Fragmentation Phase Transition in Atomic Clusters IV
— Liquid–gas transition in finite metal clusters and in the bulk —

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Within the micro-canonical ensemble it is well possible to identify phase-transitions in small systems. The consequences for the understanding of phase transitions in general are discussed by studying three realistic examples.

We present micro-canonical calculations of the fragmentation phase transition in Na-, K-, and Fe- clusters of \( N = 200 \) to 3000 atoms at a constant pressure of 1 atm. The transition is clearly of first order with a back-bending micro-canonical caloric curve \( T(P,E,V(E,P)) = \partial S(E,V(E,P))/\partial E \big|_P \). From the Maxwell construction of \( \beta(P/N,P) = 1/T_P \) one can simultaneously determine the transition temperature \( T_{tr} \), the specific latent heat \( q_{lat} \), and the specific entropy-loss \( \Delta s_{surf} \) linked to the creation of intra-phase surfaces.

\[
T_{tr} \Delta s_{surf} \ast N/(4\pi r_{ws}^2 N_{eff}^{2/3}) = \gamma
\]

Here \( 4\pi r_{ws}^2 N_{eff}^{2/3} = \sum N_i \ast 4\pi r_{ws}^2 m_i^{2/3} \) is the combined surface area of all fragments with a mass \( m_i \geq 2 \) and multiplicity \( N_i \). All these characteristic parameters are for \( \sim 1000 \) atoms similar to their experimentally known bulk values. This finding shows clearly that within micro-canonical thermodynamics phase transitions can unambiguously be determined without invoking the thermodynamic limit. However, one has carefully to distinguish observables which are defined for each phase-space point, like the values of the conserved quantities, from thermodynamic quantities like temperature, pressure, chemical potential, and also the concept of pure phases, which refer to the volume of the energy shell of the N-body phase-space and thus do not refer to a single phase-space point.

At the same time we present here the first successful microscopic calculation of the surface tension in liquid sodium, potassium, and iron at a constant pressure of 1 atm.

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I. INTRODUCTION

Thermodynamics is commonly believed to address to large many-body systems close to the thermodynamic limit. It is further common believe that the three popular ensembles, e.g. for simplicity here at given pressure \( P \), the micro-canonical \( \{E,N,P\} \), the canonical \( \{T,N,P\} \), and the grand-canonical \( \{T,\mu,P\} \) agree in that limit and describe the same
physical behaviour. But this is not so at first order phase transitions as e.g. the liquid–gas transition. Fixing the temperature to the boiling temperature but leaving the energy undetermined the canonical ensemble is a mixture of pure liquid and pure gas configurations with equal probabilities. Drawing different members of the canonical ensemble, the specific heat fluctuates by the amount of the specific latent heat. In the canonical representation one would not be able to see a pot of boiling water with a surface dividing the liquid from the vapor. This is only possible when the system is confined to a given specific energy \( \varepsilon = E/N \) i.e. in the micro-canonical ensemble. The energy controls what portion of the water is liquid and what is steam. Every-day macroscopic experience is represented by the micro-canonical ensemble because the energy supply is seldomly unrestricted.

Micro-canonical thermodynamics explores the topology of the N-body phase space and determines how its volume

\[
W(E, N, V) = e^S = \int_{E-\delta E}^{E} dE' \int \frac{d^{3N-6}x \ d^{3N-6}p}{(2\pi\hbar)^{3N-6}} \delta(H(x_i, p_i) - E')
\]

depends on the fundamental globally conserved quantities namely the total energy \( E = N*\varepsilon \), the angular momentum \( \mathbf{L} \), the mass (number of atoms \( N \)), charge \( Z \), the linear momentum \( \mathbf{p} \), and last not least the available spatial volume \( V \) of the system. This definition is the basic starting point of any thermodynamics since Boltzmann [1]. It is an entirely mechanistic definition. If we do not know 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. It is of course a completely separated and difficult question, outside of thermodynamics, if and how a complicated interacting many-body system may explore its entire accessible phase space. This question does not concern us here. The present work is an attempt to develop the thermodynamics of realistic systems entirely from their mechanics without invoking any additional assumption like the use of the thermodynamic limit.

Before we proceed, we have to emphasise the concept of the statistical ensemble. Each phase space cell of size \((2\pi\hbar)^{3N-6}/\delta E\) corresponds to an individual configuration (event) of our system. (The factor \( \delta E \) is the arbitrarily chosen small width of the energy shell. In the following all energy variables, also the temperature, are in units of \( \delta E \), here in 1eV.) Clearly, the volume \( e^S \) of the phase space is the sum (ensemble) of all possible phase space cells compatible with the values of energy etc.. While the conserved, excessive quantities, energy, momentum, number of particles, and charge can be determined for each individual configuration of the system, i.e. at each phase-space point or each event, this is not possible for the phase space volume \( e^S \), i.e. the entropy \( S(E, V, N) \) and all its increments like the temperature \( T = (\partial S(E, V, N)/\partial E)^{-1} \), the pressure \( P(E, V, N) = T\partial S(E, V, N)/\partial V \), and the chemical potential \( \mu = -T\partial S(E, V, N)/\partial N \). Their determination demands a measure of the phase-space volume \( e^S \) or its resp. variation. They are ensemble averages. Only in the thermodynamic limit, for systems with infinitely many particles \( N \) may e.g. the temperature be determined in a single configuration by letting the energy flow into a small thermometer.

\[1\)This is the thermodynamical definition of temperature. It is in general different from its mechanical one as \( 2/3 \) of the mean kinetic energy per particle. This is also true for the pressure.
For a finite system, e.g. a finite atomic cluster, the temperature, its entropy, its pressure can only be determined as ensemble averages over a large number of individual events. E.g. in a fusion of two nuclei one obtains the excitation energy in each event from the ground-state Q-values plus the incoming kinetic energy whereas the temperature of the fused compound nucleus is determined by measuring the kinetic energy spectrum of decay products which is an average over many decays. It is immediately clear that the size of $S$ is a measure of the fluctuations of the system.

In what follows we discuss the most dramatic phenomena in thermodynamics: the occurrence of phase transitions. We will try to interpret them micro-canonically as peculiarities of the N-body phase space. We will avoid the concept of the thermodynamic limit as we believe that this is not really essential for the understanding of phase transitions. We will see that details about the transitions become more transparent in finite systems. Then however, one needs a modified definition for the concept of phase transitions.

In the first paper of this series on micro-canonical thermodynamics and fragmentation of atomic clusters (papers I — III, [2–4]) we introduced a new criterion of phase transitions, which avoids any reference to the thermodynamic limit and can also be used for finite systems: The anomaly of the micro-canonical caloric equation of state $T(E/N)$ where $\frac{\partial T}{\partial E} \leq 0$ i.e. where the familiar monotonic rise of the temperature with energy is interrupted. Very early the anomaly of the caloric curve $T(E/N)$ was interpreted as signal for a phase transition in small systems in the statistical theory of multi-fragmentation of hot nuclei by Gross and collaborators see refs. [5,6] and the review article [7]. Challa and Hetherington came to the same conclusion at about the same time in their paper on the Gaussian ensemble [8]. Within the Gaussian ensemble one can transform smoothly from the micro-canonical to the canonical ensemble. They concluded that there is a hierarchy of ensembles: micro-canonical $\rightarrow$ canonical $\rightarrow$ grand-canonical in which the content of information about the system diminishes from left to right. They claim it is impossible to recover the fundamental micro-canonical ensemble from the canonical. I.e. if the canonical partition sum is only known with limited accuracy, may be due to some approximation, then the back-transform is dangerously inaccurate. This is a fortiori the case at the most interesting points: At phase transitions of first order, see below. Of course, this is because of the high sensitivity of the Laplace–back transform from the canonical to the micro-canonical partition sum. (E.g. as discussed below, the Laplace transform $E \rightarrow \tau T$ suppresses configurations with liquid–gas phase separation by the exponentially small factor $\exp(-N^{2/3} \sigma_{surf}/T_{tr})$. The Laplace-back transform must consequently enhance these configurations again by the inverse of this factor.) For the case of the nuclear level-density formula by Bethe this was demonstrated by ref. [9]. Bixton and Jortner [10] linked the back-bending of the micro-canonical caloric curve to strong bunching in the quantum level structure of the many-body system i.e. a sudden opening of new phase space when the energy rises. Their paper offers an interesting analytical investigation of this feature.

2)It is convenient to consider specific quantities as the energy $\varepsilon = E/N$ or the specific entropy $s = S/N$ per atom. In many cases the micro-canonical caloric curve $T(\varepsilon)$ depends only weakly on the particle number $N$ and the extrapolation to the thermodynamic limit is then easy.
FIG. 1. Micro-canonical caloric curve $T_P(E/N = \varepsilon, V(E, P, N), N)$ at constant pressure (full square points), number of fragments $N_{fr}$ with $m_i \geq 2$ atoms, and the effective number of surface atoms $N_{eff}^{2/3} = \sum m_i^{2/3} N_i = \text{total surface area divided by } 4\pi r^2_{ws}$. The two shaded areas correspond to the two equal areas between $\beta(\varepsilon) = 1/T(\varepsilon)$ and the Maxwell-line $\beta = 1/T_{tr}$. In the lower panel $s(\varepsilon) = \int_0^\varepsilon \beta(\varepsilon')d\varepsilon'$ is shown. In order to make the intruder between $\varepsilon_1$ and $\varepsilon_3$ visible, we subtracted the linear function $25 + 11.5\varepsilon$. The double-tangent to $s(\varepsilon)$ is the concave hull to $s(\varepsilon)$ between $\varepsilon_1$ and $\varepsilon_3$. Its derivative is the Maxwell-line in the upper two panels.

A phase transition of first order is characterised by a sine-like oscillation, a “back-bending” of $T(\varepsilon = E/N)$ c.f. fig. As shown below, the Maxwell-line which divides the oscillation of $\partial S/\partial E = \beta(\varepsilon) = 1/T$ into two opposite areas of equal size gives the inverse of the transition temperature $T_{tr}$, its length the specific latent heat $q_{lat}$, and the shaded area under each of the oscillations is the loss of specific entropy $\Delta s_{surf}$. The latter is connected to the creation of macroscopic intra-phase surfaces, which divide mixed configurations into separated pieces of different phases, e.g. liquid droplets in the gas or gas bubbles in the
liquid. Even nested situations are found in some other cases like liquid droplets inside of crystallised pieces which themselves are swimming in the liquid in the case of the solid – liquid transition, see e.g. the experiments reported in [11]. I.e. at phase transitions of first order inhomogeneous “macroscopic or collective” density fluctuations are common, boiling water is certainly the best known example. Phase-dividing surfaces of macroscopic size exist where many atoms collectively constitute a boundary between two phases which cause the reduction of entropy by $\Delta s_{surf}$. As the entropy is the integral of $\beta(\varepsilon)$:

$$
s(\varepsilon) = \int_0^\varepsilon \beta(\varepsilon') d\varepsilon'
$$

it is a concave function of $\varepsilon$ ($\partial^2 s/\partial \varepsilon^2 = \partial \beta/\partial \varepsilon < 0$) as long as $T(\varepsilon) = \beta^{-1}$ shows the usual monotonic rise with energy. In the pathological back-bending region of $\beta(\varepsilon)$ the entropy $s(\varepsilon)$ has a convex intruder of depth $\Delta s_{surf}$ [12](c.f. fig.1c). This has the consequence that the specific heat ($\partial T/\partial E$) becomes negative. This astonishing result was discussed early by Thirring [13]. At the beginning ($\geq \varepsilon_1$) of the intruder the specific entropy $s(\varepsilon)$ is reduced compared to its concave hull, which is the tangent to $s(\varepsilon)$ in the points $\varepsilon_1$ and $\varepsilon_3$. The derivative of the hull to $\beta(\varepsilon)$ follows the Maxwell-line in the interval $\varepsilon_1 \leq \varepsilon \leq \varepsilon_3$. In the middle, ($\varepsilon_2$), when the separation of the phases is fully established this reduction is maximal $= \Delta s_{surf}$ and at the end of the transition ($\varepsilon_3$) when the intra-phase surface disappears $\Delta s_{surf}$ is gained back. Consequently, the two equal areas in $\beta(\varepsilon)$ are the initial loss of surface entropy $\Delta s_{surf}$ and the later regain of it. Due to van Hove’s theorem [14] this convex intruder of $s(\varepsilon)$ must disappear for “thermodynamically stable systems” as we consider in this paper in the thermodynamic limit which it will do if $\Delta s_{surf} \sim N^{-1/3}$. This is why a transition of first order may easier be identified in finite systems where the intruder can still be seen. The intra-phase surface tension is related to $\Delta s_{surf}$ by $\gamma_{surf} = \Delta s_{surf} * N * T_{tr}/surf.-area.$

In conventional thermodynamics a phase transition of first order is indicated by a singularity (jump) in the specific heat $c_P(T)$ in the thermodynamic limit ($N \rightarrow \infty|_{\rho=N/V=\text{const}}$). It is easy to see the relation to our present criterion. The canonical partition sum is obtained from the micro-canonical volume $W(E)$ of the accessible N-body phase space, in units of $(2\pi\hbar)^{3N-6}/\delta E$, or the number of quantum mechanical N-body states, $W(E) = e^{Ns(\varepsilon=E/N)}$ by the Laplace transform from the extensive energy to the intensive temperature $T = 1/\beta$:

$$Z(\beta) = \int_0^\infty W(E)e^{-\beta E} dE. \quad (3)$$

In the thermodynamic limit ($N \rightarrow \infty|_{\rho=N/V=\text{const}}$) the partition function $Z(\beta)$ and the bulk specific heat $c(T)$ are obtained via the Laplace transform (3) in saddle-point approximation (see e.g. [15] App.2B):

$$Z(\beta) = \int_0^\infty W(N\varepsilon) e^{-\beta N\varepsilon} N d\varepsilon \quad (4)$$

$$\sim T e^{N[s(\varepsilon)-\beta \varepsilon]} \sqrt{2\pi N/c(\varepsilon)} \quad (5)$$

$$\frac{\partial}{\partial \varepsilon} s(\varepsilon)|_{\varepsilon} = \beta. \quad (6)$$

$$c(\varepsilon) = -\frac{\partial^2 s}{\partial \varepsilon^2} \left|_{\varepsilon} \right. \quad (7)$$
The exponent in eq. (5) is the free energy \(-N_f(T)/T\). Eq. 6 establishes a relation between \(T\) and \(\varepsilon\), the caloric equation of state. Whereas \(T(\varepsilon)\) is single valued everywhere, this is not true for its inverse \(\varepsilon(T)\) in the back-bending region. There are in general 3 solutions for \(T = T_{tr}\) of eq. (6) here c.f. fig. 1: \(\varepsilon_1\), \(\varepsilon_2\), and \(\varepsilon_3\). At the second solution \(\varepsilon_2\) of equation (6) \(s(\varepsilon)\) has a positive curvature and the saddle point is a minimum in the direction of integration not a maximum. Consequently, the Laplace transform \(P\) towards the canonical partition function \(Z(T)\) jumps over this region which becomes exponentially suppressed by a factor \(e^{-\Delta f_{surf}/T_{tr}}\) where \(\Delta f_{surf} \propto N^{2/3}\) is the positive surface free energy. In the thermodynamic limit \((N \rightarrow \infty)\) the integration follows the concave hull of \(s(\varepsilon)\) here. Then \(c(T)\) gets the singularity = \(q_{lat}\delta(T - T_{tr})\) but otherwise remains finite [16,17], which is just the conventional signal of a phase transition of first order, c.f. Ruelle [18]. This jump over the energies \((\varepsilon_1 \leq \varepsilon \leq \varepsilon_3)\) of configurations with phase-separation with the consequence of their exponential suppression is the mathematical reason for the loss of information in the canonical ensemble. It is just the crucial information about the phase transition.

Our approach to phase-transitions of first order is complementary to the conventional approaches where the separation of the system into two homogeneous phases by a — in general — geometrical interface is investigated, e.g. [19]. The problems due to the large fluctuations of this interface are numerous and severe, see e.g. the discussion on fluid interfaces by Evans [20]. These fluctuation are of course crucial for the interfacial entropy and consequently for the surface tension also. The two main differences of our approach are that

- we do not start with the geometry (planar or spherical) of the interface but focus our attention to the entropy of the phase separation. This turns out to be much simpler than the geometric approach. Moreover, it is the entropy of the interface that decides the transition not its geometrical interpretation.

- The micro-canonical ensemble allows for large scale spatial inhomogeneities, whereas the canonical ensemble suppresses spatial large scale inhomogeneities like phase-separations exponentially \(\propto \exp(-\sigma N^{2/3}/T_{tr})\), where \(\sigma\) is the surface tension parameter \((\sigma = 4\pi r_{ws}^2 \gamma)\) in the liquid drop parametrisation of the ground-state binding-energy of the clusters here of course at the boiling point, \(r_{ws}\) is the radius of the Wigner-Seitz cell [21]. This is an example of the information loss in the canonical ensemble mentioned by Challa and Hetherington [8].

This characterisation of phase transitions is purely thermodynamically. We have not yet defined what a phase is. Much effort is spent in Ruelle’s book to define pure phases as those configurations for which in the thermodynamic limit observables survive increasing coarse-graining, for which space-averaged quantities do not fluctuate, c.f. chapter 6.5 in Ruelle’s book [18]. Of course, this definition works in the thermodynamic limit only. It does not address to finite systems. For a finite system it is not possible to decide if a specific configuration corresponds to a pure phase or not. The situation is analogous to the definition of the temperature, see above. Again to be a pure phase is a feature of the whole ensemble not of a single phase-space point (configuration). We use a statistical definition of a pure phase: A configuration belongs to the ensemble of pure phases — including its fluctuations — at concave points of \(S(E, N, V(E, P))\) with \(\partial^2 S/\partial E^2 < 0\). At the two crossing points of the micro-canonical caloric curve \(T_P(E/N) = T_{tr}, \varepsilon_1, \varepsilon_3\) we say the system is in the pure “liquid”
phase or in the pure “gas” phase respectively. This is at this moment nothing more than a working hypothesis. However, we will see that for the systems we have investigated (2-dim Potts models, fragmentation of sodium, potassium, and iron clusters with $N = 200 - 3000$ atoms) these definitions give very realistic values for all parameters of the transitions quite similar to the ones in the bulk. Of course, the parameters depend weakly on the number of particles considered. However, there is no reason to emphasise any qualitative difference between the bulk transition and the “phase transition” with or without quotation marks in finite systems as defined above.

It is evident, at a phase transition of first order ($T = T_{tr}$) the members of a canonical ensemble split into two distinct groups with different energy/particle ($\varepsilon_1$ and $\varepsilon_3$) but with equal probability $e^{-f/T}$, a “liquid” and a “vapour” phase because both have the same free energy. At $T_{tr}$ the energy per particle $\varepsilon$ fluctuates by the specific latent heat whatever the coarse-graining might be. This is illustrated in fig.2. Consequently, at a first order phase transition the micro-canonical ensemble where energy does not fluctuate is different from the canonical one even in the thermodynamic limit at $T = T_{tr}$.

If the shaded area $\Delta S_{surf}$ under the oscillation of $\beta(\varepsilon)$ (see fig.1) disappears and if the latent heat $q_{lat} = 0$, we have a continuous phase transition. In the thermodynamic limit the Laplace transform eq. (4) then has only one stationary point at $T_{tr}$ in this case, which is a saddle point of the caloric curve $T(\varepsilon)$ and the specific heat $c(T) = \partial \varepsilon / \partial T$ is continuous and has a pole at $T = T_{tr}$, c.f. fig.1 of paper I [4].

FIG. 2. Probability $P_{tr}(\varepsilon)$ to find the system in the canonical ensemble at a phase transition of first order ($T = T_{tr}$) at the energy/particle $\varepsilon$. At $\varepsilon = \varepsilon_1$ it is “liquid” and at $\varepsilon = \varepsilon_3$ it is in the pure “gas” phase

In ref. [12] we showed for a two-dimensional Potts-model that all the above mentioned micro-canonical parameters of a phase transition of first order are within a few percent close to their bulk values for relatively small systems like a couple of hundreds spins. This is not only true in model systems but also in realistic continuous systems like liquid metals. In this paper (IV. of our series) we will follow the micro-canonical fragmentation transition
in clusters of sodium, potassium, and iron with increasing number of atoms towards the well known liquid-gas transition of the bulk. In contrast to the fragmentation transition in isolated clusters which have to be treated at an approximately constant volume defined by the short range of dissipation [21], the liquid-gas transition must be studied at constant pressure, here at 1 atmosphere. The rapid convergence of the three characteristic parameters, $T_{tr}$, $q_{lat}$, and $\sigma_{surf}$ towards their bulk values (c.f. tables [1] and [1]) is a further check of the validity of our characterisation of a phase transition by the anomaly of the micro-canonical caloric curve and of our numerical method (MMMC) to treat the fragmentation of small systems like nuclei or atomic clusters.

The advantage of our new signal of a phase transition is the following: As shown in [16,17,12,21] the micro-canonical caloric equation of state $T(E/N)$ gives this signal of a phase transition already for relatively small systems. Moreover, $T(E/N)$ becomes rather quickly independent of the number of particles outside the back-bending region, which itself degenerates for large $N$ towards the Maxwell-line $T = T_{tr}$. 


II. THE MICRO-CANONICAL LIQUID–GAS TRANSITION AT CONSTANT PRESSURE

The entropy of the system follows from the fundamental formula

\[ S(E, V, N) = k \ln W(E, V, N), \]

where \( W(E, V, N) \) is the number of all accessible quantum states of the N-body system in the energy interval \( E, E + \delta E \) and volume \( V \). In what follows we take Boltzmann’s constant \( k = 1 \). The thermodynamic temperature at constant volume is defined by (in the following we suppress the dependence of the number of atoms \( N \), as this is held fixed in all derivatives)

\[ \frac{1}{T(E, V)} = \beta(E, V) = \frac{\partial S(E, V)}{\partial E} \]

\[ = \langle f_{tr} - \frac{2}{2E^0} \rangle, \]

where \( f_{tr} \) denotes the number of translational-rotational degrees of freedom and \( E^0 \) is the remaining kinetic energy (c.f. eq.B43 [21]). The pressure is given by

\[ P(E, V) = T(E, V) \times \left( \frac{\partial S(E, V)}{\partial V} \right)_E \]

\[ = T(E, V) \times \frac{\partial w_m w_r}{\partial V} \]

\[ w_m w_r \text{ is the spatial weight given in eqs.B25, B30 of [21]:} \]

\[ w_m w_r = \frac{1}{N_m!} \left[ g_e \left( \frac{1}{2\pi \hbar} \right)^3 V_m \right] \prod_{j=1}^{N_f} \left\{ \frac{1}{(2\pi \hbar)^3} \frac{4\pi}{3} (R_{sys} - R_j)^3 \right\} / NCC \]

\[ P \approx T < \frac{N_f + N_m}{V} > + \text{terms due to the change of NCC}, \]

where \( NCC - 1 \) is the number of unsuccessful attempts to put the fragments \( j \) into the given volume. It takes care of the varying avoided volume. In the present calculations at a pressure of 1atm we have \( NCC \approx 1 \) so that its variation does not concern us here. At higher pressure, more close to the critical point, the pressure due to the change of the avoided volume is more important. \( N_f + N_m \) is the average number of fragments including monomers and \( V \) is the available volume of the system. (As already discussed above, in contrast to here, for the fragmentation phase transition of free finite clusters the calculations were done in papers I–III [2,12,4] at constant freeze-out volume not at constant pressure.) We can calculate the thermodynamic temperature at constant pressure by the following:

\[ \frac{1}{T_P(E, P)} = \beta_P(E, V(E, P)) = \left. \frac{\partial S(E, V(E, P))}{\partial E} \right|_P = \left. \frac{\partial (SP)}{\partial (EV)} \right|_P = \left. \frac{\partial (SP)}{\partial (EV)} \right|_P. \]

Using the Jacobian

\[ \frac{\partial (SP)}{\partial (EV)} = \left[ \left. \frac{\partial S(E, V)}{\partial E} \right|_V \frac{\partial P(E, V)}{\partial V} \right|_E - \left. \frac{\partial S(E, V)}{\partial V} \right|_E \frac{\partial P(E, V)}{\partial E} \right|_V, \]
we get
\[ \beta_P(E, P) = \left[ \frac{\partial S}{\partial E} \left|_V \right. \frac{\partial P}{\partial V} \left|_E \right. - \frac{\partial S}{\partial V} \left|_E \right. \frac{\partial P}{\partial E} \left|_V \right. \right] \frac{1}{\frac{\partial P}{\partial V} \left|_E \right.}, \tag{18} \]

and
\[ \beta_P(E, P) = \beta(E, V \ast \left[ 1 - P \frac{\partial P}{\partial V} \right]. \tag{19} \]

On the other hand we have from eqs.11,9:
\[ \frac{\partial P(E, V)}{\partial E} \left|_V \right. = \frac{\partial T(E, V)}{\partial E} \left|_V \right. + T \frac{\partial^2 S(E, V)}{\partial V \partial E} \left|_E \right. \tag{20} \]
\[ \frac{\partial P(E, V)}{\partial V} \left|_E \right. = \frac{\partial T(E, V)}{\partial V} \left|_E \right. + T \frac{\partial^2 S(E, V)}{\partial V^2} \left|_E \right. \tag{21} \]
\[ \frac{\partial T(E, V)}{\partial E} \left|_V \right. = -T^2 \frac{\partial \beta(E, V)}{\partial E} \left|_V \right. = -T^2 \frac{\partial^2 S(E, V)}{\partial E} \left|_V \right. \tag{22} \]

Using \( w_m \) and \( w_r \) given in the appendix B of the review paper \[21\] and assuming for the moment the avoided volume to keep close to the initial cluster volume (at low densities of the system), we finally get
\[ \beta_P(E, P) = \beta(E, V(E, P)) \left[ 1 - T < N_t > \left( \frac{\partial T}{\partial E} \right) \left( \frac{\partial^2 S}{\partial V \partial E} \right) \right] \]
\[ + \text{terms } \propto \frac{\partial NCC}{\partial V} \text{ at low } \varepsilon, \text{ high } P, \tag{23} \]
where \( N_t \) is the total number of fragments including neutral monomers. \( E_0 ' \) is the remaining energy and \( f_{tr} \) is the number of translational-rotational degrees of freedom.

One notes that \( \beta(E, V) = \frac{(f_{tr} - 2)}{E_0} \). In the case of vaporisation (only monomers), we find
\[ \beta_P(E, P) = \beta(E, V(E, P)) \left[ 1 + \frac{2N}{3N - 8} \right], \tag{24} \]
where \( N \) is the number of atoms. At very large number of atoms we get the same formula as derived for an ideal gas consisting of \( N \) particles
\[ \beta_P(E, P) = \beta(E, V(E, P)) \frac{5}{3}, \tag{25} \]
The corrections \( \propto \frac{\partial NCC}{\partial V} \) take care of the fact that the avoided volume is larger than the total eigenvolume of the fragments. It is bigger at low excitation energies when the fragments are larger than at higher excitation. These variations, consequently, contribute to the pressure (eq.15). These corrections turn out to be negligible at 1 atm. However, more important at higher pressure when one approaches the critical point.

The micro-canonical ensemble with given pressure \( W(E, P, N) \) must be distinguished from the (in spirit) similar constant pressure ensemble \( \{ H, P, N \} \) introduced by Andersen \[22,24\] where a molecular-dynamic calculation with the hypothetical Hamiltonian \[23\]
\[
H\{r_i, p_i\}, V, \dot{V} = \frac{V^{2/3}}{2} \sum_{i=1}^{N} m \dot{r}_i \cdot \dot{r}_i + \sum_{i=1}^{N} \sum_{j>i}^{N} \Phi(r_{ij} V^{1/3}) + \frac{M}{2} \dot{V}^2 + P_E V
\]  

is suggested. Here \( V \) is the volume of the system, taken as an additional explicit degree of freedom, \( \{r_i, p_i\} \) are the coordinates and momenta of the atoms scaled with the factor \( V^{1/3} \), \( \Phi(r_{ij}) \) is the intra-atomic two-body potential, and \( M \) is a hypothetical mass for the volume degree of freedom. \( P_E \) is the given pressure. The total “energy” \( H \), atoms plus \( V \)-degree of freedom, is conserved, not the total energy \( E \) of the atoms alone.

This is different to our micro-canonical approach with given \( E, V(E, P), N \) where the energy \( E \) of the atoms is conserved and the pressure is the correct thermodynamic pressure \( P(E, V) = T(E, V) \partial S / \partial V|_E \). At each energy the volume \( V(E, P) \) is chosen for all members of the ensemble simultaneously by the condition that \( T(E, V) \partial S(E, V) / \partial V|_E \) of the whole ensemble is the correct pressure. In this case there is a unique correlation between the energy \( E \) and the volume \( V \) which does not fluctuate within the ensemble even though the pressure is specified. At the given energy this is still the \( \{E, V(E, P, N), N\} \) ensemble. Moreover, the entropy cannot be calculated directly by molecular dynamics, whereas this is possible in our micro-canonical Metropolis Monte Carlo method.

III. THE LIQUID-GAS TRANSITION OF SODIUM, POTASSIUM, AND IRON

The microscopic simulation of the liquid–gas transition in metals is especially difficult. Due to the delocalisation of the conductance electrons metals are not bound alone by two-body forces but experience long-range many-body interactions. Moreover, at the liquid–gas transition the binding changes from metallic to covalent binding. This fact is a main obstacle for the conventional treatment by molecular dynamics [25].

In the macro-micro approach we do not follow each atom like in molecular dynamics, the basic particles are the fragments. Their ground-state binding energies are taken from experiments. The fragments are spherical and have translational, rotational, and intrinsic degrees of freedom. The internal degrees of freedom of the fragments are simulated as pieces of bulk matter. The internal density of states is calculated from the internal entropy of the fragments. It is taken as the specific bulk entropy \( s(\varepsilon) \) at excitation energies \( \varepsilon \leq \varepsilon_{\text{max}} = \varepsilon_{\text{boil}} \). The bulk entropy can be determined from the experimentally known specific heat of the solid/liquid bulk matter [26]. \( \varepsilon_{\text{boil}} \) is the specific energy where the boiling of bulk matter starts. This approximation allows to take important enharmonicities of the internal degrees of freedom into account e.g. near to the melting point. Details are discussed in [21]. Then the metallic binding poses no difficulty for us and the metal — nonmetal transition is controlled in our approach by the increasing fragmentation of the system. This leads to a decreasing mean coordination number when the transition is approached from the liquid side while the distance to the nearest neighbour remains about the same. Exactly this behaviour was recently observed experimentally [27][28]. By using the micro-canonical ensemble we do not pre-specify the intra-phase surface and allow it to take any form. Also any fragmentation of the interface is allowed. It is the entropy alone which determines the fluctuations of the interface. Here we present the first successful microscopic calculation of the surface tension in liquid sodium, potassium, and iron.
The figure shows the micro-canonical caloric curve \( T(\varepsilon) \) for a system of \( N = 200 \) and 1000 sodium atoms. The back-bending of \( T_P(\varepsilon) \) can be clearly seen. At \( \varepsilon \sim \varepsilon_2 \approx 0.7 - 0.8\text{eV} \) the thermodynamic temperature drops suddenly due to the rapid increase of the number of fragments. This induces a jump in the increment \( \partial s/\partial \varepsilon = 1/T(\varepsilon) \) of the entropy \( s(\varepsilon) \).

The number of fragments with mass \( m_i \geq 2 \) increases slowly up to \( \varepsilon_2 \) and from there on jumps up and decays continuously down to 0. \( 4\pi r_{ws}^2 N_{eff}^{2/3} = \sum 4\pi r_{ws}^2 m_i^{2/3} N_i \) is the total surface area of the fragments. For \( \varepsilon \leq \varepsilon_2 \) the size \( m_i \) of the fragments decreases due to an increasing evaporation of monomers, c.f. fig.4, but the number of fragments increases such that the total surface area decreases more weakly with rising excitation. For \( N_0 = 200 \) and 1000 it keeps even approximately constant \( \approx 4\pi r_{ws}^2 N_{eff}^{2/3} \). A more detailed investigation shows that in sodium as well as also in potassium we actually may have two interfering transitions: One from evaporation of monomers and smaller fragments with a large residue towards multi-fragmentation with several medium sized fragments at \( \sim 0.7\text{eV/atom} \) and a second one from multi-fragmentation into a pure gas of monomers at \( \varepsilon > 1.2\text{eV/atom} \). For systems with more atoms, \( N_0 \geq 3000 \) c.f. fig.3, the multi-fragmentation in sodium moves towards larger excitation and melts together with the vaporisation dip at \( \sim 1.1 - 1.2\text{eV/atom} \). In the canonical ensemble all these important details become suppressed or even hidden.
The bulk values of $\sigma$ are calculated from the experimental surface tension $\gamma$ by:

\[
\sigma_{\text{bulk}} = 4\pi r_{\text{ws}}^2 \gamma \\
r_{\text{ws}}^3 = 10^{30} \frac{3vM}{4\pi L}
\]

\[
\sigma_{\text{bulk}}(T) = 6.242 \times 10^{-5} \times 4\pi (r_{\text{ws}}^2 \gamma)|_{T_{\text{melt}}} \left\{ 1 + \left[ \frac{1}{\gamma} \frac{d\gamma}{dT} \right]_{T_{\text{melt}}} + \frac{2}{3v} \frac{dv}{dT} \right\} (T - T_{\text{melt}}),
\]

(27)

(28)

(29)

where $r_{\text{ws}}$ in [Å] is the Wigner-Seitz radius at melting, $v$ in [$m^3/kg$] is the specific volume at melting, $L$ is the number atoms per kg-mole (Loschmid’s number), and $M$ is the molecular weight. $\gamma|_{T_{\text{melt}}}$, $d\gamma/dT|_{T_{\text{melt}}}$ are the experimental surface tension in [mN/m] and $v|_{T_{\text{melt}}}$, $dv/dT|_{T_{\text{melt}}}$ are the specific volume in [m$^3$/kg] and its temperature derivative in [m$^3$/K kg] at the melting point given by [29]. The values by Iida and Gutherie [29] are slightly different from the values from
The uncertainty of the experimental values for the bulk surface tension at
the melting point are quoted \cite{29} to be $\sim 5 \text{--} 10\%$ at $T_m$ whereas
the extrapolation towards $T = 0$ resp. towards the boiling point is done
with the parameters $\frac{1}{\gamma} \frac{d\gamma}{dT}|_{\text{melt}}$ and $\frac{1}{v} \frac{dv}{dT}|_{\text{melt}}$
which have an estimated error of $\pm 50\%$. We give the in this way extrapolated
values of $\sigma_{\text{bulk}}(T_{\text{boil}})$ for iron in the last column of table II.

Inspecting these numbers we find the liquid-drop parameter $a_s = \sigma(T = 0) = 4\pi r_{ws}^2 \star \gamma|_{T=0}$ to be less by about 30\% than the values of $a_s$ determined for the ground-state binding
energies of real clusters averaged over the shell effects in \cite{31} which we have of course used
in our calculation for the ground-state binding energies of the fragments. The origin of this
experimental discrepancies is yet unknown \cite{31}. Consequently, we think we should compare
our theoretical values for $\sigma_{\text{boil}}$ with values for $\sigma_{\text{bulk}}(T)$ which are consistent at $T = 0$ with
the values given for $a_s$ by \cite{31} and than extrapolated to $T = T_{\text{boil}}$ with formula 29. These
are listed in the last column of table II.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Micro-canonical caloric curve $T_P(E/N = \varepsilon, P)$ (full square points), number of monomers}
\end{figure}
To check this conclusion we recalculated the transition parameters for Fe$^{+}_{1000}$ and Fe$^{+}_{3000}$ using instead of $a_s = 5.1\text{eV}$, $a_s = 4.0\text{eV}$, the value of $\sigma_{\text{bulk}}(T = 0)$ as estimated with the help of formula [29] from the experimental surface tension of the bulk at melting. Again the resulting transition parameters listed in TABLE II approach nicely the corresponding “experimental” bulk values at $T = T_{\text{boil}}$. As our theory uses the ground-state ($T = 0$) binding energies for the clusters as input values, the theory predicts not the total surface tension but its temperature dependence, the so called “entropic part of the surface tension”. The good reproduction of the adjusted value at boiling in TABLE II as well as the true one in TABLE II shows the high quality of our method.

Fig. 4 shows the same caloric curve $T_P(\varepsilon)$ as fig. but now the number of evaporated monomers. At $\varepsilon > 1.2\text{eV}$ the system is totally vaporised into monomers. At $\varepsilon_2 \approx 0.7\text{eV}$ the character of the decay of the system changes and this can also be seen in $N_{\text{mon}}(\varepsilon)$.

FIG. 5. Micro-canonical caloric curve $T_P(E/N = \varepsilon, P)$ (full square points), number of monomers

The decay of potassium is in all details similar to that of sodium. Therefore we don’t show here the corresponding figures. The liquid–gas transition in iron is different from that of the alkali metals: Due to the considerably larger surface energy parameter $a_s$ in the liquid
drop formula of the ground-state binding energies of iron compared to alkali metals there is no multi-fragmentation of iron clusters at \( P = 1 \) atm. Iron cluster of \( N \leq 3000 \) atoms decay by multiple monomer evaporation c.f. fig. \[ ] for iron is taken as the average of \( N^{2/3}_{\text{eff}} \) given in tables \[ ] and \[ ] for iron is taken as the average of \( N^{2/3}_{\text{eff}} \) over the energy interval \( \varepsilon_1, \varepsilon_2 \).

Table \[ ] gives a summary of all theoretical parameters for the liquid-gas transition in clusters of \( N_0 = 200 \) – 3000 Na, K, and Fe atoms and compared with their experimental bulk values. The transition-temperature \( T_{\text{tr}} \), the specific latent heat \( q_{\text{lat}} \) and the entropy gain of an evaporated atom \( s_{\text{boil}} \) are well approaching the experimental bulk values. \( \Delta s_{\text{surf}} \) is the area under the back-bend of \( \beta(\varepsilon) \). \( \Delta s_{\text{surf}} N_0 \) is the total entropy loss due to the interfaces equal to

\[
\sum 4\pi r_{ws}^2 m_i^{2/3} N_i \gamma / T_{\text{tr}} = N_{\text{eff}}^{2/3} \sigma / T_{\text{tr}}.
\]

(30)

|   | \( N_0 \) | 200 | 1000 | 3000 | bulk   |
|---|----------|-----|------|------|--------|
| Na | \( T_{\text{tr}} [K] \) | 816 | 866  | 948  | 1156   |
|   | \( q_{\text{lat}} [eV] \) | 0.791 | 0.871 | 0.91 | 0.923  |
|   | \( s_{\text{boil}} \) | 11.25 | 11.67 | 11.2 | 9.267  |
|   | \( \Delta s_{\text{surf}} \) | 0.55  | 0.56  | 0.45  |        |
|   | \( N^{2/3}_{\text{eff}} \) | 39.94 | 98.53 | 186.6 | \( \infty \) |
|   | \( \sigma / T_{\text{tr}} \) | 2.75 | 5.68  | 7.07  | 7.41   |

| K  | \( T_{\text{tr}} [K] \) | 697 | 767  | 832  | 1033   |
|    | \( q_{\text{lat}} [eV] \) | 0.62 | 0.7   | 0.73  | 0.80   |
|    | \( s_{\text{boil}} \) | 10.35 | 10.59 | 10.15 | 8.99   |
|    | \( \Delta s_{\text{surf}} \) | 0.65  | 0.65  | 0.38  |        |
|    | \( N^{2/3}_{\text{eff}} \) | 32.52 | 92.01 | 187   | \( \infty \) |
|    | \( \sigma / T_{\text{tr}} \) | 3.99 | 7.06  | 6.06  | 7.31   |

| Fe | \( T_{\text{tr}} [K] \) | 2600 | 2910 | 2971 | 3158   |
|    | \( q_{\text{lat}} [eV] \) | 2.77 | 3.18  | 3.34  | 3.55   |
|    | \( s_{\text{boil}} \) | 12.38 | 12.68 | 13.1  | 13.04  |
|    | \( \Delta s_{\text{surf}} \) | 0.75  | 0.58  | 0.77  |        |
|    | \( N^{2/3}_{\text{eff}} \) | 22.29 | 65.40 | 142.12 | \( \infty \) |
|    | \( \sigma / T_{\text{tr}} \) | 6.73 | 8.87  | 16.25 | 17.49  |

TABLE I. Parameters of the liquid-gas transition at constant pressure of 1atm. in a micro-canonical system of \( N_0 \) interacting atoms and in the bulk. \( s_{\text{boil}} = q_{\text{lat}} / T_{\text{tr}} \), it is interesting that the value of \( s_{\text{boil}} \) for all three systems and at all sizes is near to \( s_{\text{boil}} = 10 \) as proposed by the empirical Trouton’s rule \[32\], \( N^{2/3}_{\text{eff}} = \sum m_i^{2/3} N_i \) and \( \sigma / T_{\text{tr}} = N_0 \Delta s_{\text{surf}} / N^{2/3}_{\text{eff}} \). The bulk values \( \sigma / T_{\text{tr}} \) are adjusted according to formula \[29\] to the input values of \( a_s \) taken for the \( T = 0 \) liquid-drop surface parameters from ref. \[31\] which we used in the present calculation for the ground-state binding energies of the fragments.
|       | $N_0$     | 1000 | 3000 | bulk |
|-------|-----------|------|------|------|
| $T_{tr}$ [K] | 2994 | 3044 | **3158** |
| $q_{lat}$ [eV] | 3.13 | 3.27 | **3.55** |
| $s_{boil}$ | 12.13 | 12.47 | **13.04** |
| $\Delta s_{surf}$ | 0.48 | 0.39 |      |
| $\frac{N_{\text{eff}}^{2/3}}{s_{\text{eff}}}$ | 65.74 | 136.78 | $\infty$ |
| $\sigma/T_{tr}$ | 7.30 | 8.62 | **8.86** |

**TABLE II.** Same as table I, but using for the ground-state liquid-drop parameter $a_s$ the value compiled by extrapolating the experimental surface tension of bulk iron at melting down to $T = 0$ (c.f. the discussion in the text) or to $T = T_{boil}$. 
Of course, the transition temperature $T_{tr}$ and the latent heat $q_{lat}$ of small clusters are smaller than the bulk values because the average coordination number of an atom at the surface of a small cluster is smaller than at a planar surface of the bulk. It is somewhat surprising that the surface tension is rising from $N_0 = 200$ to $N_0 = 3000$. One might think it should fall as $\sigma$ is expected to be proportional to the number of broken bonds per surface area. However, this is a purely static argument and does not take the entropic (fluctuational) part of $\sigma$ into account.

IV. THE RELATION TO THE METHOD OF THE GIBBS-ENSEMBLE

The alternative method to simulate the liquid–gas transition within the canonical ensemble is by the method of the Gibbs-ensemble \[19\]. As configurations with two coexistent phases separated by an interface become asymptotically suppressed, see above, in the Gibbs–ensemble method the system is sampled in two separated containers which can communicate via particle and energy exchange. In one container the system is close to the bulk liquid density and specific energy and in the other it is in the corresponding gas phase without establishing an inner, and possibly fluctuating interface. Then the transition temperature and latent heat can be determined.

The Gibbs-ensemble method is used to investigate the critical behaviour of systems interacting via short range forces like Lennard-Jones potentials, c.f. the recent article by Bruce \[33\].

The surface tension cannot be determined by the Gibbs-ensemble method. The dramatic fluctuations of the physical interfaces between both phases at $T = T_{tr}$ which can be seen e.g. in boiling water are a clear warning of the much more complicated and strongly fluctuating microscopic topology of the interfaces. They are considerably more complicated than the geometry assumed in the Gibbs-ensemble method. The surface tension is proportional to the entropy of the interface-fluctuations and consequently it depends essentially on these fluctuations.

V. ALTERNATIVE MICROSCOPIC METHODS TO CALCULATE THE SURFACE TENSION

Microscopic canonical calculations of the surface tension have been done for Lennard–Jones systems. A detailed survey is given by Salomons and Mareschal \[34\]. They discuss the following alternatives to determine the surface tension:

1. from the virial expansion of the free-energy as function of volume conserving distortions of the interface:

$$\gamma(T) = \frac{1}{2A} \left\langle \sum_{i<j} \left( 1 - \frac{3z_{ij}^2 r_{ij}\phi'(r_{ij})}{r_{ij}^2} \right) \right\rangle ,$$

21

where $r_{ij}, z_{ij}$ are the interatomic coordinates of the atoms, $A$ is the surface area and $\phi'(r_{ij})$ is the derivative of the interatomic two-body potential,
2. from histograms of the free-energy as function of potential energy changes due to volume conserving deformations.

The authors of [34] also determine the “entropic” part of the surface tension $\partial \gamma / \partial T$ either directly from a compilation of $\gamma(T)$ at various temperatures or via the fluctuation equation

$$\frac{d \gamma}{dT} = \frac{1}{T^2} \langle (\hat{U} - U)\gamma \rangle,$$

(32)

where $U$ is the total potential energy and $\hat{U}$ its mean value.

Evidently, the virial expansion works only for systems with two-body forces. So we cannot use it for metallic systems. The second method has not been tried either.

VI. CRITICISM AND NECESSARY IMPROVEMENTS OF THE COMPUTATIONAL METHOD

Several simplifications were made:

- We use classical not quantum statistics. — We do not believe that the problems we discussed in the present paper depend essentially on that difference.

- The fragments were assumed to be spherical. — This simplification means that surface degrees of freedom of the fragments are treated like bulk excitations. The size of the fragments was assumed to be independent of the excitation energy at $\varepsilon \leq \varepsilon_{\text{max}}$. Moreover, the static deformation of dimers and trimers is quite important for decay thresholds. An improvement of these approximations was not possible in the present calculation.

- Only internal excitations of the fragments of $\varepsilon \leq \varepsilon_{\text{max}}$ were allowed. — This approximation may be justified for the decay of hot finite clusters [26,21] where we argued that only a transient equilibrium of the decaying cluster over a time $\tau_{\text{equ}}$ is achieved and states which live considerably shorter should not contribute as independent decay channels. This argument does not work in the present scenario. However, we believe that highly unbound states above the boiling excitation $\varepsilon_{\text{boil}}$ in small fragments are anyway better described by assuming an independent motion of the decay products, just as we do it here. Doubling the actual value of $\varepsilon_{\text{max}}$ had in most cases only little influence on the transition parameters obtained.

- The calculation of the total intra-phase surface area is problematic. Consequently, the determination of the surface tension per surface area $\gamma$ suffers under a great uncertainty, whereas the determination of the surface entropy $\Delta s_{\text{surf}}$ is easy. The situation is complementary to the Gibbs ensemble method [19]. However, the surface entropy is crucial for the occurrence and classification of a phase transition, not its geometrical interpretation.

- The input values of the liquid drop parameters of the ground-state binding energies of the fragments given by [31] suffer from the uncertainty of the temperature of the clusters where the experimental data were taken. The bulk measurements of the surface tension suffers from many effects c.f. [23,24]:

19
The surface tension of alkali clusters might be reduced by oxygen contamination.

The volume expansion coefficient $\frac{1}{v} dv/dT$ is only known within $\pm50\%$.

$\gamma(T = 0)$ refers to the solid phase which is most likely anisotropic and cannot easily be extrapolated from the melting point.

VII. CONCLUSION

The liquid–gas transition in metals at normal pressure of 1 atm. is experimentally well explored. Therefore, it is a good test case for our new ideas and computational methods of micro-canonical thermodynamics. By allowing a system of $N = 200 - 3000$ atoms to condense or fragment into an arbitrary number of spherical fragment clusters which are internally excited to energies of $\varepsilon \leq \varepsilon_{\text{boil}}$ per atom and into an arbitrary number of free atoms under a fixed given external pressure of 1 atmosphere we directly calculated the micro-canonical caloric curve $\beta(\varepsilon) = \partial s/\partial \varepsilon = < \partial/\partial \varepsilon >$ (c.f. the detailed formula eq.(23)) by micro-canonical Monte Carlo methods (MMMC) [21]. The volume $W(E)$ of the total accessible $N$-body phase space can then be determined from $\beta_{P}(\varepsilon)$ by $s(\varepsilon) = \int \beta(\varepsilon')d\varepsilon'$ and $W(E) = \exp[NS(E/N)]$. The anomaly of the micro-canonical caloric curve $T_{P}(\varepsilon)$ signals the liquid–gas phase-transition in the finite system. The characteristic parameters $T_{tr}$, $q_{\text{lat}}$, and the surface tension $\sigma_{\text{surf}}$ approach already for $\sim 1000 - 3000$ atoms the experimentally known values of the bulk liquid–gas transition.

This result is remarkable for several reasons:

1. It proves that a phase transition of first order in a realistic continuous system can very well be seen and classified in small mesoscopic clusters without invoking the thermodynamic limit. In fact, with the non-vanishing back-bending of $T_{P}(E/N,V(E,N,P))$ the transition is easier recognisable than in the thermodynamic limit. For the 10-states Potts model we know that the micro-canonical parameters depend less on the size of the system than the canonical ones [12]. Finite size scaling for the micro-canonical transition parameters are not known in general. However, here we want to stress that there is no reason at all not to discuss phase transitions in small systems.

2. Even though the values determined for the specific surface tension $\sigma = 4\pi r_{\text{wes}}^2 \gamma$ are somewhat uncertain because of the difficulty to fix and determine the surface area, the surface entropy $N\Delta s_{\text{surf}}$ which is the relevant quantity that determines the nature of the transition can very well be calculated.

3. Even for a realistic metallic system with its long-range many-body interactions the Microcanonical Metropolis Monte Carlo simulation method (MMMC) is able to describe the liquid–gas phase transitions quite well. This is possible because we do not use molecular dynamics with a two-body Hamiltonian but use the experimental ground-state binding energies of the fragment clusters which of course take care of the metallic bonding of their constituents.

4. The intra-phase surface entropy can be microscopically calculated. (Essentially we calculated the temperature dependent part of it. The value at $T = 0$ is an input parameter of our calculation.) The surface tension per surface area can be determined if
the intra-phase area is known. For the surface entropy the fluctuation and fragmentation of the surfaces are essential. At the liquid–gas transition of sodium and potassium clusters of sizes as considered here at normal pressure the intra-phase fluctuations are mainly due to strong inhomogeneities and clusterization and not due to homogeneous stretching. This is consistent with recent experimental evidence [27,28].

5. Micro-canonical thermodynamics gives an important insight into the details of the transition which are hidden in the canonical approach. The transition in sodium is a good example: Figs. 1 and 3 show how the transition is a combination of actually two transitions, one from evaporation of very light fragments out of a large residue into a multi-fragmentation of the system into many larger pieces, and second the complete decay into a gas of monomers.

6. The success of the Microcanonical Metropolis Monte Carlo sampling method to reproduce the known infinite matter values of the liquid–gas transition is also a promising and necessary test of MMMC to describe nuclear fragmentation correctly [7,21] and to be able to get insight into the (eventually critical) behaviour of the nuclear matter liquid–gas transition. This is important as an experimental test of the predictions of the model for nuclear matter is not available.

7. The division of the macroscopic time-independent observables of the N-body system into

(a) observables which can be determined at each phase-space point, in each individual realisation of the micro-canonical ensemble: The globally conserved quantities like the energy, the number of particles, the charge, the momentum, the angular momentum, and

(b) into the thermodynamic observables which refer to the size of the ensemble, the volume $e^S$ of the energy shell of the N-body phase space, and which cannot be determined at a single phase-space point, in a single event, like the entropy, the temperature, the pressure, the chemical potential

is very essential. Also the concept of a pure phase and of a phase-transition belongs to the second group.

8. Last not least, there is a very fundamental difference between micro-canonical and canonical ensembles. This cannot be emphasised enough: As said above, if one wants to study a configuration where two-phases coexist simultaneously and are separated by an interface one has to control energy (if pressure is fixed). Thus the the micro ensemble \(\{E,P,N\}\) is the adequate ensemble at phase transitions of first order in the bulk, not the canonical, at least if the energy resources are not unlimited as they usually are.

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