Non-extensive Hamiltonian systems follow Boltzmann’s principle not Tsallis statistics. – Phase Transitions, Second Law of Thermodynamics

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Abstract: Boltzmann’s principle \( S(E, N, V) = k \ln W(E, N, V) \) relates the entropy to the geometric area \( e^{S(E,N,V)} \) of the manifold of constant energy in the N-body phase space. From the principle all thermodynamics and especially all phenomena of phase transitions and critical phenomena can be deduced. The topology of the curvature matrix \( C(E, N) \) (Hessian) of \( S(E, N) \) determines regions of pure phases, regions of phase separation, and (multi-)critical points and lines. Thus, \( C(E, N) \) describes all kind of phase-transitions with all their flavor. No assumptions of extensivity, concavity of \( S(E) \), additivity have to be invoked. Thus Boltzmann’s principle and not Tsallis statistics describes the equilibrium properties as well the approach to equilibrium of extensive and non-extensive Hamiltonian systems. No thermodynamic limit must be invoked

PACS numbers: 05.20.Gg, 05.70Ln

1 Introduction

There are many attempts to derive Statistical Mechanics from first principles. The earliest are by Boltzmann [1], Gibbs [2], and Einstein [3]. The two central issues of Statistical Mechanics according to the deep and illuminating article by Lebowitz [4] are to be explained: How irreversibility (the Second Law of Thermodynamics) arises from fully reversible microscopic dynamics, and the other astonishing phenomenon of Statistical Mechanics: the appearance of phase transitions. Moreover, conventional statistical mechanics works in the thermodynamic limit. i.e. all non-extensive, ”Small” systems having linear dimensions comparable
to the range of the forces are excluded.

2 Minimum-bias deduction of Statistical Mechanics

Thermodynamics presents an economic but reduced description of a $N$-body system with a typical size of $N \sim 10^{23}$ particles in terms of a very few ($M \sim 3-8$) “macroscopic” degrees of freedom ($dofs$). In order to address also "Small" systems I will allow for much smaller systems of some 100 particles like nucleons in a nucleus. However, I assume that always $6N \gg M$. The believe that phase transitions and the Second Law can exist only in the thermodynamic limit turns out to be false.

Evidently, determining only $M dofs$ leaves the overwhelming number $6N - M dofs$ undetermined. *All* $N$-body systems with the same macroscopic constraints are *simultaneously* described by Thermodynamics. These systems define an *ensemble* $\mathcal{M}$ of points in the $N$-body phase space. Thermodynamics can only describe the *average* behavior of this whole group of systems. I.e. it is a *statistical* or *probabilistic* theory. Macroscopic quantities are averages over $\mathcal{M}$.

The dynamics of the (eventually interacting) $N$-body system is ruled by its Hamiltonian $\hat{H}_N$. Let us in the following assume that our system is trapped in an inert rectangular box of volume $V$ and there is no further conservation law than the total energy. The motion in time of all points of the ensemble follows trajectories in $N$-body phase space $\{q_i(t), p_i(t)\}_{i=1}^{N}$ which will never leave the $(6N-1)$-dimensional shell (or manifold) $\mathcal{E}$ of constant energy $E$ in phase space. We call this manifold the *micro-canonical* ensemble.

An important information which contains the whole equilibrium Statistical Mechanics including all phase transition phenomena is the area $W(E, N) =: e^S$ of this manifold $\mathcal{E}$. Boltzmann has

* In this paper I denote ensembles or manifold in phase space by calligraphic letters like $\mathcal{M}$. 
shown that $S(E, N)$ is the entropy of our system. Thus the entropy and with it equilibrium thermodynamics has a geometric interpretation.

Einstein called Boltzmann’s definition of entropy as e.g. written on his famous epitaph

$$S = k \cdot \ln W$$  \hspace{1cm} (1)

Boltzmann’s principle [5] from which Boltzmann was able to deduce thermodynamics. Precisely $W$ is the number of micro-states of the $N$-body system at given energy $E$ in the spatial volume $V$ and further-on I put Boltzmann’s constant $k = 1$:

$$W(E, N, V) = \text{tr}[\epsilon_0 \delta(E - \hat{H}_N)]$$  \hspace{1cm} (2)

$$\text{tr}[\delta(E - \hat{H}_N)] = \int_{\{q_\alpha \in V\}} \frac{1}{N!} \left(\frac{d^3 q_\alpha \ d^3 p_\alpha}{(2\pi \hbar)^3}\right)^N \delta(E - \hat{H}_N),$$  \hspace{1cm} (3)

$\epsilon_0$ is a suitable energy constant to make $W$ dimensionless, the $N$ positions $q_\alpha$ are restricted to the volume $V$, whereas the momenta $p_\alpha$ are unrestricted. In what follows, I remain on the level of classical mechanics. The only reminders of the underlying quantum mechanics are the measure of the phase space in units of $2\pi \hbar$ and the factor $1/N!$ which respects the indistinguishability of the particles (Gibbs paradoxon). With this definition, eq.1, the entropy $S(E, N, V)$ is an everywhere multiple differentiable, one-valued function of its arguments. This is certainly not the least important difference to the conventional canonical definition.

In contrast to Boltzmann [1] who used the principle only for dilute gases and to Schrödinger [6], who thought equation (1) is useless otherwise, I take the principle as the fundamental, generic definition of entropy. In a recent book [7] cf. also [8,9] I demonstrated that this definition of thermo-statistics works well especially also at higher densities and at phase transitions without invoking the thermodynamic limit. This is important: Elliot Lieb [10] considers
the additivity of \( S(E) \) and Lebowitz \([4,11]\) the thermodynamic limit as essential for the deduction of thermo-statistics. However, neither is demanded if one starts from Boltzmann’s principle.

This is all that Statistical Mechanics demands, no further assumption must be invoked. Neither does one need extensivity, nor additivity, nor concavity of \( S(E) \) c.f. \([12]\). Boltzmann’s principle eq. (1) is the only axiomatic assumption necessary for thermo-statistics.

3 The micro-canonical ensemble is the fundament ensemble

During the dynamical evolution of a many-body system interacting by short-range forces the internal energy is conserved. Only perturbations by an external “container” can change the energy. I.e. the fluctuations of the energy are \( \Delta E \propto V^{-1/3} \). If, however, the diameter of the system is of the order of the range of the force, i.e. the system is “Small”, non-extensive, details of the coupling to the container cannot be ignored. The canonical ensemble does not care about these details, assumes the system is homogeneous, averages over a Boltzmann-Gibbs (exponential) distribution

\[
P_E\{q_\alpha, p_\alpha\} = \frac{1}{Z(\beta)} e^{-\beta \hat{H}\{q_\alpha, p_\alpha\}}
\]

of energy and fixes only the mean value of the energy by the temperature \( 1/\beta \). In order to agree with the micro, \( e^{-\beta E} W(E) \) must be sharp in \( E \) i.e. self-averaging, what is usually not the case in non-extensive systems. Then one must work in the micro, the only orthode ensemble.

In this conference it is suggested to describe the equilibrium of non-extensive systems by Tsallis q-entropy \([13–16]\):

\[
S_q = k \left( 1 - \frac{\sum_{i=1}^{W} P_i^q}{q - 1} \right).
\]

(4)

For a closed Hamiltonian system at energy \( E \), the \( P_i \) are the probabilities for each of the \( W(E) \) microscopic configurations (quantum states). Following Toral \([17]\) this has of course the following
consequences: After maximizing $S_q(E)$ under variation of $P_i$ with the constraint of $\sum P_i = 1$ one obtains the equal probability distribution characterized by Boltzmann’s entropy $W(E) = e^{S(E)}$:

$$P_i(\epsilon) = \begin{cases} 
e^{-S(E)} , & \epsilon_i = E \\ 0 , & \text{otherwise} \end{cases}, \quad S_q = k \frac{1 - e^{(1-q)S(E)}}{q - 1}. \quad (5)$$

Moreover, following Abe and Toral [16,17] the original definitions of the microcanonical temperature and pressure, eq. (7) below, through Boltzmann’s entropy $S(E, N, V)$, eq.(4), are the only way within Tsallis statistics to define the equilibrium of two systems in weak contact and to fulfill the zeroth law under energy- and volume exchange:

$$S(E, N, V) = \ln W(E, N, V) \quad (6)$$

$$T_{\text{phys}} = \left( \frac{\partial S}{\partial E} \right)^{-1} \quad P_{\text{phys}} = \frac{\partial S}{\partial V} \frac{\partial S}{\partial E} \quad (7)$$

I.e. the physical quantity relevant for equilibrium of Hamiltonian systems, extensive or not, is the original Boltzmann entropy $S(E) = \ln[W(E)]$, eq.(4), whatever the non-extensivity index $q$. Therefore, for closed Hamiltonian many-body systems at statistical equilibrium, extensive or not, the thermo-statistical behavior is entirely controlled by Boltzmann’s principle and the microcanonical ensemble as discussed in this paper. Tsallis statistics seems to apply to non-equilibrium situations like turbulence etc.

4 Phase transitions within Boltzmann’s principle

At phase-separation the system becomes inhomogeneous and splits into different regions with different structure. This is the main generic effect of phase transitions of first order. Evidently, phase transitions are foreign to the (grand-) canonical theory with homogeneous density distributions. Therefore, in the conventional Yang-Lee theory phase transitions [18] are indicated by the zeros
of the grand-canonical partition sum where the grand-canonical formalism breaks down (Yang–Lee singularities).

Within Boltzmann’s principle phase-transitions are generically classified in terms of the topology of curvatures of $S(E, N)$ i.e. by its Hessian and its eigenvalues $\lambda_{1,2}$. This works also for “Small”, non-extensive systems, details in [7]:

$$\det(E, N) = \begin{vmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial N \partial E} \\ \frac{\partial^2 S}{\partial E \partial N} & \frac{\partial^2 S}{\partial N^2} \end{vmatrix} = \begin{vmatrix} S_{EE} & S_{EN} \\ S_{NE} & S_{NN} \end{vmatrix} = \lambda_1 \lambda_2, \quad \lambda_1 \geq \lambda_2, \quad (8)$$

- **A single stable** phase by $\lambda_1 < 0$. Here $S(E, N)$ is locally concave (downwards bended) in both directions and if the $T, \mu$-analogue to eqs.(7) have a single solution $E_s, N_s$, then there is a one to one mapping of the grand-canonical ↔ the micro-ensemble.

- **A transition of first order** with phase separation and surface tension is indicated by $\lambda_1 > 0$. $S(E, N)$ has a convex intruder (upwards bended) in the direction $v_1$ of the largest curvature (order parameter). The depth of the intruder is a measure of the inter-phase surface tension. Then the $T, \mu$-analogue to eqs.(7) have multiple solutions, at least three. The whole convex area of $\{E,N\}$ is mapped into a single point $(T, \mu)$ in the grand-canonical ensemble (non-locality). I.e. here both ensembles are not equivalent and the (grand-)canonical ensemble is non-local in the order parameter and violates basic conservation laws [7–9, 19]. The region in $\{E, N\}$ of separation of different phases, $\lambda_1 > 0$, is bounded by lines with $\lambda_1(E, N) = 0$.

- On this boundary is the end-point of the transition of first order, here the three solutions of eqs.(7) move into one another in the direction $v_1$, into the critical end-point of the first order transition ($v_{1,2}$ are the eigenvectors of the Hessian). Here, we have a continuous (“second order”) transition with vanishing surface tension, where two neighboring phases become indistinguishable, here $\lambda_1(E, N) = 0$ and $v_1 \cdot \nabla \lambda_1 = 0$. These are the catastrophes of the Laplace transform $E \rightarrow T$. Further-
more, there may be also whole lines of second-order transitions like in the antiferro-magnetic Ising model c.f.\[7\].

- Finally, a **multi-critical point** where more than two phases become indistinguishable is at the branching of several lines in the \{E, N\}-phase-diagram with \(\lambda_1 = 0, \nabla \lambda_1 = 0\).

## 5 Fractal distributions in phase space, approach to equilibrium, Second Law

Let us examine the following Gedanken experiment: Suppose the probability to find our system at points \(\{q_t, p_t\}_1^N\) in phase space is uniformly distributed at time \(t_0\) over the sub-manifold \(\mathcal{M}(t_0, t_0) \equiv \mathcal{E}(N, V_1)\) of the \(N\)-body phase space at energy \(E\) and spatial volume \(V_1\). At time \(t > t_0\) we allow the system to spread over the larger volume \(V_2 > V_1\) without changing its energy. If the system is *dynamically mixing*, the majority of trajectories \(\{q_t, p_t\}_1^N\) in phase space starting from points \(\{q_0, p_0\}_1^N\) with \(q_0 \in V_1\) at \(t_0\) will now spread over the larger volume \(V_2\). Of course the Liouvillean measure of the distribution \(\mathcal{M}(t, t_0)\) in phase space at \(t > t_0\) remains the same (= \(\text{tr}[\mathcal{E}(N, V_1)]\)). But as already argued by Gibbs the distribution \(\mathcal{M}(t, t_0)\) will be filamented like ink in water and will approach any point of \(\mathcal{E}(N, V_2)\) arbitrarily close. \(\lim_{t \to \infty} \mathcal{M}(t, t_0)\) becomes dense in the new, larger \(\mathcal{E}(N, V_2)\). The closure \(\overline{\mathcal{M}(t = \infty, t_0)}\) becomes equal to \(\mathcal{E}(N, V_2)\). This is clearly expressed by Lebowitz [4,11], and illustrated by the figure [4]. Thermodynamics cannot distinguish \(\mathcal{M}\) from \(\overline{\mathcal{M}}\). **Thus the closed manifolds \(\overline{\mathcal{M}}\) are the real objects of thermodynamics.**

To calculate \(\overline{\mathcal{M}}\) we introduce the box-counting “measure” \(M_\delta \propto N_\delta^{6N-1}\) for the distribution in phase-space as indicated in fig.4. We cover \(\mathcal{M}\) with a rectangular grid with spacing \(\delta\) and and count the number \(N_\delta\) of boxes which overlap with \(\mathcal{M}\) with the convention taking \(\delta \to 0\) after taking averages, see [19,20]. For
finite times because of Liouville’s theorem we have

$$\lim_{\delta \to 0} M_\delta(t, t_0) = W(E, N, t_0, t_0) = W(E, N, V_1) \quad (9)$$

At $t \to \infty$ the two limits $\delta \to 0, t \to \infty$ do in general not commute and as assumed by Gibbs the manifold $\mathcal{M}(t \to \infty, t_0)$ becomes dense in the new micro-canonical manifold $\mathcal{E}(V_2)$. Then

$$\lim_{\delta \to 0} \lim_{t \to \infty} M_\delta(t, t_0) = W(E, N, V_2) \geq W(E, N, V_1). \quad (10)$$

This is the Second Law of Thermodynamics. For a more detailed mathematical discussion c.f. [19,20].

6 Conclusion

Macroscopic measurements $\hat{M}$ determine only a very few of all $6N$ dofs. Any macroscopic theory like thermodynamics deals with the volumes $W = e^S$ of the corresponding closed sub-manifolds $\overline{\mathcal{M}}$ in the $6N$-dim. phase space not with single points. The averaging over ensembles or finite sub-manifolds in phase space becomes especially important for the micro-canonical ensemble of a non-extensive or any other non-self-averaging system. Entropy $S(E, N, V)$ is the natural measure of the geometric size of the ensemble. The topology of its curvature indicates all phenomena of phase transitions independently of whether the system is extensive or non-extensive.

Several miss-interpretation of Statistical Mechanics are pointed out: The existence of phase transitions and critical phenomena are not linked to the thermodynamic limit. They exist clearly and sharply in “Small”, non-extensive systems as well. Non-extensive Hamiltonian systems do not demand a new entropy formalism like that by Tsallis [13,21]. Boltzmann’s principle, the microcanonical ensemble, covers all equilibrium properties as well as the approach towards equilibrium i.e. the Second Law.

By our derivation of micro-canonical Statistical Mechanics for fi-
nite, non-extensive systems various non-trivial limiting processes are avoided. Neither does one invoke the thermodynamic limit of a homogeneous system with infinitely many particles nor does one rely on the ergodic hypothesis of the equivalence of (very long) time averages and ensemble averages. As Bricmont \cite{22} remarked Boltzmann’s principle is the most conservative way to Thermodynamics but more than that it is the most straight one also. The single axiomatic assumption of Boltzmann’s principle, which has a straight geometric interpretation, leads to the full spectrum of equilibrium thermodynamics including all kinds of phase transitions and including the Second Law of Thermodynamics.

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Fig. 1. The compact set $\mathcal{M}(t_0)$, left side, develops into an increasingly folded “spaghetti”-like distribution $\mathcal{M}(t, t_0)$ in the phase-space with rising time $t$. The right figure shows only the early form of the distribution. At much later times it will become more and more fractal and finally dense in the new phase space. The grid illustrates the boxes of the box-counting method. All boxes which overlap with $\mathcal{M}(t, t_0)$ contribute to the box-counting volume $\text{vol}_{\text{box}, \delta}$ and are shaded gray. Their number is $N_\delta$.  

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