Second Law of Thermodynamics and Macroscopic Observables within Boltzmann’s principle, an attempt

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Boltzmann’s principle $S = k \ln W$ is generalized to non-equilibrium Hamiltonian systems with possibly fractal distributions in phase space by the box-counting volume. The probabilities $P(M)$ of macroscopic observables $\hat{M}$ 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. With this extension of the phase-space integral 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 possibly fractal sub-manifold $M$ by the volume of its closure $\overline{M}$. In contrast to conventional coarse graining the box-counting volume is defined by the limit of infinite resolution.

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I. INTRODUCTION

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

$$[S = k \ln W]$$

as the fundamental microscopic definition of entropy, Boltzmann’s principle, [1]. 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, and $\hat{H}_N$ is the $N$-particle Hamilton-function. 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 $2\pi\hbar$ and the factor $1/N!$ which respects the indistinguishability of the particles (Gibbs paradox). In contrast to Boltzmann [2,3] who used the principle only for diluted gases and to Schrödinger [4], who thought equation (1) is useless otherwise, I take the principle as the fundamental, generic definition of entropy. In a recent book [5] cf. also [6,7] I demonstrated that this definition of thermo-statistics works well especially also at higher densities and at phase transitions without invoking the thermodynamic limit.

After succeeding to deduce all phenomena of phase transitions from Boltzmann’s principle even for “Small”, i.e. non-extensive many-body systems, it is challenging to explore how far this “most conservative and restrictive way to Thermodynamics” [8] is able to describe also (eventually “Small”) systems approaching equilibrium and the Second Law of Thermodynamics. In the following such an attempt is undertaken.

Thermodynamics describes the development of macroscopic features of many-body systems without specifying them microscopically to 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

A single point \{${q_i(t), p_i(t)}$\}$_{i=1...N}$ in the $N$-body phase space corresponds to a detailed microscopic specification of the system with all degrees of freedom (d.o.f.) completely fixed at time $t$
the submanifold determined by a macroscopic theory like thermodynamics must be the artificially
information about
δ
small
e.g. by ref. [10,11]. Then no macroscopic (incomplete) measurement at time
likely that
to be the case for
\<A\>
small systems i.e. we are interested in the whole distribution
\( P \)
i.e. the probability
\( E \)
further to the cross-section \( \mathcal{E} \cap \mathcal{B} \), a subset of points in \( \mathcal{E} \) with the volume:

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

(4)

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.

Microcanonical thermostatics gives the probability \( P(B,E,N,V) \) of the \( N \)-body system, specified only by the prescribed energy \( E \), to be found in the submanifold \( \mathcal{B}(E,N,V) \subset \mathcal{E}(N,V) \):

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

(5)

This is what Krylov seemed to have in mind [9].

Similarly therodynamics describes the development of some macroscopic observables \( \hat{B} \{q_0,p_0\} \), i.e. the probability \( P(B(t)) \) of the system to be at time \( t \) in the submanifold \( \mathcal{B}(t) \) after it was specified by another macroscopic observable \( \hat{A} \{q_0,p_0\} \) at the earlier time \( t_0 \). It is related to the volume of the submanifold \( \mathcal{A}(t) = \mathcal{A}(t_0) \cap \mathcal{B}(t) \cap \mathcal{E} \):

\[ W(A,B,E,t) = \frac{1}{N!} \int \left( \frac{d^3q_t \, d^3p_t}{(2\pi\hbar)^3} \right)^N \delta(B - \hat{B} \{q_t,p_t\}) \delta(A - \hat{A} \{q_0,p_0\}) \epsilon_0 \delta(E - \hat{H} \{q_t,p_t\}) \]

(6)

where \( \{q_t(q_0,p_0), p_t(q_0,p_0)\} \) is the set of trajectories solving the Hamilton-Jacobi equations

\[ \dot{q}_i = \frac{\partial \hat{H}}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial \hat{H}}{\partial q_i}, \]

(7)

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 \( P(B(t)) \) is usually sharply peaked as function of \( B \). Ordinary therodynamics treats systems in the thermodynamic limit \( N \to \infty \) and gives only \( <B(t)> \). However, here we are interested in a general application eventually also to small systems i.e. we are interested in the whole distribution \( P(B(t)) \) not only in its mean value \( <B(t)> \). Therodynamics does not describe the temporal development of a single system (single point in the 6\( N \)-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 its arguments this does not need to be the case for \( \mathcal{A}(t) \) given by \( \hat{A} \{q_0(q,t),p_0(q_t,p_t)\} \) as function of \( \{q_t,p_t\} \) at time \( t \gg t_0 \). It is likely that \( \mathcal{A}(t) \) is a fractal (e.g. spaghetti-like) submanifold of \( \{q_t,p_t\} \) in \( \mathcal{E} \). I.e. there are series of points \( \alpha_n \in \mathcal{A}(t) \) which converge to a point \( \alpha_\infty \) not in \( \mathcal{A}(t) \). E.g. such points may have intruded from outside. Nice examples for this evolution to fractal distributions in phase space are given e.g. by ref. [10,11]. Then no macroscopic (incomplete) measurement at time \( t \) can resolve \( \alpha_\infty \) from its immediate neighbors \( \alpha_n \) in phase space with distances \( |\alpha_n - \alpha_\infty| \) less than any arbitrary small \( \delta \). In other words, at the time \( t \gg t_0 \) no macroscopic measurement with its incomplete information about \( \{q_t,p_t\} \) can decide whether \( q_0 \{q_t,p_t\}, p_0 \{q_t,p_t\} \in \mathcal{A}(t_0) \) or not. If necessary, the submanifold determined from a macroscopic theory like therodynamics must be the artificially closed \( \overline{\mathcal{M}}(t) \). Clearly, this is the origin of irreversibility. We come back to this in the next section.
III. 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 \( \{q_t, p_t\}_t \) in phase space is uniformly distributed for times \( t < t_0 \) over the submanifold \( \mathcal{E}(N, V_t) \) of the \( N \)-body phase space at energy \( E \) and spatial volume \( V_t \). At time \( t_0 \) we allow the system to spread over the larger volume \( V_2 > V_1 \) without changing its energy. If the system is \textit{dynamically mixing}, i.e.: the majority of trajectories \( \{q_t, p_t\}_t \) 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]:

\[
\text{tr}[\mathcal{M}\{q_t(q_0, p_0), p_t(q_0, p_0)\}]|_{q_0 \subset V_1} = \int_{\{q_t(q_0, p_0) \subset V_1\}} \frac{1}{N!} \left( \frac{d^3q_t \; d^3p_t}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_t, p_t\})
\]

\[
= \int_{\{q_0 \subset V_1\}} \frac{1}{N!} \left( \frac{d^3q_0 \; d^3p_0}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_0, p_0\}) \tag{8}
\]

because of: \( \frac{\partial q_t}{\partial q_0} = \frac{\partial p_t}{\partial p_0} = 1. \tag{9} \)

But as already argued by Boltzmann 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 [13].

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

\[
M(E, N, t \gg t_0) = \frac{1}{N!} \int_{\{q_t(q_0, p_0) \subset V_1\}} \left( \frac{d^3q_t \; d^3p_t}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N\{q_t, p_t\}) \tag{10}
\]

With the transformation:

\[
\int (d^3q_t \; d^3p_t)^N \cdots = \int d\sigma_1 \cdots d\sigma_{6N} \cdots \tag{11}
\]

\[
d\sigma_{6N} := \frac{1}{||\nabla H||} \sum_i \left( \frac{\partial \hat{H}}{\partial q_i} dq_i + \frac{\partial \hat{H}}{\partial p_i} dp_i \right) = \frac{1}{||\nabla H||} dE \tag{12}
\]

\[
||\nabla \hat{H}|| = \sqrt{\sum_i \left( \frac{\partial \hat{H}}{\partial q_i} \right)^2 + \sum_i \left( \frac{\partial \hat{H}}{\partial p_i} \right)^2} \tag{13}
\]

\[
M(E, N, t \gg t_0) = \frac{1}{N! (2\pi \hbar)^{3N}} \int_{\{q_0 \subset V_1\}} d\sigma_1 \cdots d\sigma_{6N-1} \frac{\epsilon_0}{||\nabla H||} \tag{14}
\]

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

\[
M(E, N, t \gg t_0) \rightarrow < G(\mathcal{E}(N, V_2) \times \text{vol}_{\text{box}}[M(E, N, t \gg t_0)] \tag{15}
\]

where \( < G(\mathcal{E}(N, V_2) \times \text{vol}_{\text{box}}[M(E, N, t \gg t_0)] \) is the box-counting volume of \( \mathcal{M}(E, N, t \gg t_0) \).

To obtain \( \text{vol}_{\text{box}}[M(E, N, t \gg t_0)] \) we cover the \( d \)-dim. submanifold \( M(t) \), here with \( d = (6N - 1) \), of the phase space by a grid with spacing \( \delta \) and count the number \( N_3 \propto \delta^{-d} \) of boxes, of size \( \delta^{6N} \), which contain points of \( M \). Then we determine
\[
\text{vol_{box}}[\mathcal{M}(E, N, t \gg t_0)] := \lim_{\delta \to 0} \delta^d N_\delta[\mathcal{M}(E, N, t \gg t_0)]
\]
with \( \lim \ast = \inf[\lim *] \) or symbolically:

\[
\mathcal{M}(E, N, t \gg t_0) =: \int_{d} \frac{1}{N!} \left( \frac{d^3 q_0 d^3 p_0}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N)
\]
\[
= \int_{\{q_0 \subset V_1\}} \frac{1}{N!} \left( \frac{d^3 q_0 d^3 p_0}{(2\pi \hbar)^3} \right)^N \epsilon_0 \delta(E - \hat{H}_N)
\]
\[
= W(E, N, V_2) \geq W(E, N, V_1),
\]

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

With this extension of eq. (10) Boltzmann’s entropy (5) 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.

Of course still at \( t_0 \) \( \mathcal{M}(t_0) = \mathcal{M}(t_0) = \mathcal{E}(N, V_1) \):

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

The box-counting volume is analogous to the standard method to determine the fractal dimension of a set of points \( Q \) by the box-counting dimension which is itself closely related to the Kolmogorov entropy \( \{14, 15\} \):

\[
\text{dim}_{box}[\mathcal{M}(E, N, t \gg t_0)] := \lim_{\delta \to 0} \frac{\ln N_\delta[\mathcal{M}(E, N, t \gg t_0)]}{-\ln \delta}
\]

Like the box-counting dimension, \( \text{vol}_{box} \) 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 \( \{Q\} \) between 0 and 1, is \( \text{vol}_{box} \{Q\} = 1 \), and thus equal to the measure of the real numbers , c.f. Falconer \( \{14\} \) section 3.1. This is the reason why \( \text{vol}_{box} \) is not a measure in its mathematical definition because then we should have

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

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

Coming back to the end of the previous section, the volume \( W(A, B, \cdots, t) \) of the relevant ensemble, the closure \( \overline{\mathcal{M}(\tilde{t})} \) must be “measured” by something like the box-counting “measure” \( \{14, 17\} \) with the box-counting integral \( \int d \) which must replace the integral in eq.(13).

IV. 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 of the corresponding submanifolds \( \mathcal{M} \) in the \( 6N \)-dim. phase space not with single points. This fact becomes especially clear 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, the proper manifolds determined by a macroscopic theory like thermodynamics are the closed \( \overline{\mathcal{M}} \). However, an initially closed subset of points at time \( t_0 \) does not necessarily evolve again into a closed subset at \( t > t_0 \). I.e. the closure operation does not commute with the dynamics of a set of points in phase space, and the macroscopic dynamics becomes irreversible.
The use of the box-counting volume $\int B_d$ in Boltzmann’s principle (eq.1 together with eq.3) allows to derive the Second Law without invoking the thermodynamic limit $N \to \infty$. We must only demand that $N \gg \text{the small number of explicit macroscopic d.o.f.} \ (\sim 3)$, the control parameters. This is in contrast to Lebowitz [13]. Also no finite coarse graining is needed. The resolution $\delta$ can be chosen arbitrarily small. The prize to be paid is that $\int B_d$ is not a measure, see above. Evidently, due to this replacement of $\mathcal{M}$ by $\overline{\mathcal{M}}$ or the integral over phase space, eq.(3), by its box-counting variant, eq.(17), the irreversibility and the increase of entropy comes about in our formalism.

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