion. The deduced temperature is plotted as a function of the excitation energy. For small sizes $n < 7$ a general increase is observed. For cluster sizes larger than $n = 9$, the deduced caloric curves first increase, and then show evidence of a plateau regime as excitation energy increases. This limiting temperature in neutral atom ejection is consistent with a bound cluster-vapor phase transition in a microcanonical system.

DOI: 10.1103/PhysRevLett.89.203401

PACS numbers: 36.40.Ei, 36.40.Qv, 64.70.-p

Investigation of phase transitions in small systems, beyond the thermodynamic limit of macroscopic systems, has attracted conceptual interest for many years, both in atomic clusters and in nuclei. Since the early 1900s, theoretical attempts were made to evaluate, within a macroscopic framework, the melting of small particles, showing a monotonic decrease in the melting temperature with decreasing particle size [1–3]. When computational resources made possible numerical simulations, they showed evidence of a clear transition from solidlike to a disorder liquidlike phase in atomic clusters consisting of a few atoms [4]. To probe the dynamic nature of the transition, more extensive time dependent calculations have been performed on isomerization and melting of very small atom-clusters. It has been found that the system fluctuates in time between the two phases without phase separation [5–7]. The liquid-gas transition has been less investigated although microcanonical Metropolis Monte Carlo computational methods allowed calculation of the parameters of such a transition at a constant pressure of 1 atm [8]. Searching phase transition in nuclei is more recent. It was inspired two decades ago by a calculation of hot dense matter, based on the compressible-liquid-drop model of the nucleus [9]. Such a result, which is of crucial interest for understanding supernovae and neutron-star formation, has also renewed the interest in the fragmentation of hot nuclear matter [10–12].

Most of the experiments dealing with phase transition in small finite systems have been devoted to their melting temperature in contact with a large energy reservoir. This situation confers a canonical description of the temperature. It has been explored for supported particles, containing at least 100 atoms. A regular decrease of melting temperature was shown as the particle size decreases, in agreement with the theoretical predictions [13,14]. A new step in exploring the solid-liquid transition in small systems has been achieved using a buffer gas as a reservoir [15–17], providing the first canonical determination of the caloric curves of size selected cluster ions [15,16]. In nuclear physics, an experimental effort has been done in the last few years in the search for a nuclear liquid-gas

transition from multifragmentation in high energy collisions. Even if some divergence exists concerning the interpretation of the data [18], the deduced nuclear caloric curve shows evidence of a critical temperature for nuclear matter [19]. Similarly the multifragmentation of hydrogen cluster ions with helium target [20] shows a caloric curve in agreement with a bound cluster-gas transition generated by coulombic forces.

Here we report on a quite different approach to the exploration of caloric curves in small isolated systems. In order to avoid the long range coulombic repulsion forces among the ionic fragments in collisional excitation experiment [20], we photoexcited mass selected singly charged strontium clusters and we measured the translational kinetic energy release of the ejected neutral atoms from hot clusters by time-of-flight (TOF) spectroscopy. Hence, for well-defined excitation, we found that the velocity of the emitted atom has a Maxwellian probability distribution. We demonstrate that at low input energy, the deduced temperature of the emitted atom is equal to the microcanonical temperature of the remaining fragment. At high energy, for cluster sizes larger than $n = 9$, we show evidence of a limiting temperature, which does not result from an evaporative cooling, but occurs as a phase transition in a microcanonical system.

The experimental setup consists of a gas aggregation strontium cluster source [21]. The neutral clusters enter an ionization-acceleration region where they are first ionized and excited by a 15 ns laser pulse duration at a photon energy 3.5 eV. Rapid evaporative cooling occurs during the 1 μs residence time in the ionizing region resulting in an “evaporative ensemble” of cluster ions at a temperature $T_0 = 700 \text{ K} \pm 50 \text{ K}$ [22,23]. The charged clusters are then accelerated with a kinetic energy of 9 keV before entering the 2.5 m TOF mass spectrometer. As entering the field free region of the drift tube, a second pulsed laser, appropriately time delayed from the first one, excites the cluster packet of interest at an energy $h\nu$, inducing cluster fragmentation. Then, parents and fragments proceed further with the same center of mass velocity. A retarding potential allows their time dispersion, showing

that ion fragments result from the ejection of neutral atoms, with a number of atoms proportional to $h\nu$ [23]. By varying $h\nu$ from 1.17 to 6.42 eV, the number of ejected atoms from clusters with a tenth of atoms varies from one to six in agreement with a mean binding energy of about 1.15 eV per atom [24]. The deflection of all ions allows the detection of the ejected neutral. In this experimental configuration the TOF is used to measure the kinetic energy release of the ejected atoms for answering the question of the kinetic energy of the ejected atom varies when the total energy of the fragmenting cluster increases.

For warm n -atom clusters, which undergo a single step of unimolecular decay, i.e., only one atom is ejected from each cluster, the temperature of the evaporating clusters may be obtained via the kinetic energy release of the fragments during evaporation [25–27]. The measurement of the average kinetic energy release of the fragment is based on the peak shape analysis of the TOF spectra. Since the process is assumed to be statistical in nature, the fragmenting cluster is in local equilibrium. The velocity distribution of the fragments, either neutral or ionic ones, follows a Maxwell-Boltzmann distribution:

$$I(v) = Av^2 \exp\left(-\left(\frac{v}{v_{\max}}\right)^2\right). \quad (1)$$

In the time-of-flight spectra each fragment peak signal displays a Gaussian shape as follows:

$$I(t) = A \exp\left(-\frac{(t - t_n)^2 v_n^4}{(Dv_{\max})^2}\right), \quad (2)$$

where t_n and v_n are the time of flight and the velocity of the center of mass of the fragmenting cluster parent, respectively, D is the distance between the fragmentation region and the detector, and v_{\max} is the relative velocity of the observed fragment in the center of mass, at the maximum of the probability of its velocity distribution. The translational temperature, at the breakup time, can be defined as $kT = \frac{1}{2}mv_{\max}^2$, where m is the mass of the fragment. Since the velocity of the neutral atom is larger than the one of the heavy ionic fragment, we performed shape analysis of the emitted atom signal.

In a first experiment, we considered the unimolecular decay during the TOF of a mass selected Sr_n^+ ion packet, keeping off the second laser. As previously shown the evaporating clusters have an internal energy relative to the upper part of the internal energy distribution of the selected ion packet [23]. We successively recorded the parent ion signal as well as the corresponding neutral atom peak, after deflecting the ions. Both normalized profiles [Fig. 1, traces (a) and (b)] display a Gaussian shape. It is clearly seen that the neutral atom peak is broader than the parent ion peak due to the kinetic energy release involved in the dissociation process. The measured ion parent peak gives the apparatus function. The measured neutral peak is fitted by a Gaussian profile, which is the convolution of $I(t)$ with the apparatus func-

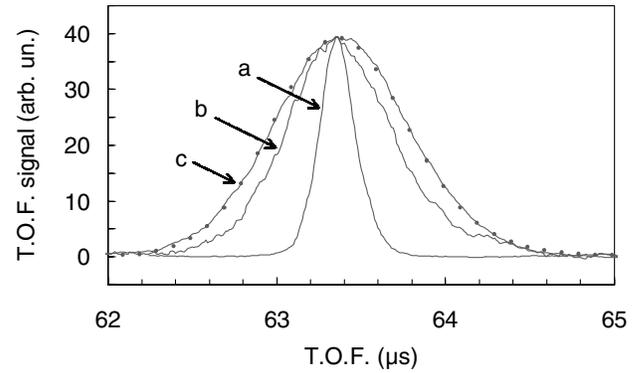


FIG. 1. Normalized experimental signals of the mass selected ions Sr_{11}^+ [trace (a)] and their neutral daughter atoms: from unimolecular decay [trace (b)], and from photoexcited parents at $h\nu = 1.16$ eV [trace (c)]. The dots are the best fit over the internal energy of the photoexcited parent.

tion [26]. Only v_{\max} in the exponent of Eq. (2) is used as a fitting parameter, t_n , v_n , D , are given from the experimental device. We deduced a translational temperature, defined as $kT = \frac{1}{2}mv_{\max}^2$. Assuming a microcanonical description of the clusters, the vibrational temperature T_v of the Sr_{n-1}^+ ionic fragments at the breaking point can be evaluated as $kT_v = (E_i - E_b)/[3(n-1) - 6]$, where E_i is the initial internal energy of the evaporating parents, and E_b its dissociation energy [27]. The vibrational temperatures, that we estimated from a mean binding energy per atom of 1.15 eV, are plotted together with the measured translational temperatures for different cluster sizes in Fig. 2, lower points. For $n > 6$ these two sets of temperatures are consistent with each other, presenting similar trends with size. This remarkable finding is interpreted as evidence for equipartition of kinetic energy at the transition state. In fact, the capability of the kinetic energy release to reflect the internal temperature of the fragment is in agreement with the predictions

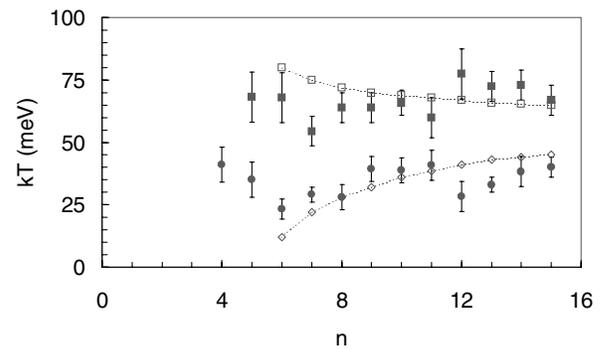
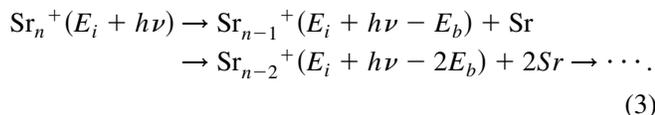


FIG. 2. Translational temperatures measured from the shape analysis of the neutral profiles versus cluster size. Solid dots and solid squares are the temperatures from unimolecular decay and photoexcited parents at $h\nu = 1.16$ eV, respectively. The irregularities at $n = 7$ and $n = 12$ reflect irregularities in the dissociation energies for these masses. Open squares are the estimated vibrational temperatures of the daughter ions from a microcanonical model.

of the phase space theory in the context of the loose transition state for evaporating atom-clusters having a reasonably large number of degrees of freedom [28].

In a second set of experiments, we increased the internal energy of the parent clusters by photoexcitation at $h\nu = 1.17$ eV. This shifts its internal energy by about one binding energy. Each photoexcited parent evaporates one atom, as verified from the fragmentation ion spectrum. After activating the ion deflection, the neutral atoms are detected. The neutral signal broadens out the “unimolecular” one, as seen in Fig. 1, trace (c), for $n = 11$. Again for all masses with $n > 6$ the trend of the translational temperature is consistent with the vibrational one, as shown in Fig. 2, upper points. For photon energy higher than 1.17 eV, more than one atom per photoexcited cluster parent is rejected before reaching the detector. The neutral experimental profile, which results from all the ejected atoms, is compared to a sequential evaporative cooling, as described in Ref. [27].



Assuming at each step of the process that the translational temperature of the emitted neutral atom equates the vibrational temperature of the remaining ionic fragment, and that the directions of neutral emissions are uncorrelated, the result of a sequential evaporative cooling on the neutral signal is the sum of the contributions of the successive evaporative events. For a given photon energy, we calculated the sum of the Gaussian contributions with decreasing vibrational temperatures corresponding to successive evaporations. As aforementioned, the vibrational temperature of the fragmenting cluster depends on its binding energy. However, in our simulations, we used the mean binding energy since the variations of E_b do not exceed 10% of its mean value in the studied size range. Two experimental profiles of neutral signals resulting from photoexcited Sr_{10}^+ at two different photon energies $h\nu = 2.33$ eV [trace (a)] and $h\nu = 5$ eV [trace (b)] are depicted in Fig. 3 together with the results of our simulations. At $h\nu = 2.33$ eV, the good agreement between experimental and calculated profiles insures a two step sequential evaporative cooling. At $h\nu = 5$ eV, our simulation leads to a profile larger than the one observed, showing evidence that clusters cannot be heated above a limit temperature. By increasing step by step the photon energy from 2.33 to 6.42 eV, experimental neutral profiles show evidence of a saturation in width for photon energy above 2.33 eV and for cluster sizes larger than 9 atom-clusters. This saturation is understood by keeping constant the kinetic energy release of neutral atoms in the first steps of the evaporation process. The deduced mean translational temperature is plotted in Fig. 4 for $n = 10, 11$ (lower traces). For smaller masses no saturation can be established in the shape profile width. In order to obtain caloric curves we plot the temperature

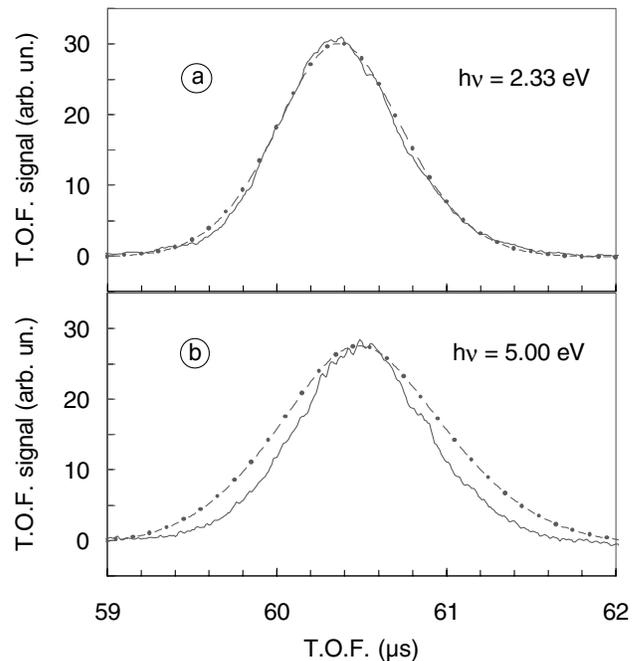


FIG. 3. Experimental profiles of neutral signals from Sr_{10}^+ after photoexcitation at $h\nu = 2.33$ eV [trace (a)] and $h\nu = 5.0$ eV [trace (b)] together with the results of our simulation for a sequential evaporative cooling (dot dashed lines). The discrepancy between simulation and experimental curve for 5 eV shows evidence of a limiting temperature as the internal energy of the parent is increased.

derived in absolute scale versus the energy deposited per atom in the cluster prior to fragmentation, as shown in Fig. 4 for cluster sizes $n = 5, 7, 10,$ and 11 . For sizes as small as $n = 5, 7$ a general increase is observed with a marked curvature at high energy. For larger sizes ($n = 10, 11$) the caloric curves can be clearly divided into two parts. After an initial rising with a slope of $1/(3 \pm 0.5)$ similar to a traditional bulk caloric curve with $C_p = 3$ (dashed line of Fig. 4), an almost constant value for kT of about 85–110 meV is obtained. Such a plateau in the caloric curve indicates a phase transition occurring here at a temperature $T = 1000$ – 1300 K. This is on average above the melting temperature (1050 K) and below the boiling point of the bulk (1655 K). A plateau in the caloric curve indicates that only part of internal energy is available for kinetic energy (i.e., internal temperature), the remainder increases the potential energy, opening a new region in the phase space. The length of the plateau gives the latent heat of the phase transition. From Fig. 4, although the plateau is not completely explored, one can deduce that its length exceeds 0.4 eV per atom, which is 5 times larger than the solid-liquid latent heat in the bulk, making unlikely a solid-liquid phase transition. As calculated for Lennard-Jones drops [29] a sudden increase in the internal energy of an isolated system should lead to its collective expansion and the system will break into smaller fragments keeping a constant breakup temperature. In our case, after a sudden increase

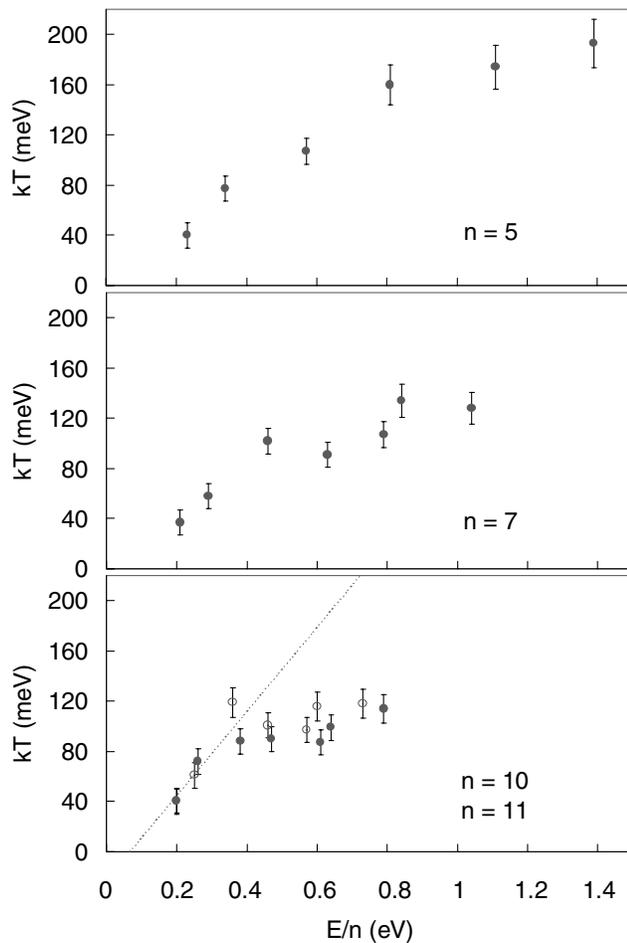


FIG. 4. Caloric curves for Sr_n^+ determined from the kinetic energy release of neutral emitted atoms versus excitation energy per atom. For $n = 5$ a general rising curve is obtained. For $n = 10, 11$ (solid and open dots, respectively) the caloric curves rise first strongly and saturate to a limiting temperature in agreement with a bound-gas transition. $n = 7$ appears as an intermediate case.

of the internal cluster energy by photoexcitation, the system emits neutral atoms, decreasing its internal energy but keeping constant its temperature as expected for an ideal bound-gas transition in a finite system.

The comparison with multifragmentation of highly ionized clusters [20] or nuclei [19] is fruitful, since they depicted phase transition in microcanonical systems. In the last case the caloric curve also presents a rising part and a plateau regime which starts at an internal energy per nucleon of about one third of the binding energy. In our case the plateau regime also starts when the internal energy per atom is about one third of the binding energy. However, the corresponding limiting temperature is only 30% smaller than the boiling temperature of the bulk, whereas in the nuclei case the critical temperature is shifted down from the bulk value by a factor of 3–4. To complete the comparison it would be interesting to increase the internal cluster energy above the atomization value to see if the caloric curve starts to increase again in

a “gas branch.” Unfortunately, increasing the photon energy deposit will lead to multiple ionization. Only multiple photon excitation should be done, but the interpretation of the data is not straightforward.

In summary, our measurements of the kinetic energy release of the neutral atoms ejected from photoexcited Sr_n^+ allowed the determination of the caloric curve of the fragmenting clusters. The plateau observed for n larger than 9, and for excitation energies larger than 0.35 eV per atom, can be viewed as a signature of a bound cluster to gas phase transition in a microcanonical system. As opposed to multifragmenting systems involving Coulomb explosion, our system by emitting only atoms is more related to the bulk-vapor transition.

- [1] P. Pawlow, *Z. Phys. Chem.* **65**, 1 (1908).
- [2] E. Rie, *Z. Phys. Chem.* **104**, 354 (1923).
- [3] P. R. Couchman and W. A. Jesser, *Nature (London)* **269**, 481 (1977).
- [4] C. L. Briant and J. J. Burton, *J. Chem. Phys.* **63**, 2045 (1975).
- [5] J. Luo, U. Landman, and J. Jortner, in *Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. Khana (Plenum, New York, 1987), pp. 201–206.
- [6] P. Labastie and R. Whetten, *Phys. Rev. Lett.* **65**, 1567 (1990).
- [7] R. E. Kunz and R. S. Berry, *Phys. Rev. E* **49**, 1895 (1994).
- [8] D. H. E. Gross and M. E. Madjet, in *Similarities and Differences between Atomic Nuclei and Clusters*, edited by Y. Abe, I. Arai, S. M. Lee, and K. Yabana (AIP, New York, 1997), pp. 203–214.
- [9] D. Q. Lamb *et al.*, *Phys. Rev. Lett.* **41**, 1623 (1978).
- [10] D. H. E. Gross, *Phys. Rep.* **279**, 119 (1997).
- [11] X. Campi and H. Krivine, *Nucl. Phys. A* **620**, 46 (1997).
- [12] Ph. Chomaz, V. Duflot, and F. Gulminelli, *Phys. Rev. Lett.* **85**, 3587 (2000).
- [13] Ph. Buffat and J. P. Borel, *Phys. Rev. A* **13**, 2287 (1976).
- [14] S. L. Lai *et al.*, *Phys. Rev. Lett.* **77**, 99 (1996).
- [15] M. Schmidt *et al.*, *Phys. Rev. Lett.* **79**, 99 (1997).
- [16] M. Schmidt *et al.*, *Nature (London)* **393**, 238 (1998).
- [17] A. Shvartsburg and M. F. Jarrold, *Phys. Rev. Lett.* **85**, 2530 (2000).
- [18] J. Pochodzalla *et al.*, *Phys. Rev. Lett.* **75**, 1040 (1995).
- [19] J. Pochodzalla, *Prog. Part. Nucl. Phys.* **39**, 443 (1997).
- [20] F. Gobet *et al.*, *Phys. Rev. Lett.* **87**, 203401 (2001).
- [21] C. Bréchnignac *et al.*, *Phys. Rev. Lett.* **81**, 4612 (1998).
- [22] C. E. Klots, *J. Chem. Phys.* **83**, 5854 (1985).
- [23] C. Bréchnignac *et al.*, *J. Chem. Phys.* **88**, 3022 (1988).
- [24] C. Bréchnignac *et al.*, *Phys. Rev. B* **61**, 7280 (2000).
- [25] C. Lifshitz and F. Louage, *J. Phys. Chem.* **93**, 5633 (1989).
- [26] S. Wei, W. B. Tzeng, and A. W. Castleman, *J. Chem. Phys.* **92**, 332 (1990).
- [27] P. Brockhaus *et al.*, *Phys. Rev. A* **59**, 495 (1999).
- [28] P. Parneix and Ph. Bréchnignac, *Eur. Phys. J. D* **13**, 43 (2001).
- [29] A. Strachan and C. O. Dorso, *Phys. Rev. C* **59**, 285 (1999).