Abstract

The volume $W$ of the accessible N-body phase space and its dependence on the total energy is directly calculated. The famous Boltzmann relation $S = k \ast \ln(W)$ defines microcanonical thermodynamics (MT). We study how phase transitions appear in MT. Here we first develop the thermodynamics of microcanonical phase transitions of first and second order in systems which are thermodynamically stable in the sense of van Hove. We show how both kinds of phase transitions can unambiguously be identified in relatively small isolated systems of $\sim 100$ atoms by the shape of the microcanonical caloric equation of state $< T(E/N) >$ and not so well by the coexistence of two spatially clearly separated phases. I.e. within microcanonical thermodynamics one does not need to go to the thermodynamic limit in order to identify phase transitions. In contrast to ordinary (canonical) thermodynamics of the bulk microcanonical thermodynamics (MT) gives an insight into the coexistence region. Here the form of the specific heat $c(E/N)$ connects transitions of first and second order in a natural way. The essential three parameters which identify the transition to be of first order, the transition temperature $T_{tr}$, the latent heat $q_{lat}$, and the interphase surface entropy $\Delta s_{surf}$ can very well be
determined in relatively small systems like clusters by $MT$. It turns out to be essential whether the cluster is studied canonically at constant temperature or microcanonically at constant energy. Especially the study of phase separations like solid and liquid or, as studied here, liquid and gas is very natural in the microcanonical ensemble, whereas phase separations become exponentially suppressed within the canonical description. The phase transition towards fragmentation is introduced. The general features of $MT$ as applied to the fragmentation of atomic clusters are discussed. The similarities and differences to the boiling of macrosystems are pointed out.

I. INTRODUCTION

This is the first paper in a series of papers treating the topological structure of the N-body phase space of atomic clusters by microcanonical thermodynamics ($MT$). It was one of the primary issues of cluster physics to understand macrosystems starting from the properties and interactions of its constituents, the single atoms or molecules. Especially one likes to understand how the most spectacular changes in the thermodynamical behavior of macro systems, phase transitions, develop with increasing number of atoms from atomic dimensions towards the bulk. However, small clusters have also their specific features. They can be charged, their shape (surface) is important, they can fragment, they can rotate, etc.

Studying clusters as thermodynamical systems we consider the phase space which can be reached by all constituents of the cluster. The topology of this total accessible N-body phase space reflects (or implies?) the behavior of many interacting systems because the dynamics is often chaotic. Then the evolution of many replica of the same system under identical macroscopic initial conditions follows the structure of the underlying N-body phase space. It is ergodic. In nuclear fragmentation the ergodicity is presumably due to the strong and short ranged friction between moving nuclei in close proximity. Friction between atomic clusters is yet unknown but probably it exists there also.
First we have to discuss the concept of thermodynamics of small systems in general and especially of phase transitions. It is important to realize that isolated clusters must be treated microcanonically. Usually there is no external heat- or particle bath which defines temperature, pressure, or chemical potential. Microcanonical thermodynamics is the proper theory for isolated small systems.

Phase transitions are well defined as singularities in various canonical or grandcanonical expectation values as function of e.g. the temperature in the thermodynamic limit \( \lim_{N \to \infty} \frac{N}{V} = \varrho \). E.g. the melting transition of bulk sodium at normal pressure shows up as a peak in the specific heat in the neighborhood of \( T_m = 371 \text{K} \) on top of which there is a \( q_{\text{lat}} \delta(T - T_m) \) singularity c.f. fig.\[1\]. With the normal finite resolution the delta-function manifests itself by a jump in the bulk-specific heat by \( q_{\text{lat}} \), the specific latent heat, see fig.\[1\]. There are different ways to identify the phase transition of melting: First one realises that the systems changes its structure, it melts. Another way is to measure e.g. the specific heat \( c(T) \) or the caloric equation of state \( \langle T(E/N) \rangle \) and realizing that at the melting the temperature does not rise if more energy is put into the system up to the point where the whole system becomes liquid. I.e. that the caloric equation of state \( \langle T(E/N) \rangle \) has an anomaly (here a plateau).

The basic questions are now: Can one define phase transitions in finite, eventually small systems like atomic clusters. Is it possible to define phase transitions of small isolated systems microcanonically as function of the energy not as function of the temperature? From which size on do phase transitions exist in such small systems? Is a cluster of some 50 to 100 atoms big enough? We will show that it is in fact much easier to identify phase transitions in

\[1\]It is possible to prepare atomic clusters initially in a canonical ensemble by embedding them in an inert carrier gas. However, most probe-reactions on these clusters are too fast to keep the cluster during this time at constant temperature. Moreover frequent collisions with the carrier gas will distort the cluster so that one would not measure the properties of the cluster alone.
the microcanonical ensemble and that this is possible in astonishingly small systems. Small clusters can undergo a phase transition and one can unambiguously distinguish continuous (second order) from discontinuous (first order) transitions by the form of the microcanonical caloric equation of state \( < T(E/N) > \). We will see that the main signal of a transition in finite systems is not the singularity of some canonical expectation value in the thermodynamic limit but a specific anomaly in the smooth microcanonical equation of state \( < T(E/N) > \) which can be well identified already in pretty small systems. Of course, the transition may change its character when the number of particles increases. However, in the case of the 10-states Potts model as well in the case of the boiling of sodium or potassium the bulk values of the three quantities above are clearly approached by the corresponding transitions in small systems/clusters \( 2 \) of some 100 atoms.

A microcanonical ensemble has some peculiarities: It does not have a positive definite heat capacity. In fact at a phase transition of first order the specific heat \( c(\varepsilon) \) becomes negative in general. Therefore the classical signal of a peak in the specific heat is not useful to characterize a phase transition in small systems.

The second peculiarity of small bound systems like atomic clusters is a new structural phase transition which does not exist in infinite homogeneous systems: At higher excitation they often do not simply boil into a gas of monomers. On the contrary, they may fragment into few relatively large fragments. In this case the size of the droplets at the transition point can be of the order of the size of the system itself e.g. in the case of fission. The fluctuation of the fragment sizes is substantial. Then one cannot ignore the droplets compared to the monatomic vapor anymore. The phase transition is not determined alone by the equilibrium of the homogeneous liquid with the homogeneous monatomic gas controlled by the equality of the chemical potentials of liquid and gas as we are used to in conventional (grandcanonical) thermodynamics. Often the number of droplets is similar to the number of monomers or even larger. Such a process was found recently in the decay of hot nuclei and is called multifragmentation.

It is one of the aims of this series of papers to study the conditions for fragmentation
of hot and/or highly charged atomic clusters. However, also rapidly rotating clusters could fragment or even fission symmetrically. Therefore it is important to develop microcanonical thermodynamics including angular momentum as a fundamentally conserved quantity or order parameter.

As today one is not familiar to microcanonical thermodynamics we will discuss in the following sections some of its basic features and show how phase coexistence and phase separations show up in $MT$. Canonical and grandcanonical ensembles have the great advantage that one can treat many simple examples like systems which can be transformed into ideal noninteracting gases analytical. The prize one has to pay is that both ensembles average in the limit of large particle numbers over spatial inhomogeneities like e.g. phase separation and interphase surfaces. Only under simple geometrical conditions this defect can be cured by the Maxwell construction. In contrast to this $MT$ allows for such inhomogeneous situations in a natural way.

II. MICROCANONICAL THERMODYNAMICS

Statistical mechanics as foundation of thermodynamics goes back to the works of Boltzmann and of Gibbs. Boltzmann’s gravestone has the famous epigraph:

$$S = k \ln W$$

which is the most concise formulation of the essence of thermodynamics. $W$ is the volume of the N-body phase space of the system (here in units of $((2\pi\hbar)^3)^N$) or the partition sum of all possible quantum states of the N-body system:

$$\Omega_N(E) = \sum_{\nu} \delta_{E,E_{\nu}},$$

and $S$ is the N-body entropy of the system.

Microcanonical thermodynamics explores the topology of the N-body phase space and determines how $\Omega_N$ depends on the fundamental globally conserved quantities namely total energy $E = N \varepsilon$, angular momentum $L$, mass (number of atoms) $N$, charge $Z$, linear
momentum \( p \), and last not least the available spatial volume \( V \) of the system. This definition is the basic starting point of any thermodynamics since Boltzmann, see e.g. \[3\]. In his “Vorlesungen über Gastheorie, II. Teil” he calls the microcanonical ensemble the “Ergode” \[4\]. It is an entirely mechanistic definition saying that if we do not know anything more about a complicated interacting N-body system but the values of its globally conserved macroscopic parameters the probability to find it in a special phase space point (N-body quantum state) is uniform in the accessible phase space.

The entropy is defined as the logarithm of \( \Omega \) see Boltzmann’s epigraph

\[
S(E, V, N) = Ns(\varepsilon = E/N) = \ln(\Omega(E, V, N)),
\]

we take Boltzmann’s constant \( k = 1 \). The thermodynamic temperature \( T_{thd} \) is defined by

\[
\beta = \frac{\partial S(E, V, N)}{\partial E} = \frac{\partial s(\varepsilon)}{\partial \varepsilon},
\]

\[
T_{thd} = \frac{1}{\beta}.
\]

By Laplace transform of \( \Omega(E, V, N) \) one steps from the “extensive” variables like \( E, V, N \) to the intensive ones like \( T, P, \mu \). E.g. the Gibbs grand partition function and the Gibbs grand potential are then

\[
Z(\beta, P, \mu) = \int_0^\infty \int_0^\infty \Omega(E, V, N)e^{-\beta(E+PV-\mu N)} \, dE \, dV \, dN,
\]

\[
G(\beta, P, \mu) = -T \ln[Z(\beta, P, \mu)].
\]

I.e. Any sufficiently isolated part of the system has the same grand partition function \( G(T, P, \mu) \), i.e. the system becomes translationally invariant or homogeneous in the bulk limit. In the same way one gets the canonical partition function and the Gibbs free energy as

\[
Z(\beta, P, N) = \int_0^\infty \int_0^\infty \Omega(E, V, N)e^{-\beta N(\varepsilon+PV)} \, dE \, dV,
\]

\[
GF(T, P, N) = -T \ln[Z(\beta, P, N)].
\]
Phase transitions in atomic clusters were quite early investigated microcanonically by molecular dynamical simulation of e.g. the melting transition in Ar_{13} clusters see the pioneering work by Jellinek, Beck and Berry [5]. In these early calculations the transition energy could be fixed by the anomaly of the “caloric” curve $E_{\text{kin}}/N$ vs. $E_{\text{tot}}/N$. Neither the entropy, nor the proper thermodynamic temperature, nor the order of the transition was determined. In contrast to these early work we will here present a proper calculation of the volume $W$ resp. $\Omega_N$ of the accessible N-body phase space and its dependence on the total energy. We thus follow literally the prescription of Boltzmann’s epigraph. This way, we will be able to determine all decisive parameters of the phase transition in question: $T_{tr}$, $q_{\text{lat}}$, $\sigma_{\text{surf}}$ and $\Delta s_{\text{boil}}$, the gain of entropy per evaporated atom, for the clusters.

III. DIFFERENCES BETWEEN MICROCANONICAL AND CANONICAL ENSEMBLE

According to van Hove a system of $N$ particles interacting via short range two-body attractive forces with hard cores is thermodynamically stable, the thermodynamic limit of $N,V \to \infty |N/V=\tilde{\rho}$ exists for such systems, intensive quantities like the specific energy have finite limiting values [6] see also [3]. Then, the thermodynamics derived from the microcanonical partition sum $\Omega(E,N,V)$ and the one derived from the canonical $Z(\beta,P,N)$ or the grand canonical partition function $Z(\beta,P,\mu)$ (usually) coincide. Outside of phase transitions of first order, the relative fluctuations $\Delta E/E$, or $\Delta \rho/\rho$ vanish $\propto 1/\sqrt{N}$.

This is naturally quite different for finite systems. However, even for bulk systems at phase transitions ($T = T_{tr}$) of first order do the microcanonical and the (grand)canonical ensemble differ essentially. In the (grand)canonical ensemble the energy fluctuations $\Delta \varepsilon$ per particle remain finite even in the thermodynamic limit $((\Delta \varepsilon)^2|_{T_{tr}} \propto q_{\text{lat}}^2$, the specific latent heat). Consequently, the difference between the microcanonical and the (grand)canonical ensemble persists at transitions of first order and we must expect both ensembles to describe different physical situations. In section [V] and especially in the subsection [VA] we will
illuminates this important point in more detail.

Systems interacting via long range forces like unscreened Coulomb repulsion between charged parts of equal sign, or the centrifugal force when they are rotating, or under the long range gravity, don’t have a thermodynamic limit and must be described by the microcanonical ensemble. Such systems fragment macroscopically into, in general, several regions of high density — condensed matter — and also into, in general, several regions of low density — vapor or may be empty space. Even though in the first two examples, Coulomb repulsion or repulsive centrifugal force, the systems are unstable they may disintegrate initially slowly enough to establish a transient statistical equilibrium. This is evidently the case in the fragmentation of hot nuclei and we expect this to be quite similar in the case of fragmentation of atomic clusters. Differently from conventional thermodynamics where systems must be in a homogeneous phase at fixed temperature everywhere, here the system is most likely inhomogeneous. The inhomogeneities and their fluctuations are more important in characterizing the state of the system than any mean values. In contrast to thermodynamics of the homogeneous bulk, in small systems or large systems with long range forces the entropy connected to different partitions of the system is an important part of the total entropy. Familiar formulas like the one-particle entropy

\[ s_{sp} = -\sum_a n_a \ln(n_a) \]  

are useless for calculating the total entropy.

IV. FIRST AND SECOND ORDER PHASE TRANSITIONS IN SMALL SYSTEMS

Macroscopic systems have a discontinuity in the specific heat \( c_{\text{bulk}}(T) \) at first order phase transitions. \( c_{\text{bulk}}(T) \) may have a finite peak at \( T \approx T_{tr} \). On top of this there is a spike \( q_{lat}\delta(T - T_{tr}) \). With finite resolution it shows up as a jump in \( c_{\text{bulk}}(T) \) by the latent heat \( q_{lat} \). A typical example is the specific heat of bulk sodium at the melting transition, fig. [4]. In contrast, a transition of second order is continuous at the transition temperature where \( c_{\text{bulk}}(T) \) has (in the example of the Ising model) a logarithmic singularity in \( T - T_{tr} \).
Microcanonical thermodynamics gives new and deep insight into this. It will further allow to extend the concept of phase transitions to systems not treated before by thermodynamics like systems with long range forces or strongly rotating systems. We begin with the discussion of microcanonical phase transitions in standard model systems in which phase transitions of first and second order are well known. As an example we take the 2-dimensional 10-states Potts model for which the asymptotic thermodynamics is even known analytically [7]. The q-states Potts model is a generalization of the Ising model by allowing q instead of only 2 spin values at each lattice point. In two dimensions it has a second order phase transition for \( q \leq 4 \) and a first order transition for \( q > 4 \) from a spin-ordered (in the following often called colloquially “liquid”) to spin-disordered phase (called “gas”).

In ref. [8] we determined the three basic parameters of phase transitions of first order within microcanonical thermodynamics, the transition temperature \( T_{tr} \), the specific latent heat \( q_{lat} \), and the specific interphase surface entropy \( \Delta s_{surf} \) for the 10-states Potts model, i.e. a systems with a nearest neighbor coupling. It was demonstrated that for surprisingly small systems the values of these three parameters are closer to their asymptotic values than in the canonical ensemble. This is so because most of the finite-size scaling is due to the large, but trivial, exponent in the Laplace transform, eq.(7), from the microcanonical to the canonical partition sum [9,10].

From our studies of the Potts model [8] we made the plausible conjecture, which will serve us as working hypothesis: The two types of phase transitions in thermodynamically stable finite systems are distinguished by the form of the microcanonical caloric equation of state \( T_{thd}(\varepsilon) \): A transition of first order has a backbending caloric equation of state \( T^{-1} = \beta(\varepsilon) \), see figure 2b. In contrast a phase transition of second order has only a horizontal saddle point in \( < T(E/N) > \). For a system with nearest neighbor interactions the area between \( \beta(\varepsilon) \) and the “Maxwell” line \( \beta_{tr} = 1/T_{tr} \) is twice the interphase surface entropy \( \Delta s_{surf} \) and the coefficient of surface tension is \( \sigma_{surf} = T_{tr} N^{1/3} \Delta s_{surf} \). Following M.Fisher a nonvanishing surface tension qualifies the transition to be of first order [11], in other words our experience with the Potts model suggests that the backbending (or S-bend) [12 14] is a
necessary signature for a phase transition of first order in a finite thermodynamically stable system. It is interesting to notice that the suppression of the configurations with phase coexistence compared to those with pure phases in the canonical ensemble is used since long to calculate the surface tension in general thermodynamical stable systems cf.e.g. [15]:

\[ P(\text{pure}) = \frac{e^{-GF_{\text{pure}}/T}}{Z(T)} \]  
\[ P(\text{mix}) = \frac{e^{-GF_{\text{mix}}/T}}{Z(T)} \]  
\[ GF_{\text{mix}} = GF_{\text{pure}} + GF_{\text{surf}} \]  
\[ GF_{\text{surf}} = \frac{N^2}{3}\sigma_{\text{surf}} \]  
\[ \frac{P_{tr}(\text{mix})}{\sqrt{P_{tr}(\text{phase1})P_{tr}(\text{phase2})}} = e^{-N*\Delta s_{\text{surf}}} = e^{-N^2/3\sigma_{\text{surf}}/T_{tr}}, \]

where \( P(\text{pure}) \) is the probability to find the system at \( T_{tr} \) in one of the pure phases, whereas \( P(\text{mix}) \) is the probability to find it in configurations with two separated phases. This generalizes to other systems our conjecture that the backbending of \( T(\varepsilon) \) is a necessary condition for the surface tension and for a transition of first order. Of course, there may also be other reasons for a backbending of \( T(\varepsilon) \).

The left darkened area is the defect of entropy \( \Delta s_{\text{surf}} = \int_{\varepsilon_1}^{\varepsilon_2} \beta d\varepsilon \) that the system ‘pays’ for introducing interphase surfaces, which it finally gets back when the whole system is converted to the new phase at \( \varepsilon = \varepsilon_3 \), right darkened area, and the interphase surface disappears [5]. In the bulk the transition is discontinuous as function of \( T \) or \( \beta \) and “jumps” from the liquid \((\varepsilon \leq \varepsilon_1)\) to the gas branch \((\varepsilon \geq \varepsilon_3)\) of the caloric curve, fig.2. As a function of the specific energy \( \varepsilon \) the transition is however continuous. With rising \( \varepsilon \) the system passes smoothly from the liquid phase over a mixed phase with large coexisting fluctuations of the two phases (“gas bubbles” and “liquid droplets”) towards the pure gas phase when the specific energy is increased by the specific latent heat \( q_{\text{lat}} \). Figure 2a shows the corresponding specific entropy \( s(\varepsilon) = \int_0^\varepsilon \beta(\varepsilon')d\varepsilon' \). Notice that the entropy is a monotonously rising function with rising energy in the region of energies shown. In figure 2a we subtracted a linear function \( a + b\varepsilon \) in order to visualize the transition. Otherwise, on the scale of fig.2a one would not be able to
distinguish \( s(\varepsilon) \) from a straight line. The transition is characterized by the convex intruder in \( s(\varepsilon) \) of depth \( \Delta s_{\text{surf}} \). The effect of the interphase surface tension is a somewhat slower increase of the entropy with rising specific energy as the system prefers to create interfaces between regions of different phases, spin-aligned and disordered ones. Figure 2c shows the specific heat capacity

\[
    c(\varepsilon) = \frac{\partial \varepsilon}{\partial < T >} = -\frac{\beta^2}{\partial \beta / \partial \varepsilon}
\]

(15)
as a function of the specific energy \( \varepsilon \). (Here numerical fluctuations in \( \beta(\varepsilon) \) in figure 2b have been smoothed). One can see within the coexistence region of \( \varepsilon_1 \leq \varepsilon \leq \varepsilon_3 \) (shaded area in fig.2), the microcanonical specific heat has two poles and becomes even negative in between.

The convex intruder in the specific entropy \( s(\varepsilon) \), fig.2a, is forbidden by van Hove’s theorem in the canonical ensemble for an infinite number of particles see also e.g. 3. At energies in the region of the intruder, an infinite system is unstable against spontaneous devision into two parts. Conventional thermodynamics of the bulk is blind in this energy interval. The Laplace transform eq.(7) has no stationary point on the branch with the positive slope of \( \beta(\varepsilon) \). It can only see the branches of \( c(\varepsilon) \) in the regions \( \varepsilon \leq \varepsilon_1 \) and \( \varepsilon \geq \varepsilon_3 \). Thus the canonical specific heat \( c_{\text{bulk}}(T) \) will be positive and approach finite values at the transition of first order. At \( T = T_{tr} \) \( c_{\text{bulk}}(T) \) has an additional peak = \( q_{\text{lat}} \delta(T - T_{tr}) \).

In the canonical ensemble the phase transition is a sharp transition (the sharp \( \delta(T - T_{tr}) \) in the specific heat) only in the thermodynamic limit. However, as a function of the specific energy the microcanonical ensemble transforms smoothly from one phase over the coexistence region into the other phase, see above, even in the thermodynamic limit. The nonvanishing width in energy of the phase coexistence persists even in the thermodynamic limit. Therefore it seems to me the singularity of \( c(T) \) reflects more a — sometimes even unpleasant — mathematical feature of the canonical ensemble to suppress inhomogeneities like phase coexistence than it does illuminate the underlying physics of the transition. This is completely contained in the (smooth) microcanonical equation of state. In fact it is exactly here where important information becomes hidden in the canonical ensemble.
Even though our conclusion from the Potts model is very convincing esp. in view of our remarks to eq.(14), it is not a general proof that the S-bend of the microcanonical caloric curve is necessary for a phase transition of first order. S. Berry and others give some sufficient conditions for the backbending of the caloric curve in several model systems [13,14,16–18]. These give a lot of insight into the mechanism that produces the S-bend of $< T(E/N) >$. Berry uses Nosé-molecular dynamics to work with intensive variables like the temperature whereas we emphasize the advantages of the microcanonical ensemble and the use of the conserved extensive quantities like the total energy per particle $\varepsilon$ which are better suited especially for the study of phase separation.

If the specific latent heat $q_{lat} \rightarrow 0$ and the specific interphase surface entropy $\Delta s_{surf} \rightarrow 0$ the caloric equation of state gets only a saddle point at the transition. Then $< E(T) > /N$ as well as $< T(E/N = \varepsilon) >$ become single valued, the transition is continuous in the canonical as well as in the microcanonical ensemble. We have a phase transition of second order. The two poles of $c(\varepsilon)$ merge and $c(\varepsilon)$ or $c_{bulk}(T)$ has a singularity at the transition point $\varepsilon_{tr}, T_{tr}$. Both slopes of $c(\varepsilon)$ are fully accessible in the canonical treatment of the heat capacity. Consequently, from the microcanonical caloric equation of state $T(\varepsilon)$ it is possible to identify and distinguish both kinds of transitions. In microcanonical thermodynamics the close relation between the two is very natural, transparent and simple.

It is further instructive that in finite realizations of the two-dimensional Potts model with $q = 10$ spin orientations at each lattice point it was not possible to see a clean separation into a compact region of ordered spins and a compact region of disordered spins at energies inside the coexistence region even for a lattice of $100 \times 100$ points. There were always several “gas bubbles” and “droplets” fluctuating over the lattice and prohibiting large interphase surfaces. A clean interphase surface, another signal of a first order phase transition in bulk systems, cannot be seen in such small systems. Nevertheless the caloric equation of state $T(\varepsilon)$ is already close to its asymptotic form. (This is also the reason why it is possible to study many-body phenomena like phase transitions in relatively small systems with some 100 atoms like we do here.) We can conclude from this observation that the other classical
signal of a transition of first order, a clear separation of the two phases, is not a useful signal of a transition of first order in small systems.

A. Phase separation of macroscopic systems in the canonical ensemble

According to eq.14 inhomogeneous configurations like configurations with two separated phases become exponentially suppressed by a factor $\exp\left(-\Delta \sigma_{\text{surf}} N^{2/3}/T\right)$ in the canonical ensemble. Nevertheless such configurations are frequently treated by conventional thermodynamics with the help of the Maxwell-construction. This is a method to construct the microcanonical, not the canonical ensemble at energies where both phases coexist: Homogeneous configurations with $N\nu_l$ particles in the lower phase (“liquid”) are linked to homogeneous configurations with $N\nu_g$ particles in the energetically higher (“gas”) phase by the condition of equal chemical potentials $\mu_l = \mu_g$ with $\mu = T\partial G\mu / \partial N$ along a well-defined interphase surface. After taking the thermodynamic limit $N \to \infty$ these homogeneous configurations can be obtained from the homogeneous canonical distributions at the lower (higher) temperature in the limit $T \to T^-_{\text{tr}}$ ($T \to T^+_{\text{tr}}$). The mean total energy can be split into the energy of the homogeneous liquid with specific energy $\nu_l \varepsilon_l$ and the homogeneous gas part with specific energy $\nu_g \varepsilon_g$ and vanishing fluctuations. Consequently the fluctuation of the total energy vanishes as well and the combinedensemble is the microcanonical ensemble with the specific total energy $\varepsilon = \nu_l \varepsilon_l + \nu_g \varepsilon_g$.

This is in contrast to a situation where the total system is treated as a single canonical ensemble without a forced phase separation. There the fluctuation of the total energy per particle remains proportional to the specific latent heat. In the latter case configurations with phase separation disappear.

Clearly this method works only if an external field like the gravitational field orders the liquid below a given surface and the gas above. In a free cluster such a simple interphase surface can usually not be fixed and the above method to circumvent the exponential suppression of the inhomogeneous configuration with separated phases (liquid and gas or solid...
and liquid) by the canonical ensemble is not possible.

V. PHASE TRANSITION TOWARDS CLUSTER FRAGMENTATION

There is a lot of interest in cluster fragmentation. Most of the work done considered the dynamical evolution of fragmentation. Starting with the atom-atom interaction one studies the explicit time-evolution of some small clusters with the help of Molecular Dynamics (MD) [19–25]. We know from other systems that the dynamical evolution of a complicated many-body system is very much guided by the accessible phase-space. Then a statistical treatment explains the main outcome of such reactions. Moreover, a thermodynamic approach of cluster fragmentation offers the immediate connection to the thermodynamics of the bulk and especially to the most interesting thermodynamic phenomena: phase transitions. With finite clusters one can study the development of structural transitions like melting with increasing number of atoms see for example the illuminating review article by S.Berry in [16] or the work of [12,13,26,17,18].

Most of these studies have been performed by embedding the cluster in a constant temperature heat bath. This is done in MD by using the Nosé dynamics. From what was discussed above in the example of the Potts model the use of the canonical ensemble to describe phase transitions in finite clusters is not only unnatural but it seems especially inconvenient for discussing phase coexistence. We saw that inhomogeneous configuration are suppressed $\propto \exp(-\sigma_{surf}N^{2/3}/T)$ relative to configurations with homogeneous phases in constant temperature realizations. Presumably this exponential suppression is the main reason for the vanishing of $\Delta T_c = T_m - T_f$, the difference of the melting and freezing temperatures for large systems ($N \to \infty$) discussed by Berry [16]. Here microcanonical thermodynamics offers a promising and quite natural alternative to investigate this problem.

Fragmentation is a new phase transition of finite systems. As other phase transitions of first order it is intimately linked to the ability of finite systems to become inhomogeneous [39]. For infinitely many atoms it may become the liquid-gas transition. This will be the topic
of the fourth paper in this series \cite{2}. Here we are not so much interested in the well known physics of macroscopic phase-transitions but more in phase transitions and thermodynamics of finite systems.

The thermodynamics of isolated metal clusters has many similarities with that of hot nuclei see ref. \cite{27}. A new aspect of atomic cluster fragmentation, however, is the fact that charge and mass degrees of freedom are nearly decoupled. This is in sharp contrast to nuclear fragmentation where neutrons and protons are strongly coupled by the symmetry energy. It leads to a predominantly symmetric nuclear fission whereas for example doubly charged alkali clusters fission highly asymmetrically until strong shell effects of the daughters favor a more symmetrical split. The conditions for symmetric versus asymmetric fission will be discussed in the next paper of this series \cite{28}. A further peculiarity of clusters plays an important role in fragmentation: Atomic clusters have a much higher internal density of states than nuclei. The internal entropy $s_{\text{int}}$ can easily become larger than 10 per atom whereas in nuclei it is rarely $s_{\text{int}} > 2$ per nucleon. This difference is of course due to the different statistics, fermionic statistics in a nucleus and bosonic statistics for the phonons in the cluster. Moreover, the internal structure of larger clusters has significant transitions like melting at which the internal spectrum shows strong enharmonicities. The bulk specific heat $c_p(T)$ is often considerably larger near the melting transition than the Debye limit for harmonic vibrations see fig.1. As shown in refs. \cite{29,30} this additional internal entropy leads to an enhancement of fragmentation and also may enlarge the evaporation times by up to three orders of magnitude.

As the charge and mass degrees of freedom are nearly decoupled in alkali clusters, it is possible to drive the system through the phase transition not only by increasing the excitation energy $\varepsilon$ but also by increasing its charge $Z$. Multiply charged but cold alkali clusters may Coulomb-explode, e.g. \cite{31,32}. This is the topic of the third paper in this series \cite{33}. A third way to explore the fragmentation transition would be to subject the cluster to large rotations and disrupt it by the centrifugal force. All three conserved quantities, the energy $E$, the charge $Z$, and the angular momentum $L$ are possible nonfluctuating order
parameters of this transition. At present it is experimentally not possible to transfer a large
known angular momentum to a cluster. In the analogous case of nuclear fragmentation
the disruptive effect of large rotations has just started to be discussed see e.g. [34]. In a
couple of papers Jellinek and collaborators explored very early the effect of rotation on the
isomerization and the behavior of clusters at low temperatures [35–37,22]. Their interest
aims into a similar direction as ours. They are concerned with the important problem how
the low energetic properties of a cluster becomes modified by the rotation. We here want to
study the effect of the two-dimensional stress by the centrifugal force on the fragmentation.
It is further important to realize that the longrange centrifugal force induces inhomogeneities
in the system which again demand a statistical treatment by microcanonical thermodynamics
which leads to interesting peculiarities as a kinetic temperature that can considerably exceed
the thermodynamic temperature [34].

We sample the accessible N-body phase space by Microcanonical Metropolis Monte Carlo,
MMMC. Its basic idea is as follows: Since every quantum state of the N-body system has
an equal probability in the microcanonical ensemble one has to sample each quantum state.
There is no hierarchy of a few important ones representing the main behavior of the system.
In view of the tremendously large number of participating states this is impossible to do.
Therefore it is essential to group the states by some common quality. In most experiments
there are several observables which remain undetermined. In a typical atomic cluster ex-
periment one counts the number of charged fragments but usually does not specify their
internal excited state. Also one will usually not determine the momentum of each neutral
evaporated monomer. Consequently, the natural sorting principle is the size of the unob-
served phase space. As explained in great detail in refs. [29,38,39] MMMC samples only
the relevant number of degrees of freedom. It treats the internal degrees of freedom of the
fragments using the known internal specific heat. Each set of explicit degrees of freedom
represents a whole subset of quantum states of the system and is weighted by the size of the
corresponding part of the phase space. There are only a few millions of different configura-
tions which are important for a specific reaction. MMMC gives a systematic method to find
them. It is thus possible to determine the size of the accessible N-body phase space i.e. the total entropy which is rather difficult to get e.g. by molecular dynamics.

Let us now consider the fragmentation of sodium clusters with increasing number of atoms and charges. Figure 3 shows the average mass of the three largest fragments versus the specific excitation energy for the fragmentation of Na\textsuperscript{2+}\textsubscript{100}. The thick solid curve gives the thermodynamic temperature in Kelvin (right scale). Below \( \varepsilon = 0.5 \) eV/atom a singly charged big “evaporation” residue with dominating mass and additionally a small charged as well as several small neutral fragments are produced. Above 0.5eV/atom we find two small singly charged and several uncharged fragments of similar size (\( \leq 10 \)) (multifragmentation). The caloric equation of state \( < T(E/N) > \) shows a significant backbending, which is a clear signal for a phase transition of first order at \( \varepsilon \approx 0.5 \) eV/atom. The two phases are characterized by the presence or absence of a dominating large fragment.

Doubling the size of the cluster gives an even more pronounced phase transition, fig.4. The transition is shifted to slightly higher excitation energies. Evidently, fragmentation is easier in a smaller cluster with a large surface to volume ratio. The behavior of the mass distribution with excitation energy is very similar to the smaller cluster. In fig.3 we show the fragmentation of an even larger cluster, Na\textsuperscript{2+}\textsubscript{500}. The mass distribution is like in the two previous cases, the transition is shifted further up to \( \approx 0.7 \) eV/atom.

Rising the charge from \( Z = 2+ \) to \( Z = 5+ \) shifts the transition point again down to \( \varepsilon = 0.55 \) eV/atom, fig.3. Rising the charge has a similar effect on the fragmentation transition as dropping the size of the cluster. All calculations were performed in the conducting sphere approximation to include the polarization of the charge distribution of Na\textsubscript{n}, see paper III [33] of this series for a detailed explanation of the method.

Figure 7 shows a calculation using only the monopole-monopole (point charge) Coulomb interactions without the higher multipoles by the induced image charges. The transition is shifted towards slightly higher energies. The polarization (mirror charges) induces a net attraction. In contrast to similar calculations in ref. [29] we used here the experimental binding energies for Na\textsuperscript{q}\textsubscript{n} with \( q = 0, 1+ \) and \( 2 \leq n \leq 21 \) given by ref. [10,11], whereas in [29]
we had only experimental values for neutral and charged dimers and trimers. This change induces a stronger upwards shift of the transition than the difference between conducting and point-charge distribution. The simple reason is the predominant production of small fragments with masses between \( n = 1 \) and \( n = 10 \), so that the transition is especially sensitive to small changes in the binding energies of these small fragments.

**VI. CONCLUSION**

Microcanonical thermodynamics is the basics of all thermodynamics, but only recently we came into the position to explore it for nontrivial situations. In contrast to the more familiar canonical thermodynamics it is the only formulation which is valid for small isolated systems like free atomic clusters. We can now study how phase transitions evolve in systems with rising number of atoms from small towards the macroscopic ones.

Fragmentation phase transition is a new but generic phase transition of first order in small systems. Like other more familiar first order transitions as melting or boiling they lead to strong spatial inhomogeneities. However, unlike to the macroscopic transitions as boiling under the presence of an external gravity field, the inhomogeneities in microcanonical small systems are strongly fluctuating and the partition entropy plays an important role. Besides of being the correct ensemble for isolated systems the microcanonical ensemble is more suited to describe configurations with eventual phase separation than the canonical ensemble in which such configuration are exponentially suppressed \( \propto \exp(-N^{2/3} \sigma_{surf}/T) \). A fact that is especially important if one wants to study the evolution with rising particle numbers of configurations with two coexistent phase as e.g. the solid clusters with a molten surface or for the evolution of the liquid – gas transition as will be discussed in \([2]\).

The fragmentation transition was first described for the multifragmentation of hot nuclei \([42,43,38,27]\). In this series of papers we will discuss the fragmentation phase transition in clusters under various external conditions. As we have seen this transition is well defined in sodium clusters of some 100 atoms. With rising size and increasing volume to surface ratio
it shifts towards higher excitation per atom. Charging the cluster leads to a lowering of the critical excitation energy per atom.

In contrast to nuclear multifragmentation, the fragmentation of alkali clusters is very asymmetric if not special magic shell closures in the fragments favor more symmetric splitting. This topic will be discussed in the next paper of this series [28].

All our results concern the topological structure of the N-atom phase space only. Whether a realistic dynamical system can explore all the topological details of the phase space depends on how ergodic the dynamics is. The strong friction between nuclei moving one against another at close distances certainly helps to equilibrate the various degrees of freedom in nuclear fragmentation. Whether there is a similar strong friction between moving atomic clusters is not known. However, this is to be expected since atomic clusters have normally a less compact surface than nuclei.

The basic limitations and approximations which we had to use in our analysis are discussed in [27] and will be listed at relevant places in the following papers.

VII. ACKNOWLEDGMENTS

D.H.E.G. is very grateful to A. Hüller, S. Großmann, S. Berry and J. Jellinek for enlightening discussions about the basic principles of thermodynamics. We thank the Sonderforschungsbereich SFB 337 of the Deutsche Forschungsgemeinschaft for substantial support. We are also grateful to the Freie Universität Berlin for supporting us with computer time.
FIGURES

FIG. 1. Specific heat of bulk sodium at atmospheric pressure from [44,45]. The dashed line represents the specific heat calculated within the Debye model. $T_m$ is the melting and $T_v$ is the boiling transition. Notice the overshooting of $c(T)$ over the Debye limit of harmonic vibrations at the melting point.

FIG. 2. a) Specific entropy $s(\varepsilon) = \int_0^\varepsilon \beta_{\text{micro}}(\varepsilon) d\varepsilon$ versus the specific energy $\varepsilon$ for the 2-dim. Potts model with $q = 10$ on a 100*100 lattice. In order to visualize the anomaly of the entropy the linear function $a + b\varepsilon$ ($a = 0.2119$, $b = 1.4185$) was subtracted. Because we use periodic boundary conditions one needs two cuts to separate the phases and the depth of the convex intruder is twice the surface-entropy.

b) Microcanonical caloric equation of state, $\beta_{\text{micro}}(\varepsilon) = 1/T(\varepsilon)$ as directly calculated by MMMC.

c) Specific heat $c(\varepsilon) = -\beta^2/(\partial \beta/\partial \varepsilon)$. The canonical ensemble of the bulk jumps over the shaded region between the vertical lines at $\varepsilon_1$ and $\varepsilon_3$. This is the region of the coexistence of two phases, one with ordered spins, the other with disordered spins. Here $c(\varepsilon)$ has two poles and becomes negative in-between. The canonical thermodynamics is blind to this region. Notice that the poles are inside $\varepsilon_1 \leq \varepsilon \leq \varepsilon_3$, i.e the canonical specific heat remains finite and positive as it should.

FIG. 3. Average masses of the three largest fragments and the thermodynamic temperature $T$ as function of the excitation energy per atom for the fragmentation of Na$_{100}^{2+}$.

FIG. 4. Same as figure 3 but for Na$_{200}^{2+}$.

FIG. 5. Same as figure 3 but for Na$_{500}^{2+}$.

FIG. 6. Same as figure 3 but for Na$_{200}^{5+}$.

FIG. 7. Same as figure 3 but for Na$_{200}^{5+}$ and point charge Coulomb interaction.
REFERENCES

[1] C. Ellert, M. Schmidt, C. Schmitt, T. Reiners, and H. Haberland. Temperature dependence of the optical response of small open shell sodium clusters. *Phys. Rev. Lett.*, 75:1731, 1995.

[2] D.H.E. Gross and M.E. Madjet. Fragmentation phase transition in atomic clusters IV — the relation of the fragmentation phase transition to the bulk liquid-gas transition. *HMI-preprint*, in preparation, 1996.

[3] C.J. Thompson. *Classical Equilibrium Statistical Mechanics*. Clarendon Press, Oxford, 1988.

[4] Ludwig Boltzmann. *Vorlesung über Gastheorie*. Number 1. Akademische Druck-u. Verlagsanstalt, Graz, 1981.

[5] J. Jellinek, T.L. Beck, and R.S. Berry. Solid-liquid phase changes in simulated isoenergetic ar$_{13}$. *J.Chem.Phys.*, 84:2783, 1986.

[6] L. van Hove. Quelques propriétés générales de l’intégrale de configuration d’un système de particules avec interaction. *Physica*, 15:951, 1949.

[7] R.J. Baxter. *J. Phys.*, C6:L445, 1973.

[8] D.H.E. Gross, A. Ecker, and X.Z. Zhang. Microcanonical thermodynamics of first order phase transitions studied in the potts model. *Ann. Physik*, 5:446–452, 1996.

[9] A. Hüller. Finite size scaling at first order phase transitions? *Z.Phys.B*, 95:63–66, 1994.

[10] M. Promberger. On a trivial aspect of canonical specific heat scaling. *preprint, Erlangen*, 1996.

[11] M.E. Fisher. *Physics*, 3:255, 1967.

[12] J.P.K. Doye, D.J. Wales, and R.S. Berry. The effect of the range of the potential on the structures of clusters. *J. Chem. Phys.*, 103:4234–4249, 1995.
[13] R. E. Kunz and R.S. Berry. Multiple phase coexistence in finite systems. *Phys.Rev.*, E49:1895, 1994.

[14] D.J. Wales and J.P.K. Doye. Coexistence and phase separation in clusters: From the small to the not-so-small regime. *J. Chem. Phys.*, 103:3061–3070, 1995.

[15] K. Binder. Monte carlo calculation of the surface tension for two- and three-dimensional lattice-gas models. *Phys. Rev. A*, 25:1699–1709, 1982.

[16] H. Haberland (Ed). *Clusters of Atoms and Molecules*. Springer-Verlag, Berlin, Heidelberg, New York, 1994.

[17] R.M. Lynden-Bell. Negative specific heat in clusters of atoms. *to be published in Galactic Dynamics*, 1995.

[18] J.P.K. Doye and D.J. Wales. An order parameter aproach to coexistence in atomic clusters. *J. Chem. Phys.*, 102:9673–9688, 1995.

[19] B.K. Rao, P. Jena, M. Manninen, and R.M. Nieminen. Spontaneous fragmentation of multiply charged metal clusters. *Phys. Rev. Lett.*, 58:1188–1191, 1987.

[20] R.N. Barnett, U. Landman, and G. Rajagopal. Patterns and barriers for fission of charged small metal clusters. *Phys.Rev.Lett.*, 67:3058, 1991.

[21] M. Brack. *Rev.Mod.Phys.*, 65:677, 1993.

[22] M.J. López and J. Jellinek. Fragmentation of atomic clusters: A theoretical study. *Phys.Rev.A*, 50:1445, 1994.

[23] C. Yannouleas and Uzi Landman. *Phys. Rev. B*, 51:1962, 1995.

[24] C. Yannouleas, R.N. Barnett, and Uzi Landman. Electronic shell effects in fission barriers and fission dynamics of metal clusters. *Com.At.Mol.Phys.*, 31:445–460, 1995.

[25] F. Rhomund, E.E.B. Campbell, O. Knospe, G. Seifert, and R. Schmidt. Collision energy
dependence of molecular fusion and fragmentation in $C_{60}^+ + C_{60}$ collisions. Phys. Rev. Lett., in print, 1996.

[26] R.M. Lynden-Bell and D.J. Wales. Free energy barriers to melting in atomic clusters. J. Chem. Phys., 101:1460–1476, 1994.

[27] D.H.E. Gross. Microcanonical thermodynamics, fragmentation “phase-transition”, and the topology of the n-body phase space. In S.Albergio, S.Costa, A.Insolia, and C.Tuve, editors, Proceedings of CRIS96 ”Critical Phenomena and Collective Observables”, http://xxx.lanl.gov/nucl-th/9607038. Acicastello, Sicily, Italia, 27.5.-31.5.96, 1996. World Scientific, Singapore.

[28] M.E. Madjet, D.H.E. Gross, P.A. Hervieux, and O. Schapiro. Fragmentation phase transition in atomic clusters II — symmetry of coulombic fission. HMI-preprint, in preparation, 1996.

[29] D.H.E. Gross and P.A. Hervieux. Statistical fragmentation of hot atomic metal clusters. Z. Phys. D, 35:27–42, 1995.

[30] P.A. Hervieux and D.H.E. Gross. Evaporation of hot mesoscopic metal cluster. Z. Phys.D, 33:295–299, 1995.

[31] F. Chandezon, C. Guet, B.A. Huber, D. Jalabert, M. Maurel, E. Monnand, C. Ristori, and J.C. Rocco. Phys. Rev. Lett., 74:3784, 1995.

[32] G. Seifert, R. Gutierrez, and R. Schmidt. Ionization energies and coulomb explosion of highly charged $c_{60}$. Phys. Lett., A 211:357, 1996.

[33] O. Schapiro, P.J. Kuntz, K. Möhring, P.A. Hervieux, M.E. Madjet, and D.H.E. Gross. Fragmentation phase transition in atomic clusters III — coulomb explosion of cold clusters. HMI-preprint, in preparation, 1996.

[34] A.S. Botvina and D.H.E. Gross. The effect of large angular momenta on multifragment-
tation of hot nuclei. *Nucl.Phys.*, A 592:257–270, 1995.

[35] D.H. Li and J. Jellinek. Rotating clusters: centrifugal distortion, isomerization, fragmentation. *Z.Phys.D*, 12:177–180, 1988.

[36] J. Jellinek and D.H. Li. Separation of the energy of overall rotation in any n-body system. *Phys.Rev.Lett*, 62:241, 1989.

[37] J. Jellinek and D.H. Li. Vibrations of rapidly rotating n-body systems. *Chem.Phys.Lett.*, 169:380, 1990.

[38] D.H.E. Gross. Statistical decay of very hot nuclei, the production of large clusters. *Rep.Progr.Phys.*, 53:605–658, 1990.

[39] D.H.E. Gross. Microcanonical thermodynamics and statistical fragmentation of dissipative systems — the topological structure of the n-body phase space. *Physics Reports*, in preparation, 1996.

[40] M.M. Kappes, M. Schär, U. Röthlisberger, G. Yeretzian, and E. Schumacher. Sodium cluster ionisation potentials revisited: Higher-resolution measurements for na<sub>n</sub> (n < 23) and their relation to bonding models. *Chem. Phys. Lett.*, 143:251, 1988.

[41] C. Bréchignac, Ph. Cahuzac, J. Leygnier, and J. Weiner. Dynamics of unimolecular dissociation of sodium cluster ions. *J. Chem. Phys.*, 90:1492, 1989.

[42] D.H.E. Gross and Meng Ta-chung. Production mechanism of large fragments in high energy nuclear reactions. In *4th Nordic Meeting on Intermediate and High Energy Physics*, page 29, Geilo Sportell, Norway, January 1981.

[43] J.P. Bondorf. A model for fragmentation in intermediate energy heavy ion reactions. In C.H. Dasso, editor, *Nuclear Physics, Proceedings of the Nuclear Physics Workshop, I.C.T.P., Trieste, Miramare, Italy, 5-30 October, 1981*, pages 765–770, Amsterdam, New York, Oxford, 1982. North Holland.
[44] G. Borelius. The changes in energy content, volume, and resistivity with temperature in simple solids and liquids. *Solid State Physics*, 15:1, 1963.

[45] R. Hultgren, R.L. Orr, P.D. Anderson, and K.K. Kelley. *Selected Values of Thermodynamic Properties of Metals and Alloys*. John Wiley ans Sons, New York, 1963.
Specific Heat of bulk sodium

$p=1$ atm.
Figure 2
Figure 4: Graph showing specific excitation energy (eV) plotted against temperature (Kelvin) for Na$^{2+}_{200}$ with three different masses labeled M1, M2, and M3.
