Second Law of Thermodynamics, Macroscopic Observables within Boltzmann’s Principle but without Thermodynamic Limit

D.H.E. Gross
Hahn-Meitner-Institut Berlin, Bereich Theoretische Physik, Glienickerstr. 100
14109 Berlin, Germany and Freie Universität Berlin, Fachbereich Physik; January 10, 2022

Boltzmann’s principle \( S = k \ln W \) allows to extend equilibrium thermo-statistics to “Small” systems without invoking the thermodynamic limit \([1–3]\). Here we show that the formulation of non-equilibrium statistics and the Second Law can be easier formulated than by conventional theory. A deeper and more transparent understanding is thus possible. The main clue is to base statistical probability on ensemble averaging and not on time averaging. It is argued that due to the incomplete information obtained by macroscopic measurements thermodynamics handles ensembles or finite-sized sub-manifolds in phase space and not single time-dependent trajectories. Therefore, ensemble averages are the natural objects of statistical probabilities. This is the physical origin of coarse-graining which is anymore a mathematical ad hoc assumption. The probabilities \( P(M) \) of macroscopic measurements are given by the ratio \( P(M) = W(M)/W \) of these volumes of the sub-manifold \( M \) of the microcanonical ensemble with the constraint \( M \) to the one without. From this concept all equilibrium thermodynamics can be deduced quite naturally including the most sophisticated phenomena of phase transitions for “Small” systems.

Boltzmann’s principle is generalized to non-equilibrium Hamiltonian systems with possibly fractal distributions \( M \) in \( 6N \)-dim. phase space by replacing the conventional Riemann integral for the volume in phase space by its corresponding box-counting volume. This is equal to the volume of the closure \( \overline{M} \). With this extension the Second Law is derived without invoking the thermodynamic limit.

The irreversibility in this approach is due to the replacement of the phase-space volume of the fractal sub-manifold \( M \) by the volume of its closure \( \overline{M} \). The physical reason for this replacement is that macroscopic measurements cannot distinguish \( M \) from \( \overline{M} \). Whereas the former is not changing in time due to Liouville’s theorem, the volume of the closure can be larger. In contrast to conventional coarse graining the box-counting volume is defined in the limit of infinite resolution. I.e. there is no artificial loss of information.

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I. INTRODUCTION

Recently the interest in the thermo-statistical behaviour of non-extensive many-body systems, like atomic nuclei, atomic clusters, soft-matter, biological systems — and also self-gravitating astrophysical systems lead to consider thermo-statistics without using the thermodynamic limit. This is most safely done by going back to Boltzmann.

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

\[
S = k \ln W
\]  

as Boltzmann’s principle \([4]\) from which Boltzmann was able to deduce thermodynamics. Here \( W \) is the number of micro-states at given energy \( E \) of the \( N \)-body system in the spatial volume \( V \):

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

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

\( \epsilon_0 \) is a suitable energy constant to make \( W \) dimensionless, \( \hat{H}_N \) is the \( N \)-particle Hamilton-function and the \( N \) positions \( q \) are restricted to the volume \( V \), whereas the momenta \( p \) are unrestricted. In
what follows, we 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 $2\pi h$ and the factor $1/N!$ which respects the indistinguishability of the particles (Gibbs paradoxon). In contrast to Boltzmann who used the principle only for dilute gases and to Schrödinger, who thought equation (4) is useless otherwise, I take the principle as the fundamental, generic definition of entropy. In a recent book [1] I demonstrated that this definition of thermo-statistics works well especially at higher densities and at phase transitions without invoking the thermodynamic limit. 

Before we proceed we must comment on Einstein’s attitude to the principle [8]): 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 $GN$-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 as artificial. It is exactly that criticized interpretation of $W$ which I use here and which works so excellently [1]. In section III I will come back to this fundamental point.

After succeeding to deduce equilibrium statistics including all phenomena of phase transitions from Boltzmann’s principle even for “Small” systems, i.e. non-extensive many-body systems, it is challenging to explore how far this “most conservative and restrictive way to thermodynamics” is able to describe also the approach of (eventually “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 we address the Second Law, we have to clarify what we mean with the label “macroscopic observable”.

II. MEASURING A MACROSCOPIC OBSERVABLE, THE “EPS-FORMULATION”

A single point $\{q_i(t), p_i(t)\}_{i=1...N}$ in the $N$-body phase space corresponds to a detailed specification of the system with all degrees of freedom (d.o.f) completely fixed at time $t$ (microscopic determination). 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 d.o.f. will be different. I.e. the measurement of the total energy $\hat{H}_N$, or any other macroscopic observable $M$, determines a $(6N-1)$-dimensional sub-manifold $\mathcal{E}$ or $\mathcal{M}$ in phase space. All points 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 microcanonical 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:

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

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

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

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

This is what Krylov seems to have had in mind [10] 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 a system which was 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 $\mathcal{M}(t) = \mathcal{A}(t_0) \cap \mathcal{B}(t) \cap \mathcal{E}$:
\[
W(A, B, E, t) = \frac{1}{N!} \int \left( \frac{d^3q_i \, d^3p_i}{(2\pi\hbar)^3} \right)^N \delta(B - \hat{B}\{q_i, p_i\}) \, \delta(A - \hat{A}\{q_0, p_0\}) \, \epsilon_0 \delta(E - \hat{H}\{q_i, p_i\}),
\]

where \(\{q_i(q_0, p_0), p_i(q_0, p_0)\}\) is the set of trajectories solving the Hamilton-Jacobi equations
\[
\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i = 1 \ldots N
\]

with the initial conditions \(\{q(t = t_0) = q_0; p(t = t_0) = p_0\}\). For a very large system with \(N \approx 10^{23}\) the probability to find a given value \(B(T), P(B(t))\), is usually sharply peaked as function of \(B\). Ordinary thermodynamics treats systems in the thermodynamic limit \(N \to \infty\) and gives only \(<B(t)\>\). 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 \(<B(t)\>\).

Thermodynamics does not describe the temporal development of a single system (single point in the 6N-dim phase space).

There is an important property of macroscopic measurements: Whereas the macroscopic constraint \(\hat{A}\{q_0, p_0\}\) determines (usually) a compact region \(\mathcal{A}(t_0)\) in \(\{q_0, p_0\}\) this does not need to be the case at later times \(t \gg t_0\): \(\mathcal{A}(t)\) defined by \(\mathcal{A}\{q_0\{q_i, p_i\}, p_0\{q_i, p_i\}\}\) might become a fractal i.e. “spaghetti-like” manifold as a function of \(\{q_i, p_i\}\) in \(\mathcal{E}\) at \(t \to \infty\) and loose compactness.

This can be expressed in mathematical terms: There exist series of points \(\{a_n\} \in \mathcal{A}\) which converge to a point \(a_\infty\) which is not in \(\mathcal{A}\). E.g. such points \(a_\infty\) may have intruded from the phase space complimentary to \(\mathcal{A}(t_0)\). Illustrative examples for this evolution of an initially compact sub-manifold into a fractal set are the baker transformation discussed in this context by ref. [1,2]. Then no macroscopic (incomplete) measurement at time \(t\) can resolve \(a_\infty\) from its immediate neighbors \(a_n\) in phase space with distances \(|a_n - a_\infty|\) less then any arbitrary small \(\delta\). In other words, at the time \(t \gg t_0\) no macroscopic measurement with its incomplete information about \(\{q_i, p_i\}\) can decide whether \(\{q_0\{q_i, p_i\}, p_0\{q_i, p_i\}\}\) \(\in \mathcal{A}(t_0)\) or not. I.e. any macroscopic theory like thermodynamics can only deal with the closure of \(\mathcal{A}(t)\). If necessary, the sub-manifold \(\mathcal{A}(t)\) must be artificially closed to \(\overline{\mathcal{A}(t)}\) as developed further in section [IV]. Clearly, in this approach this is the physical origin of irreversibility. We come back to this in section [IV].

### III. ON EINSTEIN’S OBJECTIONS AGAINST THE EPS-PROBABILITY

According to Abraham Pais: “Subtle is the Lord”. Einstein was critical with regard to the definition of relative probabilities by eq\[\[.\] 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” [4]. 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 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 we discussed above, thermodynamics as any other macroscopic theory handles incomplete, 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. The typical outcomes of macroscopic measurements are calculated. Nobody waits in a macroscopic measurement, e.g. of the temperature, 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 a nucleus, the excited nucleus, which then may fragment statistically later on, is produced by a multiple repetition of scattering events and statistical averages are taken. No ergodic covering of the whole phase space by a single trajectory in time is demanded. At the high excitations of the nuclei in the fragmentation region their life-time would be too short for that. This is analogous to the statistics of a falling ball on a Galton’s nail-board where also a
single trajectory is not touching all nails but is random. Only after many repetitions the smooth binomial distribution is established. As I am discussing here the Second Law in finite systems, this is the correct scenario, not the time average over a single ergodic trajectory.

IV. FRACTAL DISTRIBUTIONS IN PHASE SPACE, SECOND LAW

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

Let us examine the following Gedanken experiment: Suppose the probability to find our system at points \( \{q_0, p_0\}_1^N \) 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 \( \{q_0, p_0\}_1^N \) in phase space starting from points \( \{q_0, p_0\} \) with \( q_0 \subset V_1 \) at \( t_0 \) will now spread over the larger volume \( V_2 \). Of course the Liouvillean measure of the distribution \( \mathcal{M}\{q_t, p_t\} \) in phase space at \( t > t_0 \) will remain the same (= \( \text{tr}[\mathcal{E}(N, V_1)] \)) \([13]\). (The label \( \{q_0 \subset V_1\} \) of the integral means that the positions \( \{q_0\}_1^N \) are restricted to the volume \( V_1 \), the momenta \( \{p_0\}_1^N \) are unrestricted.)

\[
\text{tr}[\mathcal{M}\{q_t, p_0\}_1^N, p_t\{q_0, p_0\}] = \int_{\{q_0, p_0\} \subset V_1} \frac{1}{N!} \left( \frac{d^3 q_t \; d^3 p_t}{(2\pi \hbar)^3} \right)^N \delta_0(E - \hat{H}_N\{q_t, p_t\})
\]

because of: \[\frac{\partial q_t}{\partial p_0} = 1.\]

But as already argued by Gibbs the distribution \( \mathcal{M}\{q_t, p_t\} \) will be filamented like ink in water and will approach any point of \( \mathcal{E}(N, V_2) \) arbitrarily close. \( \mathcal{M}\{q_t, p_t\} \) becomes dense in the new, larger \( \mathcal{E}(N, V_2) \) for times sufficiently larger than \( t_0 \). The closure \( \overline{\mathcal{M}} \) becomes equal to \( \mathcal{E}(N, V_2) \). This is clearly expressed by Lebowitz \([4, 13]\).

In order to express this fact mathematically, we have to redefine Boltzmann’s definition of entropy eq.(3) and introduce the following fractal “measure” for integrals like \([3]\) or \([4]\):

\[
W(E, N, t \gg t_0) = \frac{1}{N!} \int_{\{q_0, p_0\} \subset V_1} \left( \frac{d^3 q_t \; d^3 p_t}{(2\pi \hbar)^3} \right)^N \delta_0(E - \hat{H}_N\{q_t, p_t\})
\]

With the transformation:

\[
\int (d^3 q_t \; d^3 p_t)^N \ldots = \int d\sigma_1 \cdots d\sigma_{6N} \ldots
\]

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

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

\[
W(E, N, t \gg t_0) = \frac{1}{N!(2\pi \hbar)^{3N}} \int_{\{q_0, p_0\} \subset V_1} d\sigma_1 \cdots d\sigma_{6N-1} \frac{\epsilon_0}{||\nabla H||},\]

we replace \( \mathcal{M} \) by its closure \( \overline{\mathcal{M}} \) and define now:

\[
W(E, N, t \gg t_0) = \text{tr}[\mathcal{E}(N, V_2)] \ast \text{vol}_{box}[\mathcal{M}(E, N, t \gg t_0)],
\]

where \( \text{vol}_{box}[\mathcal{E}(N, V_2)] \) is the box-counting volume of \( \mathcal{E}(N, V_2) \) which is the same as the volume of \( \overline{\mathcal{M}} \), see below.
To obtain $\text{vol}_{\text{box}}[\mathcal{M}(E,N,t \gg t_0)]$ we cover the $d$-dim. sub-manifold $\mathcal{M}(t)$, 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 $\delta^6N$, which contain points of $\mathcal{M}$. Then we determine

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

with $\lim^{*} = \inf[\lim^{*}]$ or symbolically:

$$M(E,N,t \gg t_0) =: \frac{1}{N!} \int_{q_0 \subset V_1} \left( \frac{d^3q_0 \ d^3p_0}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N)$$

$$\to \frac{1}{N!} \int_{q_0 \subset V_2} \left( \frac{d^3q_t \ d^3p_t}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N \{q_t, p_t\})$$

$$= W(E,N,V_2) \geq W(E,N,V_1),$$

where $\int d$ means that this integral should be evaluated via the box-counting volume (16) here with $d = 6N - 1$.

This is illustrated by the following figure.

FIG. 1. The compact set $\mathcal{M}(t_0)$, left side, develops into an increasingly folded “spaghetti”-like distribution in phase-space with rising time $t$. This figure shows only the early form of the distribution. At much larger 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 $\mathcal{M}(t)$ are counted in $N_\delta$ in eq. (16).

With this extension of eq. (3) Boltzmann’s entropy (1) is at time $t \gg t_0$ equal to the logarithm of the larger phase space $W(E,N,V_2)$. This is the Second Law of Thermodynamics. The box-counting is also used in the definition of the Kolmogorov entropy, the average rate of entropy gain [16,17]. Of course still at $t_0 \mathcal{M}(t_0) = \mathcal{M}(t_0) = \mathcal{E}(N,V_1)$:

$$M(E,N,t_0) =: \frac{1}{N!} \int_{q_0 \subset V_1} \left( \frac{d^3q_0 \ d^3p_0}{(2\pi\hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N)$$

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

$$= W(E,N,V_1).$$

The box-counting volume is analogous to the standard method to determine the fractal dimension of a set of points [14] by the box-counting dimension:
\[ \dim_{\text{box}}[\mathcal{M}(E, N, t \gg t_0)] := \lim_{\delta \to 0} \frac{\ln N_\delta[\mathcal{M}(E, N, t \gg t_0)]}{-\ln \delta} \]  

(21)

Like the box-counting dimension, \( \text{vol}_{\text{box}} \) has the peculiarity that it is equal to the volume of the smallest closed covering set. E.g.: The box-counting volume of the set of rational numbers \( \{\mathbb{Q}\} \) between 0 and 1, is \( \text{vol}_{\text{box}} \{\mathbb{Q}\} = 1 \), and thus equal to the measure of the real numbers, c.f. Falconer [16] section 3.1. This is the reason why \( \text{vol}_{\text{box}} \) is not a measure in its mathematical definition because then we should have

\[ \text{vol}_{\text{box}} \left[ \sum_{i \subset \{\mathbb{Q}\}} (\mathcal{M}_i) \right] = \sum_{i \subset \{\mathbb{Q}\}} \text{vol}_{\text{box}}[\mathcal{M}_i] = 0, \]  

therefore the quotation marks for the box-counting “measure”.

Coming back to the the end of section (II), the volume \( W(A, B, \cdots, t) \) of the relevant ensemble, the closure \( \mathcal{M}(t) \) must be “measured” by something like the box-counting “measure” \((16,17)\) with the box-counting integral \( \int d_\delta \) 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.(17) is for compact sets like the equilibrium distribution \( \mathcal{E} \) identical to the old one eq.(3) and nothing changes 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 (17).

V. CONCLUSION

Macroscopic measurements \( \hat{M} \) determine only a very few of all \( 6N \) d.o.f. Any macroscopic theory like thermodynamics deals with the volumes \( M \) of the corresponding closed sub-manifolds \( \mathcal{M} \) 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 microcanonical ensemble of a finite system.

Because of this necessarily coarsed information, macroscopic measurements, and with it also macroscopic theories are unable to distinguish fractal sets \( \mathcal{M} \) from their closures \( \overline{\mathcal{M}} \). Therefore, I make the conjecture: the proper manifolds determined by a macroscopic theory like thermodynamics are the closed \( \mathcal{M} \). However, an initially closed subset of points at time \( t_0 \) does not necessarily evolve again into a closed subset at \( t \gg t_0 \). I.e. the closure operation and the \( t \to \infty \) limit do not commute, and the macroscopic dynamics becomes irreversible.

Here is the origin of the misunderstanding by the famous reversibility paradoxes which were invented by Loschmidt [18] and Zermelo [19,20] and which bothered Boltzmann so much [21,22]. 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 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.

This way various non-trivial limiting processes can be 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. The use of ensemble averages is justified directly by the very nature of macroscopic (incomplete) measurements. Coarse-graining appears as natural consequence of this. 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 tacitly assumed here. Presumably, the rise of the entropy can then be already seen at finite times when the fractality of the distribution in phase space is not yet fully developed. The coarse-graining is no more any mathematical ad hoc assumption. Moreover the Second Law is in the EPS-formulation of statistical mechanics not linked to the thermodynamic limit as was thought up to now [14,15].

6
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