The physical meaning of entropy is analyzed in the context of statistical, nuclear, atomic physics and cosmology. Only the microcanonical Boltzmann entropy leads to no contradictions in several simple, elementary and for thermodynamics important situations. The conventional canonical statistics implies several serious errors and misinterpretations. This has far reaching consequences for phase-separations as well for the usual formulations of the second law. Applications in cosmology suffer under the ubiquitous use of canonical statistics. New reformulations in terms of microcanonical statistics are highly demanded but certainly difficult.

I. INTRODUCTION

Entropy, S, is the characteristic entity of thermodynamics and thermostatistics [1]. It distinguishes thermodynamics from all other physics; therefore, its proper understanding is essential. However, this 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 \( d_{\text{ext}}S \) and its internal production \( d_{\text{int}}S \). The main source of the confusion is of course the lack of a clear microscopic and mechanical understanding of the fundamental quantities of thermodynamics like heat, external vs. internal work, temperature, and last not least entropy, at the times of Clausius and possibly even today. I got some encouragement from reading Redlich's critique [2].

The second law of the necessary increase (or constancy) of the entropy has far reaching significance for all physics and especially for astro-physics and cosmology. This demands a new critical discussion of the basics of statistical mechanics and the use of the various ensembles.

This contribution wants to give a first glance of these challenges. Of course it is not able to go into the details. This would demand a whole course in statistical physics. The author’s work on statistical mechanics is given by [3] and some recent ones [4, 5]. His interpretation of the foundation of entropy and the second law is given in refs. [6, 7, 8, 9].

The boxes show the transparencies of my talk presented at the XLIV international winter meeting on nuclear physics in Bormio (Italy) - 2006, January 29-February 5. I add a few more explanations.

Plan of the talk

- Entropy by Clausius
- Entropy by Boltzmann
- Caratheodory
- Entropy by Prigogine
- Entropy by Tsallis
- Phase transitions
- Convexities of S(E)
- Long-range interactions, gravity
- Arrows of time
- Cosmological perspectives and speculations

Clausius [1]:

\[ S = \frac{dQ}{T} \]

“value of metamorphosis”

or ENTROPY

SECONd LAW :

“Heat only flows from hot to cold”

\[ \oint \frac{dQ}{T} \geq 0 \]

= uncompensated metamorphosis
The Boltzmann-Planck formula has a simple but deep physical interpretation: $W$ or $S$ measure our ignorance about the complete set of initial values for all $6N$ microscopic degrees of freedom which are needed to specify the $N$-body system unambiguously, ref. [11]. To have complete knowledge of the system we would need to know [within its semiclassical approximation] the initial positions and velocities of all $N$ particles in the system, which means we would need to know a total of $6N$ values. Then $W$ would be equal to one and the entropy, $S$, would be zero. However, we usually only know the values of a few macroscopic parameters that are conserved or change slowly with time, such as the energy, number of particles, volume and so on. We generally know very little about the positions and velocities of all the particles. The manifold of all these points in the $6N$-dim. phase space, consistent with the given conserved macroscopic constraints of $E, N, V, \cdots$, is the microcanonical ensemble, which has a well-defined geometrical size $W$ and, by equation 1, a non-vanishing entropy, $S(E, N, V, \cdots)$. The dependence of $S(E, N, V, \cdots)$ on its arguments determines completely thermostatics and equilibrium thermodynamics.

Clearly, Hamiltonian (Liouvillean) dynamics of the system cannot create the missing information about the initial values - i.e. the entropy $S(E, N, V, \cdots)$ cannot decrease. As has been further worked out in ref. [2] and more recently in ref. [3], the inherent finite resolution of the macroscopic description implies an increase of $W$ or $S$ with time when an external constraint is relaxed. Such is a statement of the second law of thermodynamics, ref. [12], which requires that the internal production of entropy be positive or zero for every spontaneous process.

Analysis of the consequences of the second law by the microcanonical ensemble is appropriate because, in an isolated system (which is the one relevant for the microcanonical ensemble), the changes in total entropy must represent the internal production of entropy, see below, and there are no additional uncontrolled fluctuating energy exchanges with the environment.

## II. SECOND LAW

### Second Law

P. Glansdorf and I. Prigogine [12]

\[
dS = d_{ext}S + d_{int}S
\]

\[
d_{ext}S = \text{positive, negative, or zero}
\]

\[
d_{int}S \geq 0=\text{Second Law (3)}
\]

Thus the Second Law is explicitly and most clearly defined by MICROCANONICAL STATISTICS!

From our experience (see section [III]) we know that the fundamental microcanonical ensemble is not equivalent to the conventional canonical ensemble. This is the case just in the thermodynamically most interesting situations: at phase separation see section [III]. In order to have a correct formulation of the second law we must follow Boltzmann’s or Prigogine’s [12] formulation of microcanonical entropy.

Already Clausius himself gave an illuminating example in [12] that clearly shows how the conventional (canonical) formula:

\[
dS = \frac{dE}{T}
\]

fails and is not automatically the correct expression of the entropy change:

When an ideal gas suddenly streams under insulating conditions from a small vessel with volume $V_1$ into a larger one ($V_2 > V_1$), neither its internal energy $U$ or $E$, nor its temperature changes, nor external work done, but its internal (Boltzmann-)entropy $S_{int}$ e.q. [1] with [2] rises, by $\Delta S = N \ln(V_2/V_1)$. This is also a clear example for a microcanonical situation where the entropy change by an irreversible metamorphosis of the system is absolutely internal. It has nothing to do with heat exchange with the surrounding as expressed by eq [3]. In this context see also my controversy with Jarzynski [14].

Then the second law becomes very simple and claims the increasing loss of information (rise of entropy) due the impossibility to distinguish the highly “fractal” distribution in phase-space after some mixing dynamics from its

---

**Boltzmann-Planck**:

\[ S = k \ln W \]  

(1)

as written on Boltzmann's tomb-stone, with

\[
W(E, N, V) = \int \frac{d^{3N} p}{(2\pi\hbar)^{3N}} \frac{d^{3N} q}{(2\pi\hbar)^{3N}} \delta(E - H(q, p))
\]  

(2)

= number of initial states with the same macroscopic parameters

$\equiv$ microscopic ignorance

$\Rightarrow$ no thermodynamic limit

| no extensivity | no concavity |
|---------------|-------------|
| no homogeneity | no Boltzmann-Gibbs (canonicality) |
| no Caratheodory | no Tsallis |

---
surrounding. I.e. the internal entropy à la Prigogine (12) of the necessarily redundant macroscopic description of the system becomes larger (information-loss) 3.

This example demonstrates the problematic of the canonical description of thermo-statistics. This is even more evident when the original object of thermodynamics, the description of boiling water, is addressed. This is discussed in the next section.

III. PHASE TRANSITIONS

Phase-transitions in conventional (grand-canonical) statistics in the thermodynamic limit:

Yang-Lee singularities. Why?

⇒ Only homogeneous configuration
⇒ No boiling water!

Are phase transitions really so trivial ???

Physical reason:

→ Strong inhomogeneities
→ Internal surfaces

What is the difference between

| Solid   | Liquid               | Gas    |
|---------|----------------------|--------|
| have surfaces | condensate volume less than external volume | no surface |
| surface has edges          | surface has no edges | fills any volume |
| hard fixed                  | flexible, adjusts to container |

⇒ Moral: Avoid thermodynamic limit !

BUT

Without thermodynamic limit several gospels of conventional thermodynamics become obsolete:

• Equivalence of canonical and microcanonical ensembles
• Legendre transform structure
• Phase transitions exist only in the thermodynamic limit
• Specific heat is \( \sim <(\delta E)^2> > 0 \)
• Extensivity of \( S \), scaling with \( N \)
• Concavity of \( S(E,N) \)
• Rise of entropy is connected to trend towards uniformization
• Second Law only in infinite systems
Convexity of $S(E)$

Example:
Atomic cluster fragmentation gives detailed insight into region of phase-separation, here no Coulomb $\rightarrow$ most interesting physics

![Graph of Na$^{+}$ ions](image)

Caloric curve of 3000 Na atoms at a pressure of 1 atm with realistic interaction (c.f. [3]). 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 (~ ideal gas). Color online

The above example of the liquid-gas transition of first order in a mesoscopic droplet clarifies the errors made by the recent works by [15]: Whereas the transition extends clearly over the latent heat from $\propto 0.3$ to $\propto 1.3$ electron volt, the transition temperature is below the evaporation line from point 1 to 2. This is the region of evaporation
configuration as is clearly seen by the inserts. The temperature of this piece remains above the true transition temperature $T_{tr}$. This is of course because phase separation is a microcanonical phenomenon characterized by a back-bending caloric curve, which does not exist in the canonical ensemble [3]. The final backbending is clearly seen beyond point 2. One might argue: the system is unstable in the backbending region. This is wrong as under a control of the energy fluctuations (thermos-flask, large systems like the ocean). Then the intermediate region is very well accessible.

As seen in the mass distribution of the fragments (inserts) the quality of the distribution changes over the latent heat from evaporation-like (insert 1 to insert 2, called by Bowman et al. 15 in a somewhat premature way “compound nucleus for ever”) finally to multifragmentation at 3 and 4. As function of the dynamically conserved energy the weight $e^{S(E) - E/T}$ of the configurations with energy $E$ in the definition of the canonical partition sum

$$Z(T) = \int_0^\infty e^{S(E) - E/T} \frac{dE}{\epsilon_0}$$

becomes here bimodal over the range of the latent heat.

Thus, in contrast to what was claimed at this meeting, this bimodality over the latent heat is a necessary signal of any phase separation. In nuclear fragmentation the caloric curve $T(E)$ is often dramatically modified by additional fission decays [3].

### IV. COSMOLOGICAL CHALLENGES

In very recent times possible links between general relativity and statistical mechanics became a topic of hot speculations.

First the philosophical question whether the arrow of time as expressed by the second law of thermodynamics has anything to do with the development of the universe (cosmological arrow of time) was a topic already of Clausius [1]. Recently Allahverdian and Gurzadyan discuss this in [16]. Uffink’s [17] answer to this question is: “The arrow of time has nothing to do with the second law!” This shows the wide span of controversial opinions about this question.

Allahverdian and Gurzadyan [16] assume that the system is coupled to a memory-losing bath. I.e. the time evolution operator of the bath

1. $T(t,0) = T(t)$ after a sufficiently long time $t$, which must still be short compared with the Poincaré recurrence time.

2. and the system relaxes to the stationary distribution $D_S(t) \rightarrow D_S^{(st)}$.

Both are of course strong assumptions which imply the second law.

The “ensemble probabilistic” interpretation of statistical mechanics [4] takes the fact seriously that knowing only a few macroscopic parameters of the system leaves the majority of degrees of freedom uncontrolled. Therefore this fixes only the ensemble of many microscopic realizations of the system. Thermodynamics as also thermodynamics can only describe the average (over the ensemble) behavior. Certainly there is nothing like a single “macroscopic state” with a discrete Poincaré recurrence time. In general the whole ensemble will never recur.

This, however, seems to have nothing to do with a cosmological arrow of time and in contrast to Allahverdian and Gurzadyan [16] I tend to agree with Uffink [17] that it might be an advantage to abandon the idea of a relation of the second law with the arrow of time.

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**Different arrows of time:**

Allahverdyan and Gurzadyan [16]:

1. Thermodynamic arrow of time: second law
2. Cosmological arrow of time: universe expands
3. Psychological arrow of time: we only know about the past, not future we become older and more stupid
4. Electromagnetic: retarded interaction
5. Quantum-mechanical: wave-function during measurement collapses

$1 \iff 2$?

⇒ Deeper understanding of entropy !≤

**Cosmological perspectives and speculations**

Common wisdom:
Specific heat of self-gravitating system often negative.

However, canonically:

$$C(T) = \frac{\langle (\Delta E)^2 \rangle}{T^2} \geq 0$$

⇒ gravitating systems are not canonical ≤
Moretto \[20, 21\].
as recently discussed and beautifully demonstrated by the surdity of the Hagedorn constant temperature spectrum implodes into a black hole. This also illuminates the ab-



system becomes too large it becomes so heavy that it systematically an upper end to the spectrum of any system.\[3\] D.H.E. Gross. Microcanonical thermodynamics: Phase transitions in “Small” systems, volume 66 of Lecture Notes in Physics. World Scientific, Singapore, 2001.



In \[19\] is the remarkable sentence: “Entropy costs energy and energy focuses light into a caustics of space-time. The caustics prevent light-sheets going on for ever.” The finite size of light-sheets and the surface-area of the corresponding system determines entropy. This sentence characterizes the deep link between entropy and space-time and the specific significance of the micro-canonical statistics in contrast to any intensive (canonical) description. There is a further important statement in \[19\]: “Entropy is a non-local phenomenon. Only in some approximation entropy can be described by a local flow of entropy density”, i.e. by an intensive (canonical) description. It is fascinating how the experience from ordinary condensed matter and especially phase-transitions points to the same conclusion as cosmology: Entropy is non-local and depends primarily on the “extensive” control parameters as energy. One may argue in view of the large scales of the universe, a local canonical approximation might be acceptable. However, gravity has also a long range. The ubiquitous negative heat capacity of self-gravitating system should be a warning.

\[\text{V. CONCLUSION}\]

The lesson I like to transfer here is that the canonical statistics is sometimes dangerously erroneous and must then be replaced by the microcanonical statistics. However, nearly all works on cosmology ignore this fact. Certainly, in general relativity a lot more work must be done along this challenge \[5\]. Examples showing some of the perspectives are \[14\] \[22\] \[23\].

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