Straight way to Thermo-Statistics, Phase Transitions, Second Law of Thermodynamics, but without Thermodynamic Limit

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Boltzmann’s principle \( S(E,N,V) = k \ln W \) relates the entropy to the geometric area \( S(E,N,V) \) of the manifold of constant energy in the (finite-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. They are linked to convex (upwards bending) intruders of \( S(E,N) \), here the canonical ensemble defined by the Laplace transform to the intensive variables becomes multi-modal, non-local, and violates the basic conservation laws (it mixes widely different conserved quantities). The one-to-one mapping of the Legendre transform gets lost. Within Boltzmann’s principle, Statistical Mechanics becomes a geometric theory addressing the whole ensemble or the manifold of all points in phase space which are consistent with the few macroscopic conserved control parameters. Moreover, this interpretation leads to a straight derivation of irreversibility and the Second Law of Thermodynamics out of the time-reversible microscopic mechanical dynamics. It is the whole ensemble that spreads irreversibly over the accessible phase space not the single \( N \)-body trajectory. This is all possible without invoking the thermodynamic limit, extensivity, or concavity of \( S(E,N,V) \) and also without invoking any cosmological constraints. Without the thermodynamic limit or at phase-transitions the systems are usually not self-averaging, do not have a single peaked distribution in phase space. It is further shown that non-extensive Hamiltonian systems at equilibrium are described by Boltzmann’s principle and not by Tsallis non-extensive statistics.

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I. INTRODUCTION

There are many attempts to derive Statistical Mechanics from first principles. The earliest are by Boltzmann [1–4], Gibbs [5,6], and Einstein [7–10]. The two central issues of Statistical Mechanics according to the deep and illuminating article by Lebowitz [11] are to explain how irreversibility (the Second Law of Thermodynamics) arises from fully reversible microscopic dynamics, and the other astonishing phenomenon of Statistical Mechanics: the occurrence of phase transitions. In this paper I want to present an easy, straightforward derivation of both aspects directly out of the microscopic time-reversal invariant Newton-mechanics invoking a minimum of assumptions. We will see how both problems are connected.

There is an important aspect of Statistical Mechanics which to my opinion was not sufficiently considered up to now: Statistical Mechanics and also Thermodynamics are macroscopic theories describing the average \(^1\) behavior of all \( N \)-body systems with the same macroscopic constraints. It is this fact and nothing else that leads in a simple and straightforward manner to the desired understanding of irreversibility, the Second Law for \( N \)-body systems, which obey a completely time reversible Hamiltonian dynamics, and leads simultaneously to the full spectrum of phase-transition phenomena. It is certainly essential to deduce the Second Law from reversible (here Newtonian) and not from dissipative dynamics as is often done because just the derivation of irreversibility from

\(^1\)Here I do not speak of the typical behavior. This would only be the same if the system is self-averaging, which I do not demand, see below.
fully reversible dynamics is the main mystery of Statistical Mechanics. Here a first hint: Whereas a single trajectory in the (finite-$N$)-body phase space returns after a finite Poincaré recurrence time a manifold of points develops in general irreversibly with time, see below.

II. 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 (dof’s). Here we will allow also 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 will turn out to be false.

Evidently, determining only $M$ dof’s leaves the overwhelming number $6N - M$ dof’s undetermined. All $N$-body systems with the same macroscopic constraints are simultaneously described by Thermodynamics. These systems define an ensemble $\mathcal{M}$ of points $^2$ 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. Considered on this level we call Thermodynamics thermo-statistics or since Gibbs Statistical Mechanics.

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 $\{(q_i(t), p_i(t))\}_{i=1}^N$ (I consider only classical mechanics) 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 $\mathcal{E}$ in the $n$-body phase space. Boltzmann has shown that $S(E, N, V)$ 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

$$S = k \ln W$$

Boltzmann’s principle $^1$ from which Boltzmann was able to deduce thermodynamics. Precisely $W$ is the number of micro-states $^3$ of the $N$-body system at given energy $E$ in the spatial volume $V$ and further-on I put Boltzmann’s constant $k = 1$:

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

$$\text{tr}[\delta(E - \hat{H}_N)] = \int_{(q,v)} \frac{1}{N!} \left(\frac{d^3 q \, d^3 p}{(2\pi \hbar)^3}\right)^N \delta(E - \hat{H}_N),$$

$\epsilon_0$ is a suitable energy constant to make $W$ dimensionless, the $N$ positions $q$ are restricted to the volume $V$, whereas the momenta $p$ 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.

$^2$In this paper I denote ensembles or manifold in phase space by calligraphic letters like $\mathcal{M}$.

$^3$In the following I will call single points in the $6N$-dim phase-space states or micro-states which are specific microscopic realizations of the $N$-body system and correspond to single $N$-body quantum states in quantum mechanics. These must be distinguished from macro-states used in phenomenological thermodynamics c.f. section V.
In contrast to Boltzmann [2,3] who used the principle only for dilute gases and to Schrödinger [13], who thought equation (1) is useless otherwise, I take the principle as the fundamental, generic definition of entropy. In a recent book [14] cf. also [15,16] I demonstrated that this definition of thermo-statistics works especially also at higher densities and at phase transitions without invoking the thermodynamic limit. This is important: Elliot Lieb [17,18] considers the additivity of $S(E)$ and Lebowitz [19,11] the thermodynamic limit as essential for the deduction of thermo-statistics. However, neither is demanded if one starts from Boltzmann’s principle. Boltzmann’s principle eq.(1) is the only axiomatic assumption necessary for thermo-statistics. This is all that Statistical Mechanics demands, no further assumption must be invoked. Neither does one need extensivity $^4$, nor additivity, nor concavity of $S(E)$ c.f. [20]. In the next section I will show how Boltzmann’s principle allows to define phase-transitions in “Small”, non-extensive as well in normal “large” extensive systems where our more general definition of phase transitions (see below) will coincide with the conventional definition by the Yang-Lee singularities [21,22].

Of course one should not wonder if some familiar features of conventional canonical thermo-statistics do not hold anymore in “Small” systems. This is discussed in some more detail in subsection III A

### III. WHY IS THE MICRO-CANONICAL ENSEMBLE FUNDAMENTAL?

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

$$\frac{\Delta E}{E} \propto V^{-1/3}. \tag{4}$$

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.

#### A. Equivalence of ensembles and self-averaging

In contrast, the canonical ensemble does not care about these details, assumes the system is homogeneous, averages over a Boltzmann-Gibbs (exponential) distribution $P_{BG}\{q_\alpha,p_\alpha\} = \frac{1}{Z(\beta)} e^{-\beta\hat{H}({q_\alpha,p_\alpha})}$ 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 or at phase transitions of first order. Then one must work in the micro, the only orthode ensemble. The micro-ensemble assumes precise – perhaps idealized – boundary conditions for each particle independently of whether the system is small or large. Therefore, already Gibbs considered the micro-ensemble as the fundamental and the canonical as approximation to it. He demonstrates clearly the failure of the canonical in cases of phase separation or other situations where both ensemble differ, footnote on page 75 of [5], see also [23,24].

There are important features where the microcanonical statistics of “Small” systems deviates from the “canonical” structure of conventional thermo-statistics of extensive systems in the thermodynamical limit:

E.g. the familiar Legendre-transform structure, a paradigm of “canonical” thermo-statistics, is lost. Clearly, without self-averaging, fixing an intensive parameter like the temperature $T$ does

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$^4$ Dividing extensive systems into larger pieces, the total energy and entropy are equal to the sum of those of the pieces. I will call non-extensive systems where this is not the case in the following also “Small” systems [14] (with a capital $S$!) to stress the paradoxical point that the largest systems in nature (globular galaxies) belong to this group as well, nevertheless, they cannot be treated in the thermodynamic limit.
not fix the energy sharply. Most evident example is a transition of first order in the canonical ensemble at the transition temperature where the energy per particle fluctuates by the specific latent heat even in the thermodynamic limit. Related is the occurrence of negative specific heat cf. section IV B found in recent experiments on nuclei [25,26] which was predicted many years before [27]. Here, there are at least three energies for the same temperature c.f. section IV C.

The present discussions of non-extensive statistics as proposed by Tsallis [28] or recently by Vives et al. [29] clearly miss this crucial point. In the Tsallis statistics the entropy is expressed by the mean-values of the extensive quantities like \( <E> \) [29,30] controlled by a Lagrange parameter \( \beta \) or \( \beta^* \). Of course, this is equivalent to the micro-ensemble (is an orthode) only if the variance of the energy is small. In one or the other way the thermodynamic limit, extensivity, and self-averaging is still demanded where Legendre transformations (may) become one to one. However, in the case of non-extensive systems the existence of the thermodynamic limit is unlikely and so is the uniqueness of the Legendre transformation.

B. Tsallis statistics does not apply to Hamiltonian systems at equilibrium

Tsallis suggested to extend the Boltzmann-Gibbs canonical energy distribution \( P_{BG}(q_i,p_i) \) by using the \( q \)-exponential [31,30]:

\[
e^q_x = [1 + (1 - q)x]^\frac{1}{1 - q},
\]

and replacing \( P_{BG}(q_i,p_i) = \frac{e^{-\beta H(q_i,p_i)}}{Z(\beta)} \)

where:

\[
Z(\beta) = \int_{\{q_i \in V\}} \frac{1}{N!} \left( \frac{d^3 q_i \, d^3 p_i}{(2\pi \hbar)^3} \right)^N e^{-\beta H(q_i,p_i)}
\]

with mean-values \( <O>_{BG} = \int_{\{q_i \in V\}} \frac{1}{N!} \left( \frac{d^3 q_i \, d^3 p_i}{(2\pi \hbar)^3} \right)^N O(q_i,p_i) P_{BG}(q_i,p_i) \)

by:

\[
P_{BG}(q_i,p_i) \rightarrow [f(q_i,p_i)]^q
\]

where:

\[
f(q_i,p_i) = \frac{e^{-\beta H(q_i,p_i)}}{Z(\beta)}
\]

and calculating mean values

\[
<O>_q = \frac{N_q}{D_q}
\]

\[
N_q = \int_{\{q_i \in V\}} \frac{1}{N!} \left( \frac{d^3 q_i \, d^3 p_i}{(2\pi \hbar)^3} \right)^N O(q_i,p_i)[f(q_i,p_i)]^q,
\]

\[
D_q = \int_{\{q_i \in V\}} \frac{1}{N!} \left( \frac{d^3 q_i \, d^3 p_i}{(2\pi \hbar)^3} \right)^N [f(q_i,p_i)]^q,
\]

\[
\lim_{q \rightarrow 1} [f(q_i,p_i)]^q = \frac{e^{-\beta H(q_i,p_i)}}{Z(\beta)},
\]

which leads to the Tsallis \( q \)-entropy [28,30,32,31]:

\[
S_q = k \frac{1 - \sum_{\alpha=1}^{W} P^q_\alpha}{q - 1} \quad \lim_{q \rightarrow 1} S_q = - \sum \alpha \, P_{\alpha} \ln P_{\alpha}.
\]

The Tsallis \( q \)-entropy is very similar to \( q \)-dimension well known in mathematics [33]. Its main purpose is to emphasize/suppress small probabilities \( P^q_\alpha \) depending on the parameter \( q < 1 \) or \( q > 1 \) resp..

For a closed Hamiltonian system at energy \( E \), the \( P_\alpha \) are the probabilities for each of the \( W(E) \) microscopic configurations (quantum states). According to Toral [34] this has of course
the following consequences: After maximizing $S_q(E)$ under variation of $P_\alpha$ with the constraint of $\sum P_\alpha = 1$ one obtains the equal probability distribution characterized by Boltzmann’s entropy $W(E) = e^{S(E)}$:

$$P_\alpha = \begin{cases} e^{-S(E)} , & \epsilon_\alpha = E \\ 0 , & \text{otherwise} \end{cases}, \quad S_q = k \frac{1 - e^{(1-q)S(E)}}{q-1}. \quad (16)$$

Moreover, following Abe [31] and Toral [34] the original definitions of the microcanonical temperature and pressure (18) through Boltzmann’s entropy $S(E, N, V)$, eq.(1), 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 see also [29]:

$$S(E, N, V) = \ln W(E, N, V) \quad (17)$$

$$T_{\text{phys}} = \left(\frac{\partial S}{\partial E}\right)^{-1} \quad P_{\text{phys}} = \frac{\partial S/\partial V}{\partial S/\partial E}. \quad (18)$$

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.(1), 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 [35] or the border of chaos [36] etc.

IV. 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. In the conventional Yang-Lee theory phase transitions [21] are indicated by the zeros of the grand-canonical partition sum where the grand-canonical formalism breaks down because of the Yang–Lee singularities of the grand-canonical potentials. In the following I show that the micro-canonical ensemble gives a much more detailed and more natural insight which moreover corresponds to the experimental identification of phase transitions by interfaces (inhomogeneities).

A. Relation of the topology of $S(E, N, V)$ to the Yang-Lee zeros of $Z(T, \mu, V)$

The grand-canonical partition sum may be obtained out of the micro-canonical one by a double Laplace transform. To explore the link to the Yang-Lee singularities I discuss it for the moment in the thermodynamic limit (large volume $V$, large number of particles $N$ but homogeneous constant density $n = N/V$). In this limit it does not matter whether $N$ is discrete or continuous.)

$$Z(T, \mu, V) = \int_0^\infty dE \int_0^\infty dN \frac{e^{-[E-\mu N-TS(E)]}}{T} \int_0^\infty d\varepsilon d\nu \frac{e^{-\varepsilon \mu - Ts(\varepsilon, \nu)}}{T} \approx \frac{V^2}{\epsilon_0} \int_0^\infty d\varepsilon d\nu e^{-V[\text{const.} + \text{lin.} + \text{quadr.}]} \quad (19)$$

and we investigate the specific free energy $f(T, \mu) = -\ln(Z)/V$ in the thermodynamic limit $V \rightarrow \infty | N/V = \text{const.}$.

The double Laplace integral (19) can be evaluated asymptotically for large $V$ by expanding the exponent as indicated in the third line to second order in $\Delta \varepsilon, \Delta \nu$ around the “stationary point” $e_s, n_s$ where the linear terms vanish:
the only terms remaining to be integrated are the quadratic ones. If the eigen-curvature $\lambda_1 < 0$ eq.(24), and eqs.(20) have a single solution $(e_s, n_s)$, this is then a Gaussian integral and yields:

$$Z(T, \mu, V) = \frac{V^2}{e_0} e^{-V[e_s - \mu n_s - TS(e_s, n_s)]/T} \int_{-\infty}^{\infty} dv_1 \int_{-\infty}^{\infty} dv_2 e^{V(\lambda_1 v_1^2 + \lambda_2 v_2^2)/2}$$  \hspace{1cm} (21)

$$f(T, \mu, V) := \frac{F(T, \mu, V)}{V} \rightarrow e_s - \mu n_s - TS_s + \frac{T \ln(\sqrt{|\det(e_s, n_s)|})}{V} + o(\ln V),$$  \hspace{1cm} (22)

Here $\det(e_s, n_s)$ is the determinant of the curvatures (Hessian) of $s(e, n)$, $v_1, v_2$ are the eigenvectors of the Hessian.

$$\det(e, n) = \begin{vmatrix} \frac{\partial^2 s}{\partial e^2} & \frac{\partial^2 s}{\partial e \partial n} \\ \frac{\partial^2 s}{\partial n \partial e} & \frac{\partial^2 s}{\partial n^2} \end{vmatrix} = \begin{vmatrix} s_{ee} & s_{en} \\ s_{ne} & s_{nn} \end{vmatrix} = \lambda_1 \lambda_2, \quad \lambda_1 \geq \lambda_2$$  \hspace{1cm} (24)

$\lambda_1$ can be positive or negative. If $\lambda_1 < 0$ and eqs.(20) have no other solution, the last two terms in eq.(23) go to 0, and we obtain in the thermodynamic limit ($V \rightarrow \infty$) the familiar result for the free energy density:

$$f(T, \mu, V \rightarrow \infty) = e_s - \mu n_s - TS_s.$$  \hspace{1cm} (25)

I.e. the curvature $\lambda_1$ of the entropy surface $s(e, n, V)$ or the largest eigenvalue of the Hessian matrix decides whether the grand-canonical ensemble agrees with the fundamental micro-ensemble in the thermodynamic limit. If this is the case and eqs.(20) have a single solution or $s(e, n)$ touches its concave hull at $e_s, n_s$, then there is a pointwise one to one mapping of the micro-canonical entropy $s(e, n)$ to the grand-canonical partition sum $Z(T, \mu)$, and $\ln[Z(T, \mu)]/V$ or $f(T, \mu)$ is analytical in $z = e^{\beta \mu}$. Due to Yang and Lee we have then a single, stable phase [22]. Otherwise, the Yang-Lee zeros of $Z(T, \mu)$ reflect anomalous points/regions of $\lambda_1 \geq 0$ ($\det(e_s, n_s) \leq 0$) where the canonical partition sum does not reflect local properties of the micro-ensemble, i.e. does not respect the conservation laws, and mixes conserved quantities. This is crucial. As $\det(e_s, n_s)$ can be studied for finite or even small systems as well, this is the only proper extension of phase transitions to “Small” systems.

**B. The physical origin of the wrong curvature**

I will now discuss the physical origin of the convex (upwards bending) intruders in the entropy surface for systems with short-range coupling in two examples.
1. Liquid-gas transition in sodium clusters

![Image of graph showing liquid-gas transition in sodium clusters]

In table (I) I compare the “liquid–gas” phase transition in sodium clusters of a few hundred atoms with that of the bulk at 1 atm. c.f. also fig.(1).

| Na   | $N_0$  | 200  | 1000 | 3000 | bulk |
|------|--------|------|------|------|------|
| $T_{tr}$ [K] | 940   | 990  | 1095 | 1156 |      |
| $q_{lat}$ [eV] | 0.82  | 0.91 | 0.94 | 0.923 |      |
| $s_{bulk}$ | 10.1  | 10.7 | 9.9  | 9.207 |      |
| $\Delta s_{surf}$ | 0.55  | 0.56 | 0.44 |      |      |
| $N_{surf}$ | 39.94 | 98.53 | 186.6 | $\infty$ |      |
| $\sigma/T_{tr}$ | 2.75  | 5.68 | 7.07 | 7.41 |      |

TABLE I. Parameters of the liquid–gas transition of small sodium clusters (MMMC-calculation) in comparison with the bulk for rising number $N_0$ of atoms, $N_{surf}$ is the average number of surface atoms (estimated here as $\sum N_{cluster}^2/3$ of all clusters together. $\sigma/T_{tr} = \Delta s_{surf} * N_0/N_{surf}$ corresponds to the surface tension. Its bulk value is adjusted to the experimental input values used for the binding energies of clusters as given by Brechignac et al. c.f. [14].

Conclusion: For systems with short range interactions a convex intruder in $s(e, n)$ appears with the fragmentation of the system into several clusters and monomers. The number of surface particles scales with the depth of the intruder (surface entropy). I.e. the convex intruder signals the preference of the system to become inhomogeneous, the characteristic signal for the separation of different phases (liquid and gas) at a phase transition of first order.

2. The topology of the entropy surface $S(E, N)$ for Potts lattice gases

Having discussed in the previous example a system with a single thermodynamic degree of freedom or control parameter (the energy $E$) we will now study more subtle features. If the system has two, or more, degrees of freedom, e.g. energy $E = V e$ and particle number $N = V n$, where $V$ is the volume, we can have phase boundaries and critical points. This is similar to the classical $P – V$ diagram of the liquid–gas phase transition in the Van der Waals theory. We are now able to identify multi-critical points. These were previously studied in the canonical ensemble only, where sophisticated finite size scaling is needed to identify these points.

As example we investigate the 3-states diluted Potts model 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:
Each lattice site $i$ is either occupied by a particle with spin $\sigma_i = -1$, 0, or 1, or it is empty (vacancy). The sum is over pairs of neighboring lattice sites $i, j$, and the occupation numbers are:

$$\alpha_i = \begin{cases} 
1, & \text{spin particle in site } i \\
0, & \text{vacancy in site } i 
\end{cases}$$

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 in the thermodynamic limit a continuous phase transition at $e_c = 1 + \frac{1}{\sqrt{q}} \approx 1.58$ [37,38]. With rising number of vacancies the probability to find a pair of particles at neighboring sites with the same spin orientation decreases. I.e. this is similar to a larger number of spin orientation $q_{eff}$ on each lattice site in the ordinary Potts model, where we know that the transition of second order becomes a transition of first order for $q > 4$.

Thus the inclusion of vacancies has the effect of an increasing effective $q_{eff} \geq 3$. 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. From here on 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).

Figure (2) shows how for a small system of 50*50 lattice points all phenomena of phase transitions can be studied from the topology of the determinant of curvatures (24) in the micro-canonical ensemble. In this example the second curvature $\lambda_2 < 0$ so $\text{sign} \text{det} = -\text{sign} \lambda_1$.

C. Systematics of phase transitions in the micro-ensemble

Now we can give a systematic and generic classification of phase transitions in terms of the topology of curvatures of $s(e, n)$ which applies also to “Small” systems.
A single stable phase by $\lambda_1 < 0$. Here $s(e,n)$ is locally concave (downwards bended) in both directions and eqs.(20) have a single solution $e_s, n_s$. Then there is a one to one mapping of the grand-canonical ↔ the micro-ensemble. The order parameter is the direction $v_1$ of the eigenvector of largest curvature $\lambda_1$. In many situations one may have only locally $\lambda_1 < 0$, however, there may be further solutions to eqs.(20) farther away. In such cases which have no equivalent in the canonical ensemble, we will still speak of regions in $\{e, n\}$ of pure phases embedded in regions of phase-separation.

A transition of first order with phase separation and surface tension (c.f. subsection IV B 1) indicated by $\lambda_1 > 0$. $s(e,n)$ has a convex intruder (upwards bended) in the direction $v_1$ of the largest curvature. Then eqs.(20) 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. if the largest curvature of $S(E,N)$ is $\lambda_1 > 0$ both ensembles are not equivalent, the (grand-) canonical ensemble is non-local in the order parameter and violates basic conservation laws. See also [14–16,39]. The region in the plane of conserved control-parameters $e, n$ where we have a separation of different phases, $\lambda_1(e,n) > 0$, is bounded by lines with $\lambda_1(e,n) = 0$. On this boundary is the end-point of the transition of first order,

where we have a continuous ("second order") transition with vanishing surface tension, where two neighboring phases become indistinguishable. This is at points where the two stationary points move into one another to become the critical end-point of the first order transition. This is then also a maximum of $\lambda_1$. I.e. where $\lambda_1(e,n) = 0$ and $v_{\lambda_1=0} \cdot \nabla \lambda_1 = 0$. These are the catastrophes of the Laplace transform $E \rightarrow T$. Here $v_{\lambda_1=0}$ is the eigenvector of the Hessian belonging to the largest curvature eigenvalue $\lambda_1 = 0$. ($v_1$ plays the role of the order parameter of the transition. In this direction one moves fastest from one phase to the other.) At the other points of $\lambda_1(e,n) = 0$ one of the two coexisting phases gets depleted. Furthermore, there may be also whole lines of second-order transitions like in the anti-ferro-magnetic Ising model c.f. [14].

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 $\lambda_1 = 0, \nabla \lambda_1 = 0$. Fig. 2 gives an illustration of a multicritical point in a small system.

Just a comment on the interesting suggestion by Pettini et al. [40] to characterize phase transitions by topological changes of the potential energy: They claim that phase transitions are signalized by sudden changes of the topology of the configurational energy. However, one has to keep in mind: In the thermodynamic limit, first order transitions are characterized by two essential things:

1. There are two or more phases (different types of configurations, liquid and gas, or ordered and disordered) which coexist at the same temperature $T = [\partial S/\partial E]^{-1}$.

2. Between both configurations the total energy per particle, or the potential energy per particle differs by the specific latent heat.

Of course not every topological jump in the configuration energy corresponds to a phase transition [40] and not every jump is accompanied by the same kinetic energy per particle (temperature) or more precisely by the same slope $T = [\partial S/\partial E]^{-1}$ of the entropy. Evidently, topological changes are likely necessary conditions (Pettini) for phase transitions to occur, however, the sufficient
condition is the same temperature $T = [\partial S/\partial E]^{-1}$ at two different values of the order-parameters, energy or magnetization etc.

Also the suggestion of Borrmann et al. [41] to characterize phase transitions in small systems by the zeros of the canonical partition sum must be commented: This idea extends the idea of Yang and Lee and the work of Grossmann [42]. First, the canonical partition sum is a derived quantity which is not an orthode at phase transitions, c.f. section III, as was already noticed by Gibbs, footnote on page 75 of [5]. Moreover, in some situations of non-extensive systems it may not even exist.

V. MEASURING A MACROSCOPIC OBSERVABLE

After succeeding to deduce equilibrium statistics including all phenomena of phase transitions from Boltzmann’s principle alone even for “Small” systems, i.e. non-extensive many-body systems [14], it is challenging to explore how far this “most conservative and restrictive way to thermodynamics” [43] is able to describe also the approach of (possible “Small”) systems to equilibrium and the Second Law of Thermodynamics.

Thermodynamics describes the development of macroscopic features of many-body systems without specifying them microscopically in all details. Before I address the Second Law, I have to clarify what I mean with the label “macroscopic observable”.

A single point $(q(t), p(t))_{i=1,\ldots,N}$ in the $N$-body phase space corresponds to a detailed specification of the system with all degrees of freedom (dof’s) completely fixed at time $t$ (microscopic determination, the curly brackets indicate the whole set of $6N$ coordinates $q_i, p_i$ of all particles $i$). Fixing only the total energy $E$ of an $N$-body system leaves the other $(6N-1)$-degrees of freedom unspecified. A second system with the same energy is most likely not in the same microscopic state as the first, it will be at another point in phase space, the other dof’s will be different. I.e. the measurement of the total energy $\hat{H}_N$, or any other macroscopic observable $\hat{M}$, determines a $(6N-1)$-dimensional sub-manifold $\mathcal{E}$ or $\mathcal{M}$ in phase space. (The manifold $\mathcal{M}$ is called by Lebowitz a macro-state [19,11] which contains $\Gamma_{\mathcal{M}} = W(M)$ micro-states. I, however, prefer to use the name “state” only for micro-states or points in phase space.) All points (the micro-states) in $N$-body phase space consistent with the given value of $E$ and volume $V$, i.e. all points in the $(6N-1)$-dimensional sub-manifold $\mathcal{E}(N,V)$ of phase space are equally consistent with this measurement. $\mathcal{E}(N,V)$ is the micro-canonical ensemble. This example tells us that any macroscopic measurement is incomplete and defines a sub-manifold of points in phase space not a single point. An additional measurement of another macroscopic quantity $\hat{B}(q,p)$ reduces $\mathcal{E}$ further to the cross-section $\mathcal{E} \cap \mathcal{B}$, a $(6N-2)$-dimensional subset of points in $\mathcal{E}$ with the volume:

$$W(B,E,N,V) = \frac{1}{N!} \int \left( \frac{d^3q \, d^3p}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N(q,p)) \delta(B - \hat{B}(q,p))$$

(28)

If $\hat{H}_N(q,p)$ as well as also $\hat{B}(q,p)$ are continuous differentiable functions of their arguments, what I assume in the following, $\mathcal{E} \cap \mathcal{B}$ is closed. In the following I use $W$ for the Riemann or Liouville volume (Hausdorff measure) of a many-fold.

Microcanonical thermostatics gives the probability $P(B,E,N,V)$ to find the $N$-body system in the sub-manifold $\mathcal{E} \cap \mathcal{B}(E,N,V)$:

$$P(B,E,N,V) = \frac{W(B,E,N,V)}{W(E,N,V)} = e^{\ln[W(B,E,N,V)] - S(E,N,V)}$$

(29)

This is what Krylov seems to have had in mind [44] and what I will call the “ensemble probabilistic formulation of Statistical Mechanics (EPS)”.

Similarly thermodynamics describes the development of some macroscopic observable $\hat{B}(q,p)$ in time of systems which were specified at an earlier time $t_0$ by another macroscopic measurement $\hat{A}(q_0,p_0)$. It is related to the volume of the sub-manifold $\mathcal{M}(t,t_0) = \mathcal{A}(t_0) \cap \mathcal{B}(t) \cap \mathcal{E}$:

$$W(A,B,E,t) = \frac{1}{N!} \int \left( \frac{d^3q_i \, d^3p_i}{(2\pi\hbar)^3} \right)^N \delta(B - \hat{B}(q,t,p)) \delta(A - \hat{A}(q_0,p_0)) \epsilon_0 \delta(E - \hat{H}(q,t,p)),$$

(30)
where \( \{q_i(t, p_0), p_i(t, p_0)\} \) is the set of trajectories solving the Hamilton-Jacobi equations

\[
\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i = 1 \cdots N
\]

with the initial conditions \( \{q(t = t_0) = q_0; \ p(t = t_0) = p_0\} \). For a large system with \( N \sim 10^{23} \) the probability to find a given value \( B(t), P(B(t)) \), is usually sharply peaked as function of \( B \) at its typical value. Such systems are called self-averaging. Ordinary thermodynamics treats systems in the thermodynamic limit \( N \to \infty \) and gives only \( \langle B(t) \rangle \). However, here we are interested to formulate the Second Law for “Small” systems i.e. we are interested in the whole distribution \( P(B(t)) \) not only in its mean value \( \langle B(t) \rangle \). There are also many situation where the system is not self-averaging, where a finite variance remains even in the thermodynamic limit. (E.g. at phase transitions of first order the energy per particle fluctuates in the canonical ensemble by the specific latent heat.)

There is an important property of macroscopic measurements: Whereas at finite times Hamilton dynamics evolves a compact region of phase space again into a compact region, this does not need to be so at infinite times. Then, at \( t \to \infty \), the set may not be closed anymore (perhaps a fractal, see below). This means there exist series of points \( \{a_n\} \in \mathcal{A}(t = \infty) \) which converge to a point \( \lim_{n \to \infty} a_n =: a_n=\infty \) which is not in \( \mathcal{A}(t = \infty) \). E.g. such points \( a_n=\infty \notin \mathcal{A}(\infty) \) may have intruded from the phase space complementary to \( \mathcal{A}(t_0) \). Illustrative examples for this evolution of an initially compact sub-manifold into a fractal set are the generalized baker transformations discussed in this context by ref. [45,46]. See reference [33] for the fractal distribution produced by the general baker transformation.(As any housewife knows, a baker dough becomes an infinitely thin (fractal) puff pastry after pounding and folding it infinitely often.) Then no macroscopic (incomplete) measurement can resolve \( a_n=\infty \notin \mathcal{A}(t = \infty) \) from its immediate neighbors \( a_n \in \mathcal{A}(t = \infty) \) in phase space with distances \( |a_n - a_n=\infty| \) less then any arbitrary small \( \delta \). In other words, at the time \( t - t_0 \to \infty \) no macroscopic measurement with its incomplete information about \( \{q_{t=\infty}, p_{t=\infty}\} \) can decide whether \( \{q_0(q_{t=\infty}, p_{t=\infty}), p_0(q_{t=\infty}, p_{t=\infty})\} \in \mathcal{A}(t_0) \) or not. I.e. any macroscopic theory like thermodynamics can only deal with the closure of \( \mathcal{A}(t \to \infty) \). If necessary, the sub-manifold \( \mathcal{A}(t \to \infty) \) must be artificially closed \(^5\) to \( \overline{\mathcal{A}(t = \infty)} \) as developed further in section VII. Clearly, in this approach this is the physical origin of irreversibility.

VI. ON EINSTEIN’S OBJECTIONS AGAINST THE EPS-PROBABILITY

Before I proceed I must comment on Einstein’s attitude to the principle [47]: Originally, Boltzmann called \( W \) the “Wahrscheinlichkeit” (probability), i.e. the relative time a system spends (along a time-dependent path) in a given region of \( 6N \)-dim. phase space. Our interpretation of \( W \) to be the number of “complexions” (Boltzmann’s second interpretation) or quantum states (trace) with the same energy was criticized by Einstein [12] as artificial. It is exactly that criticized interpretation of \( W \) which I use here and which works so excellently [14].

According to Abraham Pais: “Subtle is the Lord” [47], Einstein was critical with regard to the definition of relative probabilities by eq.(29), Boltzmann’s counting of “complexions”. He considered it as artificial and not corresponding to the immediate picture of probability used in the actual problem: “The word probability is used in a sense that does not conform to its definition as given in the theory of probability. In particular, cases of equal probability are often hypothetically defined in instances where the theoretical pictures used are sufficiently definite to give a deduction rather than a hypothetical assertion” [12]. He preferred to define probability by the relative time a system (a trajectory of a single point moving with time in the \( N \)-body phase space) spends in a given subset of the phase space. However, is this really the immediate picture of probability used in Statistical Mechanics? This definition demands the ergodicity of the trajectory in phase space. As I discussed above, thermodynamics as any other macroscopic theory handles incomplete,

\(^5\) First \( t \to \infty \) then the closure, not the other way round c.f. however, the discussion in VIII.
macroscopic informations of the $N$-body system. It handles, consequently, the temporal evolution of finite sized sub-manifolds - ensembles - not single points in phase space. In the case of a very large system the typical outcomes of macroscopic measurements are calculated. Nobody waits in a macroscopic measurement, e.g. of the temperature of a gas, long enough that an atom can cross the whole system.

In this respect, I think the EPS version of Statistical Mechanics is closer to the experimental situation than the duration-time of a single trajectory. Moreover, in an experiment on a small system like an excited nucleus, which then may fragment statistically later on, the average over a multiple repetition of scattering events is taken. No ergodic covering of the whole phase space by a single trajectory in time is demanded. Fragmenting nuclei at such high excitation have a too short lifetime. This is analogous to the statistics of a falling ball on a Galton’s nail-board where also a single trajectory does not touch all nails but is random. Only after many repetitions the smooth binomial distribution is established. For the discussion of the Second Law in finite systems, this is the correct scenario, not the time average over a single ergodic trajectory.

VII. FRACTAL DISTRIBUTIONS IN PHASE SPACE, SECOND LAW

Here I will first describe a simple working-scheme (i.e. a sufficient method) which allows to deduce mathematically the Second Law. Later, I will show how this method is necessarily implied by the reduced information obtainable by macroscopic measurements or theories.

Let us examine the following Gedanken experiment: Suppose the probability to find our system at points $\{q_t, p_t\}_t^N$ in phase space is uniformly distributed for times $t < t_0$ over the sub-manifold $\mathcal{E}(N, V_1)$ 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 $\{q_t, p_t\}_t^N$ in phase space starting from points $\{q_0, p_0\}_t^N$ 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 $t > t_0$ will remain the same ($= tr[\mathcal{E}(N, V_1)]$) [48]. (The label $\{q_0 \in V_1\}$ of the integral means that the positions $\{q_0\}_1^N$ are restricted to the volume $V_1$, whereas the momenta $\{p_0\}_1^N$ are unrestricted.)

$$tr[\mathcal{M}(t, t_0)]|_{\{q_0 \in V_1\}} = \int_{\{q_0, p_t\}_t^N \in V_1} \frac{1}{N!} \left( \frac{d^3 q_t \, d^3 p_t}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_t, p_t\})$$

$$= \int_{\{q_0 \in V_1\}} \frac{1}{N!} \left( \frac{d^3 q_0 \, d^3 p_0}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_0, p_0\}),$$

(32)

because of:

$$\frac{\partial(q_t, p_t)}{\partial(q_0, p_0)} = 1.$$  

(33)

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 $\mathcal{M}(t = \infty, t_0)$ becomes equal to $\mathcal{E}(N, V_2)$. This is clearly expressed by Lebowitz [19,11].

In order to express this fact mathematically, I transform integrals over the phase space like (3) or (28):

$$W(E, N, t, t_0) = \frac{1}{N!} \int_{\{q_t, p_t\}_t^N \subset V_1} \left( \frac{d^3 q_t \, d^3 p_t}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_t, p_t\})$$

(34)

into:
\[
\int (d^3q_i \ d^3p_i)^N \cdots = \int d\sigma_1 \cdots d\sigma_{6N} \cdots
\]

\[
d\sigma_{6N} := \frac{1}{||\nabla H||} \sum_i \left( \frac{\partial \hat{H}}{\partial q_i} dq_i + \frac{\partial \hat{H}}{\partial p_i} dp_i \right) = \frac{1}{||\nabla H||} dE
\]

\[
||\nabla \hat{H}|| = \sqrt{\sum_i \left( \frac{\partial \hat{H}}{\partial q_i} \right)^2 + \sum_i \left( \frac{\partial \hat{H}}{\partial p_i} \right)^2}
\]

\[
W(E, N, t, t_0) = \frac{1}{N! (2\pi\hbar)^{3N}} \int_{(q_t\{q_t\} \subset V_t)} d\sigma_1 \cdots d\sigma_{6N-1} \frac{\epsilon_0}{||\nabla H||}.
\]

Now, I redefine Boltzmann's definition of entropy eq. (1 to 3):

\[
S = \ln(W(E, N, V))
\]

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

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

by replacing the Riemannian integral for \( W \) by its box-counting “measure”:

\[
W(E, N, V) \to \mathcal{H}_d \int_{\{q_0\{q_t\} \subset V_t\}} \frac{1}{N!} \left( \frac{d^3q \ d^3p}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N),
\]

i.e. the volume of \( \mathcal{M} \) by that of its closure \( \overline{\mathcal{M}} \). In detail we perform the following steps:

\[
M_\delta(t, t_0) := <G>_{\delta} \ast \text{vol}_{\text{box,}\delta}[\mathcal{M}(t, t_0)],
\]

to obtain \( \text{vol}_{\text{box,}\delta}[\mathcal{M}(t, t_0)] \) we cover the \( d \)-dim. sub-manifold \( \mathcal{M}(t, t_0) \), here with \( d = (6N - 1) \), of the phase space by a grid with spacing \( \delta \) and count the number \( N_\delta \propto \delta^{-d} \) of boxes of size \( \delta^N \), which contain points of \( \mathcal{M}(t, t_0) \). This is illustrated by fig.(3). Then \( \text{vol}_{\text{box,}\delta}[\mathcal{M}(t, t_0)] := \delta^{-d} N_\delta[\mathcal{M}(t, t_0)] \) and \( <G>_{\delta} \) is the average of \( \mathcal{H}_d \int_{\mathcal{M}(t, t_0)} \frac{1}{N!} \left( \frac{d^3q \ d^3p}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N) \) over these non-empty boxes of size \( \delta \).

The \( \lim_{\delta \to 0} \text{vol}_{\text{box,}\delta}[\mathcal{M}(t, t_0)] \) is the box-counting volume of \( \mathcal{M}(t, t_0) \) which is the same as the volume of its closure \( \overline{\mathcal{M}(t, t_0)} \), see below:

\[
\text{vol}_{\text{box}}[\mathcal{M}(t, t_0)] := \lim_{\delta \to 0} \delta^d N_\delta[\mathcal{M}(t, t_0)]
\]

with \( \lim \ast = \inf \lim \ast \) and write symbolically:

\[
\lim_{\delta \to 0} M_\delta(t, t_0) =: \mathcal{H}_d \int_{\{q_0\{q_t\} \subset V_t\}} \frac{1}{N!} \left( \frac{d^3q \ d^3p}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N),
\]

where \( \mathcal{H}_d \) means that this integral should be evaluated via the box-counting volume (the limit of expression 43 with the use of 44) here with \( d = 6N - 1 \). This is illustrated by the following figure.
The box-counting integral $K(t)$, the average rate of entropy gain \[49,33\]. The box-counting is also used in the definition of the rational numbers $\vol_{\text{box}}$ to the measure of the smallest dimension of a set of points \[49\] by the box-counting dimension:

$$\dim_{\text{box}}[M(t, t_0)] := \lim_{\delta \to 0} \frac{\ln N_\delta[M(t, t_0)]}{-\ln \delta}. \quad (48)$$

Like the box-counting dimension, the box-counting “measure” has the peculiarity that it is equal to the measure of the smallest closed covering set. E.g.: The box-counting volume of the set of rational numbers $\vol_{\text{box}}\{Q\}$ between 0 and 1 is $1$, and thus equal to the measure of the real numbers, c.f. Falconer \[49\] section 3.1. This is the reason why the box-counting “measure” is not a measure in its mathematical definition because then we should have

$$\vol_{\text{box}} \left[ \sum_{i \in \{Q\}} (M_i) \right] = \sum_{i \in \{Q\}} \vol_{\text{box}}[M_i] = 0, \quad (49)$$

therefore the quotation marks for the box-counting “measure”, c.f. appendix X.

Coming back to the the end of section (V), the volume $W(A, B, \cdots, t)$ of the relevant ensemble, the closure $M(t, t_0)$ must be “measured” by something like the box-counting “measure” \(42\) with the box-counting integral $\int_{\delta}$ which must replace the integral in eq.\(3\). Due to the fact that the box-counting volume is equal to the volume of the smallest closed covering set, the new, extended, definition of the phase-space integral eq.\(42\) is for compact sets like the equilibrium distribution

\[V_a \rightarrow V_a + V_b\]
identical to the old one eq. (3) and our redefinition of the phase-space integral by box-counting changes nothing for equilibrium statistics. Therefore, one can simply replace the old Boltzmann-definition of the number of complexions and with it of the entropy by the new one (42) of course with the understanding that the closure operation with the box-counting volume (42) should be done after the times were specified.

VIII. CONCLUSION

In this paper I showed that Boltzmann’s principle eq.(1) covers in a simple and straight way both of Lebowitz’s central issues of statistical mechanics [11]. Earlier formulations of these ideas can be found in [50,51]. Lebowitz emphasises the necessity of self-averaging for thermodynamics which describes the typical outcome of a macroscopic measurement. This can only be expected for large systems, in the thermodynamic limit. However, there are many situations where even large systems are not self-averaging. E.g. at phase transitions of first order. Moreover, a whole world of non-extensive systems, like the “Small” systems, show broad, often not single peaked, phase-space distributions. E.g. in scattering experiments on nuclei or atomic clusters an average over millions of events is taken. Thus the whole distribution in the accessible phase space is measured. These are certainly the most interesting situations. An extension of statistical mechanics to cover also these is demanded.

Macroscopic measurements \( \hat{M} \) determine only a very few of all \( 6N \) dof. Any macroscopic theory like thermodynamics deals with the area \( M \) of the corresponding closed sub-manifolds \( \overline{M} \) 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 finite or any other not self-averaging system.

Because of this necessarily coarsed information, macroscopic measurements, and with it also macroscopic theories are unable to distinguish fractal sets \( M \) from their closures \( \overline{M} \). Therefore, I make the conjecture: the proper manifolds determined by a macroscopic theory like thermodynamics are the closed \( \overline{M} \). However, an initially closed subset of points at time \( t_0 \) does not necessarily evolve again into a closed subset at \( t = \infty \) and the closure operation must be explicitly done after setting the times in order to obtain a quantity that is relevant for a macroscopic theory and can be compared to thermodynamics. As the closure operation and the \( t \to \infty \) limit do not commute, the macroscopic dynamics becomes irreversible.

Here is the origin of the misunderstanding by the famous reversibility paradoxes which were invented by Loschmidt [52] and Zermelo [53,54] and which bothered Boltzmann so much [55,56]. These paradoxes address to trajectories of single points in the \( N \)-body phase space which must return after Poincaré’s recurrence time or which must run backwards if all momenta are exactly reversed. Therefore, Loschmidt and Zermelo concluded that the entropy should decrease as well as it was increasing before. The specification of a single point in \( 6N \)-dim phase-space and the reversion of all its \( 3N \) momentum components demands of course a microscopic exact specification of all \( 6N \) degrees of freedom not a determination of a few macroscopic degrees of freedom only. No entropy is defined for a single point. Thermodynamics is addressed to the whole manifold, ensemble of systems with the same macroscopic constraints. The ensemble develops irreversibly even though the underlining Newtonian dynamics of each phase-space point is fully reversible. It is highly unlikely that all points in the ensemble \( M(t, t_0) \) have commensurable recurrence times so that they can return simultaneously to their initial positions. Once the manifold has spread over the larger phase space it will never return.

Also other misinterpretation 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. Closed non-extensive Hamiltonian systems at equilibrium do not follow Tsallis non-extensive statistics [28]. Boltzmann’s principle describes the equilibrium and the approach of the equilibrium of extensive as well of non-extensive Hamiltonian systems.

By our derivation of micro-canonical Statistical Mechanics for finite, eventually “Small” 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 [43] 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 simple geometric interpretation, leads to the full spectrum of equilibrium thermodynamics including all kinds of phase transitions and including the Second Law of Thermodynamics.

In this paper, I take the fact serious that Thermodynamics as well as any other macroscopic theory handles ensembles or sub-manyfolds and not single points in phase-space. Thus the use of ensemble averages is justified directly by the very nature of macroscopic (incomplete) measurements. Entropy \( s(e, n) \) is the natural measure of the geometric size of the ensemble. With the Boltzmann definition of \( s(e, n) \) Statistical Mechanics becomes a geometric theory. The topology of its curvature indicates all phenomena of phase transitions independently of whether the system is “Small” or large.

Coarse-graining appears as natural consequence of the ensemble-nature. The box-counting method mirrors the averaging over the overwhelming number of non-determined degrees of freedom. Of course, a fully consistent theory must use this averaging explicitly. Then one would not depend on the order of the limits \( \lim_{\delta \to 0} \lim_{t \to \infty} \) as it was assumed here. Presumably, the rise of the entropy can then already be seen at finite times when the fractality of the distribution in phase space is not yet fully developed. The coarse-graining is no more a mathematical ad hoc assumption. It is the necessary consequence of the averaging over the \( 6N - M \) uncontrolled degrees of freedom. Moreover the Second Law in the EPS-formulation of Statistical Mechanics is not linked to the thermodynamic limit as was thought up to now [11,19].

In this paper I did not contribute anything to the problem of describing irreversible thermodynamics of stationary dissipative systems as it is discussed e.g. by Gilbert and Dorfman [57,46], Rondoni and Cohen [58]. As mentioned already dissipation does not exist in the microscopic dynamics. It is not clear to me how far the inclusion of dissipation predefines the arrow of time already which should have been deduced from the theory. The main problem for me was the derivation of irreversibility from fully time reversible microscopic dynamics under maximally clear conditions, i.e. of a microcanonical closed system.

Gaspard [59,60] considers systems obeying a dynamics that preserves the phase-space volume, i.e satisfying Liouville’s theorem, but under non-equilibrium steady state conditions. Similarly to the present approach he had to coarse grain (width \( \delta \)) the accessible phase space. In conformity to the standard view of thermodynamics being based on the thermodynamic limit [19] he then proves the rise of the entropy after the limits (in that order) \( \delta \to 0, V \to \infty \). However, in this limit also the Poincaré recurrence time becomes infinite and Zermelo’s piercing argument becomes blunted. So in this approach Gaspard cannot treat our problem of the Second Law in a finite closed Hamiltonian system which seems to me to be the heart of the reversibility paradox.

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X. APPENDIX

In the mathematical theory of fractals [49] one usually uses the Hausdorff measure or the Hausdorff dimension of the fractal [33]. This, however, would be wrong in Statistical Mechanics. Here I want to point out the difference between the box-counting “measure” and the proper Hausdorff measure of a manifold of points in phase space. Without going into too much mathematical details I can make this clear again with the same example as above: The Hausdorff measure of the rational numbers \( \mathbb{Q} \) is 0, whereas the Hausdorff measure of the real numbers \( \mathbb{R} \) is 1. Therefore, the Hausdorff measure of a set is a proper measure. The Hausdorff measure of the fractal distribution in phase space \( M(t \to \infty, t_0) \) is the same as that of \( M(t_0) \), \( W(E, N, V_1) \). Measured by the Hausdorff measure the phase space volume of the fractal distribution \( M(t \to \infty, t_0) \) is conserved.
and Liouville’s theorem applies. This would demand that thermodynamics could distinguish between any point inside the fractal from any point outside of it independently how close it is. This, however, is impossible for any macroscopic theory which has only macroscopic information where all unobserved degrees of freedom are averaged over. That is the deep reason why the box-counting “measure” must be taken and is a further origin for irreversibility.

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