Eur. Phys. J. D **20**, 87–92 (2002)
DOI: 10.1140/epjd/e2002-00111-6

THE EUROPEAN PHYSICAL JOURNAL D

On the fragmentation of multiply charged sodium clusters

H.I. Hidmi[1], D.H.E. Gross[2,a], and H.R. Jaqaman[1]

[1] Bethlehem University, Bethlehem, Palestine
[2] Hahn-Meitner-Institut Berlin, Bereich Theoretische Physik, 14109 Berlin, Germany
and
Freie Universität Berlin, 14109 Berlin, Germany

Received 7 November 2001 / Received in final form 4 April 2002
Published online 28 June 2002 –

Abstract. The fragmentation of multiply charged atomic sodium clusters of mass 200 is investigated using the Micro-canonical Metropolis Monte Carlo (MMMC) statistical technique for excitation energies up to 200 eV and for cluster charges up to $+9e$. In this work we present caloric curves and charged and uncharged fragment mass distributions for clusters with charges 0, 2, and 4. The caloric curves show a dip at the critical point implying a negative specific heat, as expected for finite systems, while the fragment mass distributions corroborate the picture of a phase transition from one dominant liquid-like cluster to complete vaporization.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 68.65.-k Low-dimensional, mesoscopic, and nanoscale systems: structure and nonelectronic properties

1 Introduction

The thermo-statistical investigation of atomic clusters is interesting for several reasons. On the practical side, the study of mesoscopic many-body systems is becoming increasingly important in modern technology which is very quickly approaching the nano scale where quantum and finite size effects begin to play a role. On the theoretical side, the study of small systems also gives a rich and deep insight into the fundamental concepts of statistical mechanics and tries to answer some important questions [1,2] such as how large must a system be in order to show phase transitions, or what is the microscopic origin of the second law of thermodynamics, and does it hold in small systems? Here we hope to contribute to answering the first question.

Phase transitions are identified by the shape of the caloric curve, the relation between the temperature and the excitation energy of the system. In macroscopic physics it is usually assumed that the system approaches the thermodynamic limit where the number of particles in the system $N \to \infty$ and a phase transition is characterized by the fact that the temperature at the phase transition remains constant while energy is supplied to the system. In this limit, surface effects ($\propto N^{2/3}$) can be neglected relative to the leading bulk quantities ($\propto N$).

Dealing with finite isolated systems, the picture becomes different. As the starting point of a conventional canonical description is the assumption of a homogeneous density distribution in the thermodynamic limit, the canonical description is not suited for the description of phase transitions in small clusters. The main physical effect of a phase transition of first order is the creation of inhomogeneities with a separation of two coexisting phases by interfaces. Here surface effects are important and the signal of a first order phase transition is seen as a dip in the caloric curve (temperature *versus* energy) at the critical temperature, as shown in Figure 1. This is similar to observations on small isolated nuclear systems [3–5] and was predicted by Gross *et al.* [6]. This indicates that the heat capacity is not a positive definite quantity any more and can even take negative values.

This behavior can only be obtained in a micro-canonical description which takes into account the strict conservation of mass, charge, and energy, and allows for a proper treatment of surface effects. In this approach, the phase transition can be attributed to the opening of new decay channels, *i.e.*, the population of additional regions of the phase space and the concomitant increase in the density of phase space, *i.e.* in the number $W(E_{\rm tot})$ of microstates of the system with total energy $E_{\rm tot}$. The entropy of the system is related to the phase space density through Boltzmann's Principle $S(E_{\rm tot}) = k \ln W(E_{\rm tot})$, where k is Boltzmann's constant. The thermodynamic temperature of the system can then be obtained from the entropy by the relation:

$$\frac{1}{T_{\rm ther}} \equiv \beta(E_{\rm tot}) = \frac{\partial S(E_{\rm tot})}{\partial E_{\rm tot}}. \qquad (1)$$

In the present work the fragmentation of charged atomic Na clusters of mass 200, with cluster charges ranging

[a] e-mail: gross@hmi.de

from 0 to 9, is investigated assuming that statistical equilibration is achieved at some point before the fragmentation process takes place. The statistical method used is the Micro-canonical Metropolis Monte Carlo (MMMC) technique, described in detail in [7–12]. The fundamental assumption is that, at equilibrium, all micro-canonically accessible phase-space cells $\xi_{\rm i}$ corresponding to a fixed energy (and any other conserved quantities) are equally probable. The computational simulation of the fragmentation of a sodium cluster is performed as follows: N atoms (200 in our case) are combined randomly into fragments (or subclusters) which are placed randomly inside a spherical volume of specified radius ($r \times N^{1/3}$) where r is the system radius parameter that is taken to be 6 Å in this work. Other values of r were also used and the results were found to depend weakly on the choice of r. Thus we assume that fragments explore all the accessible phase space when moving within a well defined freeze-out volume. This scenario is different from that where the fragments are in isobaric equilibrium with a pressure defined by the evaporation rate as assumed by Schmidt *et al.* [13].

The system is given a total charge Z, and a given excitation energy or heat. The charge and excitation energy are distributed randomly among the various fragments. The resulting fragment configuration corresponds to a point $\xi_{\rm i}$ in the reduced phase space of the system and the weight of the phase space at that point is calculated. So, starting from this initial phase-space point, with weight $W_{\rm i}$, one goes to a neighboring point $\xi_{\rm f}$ in phase space by, for example, repositioning one of the fragments, by combining the masses and charges of two fragments or by splitting the mass and charge of an existing fragment into two fragments and repositioning them. One then calculates the weight $W_{\rm f}$ of the new point in the reduced phase space, and the new state is accepted with a probability $\Pi = W_{\rm f}/W_{\rm i}$. It is worth mentioning that the weights are calculated using detailed balance. The states are not generated by the computer with an equal probability, but rather with an "*a priori*-probability" which depends on the way we sample the fragments. This will give different values for the transition probability from state 1 to state 2, and the transition from state 2 to state 1. So, one has to correct for this transition probability difference in order to keep detailed balance between the initial and final states. The correct inclusion of detailed balance for charged clusters is an improvement over the earlier work [10–12] where detailed balance was included only approximately for charged clusters.

Clusters of mass 200 atoms and charges ranging from zero up to 9 were studied. It was found that for charges $\geq$5 the calculation becomes unstable and this was observed as irreproducible fluctuations in the caloric curve that vary chaotically if the calculations are repeated with a different random number generator or with a different number of phase space points (typically a few millions) sampled at each energy. This puzzling behavior is due to the fact that as the charge of a fixed-mass cluster is increased, the long-range Coulomb repulsive force overwhelms the much weaker short-range van der Waals attractive forces with the result that the cluster becomes unstable even at zero excitation energy. Such a situation has been observed experimentally by Chandezon *et al.* [14,15] who investigated the critical sizes necessary for the production of multiply charged sodium clusters and found that for a charge of 5, the smallest mass of the cluster would be 200 ± 5 atoms, a result slightly dependent on the method used for producing and ionizing the cluster. For a total cluster charge of 4 the critical size is about 120. Charged clusters smaller than the critical size where found to decay immediately by emitting a light singly charged fragment and thus cannot achieve thermal equilibration. This behavior contrasts with the nuclear case where the Coulomb force has to compete with the much stronger nuclear force and where Z usually takes values close to half the number of nucleons.

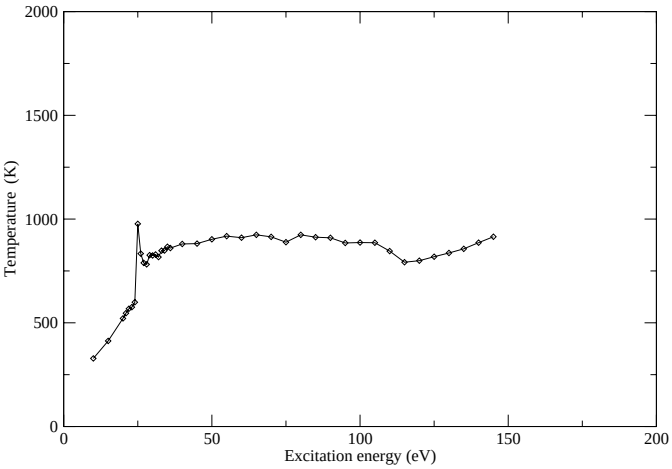

Fig. 1. Caloric curve for Na clusters of mass 200 atoms with total charge = $4e$. The temperature dip at E about 110 eV is the signature of the phase transition in small systems. This curve is obtained with statistics of 10×10^6 events per energy step.

2 Results

Figure 1 shows the caloric curve, or the thermodynamic temperature as a function of the excitation energy, that we obtained in our MMMC simulation for a cluster of sodium with a mass of 200 atoms and a charge of $+4e$. It is clear from the figure that the temperature of the system increases sharply with energy for excitation energies below 30 eV (or 0.15 eV/atom), then it reaches a plateau at a temperature of about 900 K. At energies above 100 eV the cluster starts to evaporate rapidly, its size shrinks appreciably (see also Fig. 10 below) and its temperature is reduced by about 100 K. This is indicated by the dip in the temperature curve at about 110 eV excitation energy. It corresponds to a negative specific heat capacity of a value of about -0.45 cal/gK. Similar results were obtained for clusters of charges from 0 to 3, with the dips at the end of the phase transition plateau becoming deeper as the charge is reduced. The negative heat capacity is observed in small systems, in contrast to infinite system in

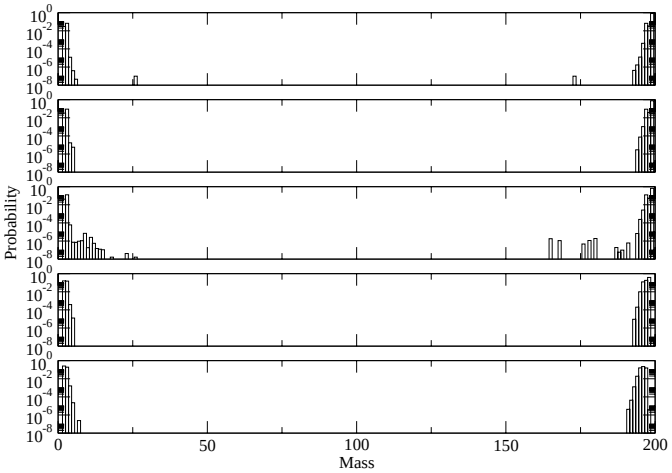

Fig. 2. Mass distribution for Na clusters of 200 atoms and a cluster charge of $2e$ near the peak of the caloric curve at 25 eV. The panels correspond to excitation energies of 23, 24, 25, 26, and 27 eV from top to bottom.

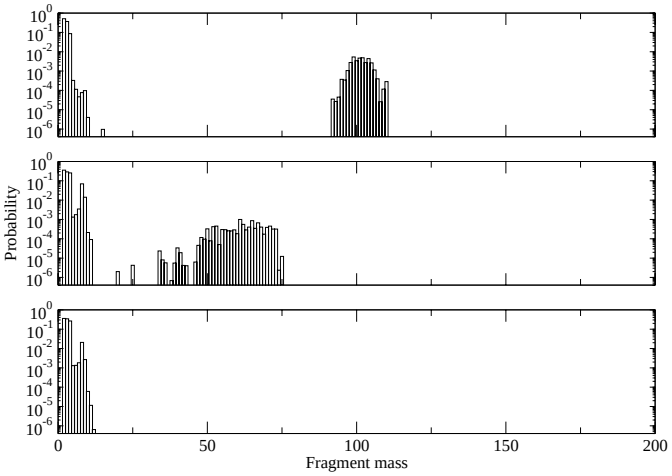

Fig. 3. The mass distribution for Na clusters of mass 200 atoms and zero charge at excitation energies of 90, 110, 130 eV from top to bottom.

which the heat capacity remains constant during phase transition.

The puzzling peak at 25 eV excitation energy in the caloric curve is reproducible and independent of the calculation. It has been verified with very high statistics, 1×10^8 events per energy step, and with small energy steps of 1 eV. This peak was also obtained by Gross *et al.* [10] who carried out similar calculations that however did include detailed balance only in average manner. The mass distribution of the cluster around the peak is shown in Figure 2 for the case of clusters with charge 2. The mass distribution at the peak, is found to have convergence problems, and to have uncertainties on the order of 1×10^{-6}.

Figure 3 shows the mass distribution for the fragmentation of uncharged Na clusters of mass 200 at three different excitation energies: before ($E = 90$ eV), in the middle of ($E = 110$ eV), and right after ($E = 130$ eV) the temperature dip. This figure excludes the abundantly produced

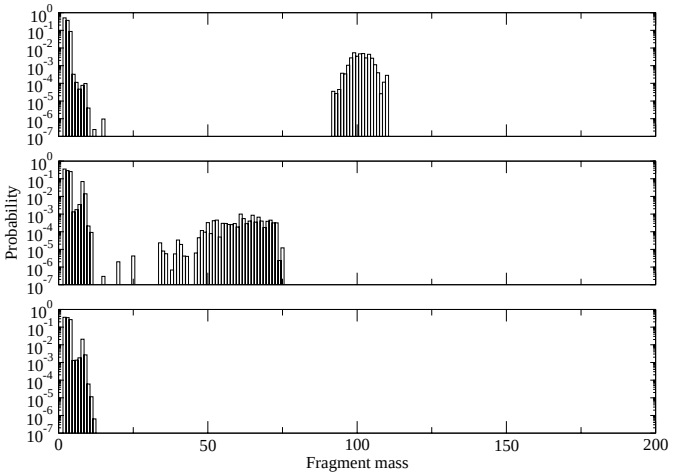

Fig. 4. Total mass distribution, excluding the neutral monomers, in the fragmentation of doubly charged Na clusters of mass 200 at energies 90, 110, 130 eV from top to bottom.

neutral monomers. We see from this figure that at all energies the dimers and trimers occur with highest probability. This figure shows how the fragmentation process takes place. For energies $\leq$90 eV large fragments containing more than 100 atoms coexist with very light fragments. At the dip energy of 110 eV we observe a broad distribution of fragments of sizes between 25 and 75 atoms, with probabilities 2–3 orders of magnitude smaller than those of the light fragments. As the excitation energy is increased to 130 eV only small fragments consisting of 10 atoms or less survive, with dimers, trimers, quadrimers and octamers singled out with relatively higher probabilities than the other multimers, in agreement with the shell model.

In Figure 4 we plot the total mass distribution for Na 200 and a cluster charge of 2 at the three different excitation energies of 90, 110, and 130 eV, from top to bottom. This figure again excludes the neutral monomers, but includes neutral and charged multimers. The total mass distribution for charge 2 is very similar to that shown in Figure 3 for the zero charge case. It is also instructive to compare Figure 4 with Figure 5, which gives the mass distribution of the charged fragments for the same system (charge 2). Only singly charged fragments are observed at the energies considered in this figure and the heavy fragments at the excitation energies of 90 and 110 eV have a higher probability than in the total mass distribution or in the neutral case. It is also noted that among the charged fragments trimers and 9-mers are present with higher probability than the others. No dimers, and very few octamers were observed as expected from shell effects, namely, neutral dimers and octamers are favored, as well as singly charged trimers and 9-mers are favored. The dominance of singly-charged trimers for such lightly charged fragments agrees with experimental evidence presented by Guet *et al.* [16] who contrast this with the sudden Coulomb explosion of highly charged clusters in which singly charged monomers dominate. These latter events cannot be generated in our statistical model because they

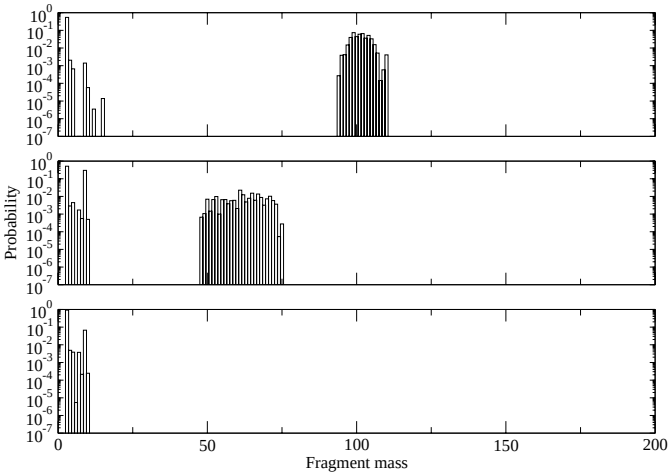

Fig. 5. The mass distribution for charged fragments resulting from the fragmentation of doubly charged Na clusters of mass 200 at energies of 90, 110, 130 eV from top to bottom. All fragments are singly charged.

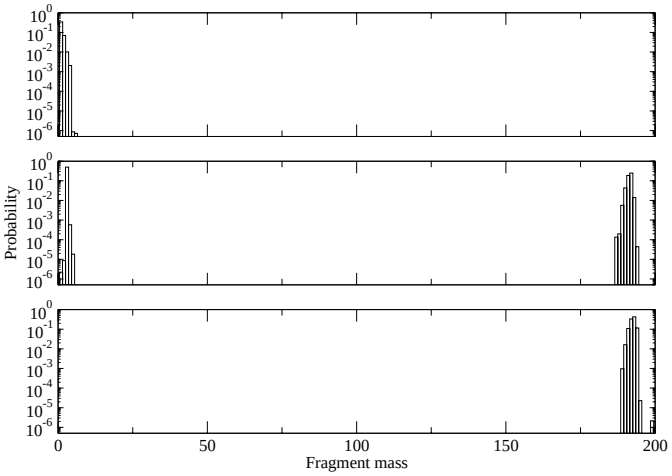

Fig. 6. Mass distribution of charged fragments from the fragmentation of Na clusters of mass 200 and a total charge = $2e$ at an excitation energy of 30 eV. The plots are for fragments with charge 0, 1, and 2 from top to bottom.

occur on a shorter time scale than that needed for the establishment of thermal equilibration.

Figure 6 shows the mass distribution of fragments resulting from the fragmentation of doubly charged Na clusters of mass 200 at an excitation energy of 30 eV. The top panel shows the distribution of neutral fragments while the middle and bottom panels show the distribution of singly and doubly charged fragments, respectively. Note that for the singly charged fragments, trimers occur with highest probability among other fragments, as expected from shell effects. It is also clear from this figure that, at this relatively low excitation energy, the system fragments by emitting a few light fragments (of mass less than 5) and leaving a heavy residual fragment of about 195 atoms. It is also noted that there are no doubly charged light fragments and no neutral heavy fragments. Because of the competition between Coulomb and surface effects, the charges prefer to reside on the heavy fragments.

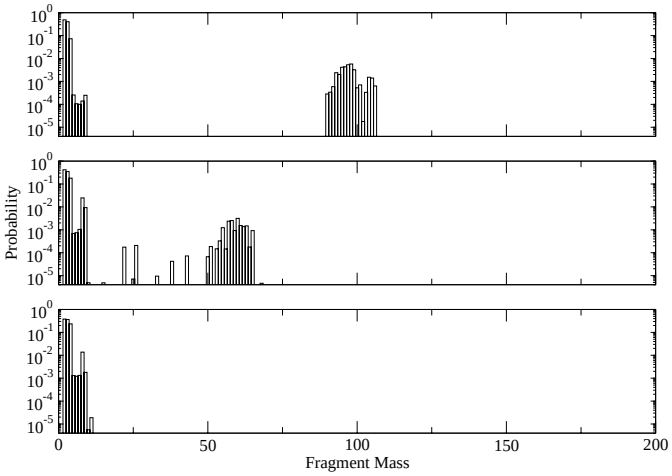

Fig. 7. Total mass distribution (excluding the neutral monomers) for Na cluster of mass 200 and total charge = $4e$. The plots are taken at energies of 90, 110, and 130 eV from top to bottom.

Figure 7 shows the total mass distribution, excluding the neutral monomers, for the fragmentation of clusters of mass 200 atoms and a cluster charge of 4 at 90, 110 at 130 eV. The excitation energies chosen are the same as those previously used for neutral and doubly charged clusters, and the results are very similar to those in Figures 3 and 4. The only notable difference is that the distribution of the heavy fragments for the charge 4 case at 110 eV has a narrower range than that for charge 0 or 2 cases at the same excitation energy. This may reflect a slight shift in the location of the temperature dip indicating that increasing the charge results in a corresponding modification in the properties of the phase transition.

In Figure 8 we present the mass distribution of the charged fragments, for a cluster of mass 200 and a total charge of 4 at energies 90, 110, and 130 eV from top to bottom. This figure also shows the fragmentation of the cluster as a function of energy around the negative heat capacity region. All fragments at these energies are singly charged. In fact we did not observe multiply charged fragments for excitation energies above 30 eV. It is clear from this figure that at these energies, the singly charged trimers are the most dominant among all others, followed by the singly charged 9-mers. This is in agreement with the electronic shell effect, which predicts that singly charged trimers and 9-mers are strongly bound (with full energy levels) and have relatively high dissociation energy. Note also in this figure that there is no charged dimers, again in agreement with the shell model. Both fission and evaporation compete in the fragmentation process, and the end result of these processes is that fragments of smaller size are produced as the energy is increased. At energies $\geq$130 eV only fragments with mass less than 10 are observed.

Figure 9 gives the mass distribution of the fragments sorted according to their charge at a total excitation energy of 30 eV. At this energy it is possible to observe

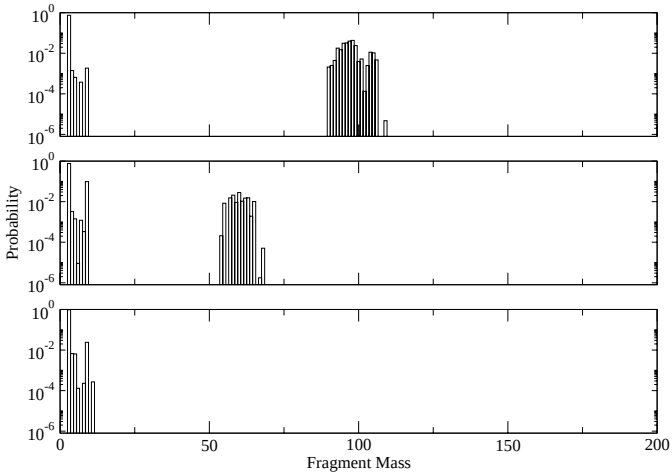

Fig. 8. Mass distribution of charged fragments for Na clusters of mass 200 and with total charge = $4e$. All the fragments are singly charged and the plots are taken at excitation energies of 90, 110, and 130 eV from top to bottom.

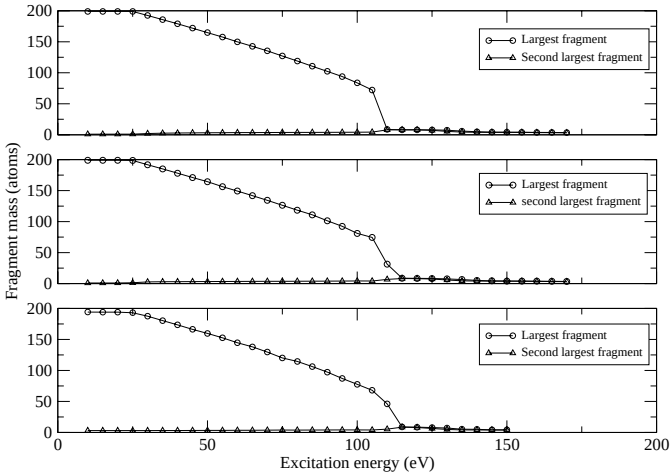

Fig. 10. The two largest fragments resulting from the fragmentation of Na clusters of mass 200 and with total charges of 0, $2e$, and $4e$, from top to bottom, respectively.

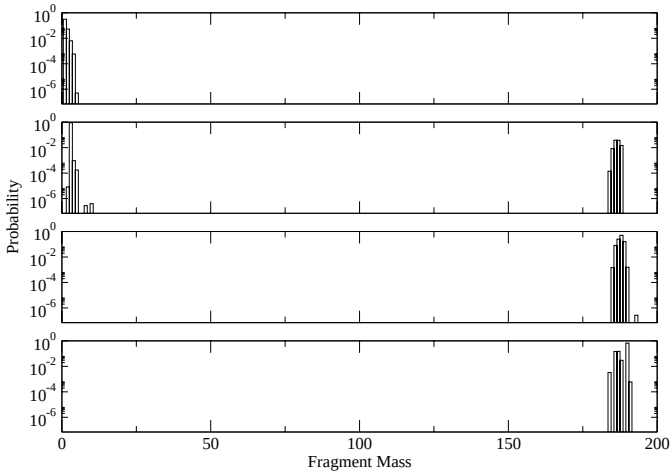

Fig. 9. Mass distribution of fragments, sorted by their charge, in the fragmentation of Na clusters of mass 200 atoms and with total charge = $4e$ at an excitation energy of 30 eV. The plots are for fragments with charge 0, 1, 2, and 3 from top to bottom, respectively.

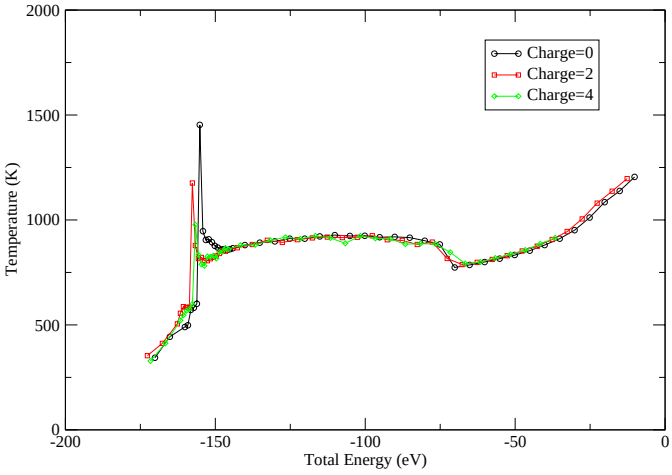

Fig. 11. Temperature curves for Na cluster of mass 200 atoms and charges of 0, $2e$, and $4e$ as a function of the total energy of the system.

multiply charged fragments. Light fragments containing less than 10 atoms are either uncharged or singly charged while the heavy fragments with masses in the range of 182–192 atoms are all charged up to a maximum charge of 3. Note that in this case there are no fragments which carry the whole charge 4, in contrast to the $Z = 2$ case. This is due to the fact that at the beginning of the excitation process, a singly charged trimer is emitted from the cluster leaving a big fragment with a maximum charge of 3. It is also clear from this figure that the singly charged trimers are the most probable species among all others. Above 30 eV only singly charged fragments can exist, and the fragment size is decreased as the excitation energy is increased.

The development of the fragmentation process as the excitation energy is increased can be seen from Figure 10 which gives the two largest fragments as a function of excitation energy for clusters with total charges of 0, 2, and 4. In the three cases the cluster remains as a big piece while a few trimers and quadrimers are evaporated up to an excitation energy of 110 eV. Of course monomers and dimers exist, and some fragments with masses up to 8 can be found but with small probability, as can be seen by comparing with Figure 9. The three panels for the different charges look very similar. Above an excitation energy of 110 eV, only fragments with mass less than 10 can exist, as can also be seen by comparing with Figures 3, 4 and 7.

In Figure 11 we show the three caloric curves for Na 200 clusters for charges of 0, 2, and 4, as a function of the total energy $E_{\rm tot} = E + E_{\rm bind}$. We note that there is not

much difference between the three curves: the plateau is the same, and the location of the phase transition is the same for these cluster charges. The slope of the dip becomes shallower as the charge of the cluster is increased.

3 Conclusion

In conclusion, we have calculated the mass distribution for the fragmentation of sodium clusters of charges ranging from 0 to 9. The calculations were carried out microcanonically and with an exact treatment of detailed balance. The caloric curves were found to be independent of the charge on the cluster for charges up to 4. Although it is not shown in the calculation presented here, the caloric curve is somewhat sensitive to the radius parameter. Increasing the volume of the system lowers the phase transition temperature, and shifts the dip at the end of the plateau to lower excitation energy since the pressure is decreased, and smaller volume favors the liquid or solid state. An increase in the system radius parameter from 4 Å to 8 Å lowers the temperature at the plateau by about 200 K. The calculation of the caloric curve was unstable for clusters of mass 200 atoms and charges ≥ 5, and this may be related to the experimentally confirmed instability [14–16] of such highly charged clusters which immediately decay by emitting light singly charged fragments and cannot therefore achieve thermal equilibration which is the fundamental assumption of our approach.

This work is supported by the Deutsche Forschungsgemeinschaft grant GR 398/6-2.

References

1. D.H.E. Gross, `http://arXiv.org/abs/cond-mat/0101281`, p. 7, 2000
2. D.H.E. Gross, `http://xxx.lanl.gov/abs/cond-mat/0105313`, 2001
3. A. Chbihi, O. Schapiro, D.H.E. Gross, S. Salou, Eur. Phys. J. A **5**, 251 (1999)
4. M. D'Agostino *et al.*, Phys. Lett. B **473**, 219 (2000), Eur. Phys. J. A **5**, 251 (1999)
5. D.H.E. Gross, *Microcanonical Thermodynamics, Phase Transitions in "Small" Systems* (World Scientific, 2001)
6. D.H.E. Gross, X.Z. Zhang, S.Y. Xu, Phys. Rev. Lett. **56**, 1544 (1986)
7. D.H.E. Gross, Rep. Progr. Phys. **53**, 605 (1990)
8. X.Z. Zhang, D.H.E. Gross, S.Y. Xu, Y.M. Zheng, Nucl. Phys. A **461**, 668 (1987)
9. D.H.E. Gross, P.A. Hervieux, Z. Phys. D **37**, 27 (1995)
10. D.H.E. Gross, M.E. Madjet, O. Schapiro, Z. Phys. D **39**, 75 (1997)
11. M.E. Madjet, P.A. Hervieux, D.H.E. Gross, O. Schapiro, Z. Phys. D **39**, 309 (1997)
12. O. Schapiro, P.J. Kuntz, K. Möhring, P.A. Hervieux, D.H.E. Gross, M.E. Madjet, Z. Phys. D **41**, 219 (1997)
13. M. Schmidt, T. Hippler, J. Donges, W. Kronmüller, B. Issendorff, H. Haberland, P. Labastie, Phys. Rev. Lett. **87**, 203402-1 (2001)
14. F. Chandezon, C. Guet, B.A. Huber, D. Jalabert, M. Maurel, E. Munnad, C. Ristori, J.C. Rocco, Phys. Rev. Lett. **74**, 3784 (1995)
15. F. Chandezon, T. Bergen, A. Brenac, C. Guet, B.A. Huber, H. Lebius, A. Pesnelle, Phys. Rev. A **63**, 051201 (2001)
16. C. Guet, X. Biquard, P. Blaise, S.A. Blundell, M. Gross, B.A. Huber, D. Jalabert, M. Maurel, L. Plagne, J.C. Rocco, Z. Phys. D **40**, 317 (1997)