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Phase transitions in “small” systems

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Abstract. Traditionally, phase transitions are defined in the thermodynamic limit only. We discuss how phase transitions of first order (with phase separation and surface tension), continuous transitions and (multi)-critical points can be seen and classified for small systems. “Small” systems are systems where the linear dimension is of the characteristic range of the interaction between the particles; *i.e.* also astrophysical systems are “small” in this sense. Boltzmann defines the entropy as the logarithm of the area $W(E,N)=\mathrm{e}^{S(E,N)}$ of the surface in the mechanical N-body phase space at total energy E. The topology of $S(E,N)$ or more precisely, of the curvature determinant $D(E,N)=\partial^2 S/\partial E^2\times\partial^2 S/\partial N^2-(\partial^2 S/\partial E\partial N)^2$ allows the classification of phase transitions without taking the thermodynamic limit. Micro-canonical thermo-statistics and phase transitions will be discussed here for a system coupled by short range forces in another situation where entropy is not extensive. The first calculation of the entire entropy surface $S(E,N)$ for the diluted Potts model (ordinary $(q=3)$-Potts model plus vacancies) on a 50×50 square lattice is shown. The regions in $\{E,N\}$ where $D>0$ correspond to pure phases, ordered resp. disordered, and $D<0$ represent transitions of first order with phase separation and “surface tension”. These regions are bordered by a line with $D=0$. A line of continuous transitions starts at the critical point of the ordinary $(q=3)$-Potts model and runs down to a branching point P_m. Along this line $\boldsymbol{\nabla} D$ vanishes in the direction of the eigenvector $\boldsymbol{v_1}$ of D with the largest eigen-value $\lambda_1\approx 0$. It characterizes a maximum of the largest eigenvalue λ_1. This corresponds to a critical line where the transition is continuous and the surface tension disappears. Here the neighboring phases are indistinguishable. The region where two or more lines with $D=0$ cross is the region of the (multi)-critical point. The micro-canonical ensemble allows to put these phenomena entirely on the level of mechanics.

PACS. 05.20.Gg Classical ensemble theory – 05.50.+q Lattice theory and statistics (Ising, Potts, etc.) – 05.70.Fh Phase transitions: general studies

1 Introduction

Nuclei, atomic clusters and astrophysical objects are not large compared to the range of their forces. Therefore, these systems are not extensive. (In the following we call systems “non-extensive” in a somewhat more general sense: If they are divided into pieces, their entropy is not the sum of the entropies of their parts in contrast to conventional extensive systems where this is assumed at least if the pieces are themselves macroscopic.) Although the largest systems possible belong to this group we call these systems “small”. But also at phase transitions in systems with short range forces does the entropy of the surface separating the different phases not scale with the size of the system. Lateron we define systems to be “small” precisely by the condition that the entropy $S(E,N,V)$ does not scale with the number of particles or the volume and especially if $S(E,N,V)$ has some convex regions.

Most applications of thermodynamics to “small” systems are more or less transcriptions from the thermodynamics of macroscopic systems, *cf.* the book by Hill [1]. Conventional thermo-statistics, however, relies heavily on the use of the thermodynamic limit ($V\rightarrow\infty|_{N/V,\text{ or }\mu\text{ const.}}$) and extensivity, *cf. e.g.* the book of Pathria [2]. This is certainly not allowed for our systems. Extensivity is nowadays considered to be an essential condition for thermodynamics to work, *cf.* Lieb and Ygnvason [3]. That the micro-canonical statistics works well also for “small” systems without invoking extensivity will be demonstrated here for finite normal systems. The use of the thermodynamic limit and of extensivity, however, is closely intervowen with the development of thermodynamics and statistical mechanics since its beginning more than hundred years ago. When we extend thermodynamics to “small” systems we should establish the formalism of thermodynamics starting from mechanics in order to remain on a firm basis. This is an old program since Boltzmann and

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Einstein [4,5]. We will see how this idea guides us to more and deeper insight into the most dramatic phenomena of thermodynamics, phase transitions. Moreover, it gives the most natural extension of thermo-statistics to some non-extensive systems without invoking any modification of the entropy like that proposed by Tsallis [6] see also [7].

In the following section we sketch a deduction of thermo-statistics from the principles of mechanics alone. Nothing outside of mechanics must be invoked. This was the starting point of Boltzmann [4], Gibbs [8], Einstein [9,5] and the Ehrenfests [10,11] at the beginning of this century. They all agreed on the logical hierarchy of the micro-canonical as the most fundamental ensemble from which the canonical, and grand-canonical ensembles can be deduced under certain conditions. According to Gibbs the latter two approximate the micro ensemble in the thermodynamic limit of infinitely many particles if the system is homogeneous. Then surface effects and fluctuations can be ignored relatively to the bulk mean values. This is the main reason why the thermodynamic limit became basic in the statistical foundation of macroscopic thermodynamics. However, it was Gibbs [12] who stressed that the equivalence of the three ensembles is not even true at phase transitions of first order, even in the thermodynamic limit.

This chapter repeats the familiar deduction of statistical mechanics as it was first formulated by Gibbs [8]. However, we will indicate at which point the main stream of logical steps towards a thermodynamics of "large" systems has to be left in order to cover also "small" and non-extensive systems.

Just a remark is neccessary here: one might think that a small system embedded in a heat bath may be described by the canonical or even the grand-canonical ensemble. A heat bath interacts with the system *via* its surface. For small systems these surface mechanisms are important. They affect the physical properties and must be specified. Certainly more must be controlled in such cases than just the mean energy (temperature) as is assumed in a canonical treatment. This would be only correct for an infinite system, with short range interactions, and if we wait an infinitely long time, then the details of the physical mechanisms in the surface contacting the system with the bath become unimportant relatively to the bulk.

The third section addresses phase transitions. First, the basics of the conventional definition of phase transitions in the thermodynamic limit ($V\to\infty|_{\mathrm{N/V,\ or\ }\mu\mathrm{\ const.}}$) by the theory of Yang and Lee [13] are reminded. Then this definition is translated into the micro-canonical picture and the source of the non-analyticities of the canonical thermodynamic potentials is traced to the topology of the micro-canonical entropy function, esp. its curvature.

In the fourth section we explain the general features of the micro-canonical phase diagram as function of fixed energy density ($e = E/V$) and particle number-($n = N/V$)/magnetization-density, at first, with the well-known example of the Ising model and the ($q = 1$) diluted Potts model. It is shown how its phase space is limited by the line of random configurations which have the maximum possible entropy. Further the region of "field driven" phase separation into spontaneously magnetized clusters (first order transition) can be well-studied in the energy-magnetization or the energy-particle number phase diagram. (Remark: the distinction between "field driven" and "temperature driven" transition makes sense only for the Ising model. Due to its intrinsic symmetry $M \to -M$ the energy-axis is also the main curvature direction for $M = 0$. This is of course not the case for systems without this symmetry.) Then the diluted Potts model with $q = 3$ is introduced. It is sketched which features of its phase diagram are to be expected in the case of a "small" system.

Section 5 gives a short discussion of the main steps of the simulation and in Section 6 the numerical results are shown. We present the first view of the entire entropy-density surface $s(e, n)$ as function of energy density (e) and particle number density (n) for the diluted ($q = 3$)-Potts model on a *finite* 2-dim lattice with "volume"[1] $V = L^2$. More insight into the phase diagram of the model is given by an overall view of the determinant of the curvature density $d(e, n)$. Various kinds of phase transitions and critical lines can be seen and classified. A subsection is addressed to the essential differences between the micro-canonical and the grand-canonical phase diagram. The information lost by the latter representation is emphasized.

The following section discusses the validity of the second law of thermodynamics in non-extensive systems with a convex $s(e, n)$. The consequences of convexity of the entropy for Weinhold's geometric interpretation of thermodynamics are discussed. It will be explained that a convexity of $S(E, N)$ is not in contradiction to the second law of thermodynamics.

Finally, our main conclusions on phase transitions in "small" non-extensive systems are summarized in Section 8.

2 On the mechanical background of thermo-statistics

An equilibrated many-body system is characterized by few macroscopic quantities:

1) its energy E, mass (number of atoms) N, volume V;
2) its entropy S;
3) its temperature T, pressure P, and chemical potential μ.

There are important qualitative differences between these three groups: All variables of the first group have a clear mechanical significance. They are conserved and well defined at each point of the N-body phase space. The internal dynamics of the system cannot leave the shell in phase space which is defined by these variables. Also entropy as the most important quantity within thermodynamics has

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[1] In the following we often skip the volume V as third variable as this is always hold fixed. Of course for finite systems the *shape* of the container matters. In the diluted Potts model we use a square lattice with periodic boundaries ("square torus").

a clear mechanical foundation since Boltzmann. His gravestone has the famous epitaph:

$$S = k\,\mathrm{ln}W$$

relating the entropy S to the size $W(E,N,V) = \epsilon_0 \mathrm{tr}\delta(E-H_N)$ of the energy (E) surface in the N-body phase space at given volume (V). Here ϵ_0 is a suitable small energy constant which does not affect any variation of the entropy, H_N is the N-particle Hamiltonian, and

$$\mathrm{tr}\delta(E-H_N) = \int \frac{\mathrm{d}^{3N}p\,\mathrm{d}^{3N}q}{N!(2\pi\hbar)^{3N}}\delta(E-H_N\{q,p\}). \quad (1)$$

The set of points on this surface defines the micro-canonical ensemble. In contrast to the conserved quantities which are defined at each phase space point, the entropy refers to the whole micro-canonical ensemble.

Remark: for a system with discrete energies E_i *e.g.* a lattice or a quantum system with energy spacing ϵ_0 one should define the micro-canonical partition sum by the number of states at this energy. When we discuss derivatives of W we imagine a suitable smoothing of this.

It is important to notice that Boltzmann's and also Einstein's formulation allows for defining the entropy entirely within mechanics by $S_{\mathrm{micro}} := \mathrm{ln}[W(E,N,V)]$. It is a single valued, non-singular, in the classical case multiply differentiable, function of all "extensive", conserved dynamical variables. No thermodynamic limit must be invoked and this definition applies to non-extensive like our "small" systems as well.

The third group of quantities which characterize the thermodynamical state of an equilibrated many-body system, temperature, pressure and chemical potential have no immediate mechanical significance. Within micro-canonical statistics they are *defined* by the derivatives of the entropy $S(E,N,V)$ *vs.* the conserved quantities:

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (2)$$

$$\mu = -T\frac{\partial S}{\partial N} \quad (3)$$

$$P = T\frac{\partial S}{\partial V}\cdot \quad (4)$$

From the mechanical point of view they are secondary, derived quantities. This difference to the two other groups of variables will turn out to be significant for "small" systems. Again, like entropy itself, these quantities characterize the whole micro-canonical ensemble, not an individual point in the N-body phase space.

Starting from this point, the conventional thermo-statistics assumes extensivity and explores the thermodynamic limit $(V \to \infty|_{N/V,\text{ or }\mu\text{ const.}})$ *cf.* [2]. This procedure follows Gibbs [8]. He introduced the canonical ensemble, which since then is the basic of all modern thermo-statistics. The link between both ensembles is established by a Laplace transform. *E.g.* the usual grand-canonical partition sum is the double Laplace transform of the micro-canonical partition sum $W(E,N,V) = \mathrm{e}^{S(E,N,V)}$:

$$\begin{aligned} Z(T,\mu,V) &= \iint_0^\infty \frac{\mathrm{d}E}{\epsilon_0}\,\mathrm{d}N\,\mathrm{e}^{-[E-\mu N-TS(E,N,V)]/T} \\ &= \frac{V^2}{\epsilon_0}\iint_0^\infty \mathrm{d}e\,\mathrm{d}n\,\mathrm{e}^{-V[e-\mu n-Ts(e,n,V)]/T}. \end{aligned} \quad (5)$$

In the thermodynamic limit it is useful to work with the energy density $e = E/V$, the particle number density $n = N/V$, and the entropy density $s = S/V$, *cf.* the right expression in equation (5).

3 Phase transitions micro-canonically

According to Yang and Lee [13] phase transitions are indicated by singularities of the grand-canonical potentials ($\propto \frac{1}{V}\mathrm{ln}[Z]$) as function of $z = \mathrm{e}^{\mu/T}$ on the positive real z-axis. These, however, can occur in the thermodynamic limit $(V \to \infty|_{\mu\text{ const.}})$ only. For finite volumes the number of particles N is finite. Consequently, Z is a sum of a finite number of powers z^N and $\frac{1}{V}\mathrm{ln}[Z]$ is analytical for positive z at any T. Are there no phase transitions in finite systems?

There are phenomena observed in finite systems which are typical for phase transitions. Sometimes this is even so in astonishingly small systems like nuclei and atomic clusters of $\sim$ 100 atoms [14–16]. In reference [17] we showed that their characteristic parameters as transition temperature, latent heat, and surface tension are – in the case of some metals – already for thousand atoms close, though of course not equal, to their known bulk values. Therefore, it seems to be fully justified to speak in these cases of phase transitions of first order.

We need an extension of thermodynamics to "small" systems which avoids the thermodynamic limit. However, here is a severe problem. The three popular ensembles, the micro-canonical, the canonical, and the grand-canonical ensembles are not equivalent for "small" systems. The energy *per particle* can fluctuate around its mean value $\langle E/N\rangle$ in the (grand-)canonical ensemble whereas the energy fluctuations are zero in the micro-canonical ensemble. Moreover, the heat capacity is strictly positive in the canonical ensembles whereas it may become *negative* in the micro ensemble. It was Gibbs himself who warned for the use of the canonical ensemble at phase transitions of first order [12]. In this situation it is certainly advisable to keep close contact with mechanics. It is helpful to realize that the fundamental micro-canonical ensemble as introduced by Boltzmann is the only one which has a clear mechanical definition [18,5] for finite systems.

To extend the definition of phase transitions by Yang and Lee to finite systems we study which feature of the micro-canonical partition sum $W(E,N,V)$ leads to singularities of the grand-canonical potentials $\frac{1}{V}\mathrm{ln}[Z]$ as function of $z = \mathrm{e}^{\mu/T}$ by the Laplace transform equation (5). In the thermodynamic limit $V \to \infty|_{\mu\text{ const.}}$ this integral can be evaluated by asymptotic methods. As far as the entropy surface $s(e,n)$ has everywhere negative curvatures the integrand of equation (5) has a single maximum. For large V the Laplace integral (r.h.s of Eq. (5)) is then dominated by the contribution of this peak. This is a stationary point $\{e_\mathrm{s},n_\mathrm{s}\}$ where $T^{-1} = \partial s/\partial e$, $\nu = -\mu/T = \partial s/\partial n$. If there is only a single stationary point then there is a one to one mapping of the grand-canonical ensemble to the micro-canonical one and energy-fluctuations disappear.

This, however, is not the case at phase transitions of first order. Here the grand-canonical ensemble contains several Gibbs states (stationary points) at the same temperature and chemical potential which contribute similarly to the integral (5). Consequently, the statistical fluctuations of e and n do not disappear in the grand-canonical ensemble even in the thermodynamic limit. This is the reason why Gibbs himself excluded phase separations [12]. Between the stationary points $s(e,n)$ *has at least one principal curvature* ≥ 0. Here van Hove's concavity condition [19] for the entropy $s(e,n)$ is violated. In the thermodynamic limit these points get jumped over by the integral (5) and $\ln[Z]$ becomes non-analytic. Consequently, we define phase transitions also for finite systems topologically by the points and regions of non-negative curvature of the entropy surface $s(e,n)$ as a function of the mechanical, conserved "extensive" quantities like energy, mass, angular momentum etc.

The central quantity of our further discussion the determinant of the curvatures of $s(e,n)$ is defined as

$$d(e,n) = \left\| \begin{matrix} \dfrac{\partial^2 s}{\partial e^2} & \dfrac{\partial^2 s}{\partial n \partial e} \\ \dfrac{\partial^2 s}{\partial e \partial n} & \dfrac{\partial^2 s}{\partial n^2} \end{matrix} \right\| = \left\| \begin{matrix} s_{ee} & s_{en} \\ s_{ne} & s_{nn} \end{matrix} \right\|. \tag{6}$$

Also critical fluctuations, *i.e.* abnormally large fluctuations of some extensive variable in the grand-canonical ensemble or the eventual divergence of some susceptibilities are micro-canonically connected to the vanishing of the curvature determinant, *e.g.* in the following examples of $d(e,n)$ or $d(e,m)$ respectively: The micro-canonical specific heat is given by:

$$c_\mathrm{micro}(e,n,V) = \left.\frac{\partial e}{\partial T}\right|_\nu = -\frac{s_{nn}}{T^2 d(e,n)}\ , \tag{7}$$

$$d = \frac{d(\beta\nu)}{d(en)} \tag{8}$$

or the isothermal magnetic susceptibility by:

$$\chi_{\mathrm{micro},T}(e,n,V) = \left.\frac{\partial m}{\partial B}\right|_T = \frac{s_{ee}}{d(e,m)}\ , \tag{9}$$

$$\text{with } s_{ee} = \frac{\partial^2 s}{\partial e \partial e} \text{ etc.} \tag{10}$$

In the case of a classical continuous system $s(e,n)$ is everywhere finite and multiply differentiable. In that case the inverse susceptibilities $[c_\mathrm{micro}(e,n,V)]^{-1}$ and $[\chi_{\mathrm{micro},T}(e,n,V)]^{-1}$ are well behaved smooth functions of their arguments even at phase transitions. Problems arise only if the susceptibilities are considered as functions of the "intensive" variables T, and ν or B [20]. In the case of lattice systems we can only assume that the inverse susceptibilities are similarly well behaved. This will be further illuminated in the Section 6.2.

Experimentally one identifies phase transitions of first order of course not by the non-analyticities of $\frac{1}{V}\ln[Z]$ but by the interfaces separating coexisting phases, *e.g.* liquid and gas, *i.e.* by the inhomogeneities of the system which become suppressed in the thermodynamic limit in the grand-canonical ensemble. This fact was early realized by Gibbs [21] and he emphasized that using S *vs.* volume at phase separation "has a substantial advantage over any other method because it shows the region of simultaneous coexistence of the vapor, liquid, and solid phases of a substance, a region which reduces to a point in the more usual pressure-temperature plane". That is also the reason why for the grand-canonical ensemble the more mathematical definition of phase transitions [13] is needed. The main advantage of the micro-canonical ensemble is that it allows for inhomogeneities as well and we can keep much closer to the experimental criteria.

Interfaces have three opposing effects on the entropy:

- An entropic gain by putting a part (N_1) of the system from the majority phase (*e.g.* solid) into the minority phase (bubbles, *e.g.* gas) with a higher entropy per particle. However, this has to be paid by additional energy ΔE to break the bonds in the "gas"-phase. As both effects are proportional to the number of particles N_1 being converted, this part of the entropy rises linearly with the additional energy.
- With rising size of the bubbles their surfaces grow. This is connected to an entropic loss (surface entropy) proportional to the interface area due to additional correlations between the particles at the interface. As the number of surface atoms is $\propto N_1^{2/3}$ this is not linear in ΔE and leads to a convex intruder in $S(E,N,V)$, the origin of surface tension [22].
- An additional mixing entropy for distributing the N_1-particles in various ways over the bubbles.

At a (multi-) critical point two (or more) phases become indistinguishable because the interface entropy (surface tension) disappears.

4 The model and its qualitative features

In this paper we want to discuss how critical and also multi-critical points manifest themselves in the micro-canonical statistics of a finite diluted Potts model.

It is helpful first to remind the main physical effects to be expected: we start with the well-known properties of the Ising model (written here as a Potts model with $q = 2$ [23]). The Hamiltonian and the magnetization are defined as:

$$H = -\sum_{i,j}^{\text{n.n.pairs}} \delta_{\sigma_i,\sigma_j} - B\sum_i \sigma_i \tag{11}$$

$$M = \sum_i \sigma_i. \tag{12}$$

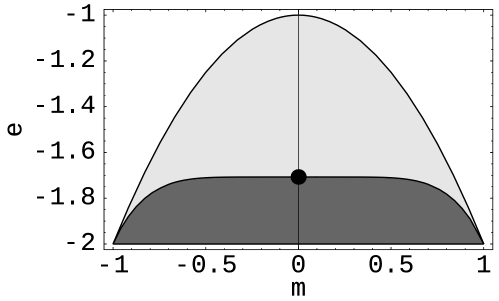

Fig. 1. Phase diagram in magnetization (m) and energy (e) per spin particle for the Ising model (ordinary ($q = 2$)-Potts model) in the thermodynamic limit. The upper parabolic line is the locus of the completely random configuration $e = -(m^2 + 1)$ with maximum entropy. The physical possible phase space points are in the two shaded regions. The darkly shaded region is the phase space of first order transition and coexistence of drops with positive and drops with negative magnetization. It is inaccessible in the grand-canonical ensemble. The dot gives the critical point ($e_\mathrm{c} = -(1 + \frac{1}{\sqrt{2}})$, $m_\mathrm{c} = 0$).

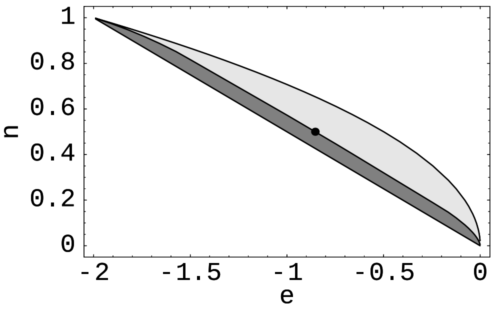

Fig. 2. Phase diagram for the diluted ($q = 1$)-Potts model in the thermodynamic limit. With the transformation $\sigma_i = 2o_i - 1$ of the two possible occupation numbers to the spin on site i and $m = \frac{1}{L^2}\sum_i \sigma_i$ this is analogous to the energy-magnetization plot of the Ising model. The dot gives the critical point ($e_\mathrm{c} \approx -0.853$, $n_\mathrm{c} = 0.5$). The darkly shaded region is the phase space of phase coexistence which is inaccessible in the grand-canonical ensemble.

The double sum runs over nearest neighbor spin-pairs only [23,24].

The two-dimensional Ising model was extensively discussed as function of temperature T and magnetic field $B = 0$ in the grand-canonical ensemble for $L \to \infty$ (thermodynamic limit) [24,2]. As known from Onsager's solution it has a continuous (second order) critical point at $B = 0$ and $\beta_\mathrm{c} = \frac{1}{T_\mathrm{c}} = 0.5\ln(\sqrt{2} + 1)$ [23,25]. Above the critical point, $T > T_\mathrm{c}$ there is a disordered phase with vanishing magnetization for $B = 0$. Below T_c there is a bifurcation of the spontaneous magnetization curve $M(T, B \to 0) = \mathrm{sign}(B)L^2 m_{\mathrm{spontan}}(T)$. As function of the extensive variables $\{E, M\}$ between $M = \pm L^2 m_{\mathrm{spontan}}(T)$ there is a whole region with phase separation which is inaccessible to the grand-canonical ensemble. Also the internal energy per lattice point $e(T, B = 0)$ is analytically known in the thermodynamic limit *cf.* [2]. This may be inverted to get the function:

$$m(e, B \to 0) = \begin{cases} 0 & , e \geq e_\mathrm{c} = -(1 + \frac{1}{\sqrt{2}}) \\ \mathrm{sign}(B) m_{\mathrm{spontan}}(e) & , e < e_\mathrm{c} \end{cases} . \tag{13}$$

Then the phase diagram in the $\{e, m\}$ plane can be drawn as in Figure 1.

At energies $e > e_\mathrm{c} = -(1 + \frac{1}{\sqrt{2}})$ one has a disordered (“gas”) phase. At $e_\mathrm{c} = -(1 + \frac{1}{\sqrt{2}}), m = 0$ there is a critical point of continuous transition with vanishing surface tension. From here an inhomogeneous region of condensed phase starts towards lower energies (several clusters of positive or negative magnetization coexist separated by interfaces). In the thermodynamic limit the overall magnetic field $\langle B \rangle$ vanishes here. This region is bordered by the curve $m_{\mathrm{spontan}}(e, B = 0)$. Approaching this border from inside with fixed e and rising m, the clusters with the opposite magnetization get depleted and the surfaces between the clusters disappears. (However, even when there are no clusters of the wrong magnetization there should still be fluctuations with the other, wrong magnetization because these states have a nonvanishing entropy. There is a general impossibility to distinguish a phase separation from a fluctuation within an individual configuration. This is a realistic example for the definition of a phase as a property of the entire ensemble only.) This region of phase separation is darkly shaded in Figure 1 and is inaccessible to the grand-canonical ensemble.

The following Gedanken-experiment may illuminate why this region cannot be accessed in the grand-canonical ensemble: suppose one prepares the system at a sharp energy and magnetization in the region with positive curvature. Then one puts the system into a heat bath with temperature T_{tr} and chemical potential (magnetic field) μ_{tr} where it will be suddenly exposed to energy- and magnetization- (particle number) fluctuations of arbitrary size. Because of the positive curvature of its entropy the system is unstable and will receive or loose sufficient energy to convert entirely into the gas or entirely into the solid phase where its free energy is lower. The latent heat which is neccessary for this will be spended (absorbed) by the bath.

The Ising model can be modified by the transformation $o_i = \frac{1}{2}(\sigma_i + 1)$ and $H_{lg} = -\frac{1}{2}\sum_{i,j}\delta_{o_i,+1}\delta_{o_j,+1}$ into the diluted ($q = 1$)-Potts model. Here the lattice points with $o_i = 0$ are vacancies. Figure 2 shows the phase diagram of the diluted ($q = 1$)-Potts model corresponding to the phase diagram of the Ising model as discussed above. The three lines indicate (from left to right) the ground state ($e_0(n) = -2n$), the critical line, and the line of random (maximum entropy) configuration ($e_{\max}(n) = -2n^2$). The dot gives the critical point which corresponds to the critical end point of the phase separation in the liquid-gas transition. Between the ground state and the critical line is the $\{e, n\}$-region (darkly shaded) of first order phase transition with phase separation. Here the system prefers inhomogeneous configurations with droplets enbedded in the gas. This corresponds to the above mentioned similar inhomogeneous region of the Ising model at energies below the Ising critical point ($e_\mathrm{c} = -(1 + \frac{1}{\sqrt{2}})$,$m_\mathrm{c} = 0$), where clusters of positive magnetization and negative magnetization coexist. In the thermodynamic limit we expect the micro-canonical entropy $s(e,n)$ to be flat in the shaded region. The whole darkly shaded region of inhomogeneities is not accessible in the grand-canonical ensemble. This is a striking example of the dramatic loss of information when the grand-canonical ensemble is addressed to phase transitions. Above the critical line we have the region of the pure disordered phase. Here $s(e,n)$ is concave.

In the following we investigate the 3-states diluted Potts model now on a finite 2-dim (here $L^2 = 50^2$) lattice with periodic boundaries in order to minimize effects of the external surfaces of the system. The model is defined by the Hamiltonian:

$$H = -\sum_{i,j}^{\text{n.n.pairs}} o_i o_j \delta_{\sigma_i,\sigma_j} \tag{14}$$

$$n = L^{-2}N = L^{-2}\sum_i o_i.$$

Each lattice site i is either occupied by a particle with spin $\sigma_i = 1, 2,$ or 3 or empty (vacancy). The sum is over neighboring lattice sites i, j, and the occupation numbers are:

$$o_i = \begin{cases} 1, & \text{spin particle in site } i \\ 0, & \text{vacancy in site } i. \end{cases} \tag{15}$$

This model is an extension of the ordinary ($q = 3$)-Potts model to allow also for vacancies. At zero concentration of vacancies ($n = 1$), the system has a continuous phase transition at $e_\mathrm{c} = 1+\frac{1}{\sqrt{q}} \approx 1.58$ [26,2]. With rising number of vacancies the probability to find a pair of particles at neighboring sites with the same spin orientation decreases. The inclusion of vacancies has the effect of an increasing effective $q_\mathrm{eff} \geq 3$. This results in an increase of the critical energy of the continuous phase transition with decreasing n and provides a line of continuous transition, which is supposed to terminate when q_eff becomes larger than 4. Here the transition becomes first order.

At smaller energies the system is in one of three ordered phases (spins predominantly parallel in one of the three possible directions). We call this the "solid" phase. This scenario gets full support by our numerical findings in the next sections.

In the following, we will show for the case of the diluted ($q = 3$)-Potts model how the total micro-canonical entropy surface $S(E, N)$ uncovers first order phase transitions, continuous phase transitions, critical, and multi critical points even for small systems and non-extensive systems. This is an extension of previous work on systems with one thermodynamic degree of freedom like the fragmentation phase transition in highly excited nuclei [14], in atomic clusters [17], and in the ordinary Potts model [22,27]. The main purpose for the study of systems with two thermodynamic degrees of freedom like $\{E, N\}$ is the possibility to localize (multi-)critical points.

5 Simulation method

The simulation methods proceeded in two steps: We first covered all space $\{E = e \times L^2, N = n \times L^2\}$, $L = 50$ by a mesh with about 1000 knots with distances of $\Delta e = 0.08$ and $\Delta n = 0.04$. At each knot $\{e_i, n_k\}$ we performed micro-canonical simulations ($\approx 2 \times 10^8$ events) to get a histogram of the probabilities $P(e_i, n_k) = \mathrm{e}^S$ for the system to be distributed in the narrow region $(E_i \pm 4) \times (N_k \pm 4)$ of phase space. Local derivatives $\beta = (\partial S(E,N)/\partial E)_N$, $-\beta\mu = \nu = (\partial S(E,N)/\partial N)_E$ in each histogram give a first "measurement" of the "intensive" quantities. These are used to interpolate β, ν over the gaps between the knots of our mesh *cf.* [28].

1) From the first interpolation we get an estimate β_0, ν_0 for the center of any region $\{\Delta e \times \Delta n\}$.
2) In a second iteration step we sample $P_1(e, n) = P(e, n)\,\mathrm{e}^{-\beta_0 L^2(e-\mu_0 n)}$ in a broader $\{e, n\}$ domain. This is chosen to touch or overlap the next neighboring region. This way a dense covering of the entire $\{e, n\}$ space is achieved.
3) A fourth order regression fit $f_4(e, n)$ in e and in n to $\ln[P_1(e, n)]$ is performed, from which we determine the two principal axes of curvature λ_1, λ_2 of $s(e, n)$ and then can rotate if desired the frame of the basic rectangle in $\{e, n\}$ to be parallel to the main curvature axes.
4) The last step is then a longer and extensive sampling of $P_2(e, n) = \mathrm{e}^{-f_4(e,n)} P_1(e, n)$ in the new basic rectangle.
5) Eventually one has to recycle steps 3 and 4 a few times up to the time one obtains a sufficiently uniform covering of $P_2(e, n)$.
6) At the end on gets back the original by $P(e, n) = \mathrm{e}^{f_4(e,n)}\mathrm{e}^{\beta_0 L^2(e-\mu_0 n)} P_2(e, n)$.

We obtain a broad and uniform covering of the whole $\{e, n\}$ space. This way one gets the most effective (and fast) "measurement" of $s(e, n)$, $\beta(e, n)$, $\nu(e, n)$ up to all third order derivatives of $s(e, n)$ *e.g.* $s_{ee}(e, n)$ or $s_{een}(e, n)$ etc.. Technical details of our method will be published in [29].

6 Results

Figure 3 shows $s_\mathrm{micro}(e, n)$. Grid lines are in the direction $[e - e_0(n)]/[e_\mathrm{max}(n) - e_0(n)] = \text{const}$ and $n = \text{const}$, ($e_0(n) = -2n, e_\mathrm{max}(n) = -\frac{2n^2}{q}$). The grey levels are determined in Figure 4: regions above $\widehat{CP_mB}$: concave, $d > 0$, pure phase (disordered, gas), in the triangle AP_mC concave, pure phase, ordered (solid); below $\widehat{AP_mB}$: convex, $d < 0$, phase-separation, first order; at the dark lines like $\widehat{AP_mB}$ we have $d(e, n) = 0$: these are termination lines of the first order transition; medium dark lines like $\widehat{CP_m}$: $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$, here the curvature determinant has an extremum in the direction of the largest curvature eigenvector $\mathbf{v}_1$ (remember: in the normal concave region of $s(e, n)$ the curvatures are both negative. A vanishing or

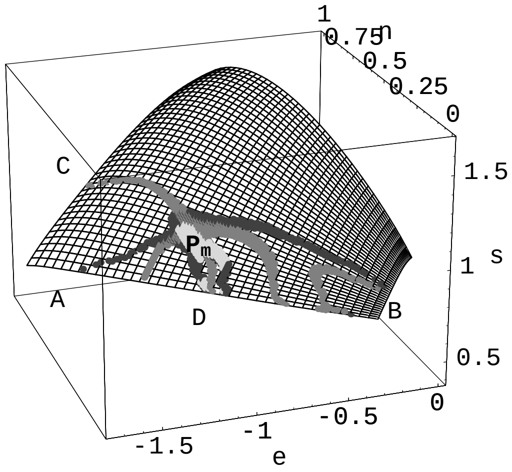

Fig. 3. Entropy $s_{\text{micro}}(e,n)$.

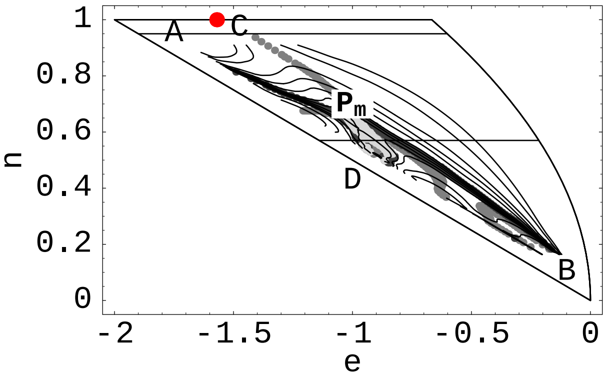

Fig. 4. Contour plot of the determinant of curvatures $d(e,n)$ defined in equation (16). The grey levels are as in Figure 3: regions above $\widehat{CP_mB}$: concave, $d>0$, pure phase (disordered, gas), in the triangle AP_mC concave, pure phase (ordered, solid); below $\widehat{AP_mB}$: convex, $d<0$, phase-separation, first order; at the dark lines $\widehat{AP_mB}$ we have $d(e,n)=0$: termination lines of the first order transition; medium dark lines *e.g.* $\widehat{CP_m}$.: $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$; here the curvature determinant has a minimum in the direction of the largest curvature eigenvector $\mathbf{v}_1$; in the cross-region (light gray) we have: $d=0 \wedge \boldsymbol{\nabla} d = \mathbf{0}$ this is the locus of the multi-critical point P_m where $s(e,n)$ is flat up to at least third order in Δe and Δn. The two horizontal lines give the positions of the two cuts shown in Figures 5, 6.

even small positive curvature is an abnormal large curvature); in the cross-region (light gray without grid) we have: $d=0 \wedge \boldsymbol{\nabla} d = \mathbf{0}$ this is the locus of the multi-critical point P_m where $s(e,n)$ is (numerically) flat up to at least third order in Δe and Δn.

The convex region of phase separation corresponds to the similar region in the Ising lattice gas, respectively the original Ising model as function of magnetization, *cf.* the darkly shaded region in Figure 2. The main new feature of the phase diagram of the diluted ($q=3$)-Potts model compared to the diluted ($q=1$)-Potts model is the critical line from C to P_m.

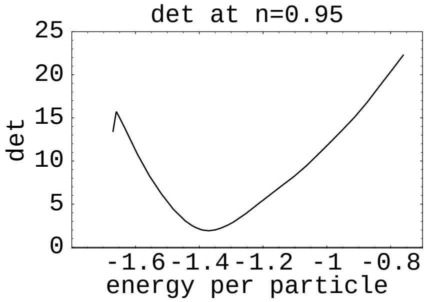

Fig. 5. Cut through the determinant $d(e,n)$ along the line shown in Figure 4 at const. $n=0.95$, through the critical line $\widehat{CP_m}$ close to the critical point C of the ordinary Potts model ($n \sim 1$).

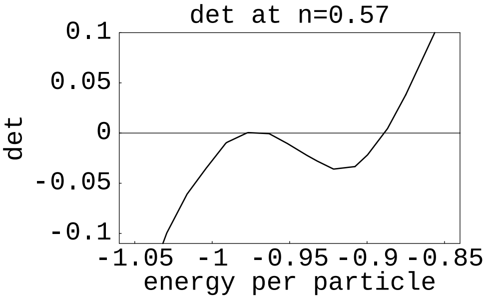

Fig. 6. Cut through the determinant $d(e,n)$ along the line shown in Figure 4 at const. $n=0.57$, slightly below the multi-critical region. There are several zero points of the determinant of curvatures: The left one is simultaneously a maximum with $\boldsymbol{\nabla}\ d=0$ and consequently critical as discussed above.

In Figure 4 the determinant of curvatures of $s(e,n)$:

$$d(e,n) = \left\| \begin{matrix} \dfrac{\partial^2 s}{\partial e^2} & \dfrac{\partial^2 s}{\partial n \partial e} \\ \dfrac{\partial^2 s}{\partial e \partial n} & \dfrac{\partial^2 s}{\partial n^2} \end{matrix} \right\| = \left\| \begin{matrix} s_{ee} & s_{en} \\ s_{ne} & s_{nn} \end{matrix} \right\| = \lambda_1 \lambda_2 \tag{16}$$

is shown. On the diagonal we have the ground-state of the 2-dim Potts lattice-gas with $e_0 = -2n$, the upper-right end is the complete random configuration (here without contour lines), with the maximum allowed excitation $e_{\text{rand}} = -\frac{2n^2}{q}$. In the region above the line $\widehat{CP_mB}$ we have the disordered, “gas”. Here the entropy $s(e,n)$ is concave ($d>0$), both curvatures are negative (we have always the smaller one $\lambda_2<0$). This is also the case inside the triangle AP_mC (ordered, “solid” phase). In these regions the Laplace integral equation (5) has a single stationary point. They correspond to pure phases.

Below $\widehat{AP_mB}$ $s(e,n)$ is convex ($d<0$) *cf.* Figure 7, corresponding to phase-separation, first order. At these $\{e,n\}$ the Laplace integral (5) has no stationary point. Here we have a separation into coexisting phases, *e.g.* solid and gas. Due to the inter-phase surface tension or the negative contribution to the entropy by the additional correlations at the phase boundaries (surface), $s(e,n)$ has a convex intruder with positive largest curvature.

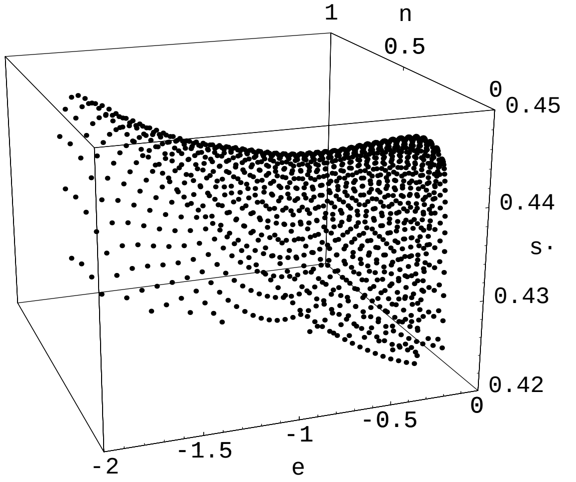

Fig. 7. Entropy surface $s' = s(e,n) - 1.85(e - e_0) - 3.61(n - n_0)$ along a strip with constant $\beta = 1.85$ (roughly parallel to the ground state $e_0(n) = -2n$ through the region of phase separation).

In [22,17] it is shown that the depth of the convex intruder in $s(e,n)$ gives the surface tension.

At the dark lines like $\widehat{AP_mB}$ we have $d(e,n) = 0$. These are the termination lines of the first order transition. At these lines one of the two phases is depleted and beyond all particles are in the other phase (solid or gas respectively).

Along the medium dark lines like $\widehat{P_mC}$ we have $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$, here the curvature determinant has a minimum in the direction of the largest curvature eigenvector $\mathbf{v}_1$. The line $\widehat{P_mC}$ goes towards the critical point of the ordinary ($q = 3$)-Potts model at $e = -1.58$, $n = 1$. It corresponds to a critical line of second order transition which terminates at the multicritical "point" P_m. It is a deep valley in $d(e,n)$ *cf.* Figure 5 which rises slightly up towards C. On the level of the present simulation we cannot decide whether this rise is due to our still finite, though otherwise sufficient, precision or is a general feature of finite size. (The largest curvature λ_1 of $s(e,n)$ has a local maximum with $\lambda_1 \lesssim 0$, or $d \gtrsim 0$). Because of our finite interpolation width of $\Delta e \sim \pm 0.04$, $\Delta n \sim \pm 0.02$ it might be that this valley of $d(e,n)$ gets a little bit filled up from its sides and the minimum is rounded, *cf.* Figure 5. The valley converts below the crossing point P_m into a flat ridge inside the convex intruder of the first order lattice-gas transition see also Figure 7.

In the cross-region (light gray in Fig. 4) we have: $d = 0 \wedge \boldsymbol{\nabla} d = \mathbf{0}$. This is the locus of the multi-critical point P_m where $s(e,n)$ is (numerically) flat up to at least third order in both directions Δe and Δn. It is at $e_m \sim -1$, $n_m \sim 0.6$ or $\beta_m = 1.48 \pm 0.03$, $\nu_m = 2.67 \pm 0.02$. Naturally, P_m spans a much broader region in $\{e,n\}$ than in $\{\beta,\nu\}$, remember $s(e,n)$ is flat near P_m. This situation reminds very much the well known phase diagram of a ^{3}He –^{4}He mixture in temperature *vs.* mole fraction of ^{3}He *cf.* Figure 3 in reference [30].

Figure 7 gives a 3D-view of the entropy-surface $s(e,n) - \beta_0(e - e_0) - \nu_0(n - n_0)$ along a broad strip with constant $\beta = -1.85$ (through the region of phase separation, roughly parallel to the ground state $e_0(n) = -2n$). The overall convex intruder of the first order transition is well seen. In its middle the narrow ridge where $s(e,n)$ is again concave can be imagined. This is the origin of the medium dark line $\widehat{P_mD}$ in Figures 3 and 4.

6.1 On the topology of curvatures

The two eigenvalues of the curvature matrix (16) are:

$$\lambda_{1,2} = \frac{s_{ee} + s_{nn}}{2} \pm \frac{1}{2}\sqrt{(s_{ee} + s_{nn})^2 - 4d} \tag{17}$$

and the corresponding eigenvectors are:

$$\mathbf{v}_\lambda = \frac{1}{\sqrt{(s_{ee} - \lambda)^2 + s_{en}^2}} \begin{pmatrix} -s_{en} \\ s_{ee} - \lambda \end{pmatrix}. \tag{18}$$

At critical points the following conditions hold:

$$d = -\frac{\partial(\beta\nu)}{\partial(en)} = L^2 D = 0 \tag{19}$$

$$s_{ee}s_{nn} = s_{en}^2. \tag{20}$$

Here the directions β =const. and $\mu =$ const. are parallel and we have:

$$\left.\frac{\partial\beta}{\partial e}\right|_\nu = \frac{d}{s_{nn}} = 0 \tag{21}$$

$$\left.\frac{\partial\nu}{\partial n}\right|_\beta = \frac{-d}{s_{ee}} = 0. \tag{22}$$

$$\lambda_1 = 0 \tag{23}$$

$$\lambda_2 = s_{ee} + s_{nn} \tag{24}$$

$$\mathbf{v}_{\lambda=0} = \frac{1}{\sqrt{s_{ee}^2 + s_{en}^2}} \begin{pmatrix} -s_{en} \\ s_{ee} \end{pmatrix} \tag{25}$$

$$\mathbf{v}_{\lambda\leq 0} = \frac{1}{\sqrt{s_{nn}^2 + s_{en}^2}} \begin{pmatrix} s_{en} \\ s_{nn} \end{pmatrix}. \tag{26}$$

The vanishing of d is not sufficient for criticality. Physically, it means that the surface entropy (tension) and with it the interface separating coexistent phases disappears. This, however, can also signalize a depletion of one of the two phases. At a critical end-point, however, the interface disappears at a non vanishing number of atoms in each of the two phases, *i.e.* in an infinitesimal neighborhood of a critical point, d must remain zero. In a topologically formulation a critical end-point of first order transition is at:

$$d = 0 \tag{27}$$

and

$$\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0. \tag{28}$$

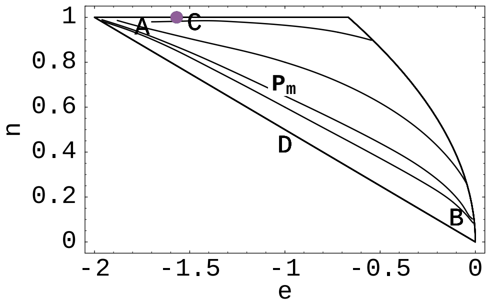

Fig. 8. Direction of the largest principal curvature $\mathbf{v}_1$.

This is a generalization of the well-known condition for a continuous transition in one dimension: the simultaneous vanishing of $\beta'(e) = 0$ and of the curvature of $\beta(e)$, $\beta''(e) = 0$.

Figure 8 shows a map of some trajectories which follow the eigen-vector $\mathbf{v}_1$ with the largest curvature eigen-value λ_1. In the region of the convex intruder ($\lambda_1 > 0$) *i.e.* the region of phase-separation $\mathbf{v}_1$ is $\sim$ parallel to the ground state $e = -2n$. Also the lines of $\beta =$ const. and $\mu =$ const. follow approximately this direction. Their Jacobian $\partial(\beta\nu)/\partial(en) = d(e,n)$ is negative but small. This reminds of the situation in the thermodynamic limit where this region of phase coexistence is flat, both intensive variables are constant and the Jacobian $d \to -0$. One can also see in Figure 8 how the direction of the largest curvature $\boldsymbol{v}_1$ turns into the e-direction when one approaches the critical point C of the ordinary ($q = 3$)-Potts model at $n = 1$.

Inspection of Figure 4 shows that along the line $\widehat{CP_m}$ of second order transition $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$, *i.e.* $d(e,n)$ has a deep and sharp valley. This line is the locus of a minimum of d in the direction of the largest eigenvalue $\mathbf{v}_1$ of the curvature. In the direction of $\widehat{CP_m}$ the determinant $d(e,n)$ is slightly growing towards the ordinary Potts critical point C. Figure 9 shows an original narrow histogram of $s(e,n)$, ($\Delta e = 0.08$ and $\Delta n = 0.04$) on the line $\widehat{CP_m}$ near to the point C which shows that the curvature of $s(e,n)$ is rather small in the direction of the larger curvature eigenvector $\mathbf{v}_1$.

At $n = 1$ we know that for an infinite system the ordinary ($n = 1$) three states Potts model has a second order transition at $e = -1.58$ where the curvature of $s(e)$ vanishes, $s_{ee} = 0$; *i.e.* the component $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d$ of $\boldsymbol{\nabla} d$ indicates nicely the locus of the second order “temperature driven” transition of the ordinary Potts model.

6.2 The information lost in the grand-canonical ensemble

Figure 10 explains what happens if one plots the entropy s *vs.* the “intensive” quantities $\beta = \partial S/\partial E$ and $\nu = \partial S/\partial N$ as one would do for the grand-canonical ensemble: as there are several points E_i, N_k with identical β, ν, $s_{\mathrm{micro}}(\beta,\nu)$ is a multivalued function of β, ν. Here the entropy surface $s_{\mathrm{micro}}(e,n)$ is folded onto itself. In the projection in Figure 10, these points show up as a black critical line (dense region). Here this black line continues over the multi-critical point P_m towards C indicating the direction to the critical point of the ordinary $q = 3$ Potts model at $n = 1$ (zero vacancies). Between P_m and C the slopes

$$\left.\frac{\partial s}{\partial \beta}\right|_{\nu} = \frac{1}{d}[\beta s_{nn} - \nu s_{ne}] \tag{29}$$

or

$$-\left.\frac{\partial s}{\partial \nu}\right|_{\beta} = \frac{1}{d}[\beta s_{en} - \nu s_{ee}] \tag{30}$$

are negative large but finite.

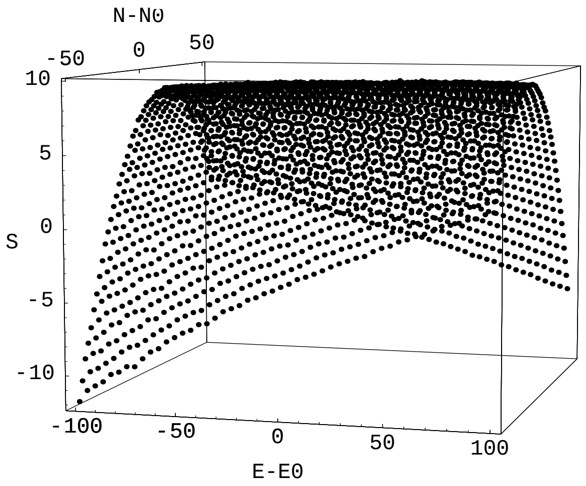

Fig. 9. Histogram of $s(e,n) - (e - e_0)\beta(e_0,n_0) - (n - n_0)\nu(e_0,n_0)$ at $e_0 = -1.48, n_0 = 0.94$ in the rectangle $e_0 \pm 0.04$, $n_0 \pm 0.02$ viewed in the direction of the valley $\widehat{P_mC}$ of $d(e,n)$, the second-order critical line towards the critical point C of the ordinary $q = 3$-Potts model at $e = -1.58$. The approximate vanishing of the largest curvature in the direction $\mathbf{v}_1$ (pointing from left to right) at this point e_0, n_0 is clearly seen.

The information given by the projection would be all information which can be obtained from the conventional grand-canonical entropy $s(T,\mu,V)$, if we would have calculated it from the Laplace transform (Eq. (5)). The shaded region will be lost.

The upper part of Figure 10 shows $s_{\mathrm{micro}}(\beta,\nu)$ in a three-dimensional plot. The lines building the entropy surface are lines of equal β. The images of the points A, D, B, C defined in Figure 4 are roughly indicated. The convex intruder between the lines $\widehat{AP_mB}$ and $\widehat{ADB}$ becomes folded back and can here be seen only from its side (shadowed). It is jumped over in equation (5) and gets consequently lost in $Z(T,\mu)$. This demonstrates the far more detailed insight into phase transitions and critical phenomena obtainable by micro-canonical thermo-statistics which is not accessible by the canonical treatment, *cf.* the similar arguments of Gibbs [21].

In the next two figures the cross-section through $s(\beta,\nu)$ at constant β is shown in Figure 11 below the multi-critical point $\beta_m = 1.48$ and in Figure 12 above it. The latter clearly shows the back-bending of $s(\beta,\nu)$.

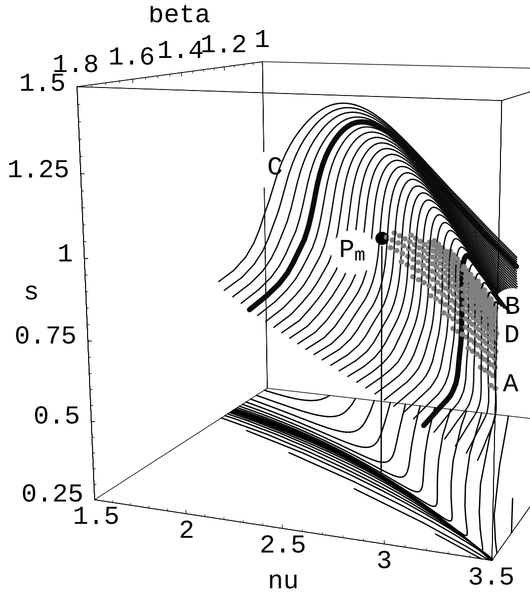

Fig. 10. Plot of the entropy $s_{\mathrm{micro}}(\beta,\nu)$ as function of the "intensive" variables ($\nu = -\beta\mu$) in the figure labeled as "nu" and β is called "beta". The lines which build the surface are lines for $\beta = \mathrm{const}$. The two bold ones indicate the cuts shown in Figures 11 and 12. The positions of the points A, D, B, C defined in Figure 4 are only roughly indicated. The convex intruder where $s_{\mathrm{micro}}(\beta,\nu)$ becomes multi-valued as function of $\nu > \nu_{P_m}$ and $\beta > \beta_{P_m}$ is indicated by shadowing. This corresponds to the first order transition. At the bottom the projection of the entropy surface onto the $\{\beta,\nu\}$ plane is shown as contour plot. The convex part (region of phase-separation) is hidden behind the dark "critical" line.

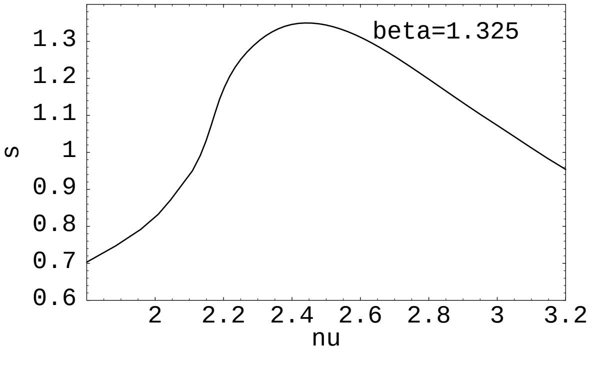

Fig. 11. Plot of the entropy $s(\beta = 1.325, \nu)$.

7 Convex entropy — Violation of the Second Law?

At this point it is worth-wile to spend some words on a popular misunderstanding connected with the eventual convexity of the entropy as function of "extensive" quantities like the energy: The convex parts of $S(E,N)$ violate van Hove's concavity condition [19,31].

One may believe that this is also in contradiction to the second law of thermodynamics: At a convex region of $S(E,N)$ a split of the system into two pieces with entropies $S_1(E_1,N_1)$ and $S_2(E_2,N_2)$ would yield $S_1(E_1,N_1) + S_2(E_2,N_2) > S(E_1+E_2,N_1+N_2)$. So the system seems to gain entropy by splitting.

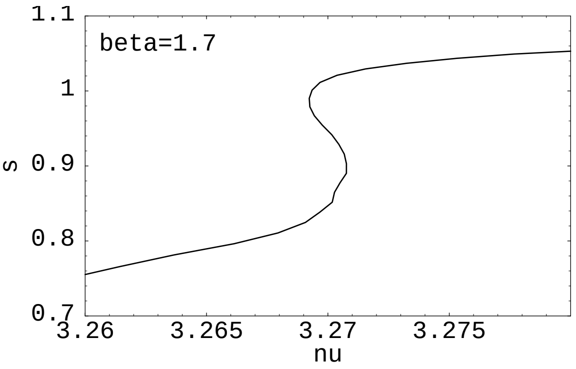

Fig. 12. Plot of the entropy $s(\beta = 1.7, \nu)$.

This, however, is an error. The Boltzmann entropy as defined in Section 2 is already the logarithm of the sum over all possible configurations of the system at the given energy. The split ones are a subset of these. Their partial phase space W_{split} is of course $\le$ the total W. The entropy $S_{\mathrm{split}} = \ln(W_{\mathrm{split}})$ is $\le$ the total entropy. Evidently, the split system looses some surface entropy S_{surf} at the separation boundary due to additional correlations imposed on the particles at the boundary, see the discussion in Section 3. The entropy after split is consequently:

$$\begin{aligned} S_{\mathrm{split}} &= S_1(E_1,N_1) + S_2(E_2,N_2) - S_{\mathrm{surf}} \\ &\le S(E_1+E_2,N_1+N_2). \end{aligned} \tag{31}$$

It is a typical finite size effect. S_{surf}/V vanishes in the limit $V \to \infty$ for interactions with finite range. The entropy is non-extensive for finite systems but becomes extensive in the limit, and van Hove's theorem [19] is fulfilled. This is of course only under the condition that $\lim_{V\to\infty} S_{\mathrm{surf}}/V = 0$.

In general this is of course a trivial conclusion: an additional constraint like an artificial cut of the system can only reduce phase space and entropy. The second law is automatically satisfied in the Boltzmann formalism whether S is concave or not, whether S is "extensive" or not.

A positive (wrong) curvature introduces problems to the geometrical interpretation of thermodynamics as formulated by Weinhold [32,33] which relies on the non-convexity of $S(E,N)$. Weinhold introduces a metric like

$$g_{ik} = -\frac{\partial^2 S}{\partial X^i \partial X^k} \tag{32}$$

where we identify:

$$\begin{aligned} X^1 &= E \\ X^2 &= N. \end{aligned}$$

The thermodynamic distance is defined as:

$$\Delta_{a,b} = \sqrt{[X^i(a) - X^i(b)]g_{ik}[X^k(a) - X^k(b)]}. \tag{33}$$

Evidently, a negative metric g_{ik} is here not allowed. Of course Weinhold's theory does not apply to finite systems with phase transitions.

8 Conclusion

Micro-canonical thermo-statistics describes how the entropy $s(e,n)$ as defined entirely in mechanical terms by Boltzmann depends on the conserved “extensive” variables: energy e, particle number n, angular momentum L etc. It is well-defined for finite systems without invoking the thermodynamic limit. Thus in contrast to the conventional theory, we can study phase transitions also in “small” systems or other non-extensive systems. In this simulation we could classify phase transitions in a “small” system by the topological properties of the determinant of curvatures $d(e,n)$, equation (16) of the micro-canonical entropy-surface $s(e,n)$:

- A single stable phase by $d(e,n) > 0$.
- A transition of first order with phase separation by $d(e,n) < 0$. The depth of the intruder is a measure of the inter-phase surface tension [34,22]. This region is bounded by a line with $d(e,n) = 0$. On this line P_m is a critical end-point where additionally $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$ in the direction of the eigenvector of $d(e,n)$ with the largest eigenvalue λ_1.
- There, the transition is continuous (“second order”) with vanishing surface tension, and no convex intruder in $s(e,n)$. Here two neighboring phases become indistinguishable, because there are no interfaces. However, we found a further line ($\widehat{P_mC}$, critical) with $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$ which does not border a region of negative $d(e,n)$. Presumably $d(e,n)$ should be 0 also. This needs further tests in other systems. It may also be that these lines signalize transitions of first order in other, but hidden conserved degrees of freedom.
- Finally a multi-critical point P_m where more than two phases become indistinguishable by the branching of several lines with $d = 0$ or with $\mathbf{v}_1 \cdot \boldsymbol{\nabla} d = 0$ to give a flat region with additionally $\boldsymbol{\nabla} d = \mathbf{0}$.

Our classification of phase transitions by the topological structure of the micro-canonical Boltzmann entropy $s(e,n)$ is close to the natural experimental way to identify phase transitions of first order by the inhomogeneities of phase separation boundaries. This is possible because the micro-canonical ensemble does not suppress inhomogeneities in contrast to the grand-canonical one, as was emphasized already by Gibbs [21]. Inter-phase boundaries are reflected in “small” systems by the convex intruder in the entropy surface. With this extension of the definition of phase transitions to “small” systems there are remarkable similarities with the transitions of the bulk. Moreover, this definition agrees with the conventional definition in the thermodynamic limit (of course, in the thermodynamic limit the largest curvature λ_1 approaches 0 from above at phase transitions of first order). The region of phase separation remains inaccessible in the conventional grand-canonical ensemble.

We believe, however, that the various kind of transitions discussed here have their immediate meaning in “small” and non-extensive systems independently whether they are the same in the thermodynamic limit (if this then exist) or not. For systems like the Potts model that have a thermodynamic limit it might well be possible that the character of the transition changes towards larger system size.

The great conceptual clarity of micro-canonical thermo-statistics compared to the grand-canonical one is clearly demonstrated. Not only that, we showed that the micro-canonical statistics gives more information about the thermodynamic behaviour and more insight into the mechanism of phase transitions than the canonical ensemble: About half of the whole $\{E,N\}$ space, the intruder of $S(E,N)$ or the region between the ground state and the line $\widehat{AP_mB}$ in Figure 4, gets lost in conventional grand-canonical thermodynamics. Without any doubts this contains the most sophisticated physics of this system. We emphasized this point already in [28] there, however, with still limited precision. Due to our refined simulation method this could be demonstrated here with uniformly good precision in the whole $\{E,N\}$ plane. Finally, we should mention that micro-canonical thermo-statistics allowed us to compute phase transitions and especially the surface tension in realistic systems like small metal clusters [17]. Our finding clearly disproves the pessimistic judgement by Schrödinger [35] who thought that Boltzmann’s entropy is only usefull for gases. A recent application of micro-canonical thermo-statistics to thermodynamically unstable, collapsing systems under high angular momentum is found at [36].

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