Ergodicity: a historical perspective.
Equilibrium and Nonequilibrium

The "second law": $\oint_{rev} \frac{dQ}{T} = 0$ & $\oint \frac{dQ}{T} \leq 0$

In 1866 Boltzmann develops the idea that second law reflects a very general property of Hamiltonian mechanics, ⇒ "theorem"

First a mechanical argument to explain why temperature should be identified with the time-averaged kinetic energy.

Then a proof is undertaken to obtain it as "entirely coincident" with the form first exposed by Clausius, namely:

$$\oint \frac{dQ}{T} \leq 0$$

over a cyclic process in which "actions and reactions are equal to each other, so that in the interior of the body either thermal equilibrium or a stationary heat flow will always be found"

The basic assumption [7, #2,p.24,(1866)], is that

”*An arbitrarily selected atom runs over every site of the region occupied by the body in a suitable time interval (no matter if very long), of which the instants t_1 and t_2 are the initial and final times, at the end of which the speeds and the directions come back to the original value in the same location, describing a closed curve and repeating, from this instant on, theirmotion.*”

B. and C. initially imagine atoms follow a closed identical path. Position of a particle on the path is identified with the “phase”: $\varphi = \frac{time}{period}$ (not phase space). The motion is periodic.

Later groups of atoms may follow closed paths, possibly divided in groups with different periods. However periodicity, hence recurrence, is an essential element.

Here I focus on the role of periodicity in the foundations.

Fundamentally motions are periodic: ⇒ averages computed simply by integrating over the period *i.e.* over the phase.

Let $t \to x(t)$ be a periodic motion developing, under the action of forces with potential $V(x) = V_{int}(x) + \widetilde{V}_{ext}(x)$, with period i

Let δx be the variation that the motion undergoes in

"*a process in which actions and reactions during the entire process are equal to each other so that in the interior of the body either termal equilibrium or a stationary heat flow will always be found*",[7, #2,(1866)].

The heat theorem then becomes a property of the variation $\delta(\overline{K} - \overline{V})$ btwn motion x and varied motion x' in the process

$$\begin{aligned} x(t) &= x(i\varphi) \overset{def}{=} \xi(\varphi), \qquad t \in [0, i], \\ x'(t) &= x'(i'\varphi) \overset{def}{=} \xi'(\varphi), \quad t \in [0, i'], \\ \delta i &= i' - i \end{aligned}$$

with ξ, ξ' two periodic functions of period 1 in the phase φ

Clausius proof, simple and general. The energy variation

$$\delta U = \delta(\overline{K} + \overline{V}) = \delta(\overline{K} + \overline{V}_{int} + \overline{\widetilde{V}}_{ext}) + \overline{\delta\widetilde{V}}_{ext}$$

(But in Boltzmann $\delta\widetilde{V}_{ext} \equiv 0$) and

$$\delta Q = \delta U - \overline{\delta\widetilde{V}}_{ext}$$

interpreted as heat received in the process $x \to x'$. Compute, proceeding as in the calculation of $\delta(\overline{K} - \overline{V})$ in the analysis of the least action principle (variation at fixed extremes t_1, t_2 and $x(t_1), x(t_2)$, resulting in $\delta(\overline{K} - \overline{V}) = 0$):

$$\delta(\overline{K} - \overline{V}) + \overline{\delta\widetilde{V}}_{ext} + 2\overline{K}\delta\log i = 0$$

so that adding and subtr. $+2\delta\overline{K}$ ([12, (1871)])

$$+2\delta\overline{K} - \delta(\overline{K} + \overline{V}) + \overline{\delta\widetilde{V}}_{ext} + 2\overline{K}\delta\log i = 0$$

$$-\delta Q + 2\delta\overline{K} + 2\overline{K}\delta\log i \equiv -\delta Q + 2(\delta\overline{K} + \overline{K}\delta\log i) = 0$$

$$-\delta Q + 2\overline{K}\delta\log(\overline{K}i) = 0$$

$$-\delta Q + 2\overline{K}\delta\log(\overline{K}\log i) = 0 \;\Rightarrow\; \frac{\delta Q}{\overline{K}} = 2\,\delta\log(\overline{K}i)$$

"*It is easily seen that our conclusion on the meaning of the quantities that intervene here is totally independent from the theory of heat, and therefore the second fundamental law is related to a theorem of pure mechanics to which it corresponds just as the "vis viva" principle corresponds to the first principle; and, as it immediately follows from our considerations, it is related to the least action principle, in a somewhat generalized form.*" [7, #2,(1866)]

"Generalization of the action principle" ??: really ??
Act. principle uniquely determines a motion as a minimum, instead heat th. does not, it only establishes a relation btwn close periodic motions if both satisfy equations of motion.

Rather shows: to "each" mechanical system it is possible to associate a "model of thermodynamics"

Remarkably in C. paper *no signs $\geq$ or $\leq$, but only equalities* !
while B. needs an extra argument to show $\oint \frac{dQ}{T} \leq 0$

The priority dispute makes clear the difference btwn the two theorems: B. does not allow varying external forces; strictly speaking it only deals with heat transfer processes.

The result of C. applies instead to a general cycle in which heat and work are involved.

B. at first claims that his analysis would work unchanged in presence of varying ext. forces, but later acknowledges the lack of them: without even insisting that the very critique of C. did show that ext. forces could be included. Instead, after promising that in the future he would care for varying external forces, proceeded to further developments.

Before going through an example of great interest (1877) it is necessary to decide whether B., C., M., really imagined microscopic motions as continuously filling the energy surface.

There is support to the claim that it is not possible to say so.

First quote Clausius (1871)

..temporarily, for the sake of simplicity we shall assume, as already before, that all points describe closed trajectories. For all considered points, and that move in a similar manner, we suppose, more specifically, that they go through equal paths with equal period ... If the initial stationary motion is changed into another, hence on a different path and with different period, nevertheless these will be still closed paths each run through by a large number of points.

This is again just "periodicity". Notice that there is no statement about visiting the whole energy surface

The discrete view of phase-space and time emerges from the "Popular Writings"

Boltzmann in “Popular Writings”, [9, p.56],[9, p.55], [9, p.227]:

‘*The concepts of differential and integral calculus separated from any atomistic idea are truly metaphysical, if by this we mean, following an appropriate definition of Mach, that we have forgotten how we acquired them*”

“*Through the symbolic manipulations of integral calculus, which have become common practice, one can temporarily forget the need to start from a finite number of elements that are at the basis of the creation of the concepts, but one cannot avoid it*”.

“*Differential equations require, just as atomism does, an initial idea of a large finite number of numerical values and points ...... Yet here again it seems to me that so far we cannot exclude the possibility that for a certain very large number of points the picture will best represent phenomena and that for greater numbers it will become again less accurate, so that atoms do exist in large but finite number*

"... *Often in the use of all such [discrete] models, created in this way, it is necessary to put aside the basic concept, from which they have overgrown, and perhaps to forget it entirely, at least temporarily. But I think that it would be a mistake to think that one could become free of it entirely.*"

At this point it seems quite clear that B. was forming his ideas about the interpretation of the physical events adopting a microscopic discrete view. [13, p.26],[19],[11, p.371].

Finally it is interesting to report a quotation by M., the closest I found to the modern ergodic hypothesis (EH): it refers to the entire energy surface as in modern form of EH.

External help is allowed (rough boundaries), which still scatter deterministically, hence it must be conceded that he too makes use of a discrete conception of the microscopic motions.

As an aside: the etimology of "ergodic" is not "ergon+odos" (as in Erhenfest) but "ergon+eidos", [14].

So Maxwell (1876), [21, p.714]:

" *The only assumption which is necessary for the direct proof* [of the kinetic energy equipartition] *is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy. Now it is manifest that there are cases in which this does not take place .... But if we suppose that the material particles, or some of them, occasionally encounter a fixed obstacle such as the sides of a vessel containing the particles, then, except for special forms of the surface of this obstacle, each encounter will introduce a disturbance into the motion of the system, so that it will pass from one undisturbed path into another...". "*

M. refers to proof of Maxwellian given by B. in [4, #5,(1868)] without using periodicity (but for a strongly rarefied gas).

By contrast the modern Ergodic H. replaces all config. → $dp\,dq$-almost all and states visit frequency = volume.

The possible discrete conception, perfectly meaningful mathematically, was apparently completely misunderstood by his critics: yet it was clearly stated in one of the replies to Zermelo, [10, #119(1896)], & in Gas Theory [2, (1896)], [14].

In 1871 B. begun to consider an approach to Thermodynamics which seemed to depart from the periodic motions: this became much more clear in 1877 and later, in 1884, where the general theory of ensembles in its modern form was completed.

Novelty (?) was B.'s conception of models of Thermodynamics.

Interestingly the first examples of such models were still drawn from periodic motions and I present below the example of (1877) which later (1884), apparently independently, was taken up and generalized by Helmoltz.

Remarkably B. did not claim his priority **?** over Helmoltz work, rather developed it to build a very general theory of the ensembles as models of Thermodynamics.

A "mechanical model of thermodynamics" is a system in which it is possible to define quantities to be called U, T, V, p as averages with respect to a "state", i.e. a distribution, depending on a few parameters $\alpha, \beta, \ldots$" and such that varying them by $d\alpha, d\beta, \ldots$ the differential $\frac{dU+pdV}{T}$ is exact.

It is not obvious that such models exist, and that there is only one if any, nor whether, when existing, they have anything to do with the thermodynamics of the mechanical system.

B.'s reply to the above questions involves deeply ergodicity:

1) models exist (B. 1866, C. 1871), with no need of dynam. details to be established (B. 1884)

2) there are many of them for most systems (B. 1884)

3) one of them describes "thermodynamics" if ergodicity holds (in the sense of periodicity)

4) the others describe the same physics because they can be shown to be equivalent (B. 1884)

Randomness and ergodicity in B., [5, #18,p.240,l.4],[18, p.13-14]:

“*Since the great regularity shown by the thermal phenomena induces to suppose that* f *is almost general and that it should be independent from the properties of the special nature of every gas; and even that the general properties depend only weakly from the form of the equations of motion, with the exception of the cases in which the complete integration does not present insuperable difficulties.*”

“*An argument against is that so far the proof that such distributions are the unique that do not change in presence of collisions is not yet complete. It remains nevertheless established that a gas in the same temperature and density state can be found in many configurations, depending on the initial conditions, a priori improbable and even that will never be experimentally observed.* ”.[5, #18,p.255].

Certainly the strict periodicity seems replaced by an apparently more reasonable stochasticity to account for the occupation of the whole energy surface, on which the new thermodynamics models depend, as it appears from the third paper of 1871

The great chaoticity of the thermal motion and the variability of the force that the body feels from the outside makes it probable that the atoms get in the motion, that we call heat, all possible positions and velocities compatible with the equation of the "vis viva", and even that the atoms of a warm body can take all positions and velocities compatible with the last equations considered.[3, #19,p.284][18, p.167].

The most complete proof of the second main law is manifestly based on the remark that, for each given mechanical system, equations that are analogous to equations of the theory of heat hold. (B. 1884)

At the end of this apparently new view it might appear that ergodicity and discreteness can be abandoned via this change of viewpoint, leading to Gibbs **?**.
However item 3), periodicity, remains in the background playing a central role: and examples of systems with periodic motions are discussed before the general ensembles.

The message is that Hamiltonian systems provide examples no matter whether they contain $N = 1$ or $N = 10^{19}$, if their motions are considered periodic.

But periodicity is not necessary its role is reduced to justify *a priori* considering classical ensembles as related to Physics, to people not willing to take the canonical ensemble as an axiom.

The prototype of a model of Thermodynamics (B877,B884) is a 1-D system in a confining potential $\varphi_V(r)$ (V=parameter).

Define *a state* a motion with given energy U and given V (*i.e.* a periodic motion). And call:

U = total energy of the system $\equiv K + \varphi_V$
T = time average of the kinetic energy K
V = the parameter on which φ_V is supposed to depend
p = $-$ time average of $\partial_V \varphi_V$.

A state (*i.e.* a periodic motion) is parameterized by U, V

and if such parameters change by dU, dV, respectively, let

$$dW = -pdV, \qquad dQ = dU + pdV, \qquad \overline{K} = T$$

Then, if $i = i(U, V)$ is the period, heat theorem is in this case:

The differential $(dU + pdV)/T$ is exact and equal to the "entropy" differential $S = 2\log(iT)$. $\longleftrightarrow$ "orthodic model"

In fact let $x_{\pm}(U,V)$ be the extremes of the oscillations of the motion with given U, V and define S as:

$$S = 2\log \int_{x_-(U,V)}^{x_+(U,V)} \sqrt{U - \varphi_V(x)}\,dx = 2\log i\overline{K}$$

by $\frac{dx}{\sqrt{K}} = \sqrt{\frac{2}{m}}dt$ to express period i and averages via $\int \cdot \frac{dx}{\sqrt{K}}$.

$$dS = \frac{\int \Big(dU - \partial_V\varphi_V(x)dV\Big)\frac{dx}{\sqrt{K}}}{\int K\frac{dx}{\sqrt{K}}} = \frac{\int \Big(dU - \partial_V\varphi_V\Big)\sqrt{\frac{m}{2}}\frac{dt}{i}}{\int K\sqrt{\frac{m}{2}}\frac{dt}{i}}$$

$$= \frac{dU + pdV}{T} \equiv \frac{dQ}{T}$$

Another example is the gravitational two body problem (1877) [1, #39,(1877)]

$$E = \frac{1}{2}m\dot{\rho}^2 + \frac{mA^2}{2\rho^2} - \frac{mg}{\rho}, \qquad \varphi(\rho) = -\frac{gm}{\rho}$$

where the parameters are E, g with A=aereal velocity constant

$$\frac{dE-\langle\,\frac{\partial_g\varphi(r)}{\partial g}\,\rangle dg}{T}=\frac{dE-2E\frac{dg}{g}}{-E}=d\log\frac{g^2}{-E}\overset{def}{=}dS$$

However B. also give a "counterexample": namely $\varphi_b(r)=\varphi(r)+\frac{b}{r^2}$. This exhibits the importance of the "physical uniqueness" question. Also A variable !

The last example is possibly responsible of the apparently relatively little interest shown so far for the 1884 paper: which starts referring to Saturn rings as an example of thermodynamics model. [15, p.36],[18].

However the B1884 is a breakthrough, [8, #73]: where the theory of ensembles as models of Thermodynamics (begun in 1871, [3, #19,(1871)]) is fully developed: with the canonical ensemble "orthodicity" obtained as follows:

B1884 thermodynamic model for N (not necessarily large):

$$K = K(\mu) = \int \left(\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \right) e^{-\beta K(\vec{p}) - \beta \Phi(\vec{q})} \frac{d\vec{p}\, d\vec{q}}{h^{3N} N! Z(\beta, V)}$$

$$v = V/N$$

$$U = U(\mu) = -\frac{\partial}{\partial \beta} \log Z(\beta, V)$$

$$p = P(\mu) = \beta^{-1} \frac{\partial}{\partial V} \log Z(\beta, V)$$

At this point a simple direct check. Let:

$$F = -\beta^{-1} \log Z(\beta, V), \qquad S = (U - F)/T \longleftrightarrow F = U - TS$$

then obtain: $T = \frac{2}{3k_B} \frac{K(\mu)}{N} = \frac{1}{k_B \beta}$ $\qquad \frac{dT}{T} = -\frac{d\beta}{\beta}$ *because* $d\vec{q}, d\vec{p}$ integrals are independent (and the $d\vec{p}$ one is gaussian):

$$dF = -S dT - p dV \;\Rightarrow\; \frac{dU + p dV}{T} = dS$$

In conclusion

(a) Ensembles theory is independent of the ergodic hypothesis

(b) The hypothesis as in B., C., M., *i.e.* a point visits all phase space of given energy, is not absurd if space is imagined discrete

(c) Recurrence times are superastronomical, hence not observable. But the small number of observables greatly reduces the "equilibration times" (as discussed by B. & Thomson)

(d) A discrete representation supposes phase space discretized on a regular lattice; hence a special status for Liouville measure: *an "experimental fact" possibly due to our perception of space-time as a translation invariant continuum.*

(e) E. hypothesis then privileges the invariant distributions really describing the thermodynamics of a large system

What can be done in nonequilibrium cases? beginning with the natural extension of equilibrium states, *i.e.* stationary states. What replaces the Liouville distr.? can entropy be defined?

Nonequilibrium & Ergodicity & Chaos ?

B's definition of H was set for approach to equilibrium. Does equality of H with thermod. entropy $\Rightarrow$ define entropy also out of equilibrium (even out of stationarity state ?) ?

B.[6, #42,p.288,(1877)]:

Let us think of an arbitrarily given system of bodies, which undergo an arbitrary change of state, without the requirement that the initial or final state be equilibrium states; then always the measure of the permutability of all bodies involved in the transformations continually increases and can at most remain constant, until all bodies during the transformation are found with infinite approximation in thermal equilibrium.

Commented by M.Klein as:

"*... $\log P$ was well defined whether or not the system is in equilibrium, so that it could serve as a suitable generalization of entropy*", [20, p.82]

Many attempts for noequilibrium entropy, in stationary or even evolving states. But as many difficulties. To begin with:

But counting configurations requires discrete phase space.

Conservation of Liouville measure no longer can offer the illusory argument offered in equilibrium as it is not conserved.

In the continuum picture dissipation implies phase space volume contraction, and motions approach the attracting set $\mathcal{A}$, a subset of phase space, and on it the attractor B (which has therefore zero volume).

In general nonconserv. motions, *nonrecurrent points will be "most" points*: $\mathcal{A} =$ may be entire phase space, and $vol(\mathcal{B}) = 0$.

E.H. can be formulated by requiring that *on the attracting set* recurrent points form a one cycle permutation. In this form

the ergodic hypothesis, for chaotic systems, is the same for conservative and dissipative systems provided phase space is identified with the attracting set.

Of course in chaotic motions the periodicity of motion is not observable as the time scale for the recurrence will remain (in equilibrium as well as out of equilibrium) out of reach.

E.H. has far reaching consequences: in equil. determines the equilibrium distribution. Out of equilibrium in stationary states it **also** determines the distr. of time averages. An idea proposed by Ruelle, for turbulence and for general chaotic systems.

B.M.G. distributions are generalized to “SRB distributions.

Simplest chaotic systems are the Anosov systems: they play a role like harmonic oscillators in ordered mechanical systems.

The key property is that “coarse grained descriptions” can be naturally defined. Of course it is **not necessary** that systems are Anosov systems in a mathematical sense.

Once the idea is grasped it becomes extendible to more general systems (from the still mathematical sounding “axiom A” attractors to the more empirically defined “chaotic hypothesis”).

How to describe the SRB distribution genesis in a coarse grained approach to chaotic motions? It is necessary to clarify some of the main properties of Anosov systems. Key: hyperbolicity.

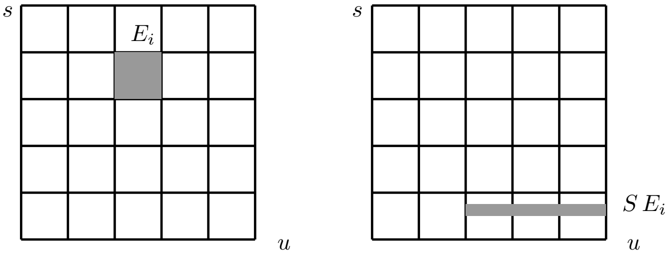

Fig.2: The figures illustrate very symbolically, as 2-dimensional squares, elements of a Markovian pavement for a map.

The evolution maps admit “partition”, $E_1, E_2, \ldots, E_n$ in “rectangles” with “expanding and contracting sides”.

Under S no new contracting sides, under S^{-1} no new expanding

The "cells" $E_1, E_2, \ldots, E_n$ are **NOT** permuted by evolution: in a discrete phase space, each contains very many points of the lattice formed by phase space points, "microcells".

"Markovian partitions", "M.P.", can be as fine as wanted because also $SE_1, SE_2, \ldots, SE_n$ is M.P. and so is the finer $\{E_{ij}\}_1^n$ formed by $E_i \cap SE_j$ or the n^k elements partition

$$E(\vec{q}) = E_{q_1} \cap SE_{q_2} \cap \ldots S^k E_{\vec{q}_k}$$

In Anosov systems the attractor $\mathcal{B}$ is associated with the unstable manifolds: in the discrete version

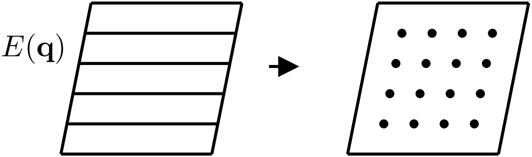

Fig3: A very schematic and idealized drawing of the intersections btwn the attractor $\mathcal{B} \cap E(\vec{q}) = \Delta(\vec{q})$ consisting of the microcells remaining, after a transient time, inside a coarse cell $E(\vec{q})$.

Ergodic hypothesis ⇒ statistics is given simply by **equal weight** $\frac{1}{\mathcal{N}}$, to the $\mathcal{N}$ attractor points, but the condition that the attractor points evolve via a cyclic permutation.

imposes a very strict constraint on the weights $w(\vec{q})$ [14, 17]

For simplicity imagine the attracting set to be a surface δ intersecting the coarse cells $E(q)$ only once: let

$$\delta_u(q) = E(q) \cap \delta$$

Then the numerical density of attractor points in $E(q')$ is

$$\rho(q') = \frac{N(q')}{\delta_u(q')}$$

Under the evolution the density is reduced by a factor $e^{-\lambda_u(q')}$

$\lambda_u(q) =$ surface expansion under evolution S

→ # discrete points ending in $E(q)$ are $(\sum_{q'} \rho(q') e^{-\lambda_u(q')})\delta_u(q)$

$$\rho(q) = \sum_{q'} e^{-\lambda_u(q')} \rho(q') T_{q,q'}, \qquad T_{q,q'} = \begin{cases} 1 & SE(q') \cap E(q) \neq \emptyset \\ 0 & else \end{cases}$$

Since the number of sets $E(q)$ is finite the condition is an eigenvalue problem and the ergodic hypothesis (in the discrete form) implies that the matrix T is irreducible *i.e.* that the eigenfunction $\rho(q) > 0$ with eigenvalue 1 exists and is unique.

SRB weights of coarse cells = eigenvectors $\rho(q)$

This means that the SRB distribution has weights $\rho(q)$ uniquely defined as the positive eigenvectors of an eigenvalue equation, [18].

The eigenvalue equation is the same that arises for Gibbs distribution in a lattice gas in which particles are labeled by q.

The SRB distribution is naturally associated with the equilibrium state of a lattice gas with "potential energy" $\lambda_u(q)$ and hard core between q, q' (if $SE(q') \cap E(q) = \emptyset$), [18].

The heuristic argument can be extended to the more interesting cases in which the attracting set intersects $E(q)$ in more "parallel surfaces".

But having seen the idea it is perhaps simpler to look at the mathematical proof (!).

This remark is at the basis of the denomination "thermodynamic formalism" of the theory of SRB states.

Finally the SRB distribution being a Gibbs state satisfies a variational property ($\max_\rho \sum_q (-\rho(q)\log\rho(q) - \lambda_u(q)\rho(q))$ in the example) and in an Anosov map, as a theorem, the SRB distribution is the μ for which

$$\max_\mu (s(\mu) - \mu(\log\lambda_u))$$

is reached over all distributions which are stationary.

It is also possible to compare the fraction of phase space volume $\frac{|E(\vec{q})|}{W}$ against the $\mu_{SRB}(E(\vec{q}))$.

Such an estimate would yield a count of the number $\mathcal{N}$ of microcells on the attractor in terms of the total number $\mathcal{N}_0$ of microcells ($\propto$ phase space volume): and

$$S = \log \frac{\mathcal{N}}{\mathcal{N}_0} \text{ could be taken as nonequilibrium entropy}$$

But this would make sense

if S depended only up to an additive constant on the microcells dimensions:

let $\theta = \frac{(dpdq)^3}{h^3}$ be the ratio between the microcells dimensions to a typical size of phase space volume, then the variation of S should only be an additive constant.

But this seems incompatible with an average phase space contraction $\sigma_+ > 0$, *i.e.* in stationary nonequilibrium states.

The estimate, [16, 18],

$$\log \mathcal{N} < \log \mathcal{N}_0 - \frac{\sigma_+}{\lambda} \log \theta^{\frac{1}{3}}$$

indicates that changing the size of θ (*i.e.* the precision by which points in phase space may be determined) the change in $\log \mathcal{N}/\mathcal{N}_0$ is not an additive constant

because σ_+, λ are dynamical quantities which are dependent on the state of the system, except in the equilibrium cases $(\sigma_+ \equiv 0)$

Conclusion: it might be impossible to define an entropy function for systems in which average phase space contraction $\sigma_+ > 0$.

Nevertheless the average number of phase space points visited will always tend **increasing** to $\log \mathcal{N}$: in other words it seems possible to define a "Lyapunov function", which reaches its maximum when the system reaches stationarity even though it may depend nontrivially on the chosen precision of the discrete representation of phase space points, [18].

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