

Deterministic thermostats in nonequilibrium statistical mechanics

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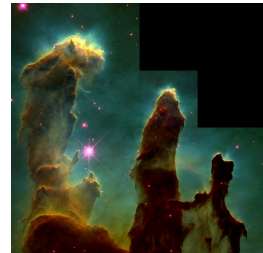
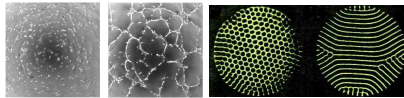
Outline

1 Background

2 Molecular Dynamics

Variety of nonequilibrium phenomena. As in equilibrium, 3 levels:

- Microscopic (mechanical; reversible);
- Mesoscopic (stochastic/kinetic; fluctuating-irreversible);
- Macroscopic (hydro-thermodynamic; deterministic-irreversible).



Somewhat unified under hypothesis of

Local Thermodynamic Equilibrium.

Local Thermodynamic Equilibrium, based on separation of scales

$$N \gg 1, \quad \ell \ll \delta L \ll L, \quad \tau \ll \delta t \ll t$$

δL^3 contains thermodynamic system (P, V, T);

δt suffices for system in δL^3 to reach equilibrium.

So fundamental to appear only in preface of De Groot – Mazur.

Then, hydrodynamic laws are given and for them container shape does **NOT** matter (just boundary conditions).

Equilibrium based on **Ergodic Hypothesis**:

Consider $\dot{\Gamma} = G(\Gamma)$ in \mathcal{M} with solution $S^\tau \Gamma$.

Observable \mathcal{O} , defined as average of appropriate microscopic quantity \mathcal{Q} , equals phase space average, with proper probability distribution (*ensembles*) μ :

$$\mathcal{O} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \mathcal{Q}(S^\tau \Gamma) d\tau = \int_{\mathcal{M}} \mathcal{Q}(\Gamma) d\mu(\Gamma) \quad \text{a.e. } \Gamma$$

Why it works, is a long story.

Mathematical ergodic theory: too much and too little.

Extremum principles & information theory, not a real justification.

Which measures? Regular: $d\mu(\Gamma) = \rho(\Gamma) d\Gamma$

Khinchin and Birkhoff, complementary approaches, address:

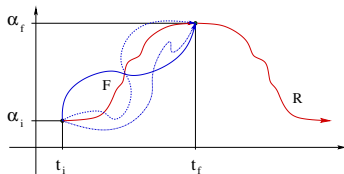
- physics questions (ubiquity & time scales, based on $N \gg 1$);
- mathematics questions (e.g. identify “ergodic” systems).

Hard to justify ensembles (micro-canonical, canonical, grand-canonical), although they work very well.

$N \gg 1$ must play a role, not obvious in chaotic dynamics.

Not fully understood, but it does work.

Onsager-Machlup: assume LTE, generalize to paths Einstein's



$$P(\Delta\alpha) \propto e^{\Delta S/K_B}$$

deterministic evolution & noise,
maximize Pr. of paths, $N \rightarrow \infty$.

Obtain hydrodynamic laws, e.g.

$$\text{Fick's law: } J = -D\nabla n$$

Green-Kubo: hamiltonian perturbed by weak field at $t = 0$;
assume LTE (phase space μ is canonical + small perturbation),
use Liouville eq. for perturbation of equilibrium density. Obtain

$$\sigma = \frac{\beta}{V} \int_0^\infty d\tau \langle J(\Gamma) J(S^\tau \Gamma) \rangle_0$$

Remarkable connection between equilibrium and
nonequilibrium properties.

Kinetic theory goes beyond LTE, and works well even in extreme situations, like neutron transport.

Rests on **stosszahl-ansatz**, and $\ell \ll L$.

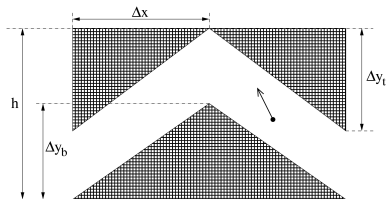
Rarefied conditions, $\ell \sim L$.

Highly confined (almost 1-D).

High gradients (reduced chaos):

Correlations destroy LTE,
produce anomalous transport,
walls affect transport law

[BJR 08].



Is pure dynamics appropriate?

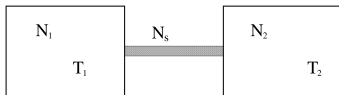
Deterministic reversible dynamics uncovered phenomena not obvious in other frameworks: **steady state (large deviation) and transient (ensemble) fluctuation relations for entropy production and work**. Cohen, Evans, Gallavotti, Morriss, Searles; Jarzynski...

Question of appropriate ensemble (if needed)

Equilibrium ensembles: micro-canonical, canonical and grand-canonical do work.

What about nonequilibrium ensembles? Need model.

Ideally, infinite reservoirs must be given. How to represent them?



Algorithms to compute transport coefficients etc.?

Need dynamical models to test various hypothesis and develop theory, in particular far from LTE.

Equilibrium molecular dynamics computes properties of systems by simulation of microscopic particle dynamics:

$$\dot{\mathbf{q}}_i = \mathbf{p}_i/m; \dot{\mathbf{p}}_i = \mathbf{F}_i; i = 1, \dots, N$$

and use of statistical mechanical relations.

Successful in calculation of rheological properties, polymers in porous media, defects in crystals, friction of surfaces, atomic clusters, biological macromolecules, etc. Difficulties only if:

- interatomic forces too complicated;
- number of simulated particles must be too large;
- simulation times must be too long.

Otherwise, commonly used to understand results of experiments; in place of (expensive or practically impossible) experiments: observation of fracture fronts *inside* solids, thermal dilation of nuclear fuel pellets, etc.

1952, Fermi and Ulam list problems amenable to numerical investigation. With Pasta, in 1953, they investigate equipartition of energy in a chain of 64 coupled anharmonic oscillators.

Calculations on which the work of the report is based were performed on desk computers and rubes. The subsequent massive and lengthy work on the electronic computer machines designed and performed by von Neumann, F. and C. Evans and others confirmed in fact, qualitatively and to a good degree quantitatively the behavior of the system estimated and predicted in our report—with its combination of intuitive analog schematic equations and hand calculations.

S. M. ULAM

266.

STUDIES OF NON LINEAR PROBLEMS

E. FERMI, J. PASTA, and S. ULAM
Document LA-1940 (May 1955).

ABSTRACT.

A one-dimensional dynamical system of 64 particles with forces between neighboring nonlinear terms has been studied on the Los Alamos computer MANIAC I. nonlinear terms considered are quadratic, cubic, and broken linear types. The result analyzed into Fourier components and plotted as a function of time.

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266. - Studies of non Linear Problems

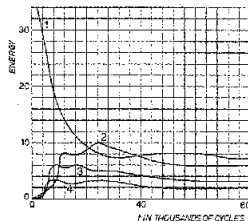
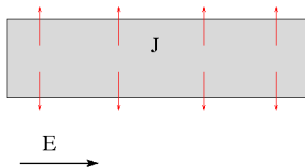
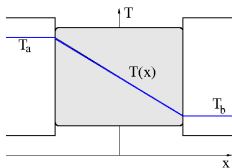


Fig. 2. This graph refers to the problem of fig. 0. The curves, numbered 1, 2, 3, 4, show the time averages of the kinetic energy contained in the first 4 modes as a function of time.

In other words, the quantity is $\frac{1}{\nu} \sum_{\nu=1}^{\nu} T_{\nu}^2$, ν is the cycle no., $k = 1, 2, 3, 4$.

Postumous internal report of Los Alamos labs, 1955, surprisingly reports no equipartition. Beginnings of Molecular Dynamics. Alder and Wainwright, J. Chem. Phys. 1957: phase diagram of hard sphere system.

To reach nonequilibrium steady state, energy pumped in system by **external drivings** must be passed to **reservoirs**.



Nonequilibrium molecular dynamics achieves goal replacing:

boundary or bulk drivings + reservoirs

by

mechanical forces + p.b.c. + *fictitious* thermostating forces

Thermostatting term added to equations of motion, introduced through appropriate constraints, dissipates excess energy. Simplest case:

Gauss' principle of least constraint (1829). Consider N point particles of mass m_i , subjected to frictionless bilateral constraints Φ_i and external forces \mathbf{F}_i . Of all motions allowed by the constraints, the **natural** one minimizes the “curvature”

$$C = \sum_{i=1}^N m_i \left(\ddot{\mathbf{q}}_i - \frac{\mathbf{F}_i}{m_i} \right)^2 = \sum_{i=1}^N \frac{1}{m_i} \Phi_i^2 .$$

According to Gauss, the “Curvature” C is minimized by the accelerations of real motions or, equivalently, real motions minimize the action of the constraints.

In case of holonomic constraints, consistent with least action principle (Hamiltonian eqs).

Non holonomic constraints result in non Hamiltonian eqs.

Diatomic molecule with constant interatomic distance D :

$\mathbf{q}_{12}^2 - D^2 = 0$, with $\mathbf{q}_{12} = \mathbf{q}_1 - \mathbf{q}_2$, \mathbf{q}_i = position of atom i .

Differentiate constraint twice w.r.t. time: $\mathbf{q}_{12} \cdot \ddot{\mathbf{q}}_{12} + \dot{\mathbf{q}}_{12}^2 = 0$

Minimize C:

$$\frac{\partial}{\partial \ddot{\mathbf{q}}_i} \left[\frac{m_1}{2} \left(\ddot{\mathbf{q}}_1 - \frac{\mathbf{F}_1}{m_1} \right)^2 + \left(\ddot{\mathbf{q}}_2 - \frac{\mathbf{F}_2}{m_2} \right)^2 - \alpha (\mathbf{q}_{12} \cdot \ddot{\mathbf{q}}_{12} + \dot{\mathbf{q}}_{12}^2) \right] = 0$$

$$\begin{cases} m_1 \ddot{\mathbf{q}}_1 = \mathbf{F}_1 + \alpha \mathbf{q}_{12} ; & m_2 \ddot{\mathbf{q}}_2 = \mathbf{F}_2 - \alpha \mathbf{q}_{12} \\ \alpha = - (\mathbf{q}_{12} \cdot (m_1 \mathbf{F}_2 - m_2 \mathbf{F}_1) + m_1 m_2 \dot{\mathbf{q}}_{12}^2) / (m_1 + m_2) \mathbf{q}_{12}^2 \end{cases}$$

N -particles with external field $\mathbf{F}_i^{\text{ext}}$, interactions $\mathbf{F}_i^{\text{int}}(\mathbf{q})$:

$$\begin{cases} \dot{\mathbf{q}}_i = \mathbf{p}_i/m \\ \dot{\mathbf{p}}_i = \mathbf{F}_i^{\text{int}}(\mathbf{q}) + \mathbf{F}_i^{\text{ext}}(\mathbf{q}) - \alpha(\Gamma)\mathbf{p}_i \end{cases}$$

Simple constraints: isokinetic fixes $K = \sum_i \mathbf{p}_i^2/2m$;
isoenergetic fixes $H_0 = K + \Phi^{\text{int}}$

$$\alpha_{IK}(\Gamma) = \frac{1}{2K} \sum_{i=1}^N \dot{\mathbf{q}}_i \cdot (\mathbf{F}_i^{\text{int}} + \mathbf{F}_i^{\text{ext}}) = \beta \dot{\Phi}^{\text{int}}(\mathbf{q}) + \beta \sum_{i=1}^N \dot{\mathbf{q}}_i \cdot \mathbf{F}_i^{\text{ext}}$$

$$\alpha_{IE}(\Gamma) = \frac{1}{2K} \sum_{i=1}^N \dot{\mathbf{q}}_i \cdot \mathbf{F}_i^{\text{ext}}$$

SLLOD for shear rate γ

$$\begin{cases} \dot{\mathbf{q}}_i = \mathbf{p}_i/m + \mathbf{n}_x \gamma y_i, & i = 1, \dots, N \\ \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{n}_x \gamma p_{yi} - \alpha \mathbf{p}_i \end{cases}$$

$$\alpha_{IE} = \frac{-\gamma P_{xy} V}{\sum_{i=1}^N \mathbf{p}_i^2 / m}, \quad \alpha_{IK} = \frac{\sum_{i=1}^N (\mathbf{F}_i \cdot \mathbf{p}_i - \gamma p_{xi} p_{yi})}{\sum_{i=1}^N \mathbf{p}_i^2 / m}$$

As phase space contraction rate $\chi = -\text{div } \dot{\Gamma} \propto -\alpha$

$$\sigma_{IE} \propto \chi_{IE}$$

$$\sigma_{IK} \propto \chi_{IK} - \text{extra (conservative) term}$$

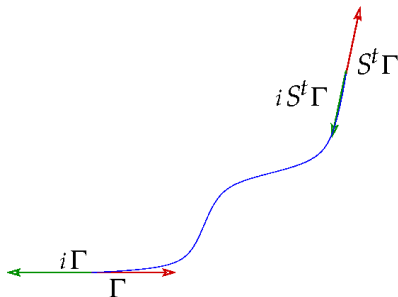
$\alpha(\Gamma)\mathbf{p}_i$ makes dynamics **dissipative**, hence system reaches steady state, but **time reversal invariant**.

$S^t : \mathcal{M} \rightarrow \mathcal{M}$ evolution operator,
 $t \in \mathbf{R}$; $S^t\Gamma$ phase after time t .

$i : \mathcal{M} \rightarrow \mathcal{M}$ time reversal
involution ($i^2 = \text{Id}$).

Time reversal invariant if

$$iS^t\Gamma = S^{-t}i\Gamma, \forall \Gamma \in \mathcal{M}$$



Nosè-Hoover thermostat

Defined by following transformations of momenta and time variables:

$$\tilde{\mathbf{p}}_i = \frac{\mathbf{p}_i}{s} ; \quad \tilde{t} = \int_0^t \frac{d\tau}{s}$$

$$\frac{d\mathbf{q}_i}{d\tilde{t}} = \frac{\tilde{\mathbf{p}}_i}{m} ; \quad \frac{d\tilde{\mathbf{p}}_i}{d\tilde{t}} = \mathbf{F}_i - \zeta \tilde{\mathbf{p}}_i ; \quad \frac{d\zeta}{d\tilde{t}} = \frac{1}{\tau^2} \left(\frac{K(\tilde{\mathbf{p}})}{K_0} - 1 \right) ; \quad \frac{ds}{dt} = \zeta s .$$

K_0 = value chosen for the time average of kinetic energy $K(\tilde{\mathbf{p}})$,
 τ = relaxation time.

In the small τ limit, Nosè-Hoover dynamics approximate Gaussian IK dynamics.

In equilibrium, Hamiltonian and reproduces canonical ensemble

Temperature for Gaussian isokinetic dynamics: Coordinate transform leads to Hamiltonian version of *IK* dynamics. One particle. Replace \mathbf{p} with $\boldsymbol{\pi} = \mathbf{p} \exp(-\phi/2R)$, $\phi = \phi^{\text{ext}} + \phi^{\text{int}}$
 $R = \text{parameter}$.

$$\mathcal{H}(\mathbf{q}, \boldsymbol{\pi}) = \frac{e^{\phi/2R}}{2m} \boldsymbol{\pi}^2 - R e^{-\phi/2R}, \quad (2.1)$$

leads to:

$$\dot{\mathbf{q}} = \frac{e^{\phi/2R} \boldsymbol{\pi}}{m}, \quad \dot{\boldsymbol{\pi}} = \frac{(\mathbf{F}^{\text{ext}} + \mathbf{F}^{\text{int}}) e^{-\phi/2R}}{2R} \left(\frac{e^{\phi/R} \boldsymbol{\pi}^2}{2m} + R \right). \quad (2.2)$$

Taking $R = K$ and $(\mathbf{q}(0), \boldsymbol{\pi}(0))$ so that $\mathcal{H} = 0$, one gets

$$\dot{\mathbf{q}} = \frac{\mathbf{p}}{m}, \quad \dot{\mathbf{p}} = \frac{d\mathbf{p}}{d\boldsymbol{\pi}} \frac{d\boldsymbol{\pi}}{dt} = \mathbf{F}^{\text{ext}} + \mathbf{F}^{\text{int}} - \frac{(\mathbf{F}^{\text{ext}} + \mathbf{F}^{\text{int}}) \cdot \mathbf{p}}{\mathbf{p}^2} \mathbf{p}. \quad (2.3)$$

the *IK* equations for a 1-particle system.

Then one may use the definition of configurational temperature T :

$$\frac{1}{T} \equiv \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t \Phi(S^\tau x) d\tau, \quad (2.4)$$

under some ergodic assumption, where

$$\Phi = \nabla \cdot \left(\frac{\nabla \mathcal{H}}{\|\nabla \mathcal{H}\|^2} \right)$$

∇ = gradient with respect to the phase variable.

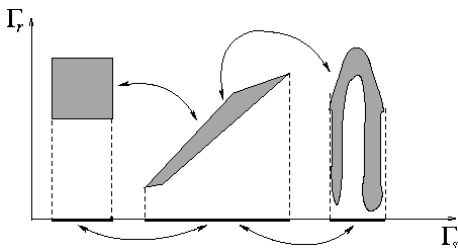
T obtained from both kinetic and configurational degrees of freedom.

Purely configurational temperatures are viable when no kinetic temperature makes sense, e.g. in nonequilibrium fluids of large, flexible polymers.

Is non-Hamiltonian dynamics fine?

System ideally obtained projecting out reservoir coordinates

$$\dot{\Gamma} = \begin{pmatrix} \dot{\Gamma}_s \\ \dot{\Gamma}_r \end{pmatrix} = G(x) = \begin{pmatrix} G_s(\Gamma_s, \Gamma_r) \\ G_r(\Gamma_s, \Gamma_r) \end{pmatrix}, \quad \begin{aligned} \Gamma_s &= (\mathbf{q}_i, \mathbf{p}_i)_{i=1}^{N_s} \\ \Gamma_r &= (\mathbf{q}_i, \mathbf{p}_i)_{i=N_s+1}^N \end{aligned}$$



Full dynamics volume preserving
and reversible,

projected dynamics is reversible.

Reservoir removes energy on
average,

**projected dynamics is dissipative
on average.**

Looks just right: dissipative & reversible dynamics, as desired.

But: not obtained through ideal projection procedure, hence spoiled by fictitious, unnatural forces.

Why bother?

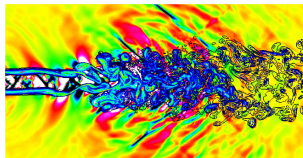
Any model is just that: **must** be simpler than described object; represent *some* feature of interest of real system.

Navier-Stokes equation

$$\dot{\mathbf{u}} + (\mathbf{u} \cdot \nabla)\mathbf{u} = -\frac{1}{\rho}\nabla p + \mathbf{g} + \alpha\Delta\mathbf{u}$$

its viscosity is a fictitious quantity.

Would anyone argue it is no good?



Deterministic thermostats devised to efficiently compute **transport coefficients**.

Idea: details of heat removal irrelevant for phenomenon of interest. Indeed NEMD “unnatural”, ad hoc models, succeed in that.

Furthermore, easy to simulate, relate purely dynamic and thermodynamic quantities:

e.g. sum of Lyapunov exponents proportional to transport coefficients.

What about properties related to details of dissipation?

NEMD “good” models in a limited sense;

for calculation of specific quantities.

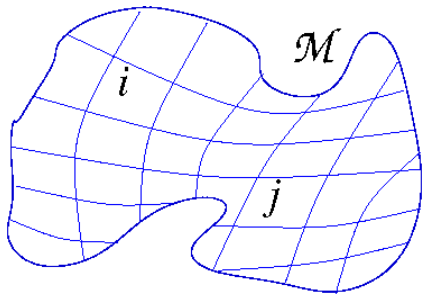
Which quantities under which conditions, yet to be understood.

Possible approach:

equivalence of nonequilibrium ensembles; role of large N .

Which probability distributions describe steady states of NEMD models? If Φ is one observable

$$\langle \Phi \rangle = \lim_{T \rightarrow \infty} \frac{1}{t} \int \Phi(S^t x) dt = \int_{\Omega} \Phi(x) \mu(dx)$$



$$\langle \Phi \rangle \approx \sum_i \Phi(x_i) P(C_i)$$

Gallavotti and Cohen, observing chaotic properties of NEMD models, and inspired by ECM2, proposed:

Chaotic Hypothesis: *A reversible N -particle system in a stationary state can be regarded as a transitive Anosov system, for the calculation of its macroscopic properties.*

Anosov flow (Ω, S^t) : smooth, and Ω is hyperbolic: $\forall x \in \Omega$

- i. $T_x \Omega = E_x^u \oplus E_x^s \oplus E_x^0$ continuous with x , E_x^0 1-dim. subspace.
- ii. E_x^s, E_x^u invariant under tangent map $D(S^t)$:

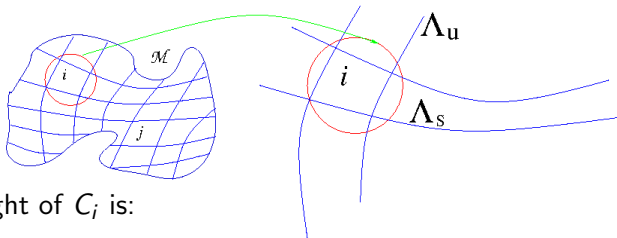
$$\forall x \in \Omega, D(S^t)(x)E_x^i \subset E_{S^t(x)}^i \text{ with}$$

$$i = s, u.$$
- iii. $\exists C > 0, \theta \in (0, 1)$ such that $\forall t \geq 0, \| D(S^t)\xi \| \leq C \theta^t \| \xi \|$,
 for all $\xi \in E_x^s$ and $\| D(S^{-t})\eta \| \leq C \theta^t \| \eta \|, \forall \eta \in E_x^u$.

Stable and unstable manifolds W_x^s, W_x^u dense in $\Omega \forall x \in \Omega$
 (transitivity), periodic orbits are dense in Ω , and physical measure has density along the unstable directions (SRB).

Theorem (Sinai, 1968): *Every transitive Anosov system admits Markov partitions.*

Attribute weights to cells of a Markov partition of Ω ;
limit of finer and finer partitions: SRB measure.



Weight of C_i is:

$$\Lambda_{w_i, u, \tau}^{-1} = 1/|\text{Jacobian of dynamics restricted to } W^u|,$$

$$w_i = \{S^t x_i\}_{t=-\tau/2}^{\tau/2}, \text{ large } \tau, x_i \in C_i.$$

$$w\text{'s can be periodic: } \Rightarrow \Lambda_{w, u}^{-1} = \exp(-\tau \sum_l^+ \lambda_{w, l}),$$

\sum^+ summation over positive $\lambda_{w, j}$

Hence, several results in nonequilibrium statistical mechanics (numerically first in ECM2; ES in '94, GC in '95).

Theorem (Gallavotti-Cohen, 1995): *For reversible Anosov diffeomorphism S on compact \mathcal{M} with SRB measure π , $\exists p^* > 0$ s.t. if $|p| < p^*$ and $\delta > 0$*

$$p - \delta \leq \lim_{\tau \rightarrow \infty} \frac{1}{\tau \langle \sigma \rangle} \log \frac{\pi(\sigma_\tau(x) \in (p - \delta, p + \delta))}{\pi(\sigma_\tau(x) \in (-p - \delta, -p + \delta))} \leq p + \delta$$

with

$$\sigma_\tau(x) = \frac{1}{\tau \langle \sigma \rangle} \sum_{i=0}^{\tau-1} \log J_f(S^i x)^{-1}$$

the dimensionless phase space contraction.

Sketch of proof. M.P. with cells C_k , $k = 1, \dots, M$.
Limit of fine M.P. and long τ on frequency of $\sigma_\tau(x_k)$ in
 $B_{p,\delta} = (p - \delta, p + \delta)$ to obtain

$$\pi(\sigma_\tau \in B_{p,\delta}) = \frac{1}{M} \sum_{C_k, \sigma_\tau \in B_{p,\delta}} \Lambda_{k,u,\tau}^{-1}$$

except for errors which can be made arbitrarily small. *If support of SRB is \mathcal{M}* , T.R.I. implies p values symmetric around 0

$$\frac{\pi(\sigma_\tau \in B_{p,\delta})}{\pi(\sigma_\tau \in B_{-p,\delta})} = \frac{\sum_{\sigma_\tau(x_k) \in B_{p,\delta}} \Lambda_{k,u,\tau}^{-1}}{\sum_{\sigma_\tau(x_k) \in B_{-p,\delta}} \Lambda_{k,u,\tau}^{-1}}$$

Let $i =$ time reversal map, $\Rightarrow \sigma(x) = -\sigma(ix)$

$$\Lambda_{iw,u,\tau} = \Lambda_{w,u,\tau}^{-1}$$

$$\Lambda_{iw,u,\tau} / \Lambda_{w,u,\tau} = \exp(\tau \langle \sigma \rangle p), \text{ if } w \text{ has } p.$$

All terms in numerator of RHS have counterpart in denominator. For small δ , division of each term in numerator by its counterpart $\approx \exp(\tau \langle \sigma \rangle p)$.

Guaranteed to converge for $p \in (-p^*, p^*)$.

Difficulties emerge when $\langle \sigma \rangle \rightarrow 0$.

Real systems not Anosov, “Anosov-like” if CH holds,
an expression to be properly interpreted.

ECM2, GNS not uniformly hyperbolic; BGG has singularities;
LRB, BR not chaotic;...

For CH, similarly to EH, microscopic dynamics must be so
“disordered” that deviations from Anosov unobservable.

But which form of “chaos” is needed?

The most important ingredients for thermodynamic behaviour are
large N and particle interactions but don't seem to play a role
in the CH... puzzling...

When $\sigma =$ entropy production rate, GCFT has physical consequences. But

1. this almost never happens;
2. how necessary is to be close to Anosov?

At the same time, relation almost ubiquitous:

They are very general and their proofs are, in most cases, disconcertingly simple (Kurchan says)

at least if one remains in the stochastic framework.

Hence numerical and experimental tests of any relation like

$$\ln \frac{p(F = A)}{p(F = -A)} = \text{constant} \times At$$

have been performed and considered tests of the GCFT.

But what does “Anosov-like” mean?

How much chaos is “sufficiently chaotic”?