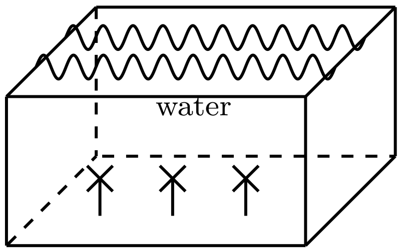
Nonequilibrium and Entropy

Ergodic hypothesis ⇒ theory of equilibrium

A nonequilibrium state ⇒ **stationary** and **transport** $\neq 0$ (electric, heat, mass, chemical currents) under **forcing E**

Examples: (a) wire with e.m. force and steady current
(b) "Joule's experiment"
(c) Developed turbulence in a liquid
(d) Goldburg et al. experiment



Lagrangian flow *on surface*
$\dot{\mathbf{x}} = \mathbf{u}(\mathbf{x}, t)$
with $\mathbf{u}$ turbulent
"Kraichnan flow"

Not to be confused with "approach" or "return" to equilibrium.

Problem: properties of (**E**-dependent) time averages?

$$\langle A \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T A(S_t x) dt = \int \mu(dy) A(y)$$

with x "random" (*with respect to volume*). μ called the SRB statistics.

Classical results (De Groot-Mazur)

(a) Onsager reciprocity and Green–Kubo formulae ($J_k = \partial_{E_k}\sigma(s)$)

$$\partial_{E_h}\langle J_k\rangle\big|_{\mathbf{E}=\mathbf{0}} = \frac{1}{2}\int_{-\infty}^{\infty}\langle J_h(\cdot)J_k(\cdot)\rangle dt$$

(b) Onsager-Machlup, results on probability of patterns

$$Probability(|J(t)-f(t)|<\delta),\ -\frac{\tau}{2}\le t\le\frac{\tau}{2}$$

No results for $\mathbf{E}\ne\mathbf{0}$!

Turbulence "same", example NS incompress. flow $x=\mathbf{u}$. $\mathbf{u}$ are finte dimensional (OK41). x random w.r. to volume $\Rightarrow$ SRB statistics

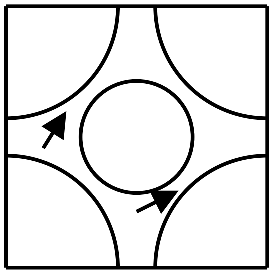
$$\frac{1}{t}\int_0^T O(S_t x)dt \xrightarrow[t\to\infty]{} \int \mu(d\mathbf{v})O(\mathbf{v})$$

Key SRB statistics is well understood in *paradigmatic cases* "hyperbolic systems". Hope to understand results of simulations or material experiments.

Non Equilibrium Thermodynamics means "finding relations between $\langle F\rangle,\langle G\rangle,\langle O\rangle,\ldots$" *model independent.*

Since 80's various attempts at connecting with the SRB theory

(I) difficult: need model of thermostat. Nosé–Hoover, Evans–Morriss. Example



$\ddot{\mathbf{x}}_i = \mathbf{f}_i(\mathbf{x}) + \mathbf{E} - \alpha(\dot{\mathbf{x}})\dot{\mathbf{x}}_i$

$\alpha = \frac{\mathbf{E}\cdot\sum_i \dot{\mathbf{x}}_i}{\sum_i \dot{\mathbf{x}}_i^2}$ "Gaussian"

$\alpha = \nu$ "viscous"

"Drude": speed renormalized at collisions to $\sqrt{3k_BT/m}$

Gaussian case is particularly interesting: **reversible** $I(\mathbf{x}, \dot{\mathbf{x}}) = (\mathbf{x}, -\dot{\mathbf{x}})$

$$I\, S_t\, \mathbf{x} \;=\; S_{-t}\, I\, \mathbf{x}$$

Important: thermostat models $\Rightarrow$ "no Liouville theorem".
The $-$ divergence is

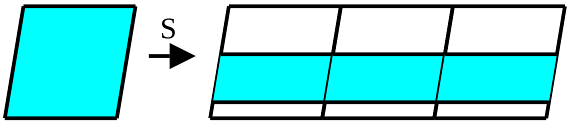
$$\mathrm{div}(x) = \frac{\mathbf{E}\cdot\mathbf{J}}{k_BT}$$

Note hysical interpretation of **entropy increase** of the thermostat.

$\Rightarrow$ difficult to imagine phase space as decomposed into "coarse grain cells" which are permuted by the evolution. But for "**hyperbolic systems**" coarse grain can be made precise.

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. So small that the *relevant observables* are constant.

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

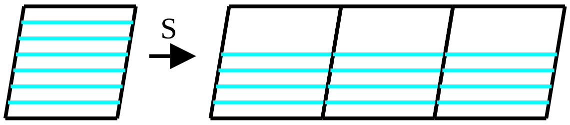
$$\lim_{\tau\to\infty} \frac{1}{\tau} \sum_{j=0}^{\tau-1} F(S^j\mathbf{x}) = \int \mu(dy)\, F(y)$$

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 div($\mathbf{x}$) has *positive* time average

$$\mathrm{div}_+ \stackrel{def}{=} \langle \mathrm{div}(x) \rangle > 0.$$

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

$$\propto \Lambda_e(\Delta, N_h)^{-1} = e^{-\lambda_e(\Delta, N_h)}$$

inv. proportional to expansion of $\Delta \Rightarrow$ privileged dist.: **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 statistics, useful for establishing relations

$$\langle F\rangle = \frac{\sum_\Delta e^{-\lambda_e(\Delta)} F(\Delta)}{\sum_\Delta e^{-\lambda_e(\Delta)}}$$

SRB = **equal weight on all microcells on the attractor** , unification equilibrium-nonequilibrium. *So what ?*

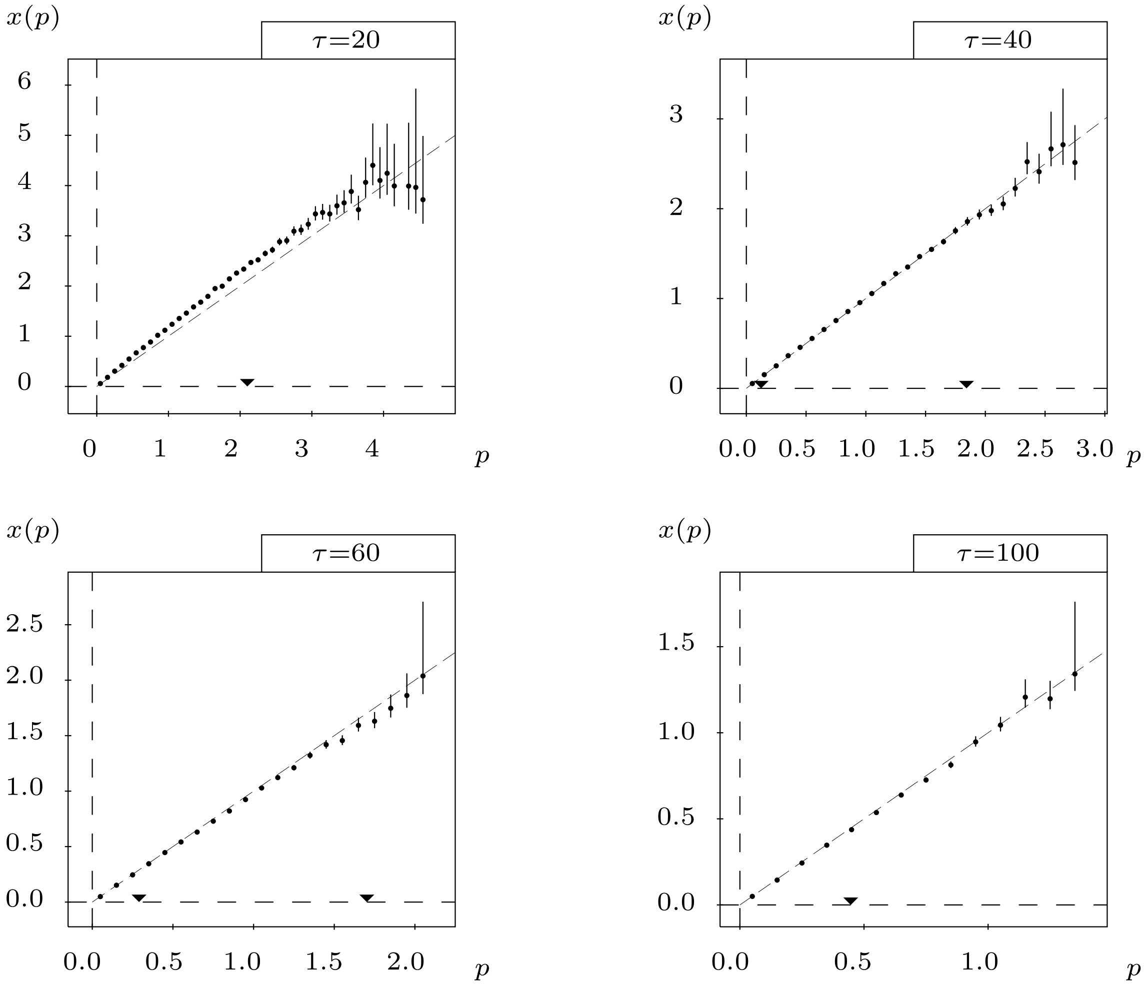
Experimental result (Evans,Cohen,Morriss 93). Study fluctuations of entropy creation rate in dissipative syst. ($\mathrm{div}_+ > 0$)

$$p = \frac{1}{\tau}\int_0^\tau \frac{\mathrm{div}(S_t x)}{\mathrm{div}_+}\, dt$$

The probability $P_\tau(p)$ is (Sinai th) $P_\tau(p) \approx e^{\tau\zeta(p)}$
The Fluctuation Theorem on reversible hyperbolic systems implies the fluctuation relation

$$\zeta(p) - \zeta(-p) = p\,\mathrm{div}_+$$

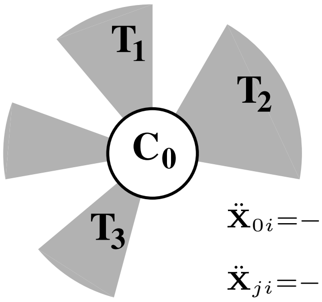
Can be tested in simulations.
This is a symmetry relation, *no free parameters.* If $\mathbf{E} \to 0$ it degerates and becomes Green-Kubo relation. Its validity $\Rightarrow$ test of the Chaotic Hypothesis.
More?



arrow marks mean square deviation of the distribution $P_\tau(p)$, $(\langle p\rangle \equiv 1)$ (Bonetto, Garrido, G., 96)

In “all” cases phase space contraction = entropy rate of increase of reservoir. Problem: reversible model of reservoir acting on all particles is unphysical. Hence theory **only** for simulations !! *Thermostats very often only act through the boundaries of the container*: only so the statistics of the system could possibly be independent of the thermostats.

Led to remarkable *mechanical interpretation of phase space contraction.* General model of thermostat:



$$\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$$

$$\ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \sum\nolimits_j \partial_i U_j(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{F}_i$$

$$\ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i U_j(\mathbf{X}_0, \mathbf{X}_j) - \alpha_j \dot{\mathbf{X}}_{ji}$$

Fig.1Reservoirs occupy finite regions outside $\mathcal{C}_0$, *e.g.* sectors $\mathcal{C}_j \subset R^3$, $j = 1, 2 \ldots.$ Their particles (with mass 1) are constrained to have a *total* kinetic energy K_j constant, by suitable forces, so that the reservoirs “temperatures” T_i are well defined. Fixed j the label i is in $1, \ldots . N_j$.

Thermostat forces $\alpha_i \dot{\mathbf{X}}_i$ are so defined that total kinetic energy $K_j = \frac{1}{2}\dot{\mathbf{X}}_j^2$ in each thermostat is strictly constant $\equiv \frac{3}{2} N_j k_B T_j$. Such forces will be imagined realized by *Gauss' principle*: $\alpha_j \equiv \frac{W_j - \dot{U}_j}{2K_j}$

Then W_j can be interpreted as the heat Q_j ceded to the thermostats and the divergence is

$$\mathrm{div}(X) = \sum_{j>0} \frac{Q_j}{k_B T_j} + \dot{R}(X) \stackrel{def}{=} \varepsilon(X) + \dot{R}(X), \qquad R(X) = \sum_{j>0} \frac{U_j}{k_B T_j}$$

The infinite time average $\langle \mathrm{div}(X) \rangle \equiv \langle \varepsilon \rangle$ (because $\langle \dot{R} \rangle_T = \frac{R(T)-R(0)}{T} \to 0$) and finite time average

$$p' = \frac{1}{t} \int_0^T \sum_{j>0} \frac{Q_j(t)}{k_B T_j} dt + \frac{R(T) - R(0)}{T} = p + O(T^{-1})$$

Therefore p' and p have the *same* asymptotic distribution with rate $\zeta(p)$ and by CH FR should hold for the **measurable** p.

Other extensions are towards the Onsager-Machlup theory. A remarkable result (CH+ reversibility): let $\varphi_1(t), \ldots, \varphi_n(t)$ be n *patterns*, defined for $-\frac{\tau}{2} < t < \frac{\tau}{2}$ and let $F_1(x), \ldots, F_n(x)$ be n observables *odd under time reversal*

$$\frac{Prob(|F_i(S_t x) - \varphi_i(t)| < \delta, p)}{Prob(|F_i(S_t x) + \varphi_i(-t)| < \delta, -p)} = e^{\tau\, p\, \varepsilon_+}$$

independent of F_i!
and (Bonetto identity) $\langle e^{p\tau\varepsilon_+} \rangle$=1 asymptotically.
Quantum ?