Microcanonical Thermostatistics, the basis for a New Thermodynamics, “heat can flow from cold to hot”, and nuclear multifragmentation. The correct treatment of Phase Separation after 150 years of statistical mechanics

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Abstract. Equilibrium statistics of finite Hamiltonian systems is fundamentally described by the microcanonical ensemble (ME) [1]. Canonical, or grand-canonical partition functions are deduced from this by Laplace transform. Only in the thermodynamic limit are they equivalent to ME for homogeneous systems. Therefore ME is the only ensemble for non-extensive/inhomogeneous systems like nuclei or stars where the \( \lim_{N \to \infty, \rho = N/V = \text{const}} \) does not exist. Conventional canonical thermo-statistic is inapplicable for non-extensive systems. This has far reaching fundamental and quite counter-intuitive consequences for thermo-statistics in general: Phase transitions of first order are signaled by convexities of \( S(E, N, Z, \cdots) \) [1]. Here the heat capacity is negative. In these cases heat can flow from cold to hot! The original task of thermodynamics, the description of boiling water in heat engines can be treated. Consequences of this basic peculiarity for nuclear statistics as well for the fundamental understanding of Statistical Mechanics in general are discussed. Experiments on hot nuclei show all these novel phenomena in a rich variety. The close similarity to inhomogeneous astro physical systems will be pointed out.

Keywords: Microcanonical statistics, first order transitions, phase separation, steam engines, nuclear multifragmentation, negative heat capacity

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1. Introduction

Boiling water drives steam engines. Steam engines were the original motive for proposing Thermodynamics some 170 years ago. About 150 years ago Boltzmann and Gibbs developed Statistical Mechanics to explain (irreversible) Thermodynamics within reversible Mechanics. Since then canonical Boltzmann-Gibbs (BG) statistics is considered to answer this task. However, BG works in the thermodynamic limit of homogeneous systems. Boiling water is inhomogeneous. Phase transitions of first order are signaled by Yang-Lee singularities in BG. Consequently, BG is inappropriate for boiling water.

The best way to understand the difference between the canonical and the microcanonical representation of first order phase transition is perhaps by studying figure (1), which shows the typical convex intruder of $S(E)$ between $e \sim 0.35$ and $1.25 \text{ eV/atom}$. This region gets completely jumped over by the canonical ensemble. Between $e \sim 0.35$ and $\sim 1. \text{ eV}$ the temperature (inverse slope of $S(E)$) is approximately constant. There is a single cluster that evaporates up to 2500 atoms. This is the region of the “compound nucleus for ever” which is emphasized so much by Moretto [2]. However, its temperature is higher than the canonical transition temperature $T_{tr}$ and these events are inaccessible to the canonical ensemble.

At $\sim 1.1 \text{ eV}$ the single cluster explodes suddenly into on average 2726 monomers, 80 dimers, about 20 quadrimers and a few heavier fragments. This corresponds to nuclear multi-fragmentation. However, as the total charge of the system is only 1+ there is no Coulomb force, and fission is missing. One can also clearly see that the total surface of the fragments $\propto N_{eff}^{2/3}$ rises steep in the fragmentation region. This leads to the steep drop of the temperature (backbending).

2. Short way to entropy

Entropy, $S$, is the fundamental entity of thermodynamics which distinguishes thermodynamics from all other physics. Therefore, its proper understanding is essential. The understanding of entropy is sometimes obscured by frequent use of the Boltzmann-Gibbs canonical ensemble, and the thermodynamic limit. Also its relationship to the second law is often beset with confusion between external transfers of entropy $dS_e$ and its internal production $dS_i$ [3].

Macroscopic systems are controlled by a few macroscopic control parameters $M$ like energy $E$, particle number $N$, and volume $V$. All $6N - M$ degrees of freedom remain unknown. Consequently, Thermodynamics describes all systems with the same macroscopic parameters $M$ simultaneously. It can only give probabilistic information about the typical behaviour of all systems in the microcanonical ensemble.

Boltzmann defined the entropy of an isolated system

$$S = k \ln W$$

(1)
Fig. 1. Microcanonical caloric curve of 3000 Na atoms at a pressure of 1 atm with realistic interaction (c.f. [1]). The temperature $T$ in Kelvin, the energy in eV/atom. $N_{fr}$ the number of fragments, $N_{eff}^{2/3} = \sum N_i^{2/3}$ the number of surface atoms of dimers and heavier ones. The four inserts give the fragment distribution at 4 characteristic energies over the intruder. E.g.: at $0.442$ eV $1:329$ means $329$ monomers, and $2:7.876$ means $7.876$ dimers, and $4:1.295$ means $1.295$ quadrimers on average. Below $e \sim 0.33$ eV 2999 atoms are condensed in a single liquid droplet and above $e \sim 1.3$ eV nearly all atoms are free (\sim ideal gas).

as written on Boltzmann’s tomb-stone. I.e. $S$ measures the size of the (microcanonical) ensemble.

This has a very simple interpretation: The size of the ensemble i.e. the number $W$ of cells of size $(2\pi\hbar)^3N$ of different initial values of positions $q_i$ and momenta $p_i$ consistent with the $M$ control parameter is measured by the entropy $S$. If we would know all $6N$ positions and momenta, $W$ would be one and the entropy $S = 0$. 
3. No phase separation without convex non-extensive $S(E)$

The weight $e^{S(E) - E/T}$ of configurations with energy $E$ in the definition of the canonical partition sum

$$Z(T) = \int_{0}^{\infty} e^{S(E) - E/T} dE$$

(2)

becomes here bimodal, at the transition temperature it has two peaks, the liquid and the gas configurations which are separated in energy by the latent heat. Consequently $S(E)$ must be convex (like $y = x^2$) and the weight in (2) has a minimum between the two pure phases. Of course, the minimum can only be seen in the microcanonical ensemble where the energy is controlled and its fluctuations forbidden. Otherwise, the system would fluctuate between the two pure phases by an, for macroscopic systems even macroscopic, energy $\Delta E \sim E_{lat} \propto N$ of the order of the latent heat. I.e. the convexity of $S(E)$ is the generic signal of a phase transition of first order and of phase-separation\[1\]. Such macroscopic energy fluctuations and the resulting negative heat capacity are already early discussed in high-energy physics by Carlitz [4].

4. Application in astrophysics

The necessity of using “extensive” instead of “intensive” control parameter is explicit in astrophysical problems. E.g.: for the description of rotating stars one conventionally works at a given temperature and fixed angular velocity $\Omega$ c.f. [5]. Of course in reality there is neither a heat bath nor a rotating disk. Moreover, the latter scenario is fundamentally wrong as at the periphery of the disk the rotational velocity may even become larger than velocity of light. Non-extensive systems like astro-physical ones do not allow a “field-theoretical” description controlled by intensive fields!

E.g. configurations with a maximum of random energy on a rotating disk, i.e. at fixed rotational velocity $\Omega$:

$$E_{random} = E - \frac{\Theta \Omega^2}{2} - E_{pot}$$

(3)

and consequently with the largest entropy are the ones with smallest moment of inertia $\Theta$, compact single stars. Just the opposite happens when the angular-momentum $L$ and not the angular velocity $\Omega$ are fixed:

$$E_{random} = E - \frac{L^2}{2\Theta} - E_{pot}.$$  (4)

Then configurations with large moment of inertia are maximizing the phase space and the entropy. I.e. eventually double or multi stars are produced, as observed in reality.
In figure 2 one clearly sees the rich and realistic microcanonical phase-diagram of a rotating gravitating system controlled by the “extensive” parameters energy and angular-momentum. [6]

![Phase diagram of rotating self-gravitating systems in the energy-angular-momentum (E, L)-plane. DC: region of double-stars, G: gas phase, SC: single stars. In the mixed region one finds various exotic configurations like ring-systems in coexistence with gas, double stars or single stars. In this region of phase-separation the heat capacity is negative and the entropy is convex. The dashed lines $E - L = -1$ (left) and $E = L$ (right) delimit the region where systematic calculations were carried out. At a few points outside of this strip some calculations like the left of fig.(3) were also done.](image)

**Fig. 2.** Phase diagram of rotating self-gravitating systems in the energy-angular-momentum (E, L)-plane. DC: region of double-stars, G: gas phase, SC: single stars. In the mixed region one finds various exotic configurations like ring-systems in coexistence with gas, double stars or single stars. In this region of phase-separation the heat capacity is negative and the entropy is convex. The dashed lines $E - L = -1$ (left) and $E = L$ (right) delimit the region where systematic calculations were carried out. At a few points outside of this strip some calculations like the left of fig.(3) were also done.

**References**

Fig. 3. Rotating multi-star-systems. The left shows a rotating double-star system in the DC phase. This is an inhomogeneous phase, analog to nuclear multifragmentation. The right is one of the many different, unstable, configurations existing in the mixed phase with negative heat capacity. Here the system fluctuates between such ring systems, systems of stars rotating around a central star but also mono-stars and eventual gas. This region is very interesting but must still be more investigated. Cover page of Phys.Rev.Lett. vol 89, (July 2002)