Probing the Liquid-to-Gas Phase Transition in a Cluster via a Caloric Curve

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High-energy collisions (60 keV/amu) of hydrogen cluster ions with a helium target have been completely analyzed on an event-by-event basis. By selecting specific decay reactions we can start after the energizing collision with a microcanonical cluster ion ensemble of fixed excitation energy and we derive corresponding temperatures of the decaying cluster ions. The relation between the temperature and the excitation energy (caloric curve) exhibits the typical prerequisites of a first-order phase transition in a finite system, in the present case signaling the transition from a bound cluster to the gas phase.

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One of the great challenges in cluster physics in the last years was the identification and characterization of critical behavior and of phase transitions, including solid-to-liquid and liquid-to-gas phase transitions. Since clusters are particles of finite size, one is confronted with the general question of how to detect and/or characterize such a transition in a finite system, a question of interest for many microscopic or mesoscopic systems such as, for instance, melting and vaporization of metallic clusters, Bose condensation of quantum fluids, and nuclear liquid-to-gas transition [1,2].

In a strict sense, sharp second-order phase transitions can occur only in the thermodynamic limit—that is, critical singularities are present only for a system with a large number of particles [3]. In small systems such as two colliding nuclear or molecular systems fluctuations may wash out the signature of the phase transition [4] (see also [1]). Nevertheless, it has been demonstrated theoretically (see [4] and references therein) and also experimentally (see [5] and references therein) that finite systems may indeed exhibit critical behavior to be seen when studying inclusive fragment size distributions, scaled factorial moments, and anomalous fractal dimensions. For instance recent heavy ion collision experiments around the Fermi energy (see [9] in Ref. [4]) and cluster collision experiments around the Bohr energy (see [6] and references therein) have shown the formation of many different fragments in the exit channel of the reaction exhibiting a power law in total fragment size distributions. Such a power law, as described by the Fisher droplet model [7,8], is expected to hold for droplet condensation/evaporation near the critical temperature, indicating a liquid-to-gas second order phase transition. However, the recent work on the lattice gas model [1] demonstrates that a critical behavior is compatible with a first-order phase transition because of the finite size effects.

As concluded by Gross and co-workers [9,10] on the basis of extensive theoretical modeling the best signature, however, of a phase transition of first or second order in a finite system is the specific shape of the caloric curve (see also [2] and the theoretical work of Berry and co-workers [11–13]), i.e., the thermodynamic temperature as a function of the total energy in the system. Pochodzalla *et al.* [14] were the first to determine experimentally a relation between the temperature of hot decaying nuclei resulting from Au + Au collisions at 600 MeV/amu and the excitation energy, the shape of this relation exhibiting the characteristic plateau expected for a phase transition. The validity of this first experimental observation of a caloric curve for a liquid-to-gas phase transition for nuclear systems (in particular, the determination of the temperature) was later questioned [3] because later experiments arrived at different shapes (see [15]and [16] and references therein). On the other hand, Haberland and co-workers [17–19] reported the first experimental determination of a caloric curve for the solid-to-liquid transition (melting) of a small cluster, i.e., a sodium cluster consisting of 139 atoms [17]. A beam of cluster ions was generated with a canonical distribution of internal energy thus fixing the temperature. One cluster size was selected (thus switching to microcanonical system), irradiated by photons, and the photofragmentation pattern (which can be related to the energy) was measured as a function of cluster temperature. Moreover, Bachels *et al.* [20] reported recently a caloric curve for a free tin cluster distribution (without mass selection) impinging a sensitive pyroelectric foil, the interpretation of their experiment was, however, later questioned [21].

In the present Letter we report a quite different approach to search for a signal of a phase transition using hydrogen cluster ions with sizes much smaller than the previously studied metal cluster ions. The protonated hydrogen clusters represent a different class of systems where a quantum solute is solvated by a quantum solvent; the added proton becomes trapped and a tightly localized H_3^+ core is surrounded by solvating H_2 molecules, $H_3^+(H_2)_{m\leq 14}$ [22]. Moreover, after the energizing collisions between 60 keV/amu ions with a helium target we select a microcanonical ensemble of cluster ions with a given energy (by selecting specific decay reactions from a host of possible decay channels) and determine from the (partial) fragment size distribution the corresponding temperature of the ensemble of decaying cluster ions. This experiment involves the complete event-by-event analysis of 29 041 collisions using a recently developed [5,6] multicoincidence technique for the simultaneous detection of the correlated, ionized and neutral, collision fragments, thus allowing us to obtain an experimental caloric curve for the transition from a bound cluster to the gas phase.

Mass selected hydrogen cluster ions with an energy of 60 keV/u are prepared in a high-energy cluster ion beam facility [5]. In the present study, the beam of mass selected $H_3^+(H_2)_{m\leq 14}$ cluster ions is crossed perpendicularly by a helium target beam effusing from a cylindrical capillary tube. The undissociated primary $H_3^+(H_2)_{m\leq 14}$ cluster projectile ion or the neutral and charged fragments resulting from reactive collisions are then passing a magnetic sector field analyzer and detected with a multidetector device consisting of an array of passivated implanted planar silicon surface barrier detectors located at different positions at the exit of the magnetic analyzer. With this instrument we are able to record for each event simultaneously the number (multiplicity) of each mass-identified fragment ion resulting from the interaction (for more experimental details, see [5,6,23]). In addition, for each event we can also monitor in coincidence with the detected ions the sum of the masses of all the neutral fragments. Moreover, by probing the angular distribution of these neutrals in front of the detector by using a movable aperture we find that the neutral products consist only of hydrogen atoms and hydrogen molecules [24], with no larger neutral clusters present. From additional measurements using a movable grid in front of the detector with the molecular projectiles H_2 or H_3^+ we can distinguish whether a resulting signal at a mass of 2 amu is due to one hydrogen molecule or two hydrogen atoms [24,25]. For larger clusters this technique cannot be directly applied and therefore additional information on relative cross sections for the various product channels needs to be used for a complete analysis of the neutral mass peak [24]. Thus we are able to analyze on an event-by-event basis the identity of all correlated fragments produced in a single collision event between the $H_3^+(H_2)_{m\leq 14}$ cluster ion and the He target atom, the fragmentation reactions having the general form

$$H_3^+(H_2)_m + \mathrm{He} \rightarrow H_3^+(H_2)_k + bH_3^+ + cH_2^+ + dH^+ + eH_2 + fH,$$

with $a-f = 0, 1, \dots$. The validity of single collision conditions has been ascertained by measurements at different He target pressures and allows us also to derive absolute cross sections for the occurrence of specific reaction channels (partial cross sections) (for details, see [26]). This complete analysis allows us to go beyond the straightforward determination of total fragment size distributions as reported previously ([6], and references therein), since we are able to generate for the first time partial fragment size distributions for selected decay reactions or classes of decay reactions.

As we need for the construction of a caloric curve the simultaneous determination of the energy and the temperature of the system, we use the ability to select certain classes of reactions to group our analyzed events into a number of different subgroups each representing collisions in which a certain amount of energy is deposited into the cluster. Thus we are generating from our large set of collisions various subsets containing only cluster ions with a certain energy (or energy range) in a microcanonical sense. The basic idea behind this is to analyze each decay reaction in terms of the energy required for all the particles produced in such a decay reaction (taking into account the well-known potential energy curves for the hydrogen molecule when calculating the energy for the Franck-Condon transitions from quasi-isolated cold ground state H_2 molecules to the various excited states involved) and to use the total energy value obtained as a measure for the internal energy prior to the decay. For instance, the observed decay reactions of the $H_3^+(H_2)_{12}$ ion into $H_9^+ + H_2^+$ plus a neutral mass totaling 16 amu. Analyzing the identity of the neutrals in these events shows that 86.1% of the cases correspond to the production of eight hydrogen molecules. In this case the necessary energy for the reaction is 15.7 eV (the ionization energy for the hydrogen molecule), neglecting the much smaller binding energy of the hydrogen molecules. Similarly, 13% of these events correspond to the production of seven hydrogen molecules and two hydrogen atoms necessitating an additional energy input of about 10.3 eV to dissociate one molecule into two atoms (with a total energy of 26 eV), 0.8% correspond to six molecules and four atoms (total energy of 36.3 eV), and 0.1% to five molecules and six atoms (total energy of 46.6 eV).

Figure 1 shows for the $H_3^+(H_2)_{12}$ cluster ion projectile for eight selected subsets each of which includes reactions of a certain energy range, e.g., 2–12 eV, 15–25 eV, etc. It is interesting to note that the shape of these distributions changes significantly as a function of the energy deposited, i.e., from a U-shaped form at low energy which is due to the occurrence of a mixture of evaporation and multifragmentation processes, to a pure power

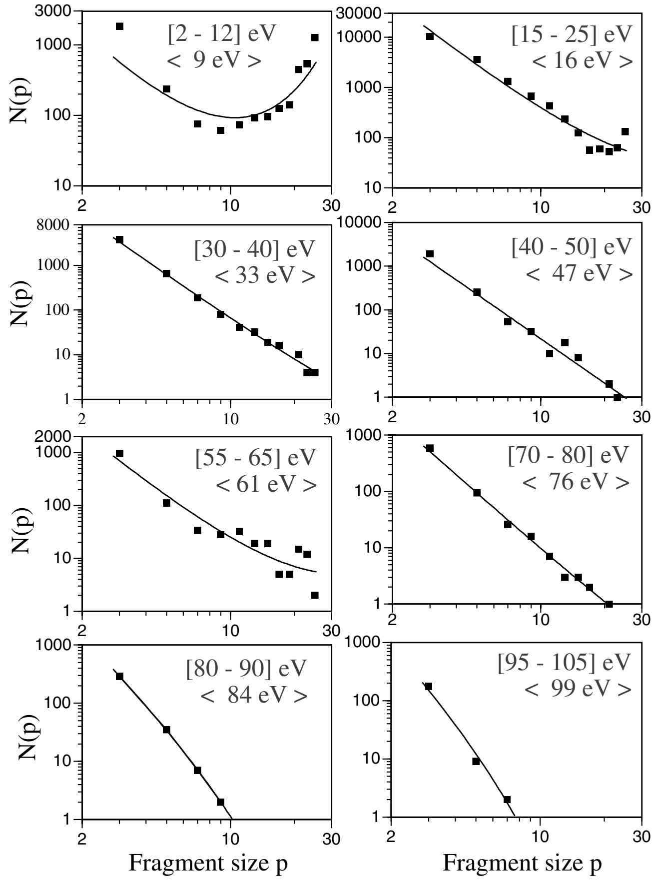

FIG. 1. Partial fragment mass distributions for different subsets of reaction channels (selected according to the energy deposited in the collision complex, i.e., 2–12 eV, 15–25 eV, etc.) occurring in collisions of 60 keV/amu H_{27}^{+} ions with He. Solid lines: fits using Fisher's formula (see text).

law at intermediate energies due to the presence of only multifragmentation reactions to finally a regime at high energies which is dominated by complete disintegration processes. So far these different regimes could be observed only by different experiments with widely different collision parameters ranging from low-energy mass spectrometer collision experiments [27], to high-energy cluster/atom or nuclear collision experiments (see [6] and references therein) and to beam foil experiments with clusters yielding only atomic fragment ions [28]. This is the first time that this characteristic change of the mass distribution as a function of energy deposited has been determined in only one experiment over the whole range of possible shapes and thus possible decay mechanisms.

Returning now to the construction of the caloric curve we need in a second step to determine for each subset of known energy the corresponding temperature of the cluster ions prior to the decay. Here we use a relationship between the characteristic shape of a fragment mass distribution and the temperature of the decaying nuclei at around the critical point reported recently by Belkacem *et al.* [4]. They were able to fit quite differing numerical mass distributions obtained by classical MD calculations for $A = 100$ nucleus at different initial canonical temperatures (by generating 2000 events per temperature) very well with Fisher's droplet formula [7]

$$dN/dA = Y_0 A^{-\tau} X^{A^{2/3}} Y^{A}, \qquad (1)$$

with Y_0, X, Y, and τ fitting parameters and A the atomic mass number, thus demonstrating a direct relationship between the shape of the mass distribution [as described by (2) and in particular by the parameter Y which is related to the temperature approaching the value 1 at the critical temperature] and the initial temperature of the decaying system (see also [29]). Following the methodology of Belkacem *et al.* [4] in fitting their mass distribution, i.e., first fixing the parameter τ using a rather pure power law distribution (e.g., the one at an energy of 47 eV in Fig. 1) and then fitting the other parameters by using all distributions (and doing this in an iterative way several times), we also tried to fit the presently obtained (partial) fragment mass distributions with formula (2). With a slope of $-(3 \pm 0.5)$ (as compared to -2.23 in the calculation of Belkacem *et al.* [4]; previous experimentally determined values for total fragment mass distribution for clusters and nuclei having values of about -2.6 [6]) we obtain a very good agreement between the experimental points and the fits shown in Fig. 1 by solid lines. In order to check the robustness of these fits we have also analyzed the decay of other cluster sizes including $m = 6$, 8, 9, 11, 12, and 14, the fits obtained were equally convincing. This then allows us by comparison with the results of Belkacem *et al.* [4] to designate for each of the subsets considered a relative measure for the temperature due to the characteristic shape of its fragment mass distribution (as expressed by the fitted parameters, in particular the parameter Y). As discussed below it turns out that for small energies the distribution is quickly changing with increasing energy from a U-shaped form to a single power law falloff. This power law containing fragments of all sizes is sustained over a broad energy range and thus this is direct evidence for a constant temperature in this energy range. Finally, at very large energies this power law is replaced by a shape which is falling off much faster than this power law signaling a sudden change (increase) in temperature. It is interesting to note that in a similar fashion, though in a different context and by different theoretical means, temperatures of decaying carbon cluster ions have been determined by measuring either the microcanical decay rate constants for monomer evaporation [30] (see also results for aniline-argon clusters [31]), the kinetic energy release distributions for monomer evaporation [32], or the fragmentation pattern in surface-induced dissociations [33].

Using this "temperature" which is only a relative measure (due to the comparison with MD calculations applied to the nuclear matter), we plot in Fig. 2 the temperature derived in reduced units versus the energy deposited. As a matter of fact we have for this purpose considered more

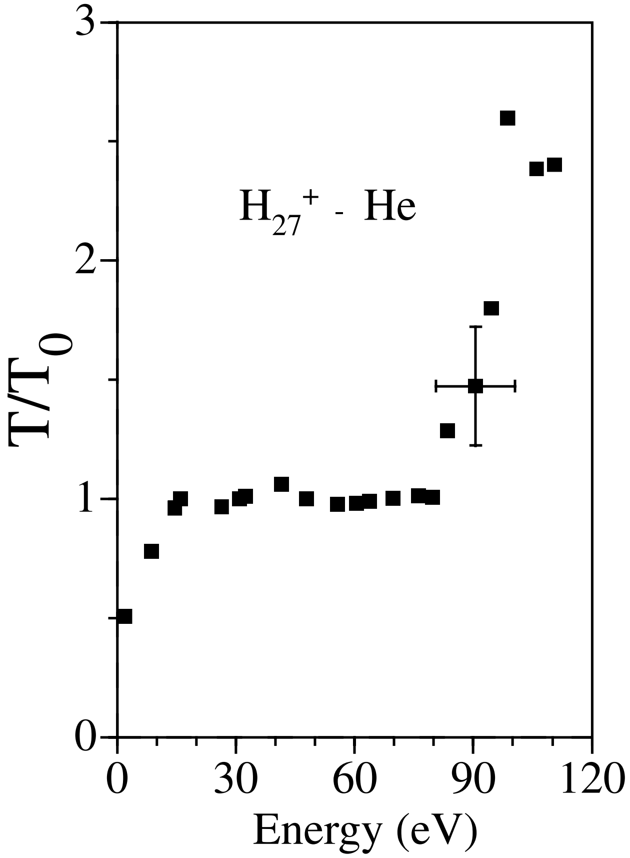

FIG. 2. Caloric curve for cluster fragmentation: temperature [given in reduced value (T/T_0), with T_0 the temperature in the plateau part of the curve] versus the energy deposited in the H_{27}^+ cluster ion.

data subsets than shown in Fig. 1. Moreover, similar results have also been obtained for other cluster ion sizes mentioned already above, thus confirming independence of this characteristic result from the finite particle size. This caloric curve can be clearly divided into three parts, after an initially rising a distinct plateau is present before the curve rises again. This curve therefore agrees qualitatively with the typical prerequisites of a first-order phase transition [9] (see also Fig. 7 in [2]) in a finite system. It thus constitutes a strong signature for a liquid-to-gas phase transition in a fragmenting cluster and thus confirms and replaces the other fingerprints [10] such as the power law in mass distributions and factorial moment analyses. It is interesting to note that this caloric curve exhibits a relatively long plateau region giving the apparent heat connected to this transition. As in the calculations discussed by Gross *et al.* using microcanonical metropolis sampling for hot atomic metal clusters [9], the transition occurs and is characterized by the interplay and transition from monomer evaporation reactions (see also Fig. 1), to multifragmentation reactions and complete vaporization events in this bound-free transition regime. The particular long plateau may be also connected to the many different degrees of freedom available in this special type of cluster being bound by a mixture of dispersion force (intermolecular binding) and covalent binding with more intramolecular excited states available than in atomic clusters.

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