Entropy, Nonequilibrium, Chaos and Infinitesimals

Ergodic hypothesis $\Rightarrow$ theory of equilibrium

Boltzmann (1868-1877) : Phase space is discrete and time evolution maps, actually permutes, "cells" Δ into cells: $S\Delta = \Delta'$.

Ergodicity $\Rightarrow$ one cycle permutation

Boltzmann (1866-1884): $\Rightarrow$ second law (see Gibbs introduction) and linked his work to Helmoltz (1884): extends and formalizes key idea of finding mechanical "analogies" of Thermodynamics.

Define quantities p, U, V, T associated with mechanical system (small or large, simple or complex) s.t. control parameters (e.g. U, V)

$$\frac{dU \,+\, p\,dV}{T} = \text{exact differential}$$

Maybe trivial (!) for small systems but interesting for large: *i.e.* Thermodynamics is a "symmetry" of Hamiltonian systems: *e.g.* for 1D

$$p = \langle -\partial_V \varphi \rangle, \qquad T = \langle K \rangle, \qquad S = 2 \log \oint p dq$$

Also (1884) $\Rightarrow$ ergodic hypothesis, actually *periodicity*, not necessary (except to interpret the value of p as a time average).

If not periodic? B. 1866: aperiodic motion = periodic with ∞ period **!**

microstate: $(\mathbf{p},\mathbf{q}) \in V^{3N} \times R^{3N}$ and *macrostates*: family $\mathcal{E}$ of prob. distr. μ on ph. sp. yielding the averages depending on two parameters (eg U, V or T, V)

B. 1884 realized $\exists$ many analogues of Thermodynamics: *i.e.*

many collections $\mathcal{E}$ of distr. such that defining p as the average force on the walls, V as the volume occupied, $T = \langle K \rangle$ as the kinetic energy and $U = \langle H \rangle$ then varying the parameters $\Rightarrow$

$$\frac{dU + pdV}{T} = \text{exact}$$

Collection $\mathcal{E}$ is an *Orthode* ("looking right"): *Ergode*=mcirocanonical and *holode*=canonical. *Equivalence.*

B was aware of the impossibility of "each point visiting the whole energy surface".

Discrete vision: phase space consists of small cells whose evolution is simply a permutation is essential: Boltzmann "counted" (following (?) Thomson) the number of cells and estimated the *recurrence time* ($10^{10^{19}}$ ages of the Universe for $1\mathrm{cm}^3$ of normal H_2) (Thomson).

Possible the "same" out of equilibrium ?

Restrict to generalize equilibrium states to stationary states

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x})$$

Cannot be $\varepsilon(\mathbf{x}) = -\sum_i \mathrm{div}\partial_{x_i} f_i(\mathbf{x}) = 0$ hence no invariant distrib. with density. **1-th :** restrict to hyperbolic systems & discrete time.

Then $\exists$ a partition $P_1, P_2, \ldots, P_n = \{P_\sigma\}_{\sigma=1}^n$ "Markovian" with transition matrix $M_{\sigma\sigma'} = 0, 1$:

(1) if $\boldsymbol{\sigma} = \{\sigma_i\}_{-\infty}^{\infty}$ and $M_{\sigma_i,\sigma_{i+1}} \equiv 1 \Rightarrow$ unique $\mathbf{x}$ s.t. $S^i\mathbf{x} \in P_{\sigma_i}$ and
(2) *viceversa* up to a set of 0 volume.

Given a precision h let $\Delta = P_{\sigma_{-N_h},\ldots,\sigma_{N_h}} = \bigcap_{j=-N_h}^{N_h} S^{-j} P_{\sigma_j}$: natural coarse cells on phase space. So small that the *relevant observables* are constant.

Th.(Sinai): a. all data $\mathbf{x}$ *have a* $\mathbf{x}$ *indep. statistics* μ*:*

$$\lim_{\tau\to\infty} \frac{1}{\tau} \sum_{j=0}^{\tau-1} F(S^j\mathbf{x}) = \int \mu(dy)\, F(y)$$

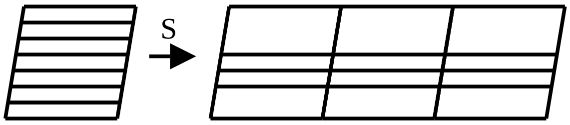
However it is not possible to regard motion as coarse cell permutation. Not even if Hamiltonian (*i.e.* in equilibrium).

To do so coarse cells must be divided into extremely small equal boxes δ "microcells" (as done in simulations). OK for Hamiltonian.

Not Hamiltonian: *Not true* that $S\delta = \delta'$ is a permutation. The microcells *merge* if $\varepsilon(\mathbf{x})$ has *positive* time average

$$\varepsilon_+ \stackrel{def}{=} \langle\varepsilon\rangle\ > 0.$$

Picture:



However *eventually* S is a permutation: $\Rightarrow$ attractor. Transitivity $\Rightarrow$ permutation can be chosen cyclic.

Consistency: The number of surviving microcells in each coarse cell Δ is $\sim \mathcal{N}\Lambda_e(\Delta, N_h)^{-1}$ proportional to expansion rate along the unstable manifold in Δ.

$\Rightarrow$ privileged distribution: equal probability $\frac{1}{\mathcal{N}}$ on the microcells: the SRB distr.

Gordian node (CG95) cut.

Chaotic hypothesis: motion of a chaotic system on its attracting set can be regarded as hyperbolic transitive ("Anosov").

Same spirit as "*while one would be very happy to prove ergodicity because it would justify the use of Gibbs' microcanonical ensemble, real-systems perhaps are not ergodic but behave nevertheless in much the same way and are well described by Gibbs' ensemble...*" (Ruelle, 72, Boltzmann conference).

$\Rightarrow$ explicit expression for the statistics. Useful for establishing relations, at least. Example:

$$p \stackrel{def}{=} \frac{1}{\tau}\sum_{j=0}^{\tau-1}\frac{\varepsilon(S^j\mathbf{x})}{\varepsilon_+}, \qquad \langle p\rangle \equiv 1, \qquad P(p\in A) \propto e^{\tau\ \max_A \zeta(p')}$$

has a large deviation rate $\zeta(p)$ (Sinai) convex and analytic in (p_1,p_2) and $-\infty$ for $p\notin[p_1,p_2]$.

If *reversible*, *i.e.* $\exists$ isometry I such that

$$IS = S^{-1}I \quad \Rightarrow (p_1,p_2) = (-p^*,p^*), \qquad p^*\ge 1$$

Fluctuation theorem (CG95): If transitive hyperbolic and reversible:

$$\zeta(-p) = \zeta(p) - p\varepsilon_+$$

Symmetry property: *no parameters.*

Given an initial distribution $p_0(\boldsymbol{\eta})$ on the microcells it evolves towards $p(\boldsymbol{\eta}) = \frac{1}{\mathcal{N}}$. Hence $-\sum_{\boldsymbol{\eta}} p_{\boldsymbol{\eta}}(t) \log p_{\boldsymbol{\eta}}(t)$ evolves towards its maximum $\log \mathcal{N}$.

Whether Hamilt. or not $\Rightarrow$: unification equilib. & stationary non equil.

Chaotic systems admit a Lyapunov function for their evolution towards stationarity

$\log P$ *was well defined whether or not the system is in equilibrium, so that it could serve as a suitable generalization of entropy* (Klein, 73)

Can this be used to define *entropy* of nonequilibrium stationary states at least?

Necessary that $\log \mathcal{N}$ is independent of the precision h: but this happens only in equilibrium where changing the precision of coarse graining changes $\log \mathcal{N}$ by an h-dependent (only) constant.

This is not the case for stationary nonequilibrium (Ga04).

The H theorem of Boltzmann can be generalized to nonequilibrium.

But H plays the role of a Lyapunov function and entropy, as a function of state, does not seem to be defined.

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