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 as time averages of suitable observable associated with mechanical system (small or large, simple or complex) s.t. varying control parameters (e.g. $U =$ energy, $V =$ volume)

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

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

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

If $V =$ volume then $p \equiv \langle -\partial_V \varphi\rangle =$ average force per unit surface, $T = \langle K\rangle$ **in general** provided the motion visits "all phase space", *e.g.* if motions are periodic.

If not periodic? B. 1866: aperiodic motion = periodic at ∞ period **!**. Meaning ? $\to$ "ergodic hypothesis"

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 $\Rightarrow$ description of equilibrium state = average are computed as integrals over the energy surface: in other words equilibrium states identified with the uniform distributions $\mu_{U,V}$ over the energy surface. Such averages (p, U, V, T) satisfy $(dU + p\,dV)/T = exact$.

The collection of the distributions $\mu_{U,V}$ generates a model of Thermodynamics *with the correct interpretation of* p, U, V, T, S. **Therefore** Boltzmann introduces *macrostates* as a family $\mathcal{E}$ of prob. distr. $\mu_{U,V}$ on ph. sp. *i.e.* on *microstates*: $(\mathbf{p}, \mathbf{q}) \in V^{3N} \times R^{3N}$ and $\mathcal{E}$ gives a model of Thermodynamics. They form what is now the *microcanonical ensemble*.

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

many collections $\mathcal{E}$ of distr. $\mu_{\alpha,\beta}$ with two parameters α, β such that defining p as the average specific force on the walls, V as the volume occupied, $T = \langle K \rangle$ as the average kinetic energy and $U = \langle H \rangle$, then varying the parameters by $d\alpha, d\beta$ it is $\frac{dU+pdV}{T}$ = exact.

Collection $\mathcal{E}$ is an *Orthode* ("looking right"): *Ergode*=microcanonical and *holode*=canonical. Many Thermodynamics? **no**: *equivalence*! *i.e.*

$$\mu^{mc}_{U,V} \sim \mu_{\beta,V} \qquad \text{if} \quad \langle H \rangle_{\mu^c_{\beta,V}} = U$$

B was aware of the impossibility of "each point visiting the whole energy surface". Erg. Hyp. *not* inconsistent because

Discrete vision *die Zahl der lendigen Kräft ist eine diskrete*, (1968): phase space consists of small cells whose evolution is simply a permutation: Boltzmann even "counted" (following (?) Thomson) the number of cells and estimated the *recurrence time* ($10^{10^{19}}$ ages of the Universe for 1cm^3 of normal H_2) (Thomson).

Question: 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: paradigm of chaotic motions.

Hyperbolic $\Rightarrow$ $\exists$ 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 $\to$ h-dependent **coarse graining**

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) unless h is very small.

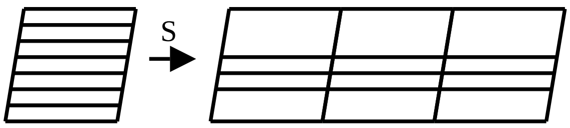
To do so coarse cells must be divided into extremely small equal boxes δ "microcells" (as done in simulations where microcells are to be identified with the machine-represented points). OK for Hamiltonian but bf not if "*dissipative*":

.

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

Not Hamiltonian and *not true* that $S\delta=\delta'$ is a permutation *no matter how small* the size of the microcells δ. The microcells *merge* if $\varepsilon(\mathbf{x})$ has *positive* time average

Picture:



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

How many cells on the cycle? $\mathcal{N}$:

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: essentially it becomes a Markov proces on the space of the symbolic sequences

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

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

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

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

Symmetry property: *no parameters.* Can be tested in simulations and recently even in real experiments.

Interest: defining $\dot{Q}$ to be the heat extracted from the system from the thermostat at temperature T per unit time the quantity p is proportional to $\frac{\dot{Q}}{T}$ *i.e.* to the entropy rate of change of the thermostat.

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 bewteen equilibrium & stationary non equilibrium.

Also: chaotic systems admit a Lyapunov function for their evolution towards stationarity: extends

$\log P$ *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.

Here it seems that we have an instance of (Pop. Schr.)

"*Differential equations require, just as atomism does, an initial idea of a large finite number of numerical values and points ...... Only afterwards it is maintained that the picture never represents phenomena exactly but merely approximates them more and more the greater the number of these points and the smaller the distance between them. 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.*"

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