Phase Transitions in “Small” Systems
– A Challenge for Thermodynamics –

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Traditionally, phase transitions are defined in the thermodynamic limit only. We propose a new formulation of equilibrium thermo-dynamics that is based entirely on mechanics and reflects just the geometry and topology of the N-body phase-space as function of the conserved quantities, energy, particle number and others. This allows to define thermo-statistics without the use of the thermodynamic limit, to apply it to “Small” systems as well and to define phase transitions unambiguously also there. “Small” systems are systems where the linear dimension is of the characteristic range of the interaction between the particles. Also astrophysical systems are “Small” in this sense. Boltzmann defines the entropy as the logarithm of the area \( W(E, N) = e^{S(E, N)} \) 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 \( D(E, N) = \partial^2 S/\partial E^2 * \partial^2 S/\partial N^2 - (\partial^2 S/\partial E \partial N)^2 \) allows the classification of phase transitions without taking the thermodynamic limit. The topology gives further a simple and transparent definition of the order parameter.

Attention: Boltzmann’s entropy \( S(E) \) as defined here is different from the information entropy c.f. [1] and can even be non-extensive and convex.

1. Fundamentals of thermo-statistics

Conventional (canonical) thermo-statistics addresses large (in the thermodynamical limit), homogeneous systems. Extensivity (i.e. if the system is divided into pieces their energy and entropy scale with the size of the pieces) is an important condition c.f.[2].

Here we propose a new, easy, and more transparent access to the thermodynamics and especially to phase transitions which applies also to “Small” systems. Only the static geometrical and topological properties of the volume of energy-shell of the N-body phase-space is investigated. No thermodynamic limit has to be invoked. It is obvious that only by this extension of thermo-statistics it is possible to discuss phase transitions in nuclei, atomic clusters and astro-physical systems.

First order transitions are distinguished from continuous transitions by the appearance of phase-separations. Here the system becomes inhomogeneous and coexistent phases are separated by interfaces. Any system at phase separation is necessarily inhomogeneous and non-extensive. This is also the case for the majority of systems in nature: hot nuclei, hot...
atomic clusters and the real big ones: astrophysical systems under self-gravity. They are inhomogeneous even away from phase transitions. There the thermodynamic limit makes no sense. We will henceforth call these systems “Small” or “non-extensive”.

To describe these non-extensive systems, we have to go back to pre-Gibbsian times. Boltzmann’s famous epitaph

\[ S = k \times \ln W \]

contains everything what can be said about equilibrium thermodynamics in its most condensed form. \( W \) is the volume of the sub-manifold of sharp energy in the 6\( N \)-dim. phase space. It defines entropy \( S \) and with it thermodynamics entirely by mechanical quantities and geometry. No thermodynamic limit, no extensivity, no concavity (downwards bending) of the entropy have to be invoked. This was largely forgotten since hundred years.

2. Thermo-statistics as geometry and topology of the mechanical phase-space

Like Boltzmann we are led by mechanics as the safe guide when we want to extend thermodynamics here to non-extensive or “Small” systems. For “Small” systems the canonical ensemble and with it the Boltzmann-Gibbs distribution have no support by mechanics anymore. A fact by the way Gibbs agreed fully with [3]. Whereas Boltzmann’s definition above opens the way to interprete thermodynamics by the topological and geometrical properties of the N-body phase space. This is new and in marked contrast to e.g. the book of Balian [1] where the entropy is derived from information theory and its extensivity as well its concavity seems to be demanded from the beginning. Boltzmann’s definition as written above is free of this. It is a purely geometric definition and therefore simple. As it allows for convexity as well for non-extensivity without contradicting the Second Law of thermodynamics [4] it is much more suited for the purpose of non-extensive thermo-statistics of “Small” systems.

Another fairy tale told to us by most textbooks of statistical mechanics and thermodynamics says: “Phase transitions exist only in the thermodynamic limit.” There, we also learn that phase transitions get smeared in finite systems. Nevertheless though, phase transitions do exist in these systems. It was the result of experiments and theoretical thoughts especially in nuclear physics that paved the way to a new and much deeper understanding of equilibrium statistical mechanics and phase transitions in “Small” systems.

I want to remind the pioneering attempts on nuclear multifragmentation, experimentally by the references [5–13], where finally Moretto [14] gave a concluding overview on the experimental situation of multifragmentation, even though he initially doubted the very existence of this new phenomenon in the paper entitled: “Complex fragment emission at 50 MeV/u - compound nuclei for ever” [15]. This development was soon theoretically accompanied and stimulated: [16–28] and others. In fact the paper [19] is the first of some 500 papers on “multifragmentation” cited in the large citation database ISI “Web of Science”. Very early, multifragmentation was discussed as a real phase transition of first order in nuclei. E.g. in [20] it was argued that multifragmentation is a transition of first order distinct from the usual liquid-gas transition. And of course this was violently attacked also. I remember some experimental colleagues who claimed the intermediate
mass fragments were coming from the silicon grease used in the vacuum chamber. Theoretically, it was warned that phase transitions cannot occur in such small systems like nuclei. They will be washed out and maybe not even recognizable. In contrast to phase transitions discussed so far in nuclear physics like the transition from spherical to deformed nuclei or the one from normal to superfluidity which are all entropy \( S = 0 \) phenomena, here the real macroscopic signals of a transition in phase-space are seen where the entropy shows some anomaly: A sudden change of the configuration, a latent heat, even a negative heat capacity is seen c.f. 20,26,27,29,28 which is linked to a convexity of the entropy, forbidden in normal extensive thermodynamics by van Hove’s concavity rule 30.

3. The whole “zoo” of phase transitions exists in “Small” systems

In this talk I will show just for demonstration how the whole “zoo” of phase transitions: first order transitions including the interphase surface tension, continuous transitions, critical and even multi-critical points are unambiguously and sharply defined in “Small” systems of some hundred particles by the curvatures of the micro-canonical entropy surface \( s(e, n) \). Details can be found in [4,31]. For an example, I show (figs.1 and 3) here only the phase diagram of the determinant of curvatures of \( s(e, n) = S/V \) vs. energy per volume (lattice point) \( e = E/V \) and density (occupation) \( n = N/V \) for a Potts lattice gas of 50 * 50 lattice points with three spin components \( (q = 3) \):

\[
\text{det}(e, n) = \begin{vmatrix}
\frac{\partial^2 s}{\partial e^2} & \frac{\partial^2 s}{\partial e \partial n} & \frac{\partial^2 s}{\partial n^2} \\
\frac{\partial^2 s}{\partial n \partial e} & s_{ee} & s_{en} \\
\frac{\partial^2 s}{\partial e \partial n} & s_{ne} & s_{nn}
\end{vmatrix} = \lambda_1 \lambda_2, \quad \lambda_1 \geq \lambda_2
\]  

\( (1) \)

The eigenvectors of the curvature matrix define the main curvature directions. Notice, the smaller of the two eigenvalues is here always \( \lambda_2 < 0 \). The larger eigenvalue \( \lambda_1 \) may be positive or negative. The direction of the eigenvector \( v_1 \) belonging to \( \lambda_1 \) gives a natural and unambiguous definition of the order parameter of the system. It is by a progression in this direction that the system changes from one phase over a region of phase-separation to the other phase. In figure (3) we see the phase transition of first order is controlled by variation roughly parallel to the ground-state (similar to the magnetization axis in the Ising model) and the phase transition of second order in the pure Potts-model by a variation \( \sim \) the energy. As can be well seen the order parameter is not always a straight line in the parameter space. The systematics of micro-canonical phase transitions will be listed in the conclusion. The multi-critical point \( P_m \) is most interesting: Here the largest curvature eigenvalue \( \lambda_1 \) and therefore also the curvature determinant \( \text{det}(e, n) \) vanishes in a two-dimensional neighborhood. The entropy surface \( s(e, n) \) has the topology of the surface of a cylinder inside this neighborhood.

As is discussed in all details in ref.[4,31] this new and more extended definition of phase transitions agrees with the Yang-Lee definition in the thermodynamic limit but it allows to define phase transition also in the much larger world of non-extensive systems. Applications of thermodynamic arguments to these systems and of course to hot nuclei make sense only within the micro-canonical theory. This is also a serious reminder for many contributions to this conference. Moreover, thermodynamics of “Small” systems like hot nuclei is naturally probabilistic and therefore requires normally a Monte Carlo kind of treatment.
4. 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. In contrast to the conventional theory, we can study phase transitions also in “Small” systems or other non-extensive systems. They are sharply defined for finite systems without invoking the thermodynamic limit.

We classify phase transitions in a “Small” system by the topological properties of the determinant of curvatures $\det(e, n)$, eq.(1), of the micro-canonical entropy-surface $s(e, n)$:

- A single stable phase by $\det(e, n) > 0$. Here $s(e, n)$ is concave (downwards bended) in both directions and there is a one to one mapping of $\{e,n\} \leftrightarrow \{T,\nu\}$ or between the micro and the grand-canonical ensemble.

- A transition of first order with phase separation by $\det(e, n) < 0$ or the largest curvature $\lambda_1 > 0$. Here the entropy surface $s(e, n)$ has a convex intruder. The depth of the intruder is a measure of the inter-phase surface tension \[32–34\]. This region is bounded by a line with $\det(e, n) = 0$.

- On this line $P_m$ is a critical end-point where additionally $v_1 \cdot \nabla \det = 0$ in the direction of the eigenvector of $\det(e, n)$ with the largest eigenvalue $\lambda_1$. I.e. $\det(e, n)$ has here a minimum. 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. Moreover, we found a further line ($P_m C$, critical) with $v_1 \cdot \nabla \det = 0$ which does not border a region of negative $\det(e, n)$. Presumably $\det(e, n)$ should be 0 also. This needs further tests in other systems. It may further be that these lines signalize transitions of first order in another, but hidden non-conserved order parameter, e.g. the staggered magnetization c.f.\[31\].

- Finally a multi-critical point $P_m$ where more than two phases become indistinguishable by the branching of several lines with $\det = 0$ or with $v_1 \cdot \nabla \det = 0$ to give a cylindrical region of $s(e, n)$ with additionally $\nabla \det = 0$, here the largest curvature $\lambda_1 = 0$ has a maximum in a 2-dim. neighborhood.

- All regions with $\det(e, n) \leq 0$ lead to the catastrophes of the Laplace transform from the micro to the grand-canonical ensemble and thus to the Yang-Lee singularities of the grand-canonical partition sum in the thermodynamic limit.

It is fair to say that the discovery of nuclear multi-fragmentation as a real phase transition of first order in a “Small” many-body system is a challenge for statistical mechanics to understand its foundation better and to become able to describe also the thermodynamics of inhomogeneous and non-extensive systems \[35\]. It opens thermo-statistics for so many applications from small systems like nuclei up to the largest like astro-physical ones. Boltzmann’s definition of entropy allows for a geometrical and topological interpretation of thermo-statistics with the virtue of great conceptional clarity and to be free of invoking the thermodynamic limit. Nuclear collisions are a beautiful testing ground of these new
ideas. This is of course an idealized description. Dynamical non-statistical features are certainly also there.

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Figure 1. Contour plot of the determinant of curvatures $\det(e, n)$ defined in eq. (1) of a $(q = 3)$ Potts lattice gas on a 50*50 lattice. Regions above $\hat{CP}_m B$: concave, $\det > 0$, $\lambda_1 < 0$ (we always have $\lambda_2 < 0$), pure phase (disordered, gas), in the triangle $\hat{AP}_m C$ concave, pure phase (ordered, solid); below $\hat{AP}_m B$: convex, $\det < 0$, $\lambda_1 > 0$, phase-separation, first order; At the dark lines $\hat{AP}_m B$ we have $\det(e, n) = 0$, $\lambda_1 = 0$: termination lines of the first order transition; Medium dark lines e.g $\hat{CP}_m$: $\mathbf{v}_1 \cdot \nabla \det = 0$; 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: $\det = 0 \land \nabla \det = 0$ this is the locus of the multi-critical point $P_m$. In a two dimensional neighborhood of which $s(e, n)$ is flat in the direction of the largest curvature and downwards curved in the other (like the surface of a cylinder) up to at least third order of $\Delta e$ and $\Delta n$ and $\det(e, n) = 0$. The two horizontal lines give the positions of the two cuts shown in fig. (2)
Cut through the determinant $\det(e, n)$ along the line shown in figure (1) at const. $n = 0.95$, through the critical line $CP_m$ close to the critical point $C$ of the ordinary Potts model ($n \sim 1$)

Figure 2.

Cut through the determinant $\det(e, n)$ along the line shown in figure (1) 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 $\nabla \det = 0$ and consequently critical as discussed above

Figure 3. Direction $v_1$ of the largest principal curvature $\lambda_1$ which defines the order parameter that tunes the system through the phase-transitions along these lines.