Ergodicity: a historical perspective. Equilibrium and Nonequilibrium

The "second law": $\oint \frac{dQ}{T} = 0$ & $\oint \frac{dQ}{T} \leq 0$
In 1866 Boltzmann develops the idea that second law reflects a very general property of Hamiltonian mechanics, $\Rightarrow$ "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 [1, Sec. IV,p.24], 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.*"

C. and B. 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.

Remark: initially motion (B., C.$\le$ 1871) covers positions space **not** phase space, (M.1876).

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

Fundamentally motions are periodic: $\Rightarrow$ 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 $V(x) = V_{int}(x) + V_{ext}(x)$, 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*",[1].

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 is

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

with dQ 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 $x(t_1), x(t_2)$, the resulting in $\delta(\overline{K} - \overline{V}) = 0$):

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

so that adding and subtr. $+2\delta\overline{K}$ ([11])

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

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

"*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.*" [1, #2,sec.IV]

"Generalization of the action principle" ???:

A. 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.

B. gives an extra argument to show $\oint \frac{dQ}{T} \le 0$.

C. *leaves the inequality,* $\oint \frac{dQ}{T} \le 0$, as implicit consequence of allowing external forces (*i.e.* $\delta V_{ext} \neq 0$).

Remarkably in C.'s paper *no signs* $\ge$ *or* $\le$, but only equalities !

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.

C. instead: a general cycle with heat and work involved.

B. acknowledged without insisting that the very critique of C. did show that ext. forces could be included. 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.

(1876) M. still relies on periodicity and explicitly on covering of entire energy surface, *i.e.* apparently on the naive form of E.H.

Aside: etimology "ergodic" not "ergon+odos" but "ergon+eidos", [13].

However B. 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 adopting a discrete microscopic view. [12, 19],[10, p.371].

The discrete conception, already in [4], and clearly in [5], perfectly meaningful mathematically, was apparently completely misunderstood by his critics: yet it was clearly stated in one reply to Zermelo, [7], and in book on gases, [8], see also [13].

But a new development seemed to set aside the periodicity-ergodicity questions just at the same time when the ergodic hyp. is formulated quite precisely (1871 quoted by Gibbs,[3], - 1877), [17].

This was B.'s new conception of models of Thermodynamics arising at least in an example of (1877) and later (1884)[5, 6], taken up+generalized by Helmoltz, independent, [18].

Remarkably B. did not claim his priority **?** over Helmoltz, but developed it to a general theory ensembles as models of Th.

The novelty is resumed in: *The most complete proof of the second main theorem 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)

It might appear that ergodicity and discreteness can be abandoned via this change of viewpoint, leading to Gibbs **?**.

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, [2].

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 (1884) to above questions involves deeply ergodicity:

1) models exist with no need of dynam. details tobe established

2) there are many of them for most systems

3) one of them may describe "thermodynamics". many others describe the same physics because they can be shown to be equivalent

4) The microcanonical e. implies Thermodynamics if ergodicity holds (in the sense of periodicity)

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

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

Define *a state* a motion with given energy $U = K + \varphi_V$ and given V (*i.e.* a periodic motion). And call:

$$\begin{aligned} U &= \text{total energy of the system} \equiv K + \varphi \\ T &= \text{time average of the kinetic energy } K \\ V &= \text{the parameter on which } \varphi \text{ is supposed to depend} \\ p &= -\text{ average of } \partial_V \varphi. \end{aligned}$$

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 heat theorem is in this case, [5, 6]):

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

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

Then elementarily $dS = \frac{dU+pdV}{T}$.

Another example is the gravitational two body problem (1877) with "state parameters" E, g (and A=aereal velocity constant.

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. [14, p.36],[17].

The main point in B1884 paper is the canonical ensemble, called "*holode*", as an "orthodic"= model of Thermodynamics, and its equivalence to the microcanonical ensemble, called "*ergode*".

The *orthodicity* of the canonical ensemble is obtained as follows.

B1884 thermodynalic model for N (not necessarily large):

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

$$v = V/N, \qquad T = \frac{2}{3k_B}\frac{K(\mu)}{N} = \frac{1}{k_B\beta}$$

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

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

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

At this point a simple direct check, elementarily:

$$dF = -SdT - pdV \quad \Rightarrow \quad \frac{dU + pdV}{T} = dS$$

In conclusion

(a) Ensembles are independent of the ergodic hypothesis

(b) The hypothesis in B., C., M., *i.e.* a point visits all energy surface, 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 the Liouville measure is an "experimental fact" possibly due to our perception of pace-time as a translation invariant continuum.

(e) E. hypothesis then selects the invariant distr. (ensembles) really describing the thermodynamics of a large system

What can be said of nonequilibrium stationary states? are really new ideas needed? what about entropy?

For instance: B's definition of H was for approach to equilibrium. But is H entropy out of equilibrium **?**

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 involvedin the transformations continually increases and can at most remain constant, until all bodies during the transformation are found with infinite approximation in thermal equilibrium. [5, p.288]

Attention to the problem of defining entropy have led to thinking that B. seemed "to have abandoned the hypothesis ... he does not even mention it in his definitive" book,[10, p.372].

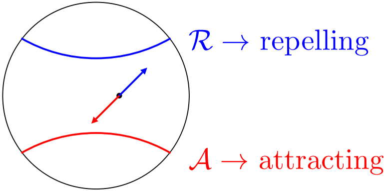
However the heritage of the early views of B. on periodicity and ergodicity and entropy as a "combinatorial problem" will not be set aside for its consequences in present studies on chaos.

Nonequilibrium & Ergodicity & Chaos ?

Counting configurations requires discrete phase space.

Discretization on a regular lattice on phase-space and time will be supposed together with time reversibility

In continuum picture dissipation $\Rightarrow$ average phase volume contraction $\boldsymbol{\sigma}_+ > \mathbf{0}$, and motions approach a subset, the attracting set $\mathcal{A}$ and on it the attractor B (with 0 vol).



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

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

Ergodic hypothesis, for chaotic systems, is the same for conservative and dissipative systems provided phase space is identified with the attracting set, regarded as a surface, [17].

E.H. has far reaching consequences: in equil. and out of equil. determines distribution controlling averages. An idea essentially proposed by Ruelle, in the case of turbulence and for general chaotic systems, [20].

Boltzmann-Maxwell-Gibbs distr. generalized to "SRB distr..

Simplest chaotic systems are Anosov systems: play a role like that of harmonic oscillators in ordered mechanical systems. The Chaotic hypothesis simply supposes that stationary states of chaotic systems share properties of Anosov systems.

Not necessary that systems are Anosov systems in a math. sense: assumption should be regarded to have same role as periodicity assumption in early days of Statistical Mechanics.

Key: Anosov $\Rightarrow$ coarse grained descriptions.

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.

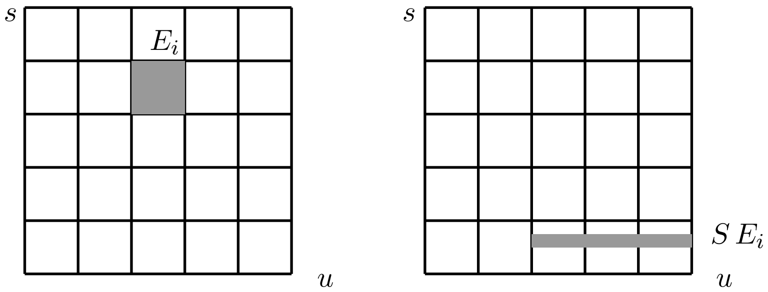


Fig.2: The figures illustrate very symbolically, as 2-dimensional squares, elements of a Markovian pavement for a map.

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 a very large number 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 $E_i \cap SE_j$. So is the partition into n^k elements

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

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

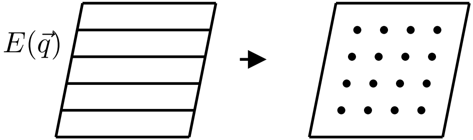


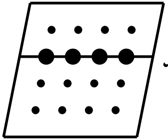
Fig3: A very schematic and idealized drawing of the intersections btwn the attractor $\mathcal{B} \cap E(\vec{q}) = \Delta(\vec{q})$ consisting of the microcells remaining, after a transient time, inside a coarse cell $E(\vec{q})$.

Ergodic hypothesis $\Rightarrow$ 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 $w(\vec{q})$ [13, 16]

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

$E(\vec{q})$



$\mathcal{A} \cap E(\vec{q}) \equiv \delta_u(\vec{q})$

Let $\delta_u(q) = E(q) \cap \delta$: then attractor numerical density in $E(q')$

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

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

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

$\Rightarrow$ # 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 $r(q)$ uniquely defined as the positive eigenvectors of an eigenvalue equation.

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 $SE(q') \cap E(q) = \emptyset$), [17].

Heuristic argument can be extended: *e.g.*to cases in which attracting set intersects $E(q)$ in more "parallel surfaces".

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

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

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 $\mu_{SRB}(E(\vec{q}))$.

Estimate would yield a count of number $\mathcal{N}$ of microcells on attractor in terms of total number $\mathcal{N}_0$ of microcells ($\propto W$): and

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

Let $\theta = \frac{(dpdq)^3}{h^3}$ =ratio btwn microcells size to typical size of phase space volume and let average phase space contraction be $\sigma_+ > 0$. The estimate [15]

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

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 dependent on the system state, 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**, [15, 17].

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