Exact & non-exact response theory from nonequilibrium molecular dynamics to stochastics

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Evans-Cohen-Morriss Phys Rev Lett 1993

These authors considered the isoenergetic SLLOD model of shear:

$$\begin{cases} \dot{\mathbf{q}}_i = \mathbf{p}_i/m + \mathbf{n}_x \gamma y_i \ , \quad i = 1, ..., N \\ \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{n}_x \gamma p_{yi} - \alpha \mathbf{p}_i \end{cases} \qquad \alpha_{_{IE}} = \frac{-\gamma P_{xy} V}{\sum_{i=1}^N \mathbf{p}_i^2/m}$$

proposed and tested first Fluctuation Relation inspired by theory of Anosov systems:

$$\frac{\mu_i}{\mu_{i^*}} = \frac{\exp\left[-\sum_n^+ \lambda_{i,n}\tau\right]}{\exp\left[-\sum_n^+ \lambda_{i^*,n}\tau\right]} = \exp\left[N d \tau \overline{\alpha}_{i,\tau}\right]$$

i, i^* conjugate segments length τ; d = dimension;
λ_i = finite time Lyapunov exponents

$$\overline{\alpha}_{i,\tau} \propto -\sum_n \lambda_{i,n} \propto \text{average energy dissipation rate (thermostat)}$$

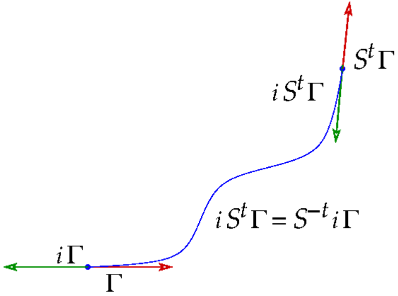
In local thermodynamic equilibrium quantifies second law, and goes beyond. First from reversible dynamics. Suitable for small systems.

Anosov dynamics physically problematic (necessary vs. sufficient conditions), so Evans-Searles alternative approach.

Thermostat made dynamics **dissipative**, allowing system to reach steady states, but **time reversal invariant in some sense.**

Let $\mathcal{M}$ = phase space and $S^t : \mathcal{M} \to \mathcal{M}$ evolution in $\mathcal{M}$
$S^t\Gamma$ phase Γ after time t.

Usual reversal operation:
$i(\mathbf{q},\mathbf{p}) = (\mathbf{q},-\mathbf{p})$ so that $i^2 = \mathrm{Id}$
For dynamics invariant under such operator, the initial conditions Γ and $\widetilde{\Gamma} = iS^t\Gamma$ trace back each other in configuration space for a time t.



More generally, take $i : \mathcal{M} \to \mathcal{M}$, with $i^2 = \mathrm{Id}$, and call dynamics time reversal invariant if

$$iS^t\Gamma = S^{-t}i\Gamma \;, \forall\Gamma \in \mathcal{M} \qquad \text{indeed} \qquad S^{-t}\Gamma = S^{-t}i(i\Gamma) = iS^ti\Gamma$$

$\dot{\Gamma} = G(\Gamma)$ in phase space $\mathcal{M}$, $S^t\Gamma$ = evolution from i.c. $\Gamma = (\mathbf{q}, \mathbf{p})$

Reversible: $S^t i = i S^{-t}$, i = time reversal involution,
but dissipative i.e.:
Λ = phase space volume variation rate = $\text{div}\, G$, $\langle \Lambda \rangle < 0$

Let $f^{(0)}$ = initial density (idea: experiments start in equilibrium).

Dissipation function:

$$\Omega^{(0)} = -G \cdot \partial_\Gamma \ln f^{(0)} - \Lambda$$

$$\Omega^{(0)}_{t,t+\tau}(\Gamma) = \int_t^{t+\tau} \Omega^{(0)}(S^s\Gamma) \mathrm{d}s = \ln \frac{f^{(0)}(S^t\Gamma)}{f^{(0)}(S^{t+\tau}\Gamma)} - \int_t^{t+\tau} \Lambda(S^s\Gamma) \mathrm{d}s$$

For equilibrium $f^{(0)}$:

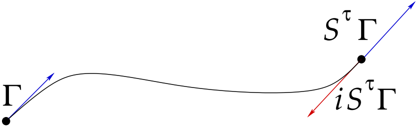
$\Omega^{(0)}$ = **dissipation rate !!** (e.g. $\sigma = FJ/k_B T$)

odd under i: $\Omega^{(0)}(i\Gamma) = -\Omega^{(0)}(\Gamma)$ like dissipative fluxes.

Transient FRs

Let $B_{A,\delta} = (A - \delta, A + \delta)$ $B_{-A,\delta} = (-A - \delta, -A + \delta)$

Observe that $\{\Gamma : \overline{\Omega}_{0,\tau}^{(0)}(\Gamma) \in B_{-A,\delta}\} = iS^\tau\{\Gamma : \overline{\Omega}_{0,\tau}^{(0)}(\Gamma) \in B_{A,\delta}\}$



Consider

$$\frac{\mu^{(0)}(\overline{\Omega}_{0,\tau}^{(0)} \in B_{A,\delta})}{\mu^{(0)}(\overline{\Omega}_{0,\tau}^{(0)} \in B_{-A,\delta})} = \frac{\int_{B_{A,\delta}} f^{(0)}(\Gamma)\mathrm{d}\Gamma}{\int_{B_{-A,\delta}} f^{(0)}(\Gamma)\mathrm{d}\Gamma}$$

and introduce $\Gamma = iS^\tau X$, with jacobian

$$J_{0,\tau}(X) = \left|\frac{\mathrm{d}\Gamma}{\mathrm{d}X}\right| = \exp\{\Lambda_{0,\tau}(X)\}$$

$$\int_{B_{-A,\delta}} f^{(0)}(\Gamma)\mathrm{d}\Gamma = \int_{B_{A,\delta}} f^{(0)}(iS^\tau X)\, e^{\Lambda_{0,\tau}(X)}\mathrm{d}X =$$

$$\int_{B_{A,\delta}} f^{(0)}(X)\, e^{-\Omega^{(0)}_{0,\tau}(X)}\mathrm{d}X = e^{-[A+\epsilon(A,\delta,\tau)]\tau} \int_{B_{A,\delta}} f^{(0)}(X)\mathrm{d}X$$

which leads to

$$\boxed{\frac{\mu^{(0)}(\overline{\Omega}^{(0)}_{0,\tau} \in B_{A,\delta})}{\mu^{(0)}(\overline{\Omega}^{(0)}_{0,\tau} \in B_{-A,\delta})} = \exp\left\{\tau\left[A + \epsilon(A,\delta,\tau)\right]\right\} \ ; \qquad \epsilon(A,\delta,\tau) \le \delta}$$

Transient Ω-FR: (unbreakable) identity for a property of $f^{(0)}$, holding $\forall\tau$.

More generally, for $\mathcal{O}(i\Gamma) = -\mathcal{O}(\Gamma)$; then $\forall\delta, \tau > 0$

$$\frac{\mu^{(0)}(\overline{\mathcal{O}}_{0,\tau} \in B_{-A,\delta})}{\mu^{(0)}(\overline{\mathcal{O}}_{0,\tau} \in B_{A,\delta})} = \left\langle e^{-\Omega^{(0)}_{0,\tau}} \right\rangle^{(0)}_{\overline{\mathcal{O}}_{0,\tau} \in B_{A,\delta}}$$

Only need time reversibility and symmetry of $f^{(0)}$.

What kind of relations are these?

Transient FRs describe **ensembles** of experiments starting in $f^{(0)}$.
Obtain equilibrium properties from nonequilibrium dynamics, closing circle with Fluctuation Dissipation Relation.
Experimentally verified (optical tweezers and colloidal particles; Evans et al. PRL 2002).

Unbreakable.

Use to debug simulations
but also experiments.
Indirect access to non-accessible quantities.

Figure 2.9: This photo was taken in June 2005, after the system was significantly modified. The components in the photo are: (1) Nikon Diaphot 300 inverted microscope, (2) Microscope objectives, (3) Microscope stage, (4) Coherrent Compass 4000M Laser, (5) BEOC Laser Stabiliser, (6) MTI IFG CCD Camera, (7) Physik Instrumente Piezo Translator, (8) replacement control computer with custom written

What about steady state FRs?

What about statistics of fluctuations along single, long evolution?

Move from statistics of $\mu^{(0)}$ to that resulting at time t by conservation of probability in phase space, $\mu^{(t)}$

$$\mu^{(t)}(E) = \mu^{(0)}(S^{-t}E)$$

and then to statistics of steady state μ_∞, *provided it exists*.

This is treating phase space probabilities objectively, like the mass of a fluid in $2dN$(!!!) dimensional space, instead of 3-dimensional space. Common postulate, but postulate...

$$\frac{1}{\tau}\ln\frac{\mu^{(t)}(\overline{\Omega}^{(0)}_{0,\tau}\in B_{A,\delta})}{\mu^{(t)}(\overline{\Omega}^{(0)}_{0,\tau}\in B_{-A,\delta})} = -\frac{1}{\tau}\ln\left\langle e^{-\Omega^{(0)}_{0,t}}\cdot e^{-\Omega^{(0)}_{t,t+\tau}}\cdot e^{-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in B_{A,\delta}}$$

$$= A+\epsilon(\delta,t,A,\tau)-\frac{1}{\tau}\ln\left\langle e^{-\Omega^{(0)}_{0,t}}\cdot e^{-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in B_{A,\delta}}$$

Take $t\to\infty$ to let $\mu_t\to\mu_\infty$. $\tau\to\infty$ should kill $\ln\langle.\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in B_{A,\delta}}$

But $t\to\infty$ before τ, hence $\Omega^{(0)}_{0,t}$, $\ln\langle\dots\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in B_{A,\delta}}$ may diverge.

Necessary condition: $\ln\langle\dots\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in B_{A,\delta}}$ **does not diverge.** Then:

steady state FR with $O(1/\tau)$ correction, for **Dissipation Function.**

What kind of condition is this?

Suppose "$f^{(0)}$-correlations" decay instantaneously:

$$\left\langle e^{-\Omega^{(0)}_{0,t}} \cdot e^{-\Omega^{(0)}_{t+\tau,2t+\tau}} \right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau} \in B_{A,\delta}} = \left\langle e^{-\Omega^{(0)}_{0,t}} \cdot e^{-\Omega^{(0)}_{t+\tau,2t+\tau}} \right\rangle^{(0)}$$

$$= \left\langle e^{-\Omega^{(0)}_{0,t}} \cdot \left(e^{-\Omega^{(0)}_{0,t}} \circ S^{t+\tau} \right) \right\rangle^{(0)} = \left\langle e^{-\Omega^{(0)}_{0,t}} \right\rangle^{(0)} \left\langle e^{-\Omega^{(0)}_{0,t}} \right\rangle^{(t+\tau)} = 1$$

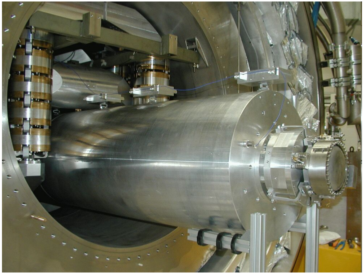
since the transient FRs yield $\left\langle e^{-\Omega^{(0)}_{0,t}} \right\rangle^{(0)} = 1$

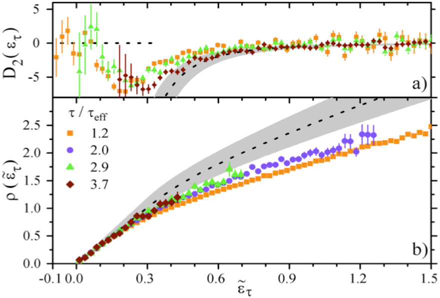
This implies that steady state is immediately reached and steady state FR is immediately verified.

If decay not immediate, results obtained after sufficiently many $f^{(0)}$-decorrelation times. If no decay, but exponential growth? (possible in simple systems) Transient valid. Steady state violated.

Only small systems?

Fluctuations even in macroscopic systems detecting gravitational waves





A 2 tons - 3 meters long - Aluminium-alloy bar cooled to an *effective* temperature of $\mathrm{O}(mK)$, via feedback currents (extra damping). Nonequilibrium state: work and dissipation.
Second derivative of PDF and FR. Three years at KHz data collection rate.
Slow correlation decay implies correction to FR.

FR in magnetic field

"The time-reversal operation **means** the transformation

$$t \to -t, \; \mathbf{p} \to -\mathbf{p}, \; \sigma \to -\sigma, \; \mathbf{B} \to -\mathbf{B}\text{"}$$

Kubo

Why?

"particles only retrace former paths if both momenta and the magnetic field are reversed. Similar situation arises for Coriolis forces where angular velocity must be reversed" De Groot-Mazur

CONSEQUENCES

Many: Onsager-Casimir relations: $L_{ij}(\mathbf{B}) = L_{ji}(-\mathbf{B})$

fluctuation relations

$$\frac{1}{\tau} \ln \frac{\mu^{(t)}(\overline{\Omega}^{(0)}_{0,\tau} \in (A-\delta, A+\delta))_{\mathbf{B}}}{\mu^{(t)}(\overline{\Omega}^{(0)}_{0,\tau} \in (-A-\delta, -A+\delta))_{-\mathbf{B}}} = A + \epsilon(\delta, t, A, \tau) + O\left(\frac{1}{\tau}\right)$$

Recover reversibility

Bonella, Ciccotti, R: equations of motion in magnetic field are formally identical to the SLLOD equations, and invariant under

$$\mathcal{M}: \quad (x, y, z, p_x, p_y, p_z, t) \longmapsto (x, -y, z, -p_x, p_y, -p_z, -t)$$

as discovered by Evans and Morriss in late 80's. We then found a huge class of time reversal transformations that preserve Hamiltonian equations of motion, without magnetic field. In presence of it, most general time reversal property we found so far is this (Carbone, De Gregorio, R 2022)

Theorem

Given $\boldsymbol{B}(\boldsymbol{x})$, take $\mathcal{M}_m \in O(3)$, so that $\mathcal{M}\boldsymbol{X} = (\mathcal{M}_m \boldsymbol{x}_1, ..., \mathcal{M}_m \boldsymbol{x}_N)$ is a time reversal map. Introduce pseudovector field rotation operator:

$$(\mathcal{M}'\boldsymbol{B})(\boldsymbol{x}) = \det(\mathcal{M}_m)\mathcal{M}_m \boldsymbol{B}(\mathcal{M}_m \boldsymbol{x})$$

$\mathcal{M}$ yields TRI in the presence of this magnetic field, **if and only if**

$$(\mathcal{M}'\boldsymbol{B})(\boldsymbol{x}) = -\boldsymbol{B}(\boldsymbol{x}) \quad \textit{(classical and quantum)}$$

More reversal operators preserve Hamiltonian dynamics under time reversal with no external field, for instance:

$$\mathcal{M}^{(1)}(x,y,z,p^x,p^y,p^z) = (x,y,z,-p^x,-p^y,-p^z)$$
$$\mathcal{M}^{(2)}(x,y,z,p^x,p^y,p^z) = (-x,-y,-z,p^x,p^y,p^z)$$
$$\mathcal{M}^{(3)}(x,y,z,p^x,p^y,p^z) = (-x,y,z,p^x,-p^y,-p^z)$$
$$\mathcal{M}^{(4)}(x,y,z,p^x,p^y,p^z) = (x,-y,z,-p^x,p^y,-p^z)$$
$$\mathcal{M}^{(5)}(x,y,z,p^x,p^y,p^z) = (x,y,-z,-p^x,-p^y,p^z)$$
$$\mathcal{M}^{(6)}(x,y,z,p^x,p^y,p^z) = (x,-y,-z,-p^x,p^y,p^z)$$
$$\mathcal{M}^{(7)}(x,y,z,p^x,p^y,p^z) = (-x,y,-z,p^x,-p^y,p^z)$$
$$\mathcal{M}^{(8)}(x,y,z,p^x,p^y,p^z) = (-x,-y,z,p^x,p^y,-p^z)$$

invert coordinate if conjugate momentum is preserved.

Electric field $(E,0,0)$, breaks $\mathcal{M}^{(2)}$, $\mathcal{M}^{(3)}$, $\mathcal{M}^{(7)}$, $\mathcal{M}^{(8)}$ symmetries (preserves the usual symmetry $\mathcal{M}^{(1)}$, polar vector)

Magnetic field along $(0,0,B)$ breaks $\mathcal{M}^{(1)}$, $\mathcal{M}^{(2)}$, $\mathcal{M}^{(5)}$, $\mathcal{M}^{(8)}$ (breaks $\mathcal{M}^{(1)}$ symmetry, pseudovector).

For $(0,0,B^z)$ and $(E^x,0,E^z)$, $\mathcal{M}^{(4)}$ only surviving symmetry.

YES! Onsager and Fluctuation relations, together with others, hold even in presence of magnetic fields. Furthermore:

- $\Psi = \Phi$ right away implies $\langle \Phi(0)\Phi(t)\rangle_{\mathbf{B}} = \langle \Phi(0)\Phi(-t)\rangle_{\mathbf{B}}$ which means that autocorrelation functions are even functions of time even in a magnetic field.
- Suppose there exist $\mathcal{M}$ and $\widetilde{\mathcal{M}}$ such that

$$\langle \Phi(0)\Psi(t)\rangle_{\mathbf{B}} = \eta_\Phi \eta_\Psi \langle \Phi(0)\Psi(-t)\rangle_{\mathbf{B}} = \eta_\Phi \eta_\Psi \langle \Phi(t)\Psi(0)\rangle_{\mathbf{B}} , \text{ under} \mathcal{M}$$

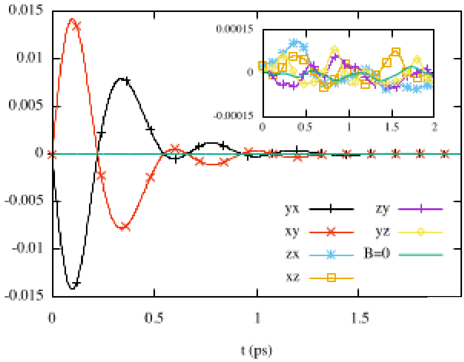
$$\langle \Phi(0)\Psi(t)\rangle_{\mathbf{B}} = \epsilon_\Phi \epsilon_\Psi \langle \Phi(0)\Psi(-t)\rangle_{\mathbf{B}} = \epsilon_\Phi \epsilon_\Psi \langle \Phi(t)\Psi(0)\rangle_{\mathbf{B}} , \text{ under} \widetilde{\mathcal{M}}$$

Then either $\eta_\Phi \eta_\Psi = \epsilon_\Phi \epsilon_\Psi$, or $\langle \Phi(0)\Psi(t)\rangle_{\mathbf{B}} = 0$

A single system, not two, and is considered, so one may draw conclusions on $\langle \Phi(0)\Psi(t)\rangle_{\mathbf{B}}$ *e.g.* implying:

$$D_{xz} = D_{zx} = D_{yz} = D_{zy} = 0; \qquad D_{xy} = -D_{yx}$$

Actually, this applies even in absence of magnetic field!



Cross components of velocity of Ag in superionic AgI conductor.

xy means $\langle v^x(0) v^y(t) \rangle$

Main: nonzero components of correlation function

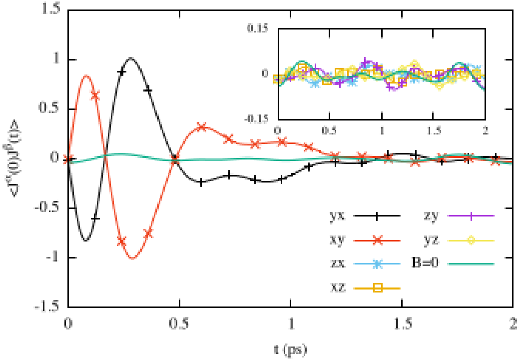
inset: null components

$B_0 = 100u$ except for green curve with $B_0 = 0$ as reference for noise

Cross components of current

Main plot: nonzero components of time-correlation function

Inset: null components



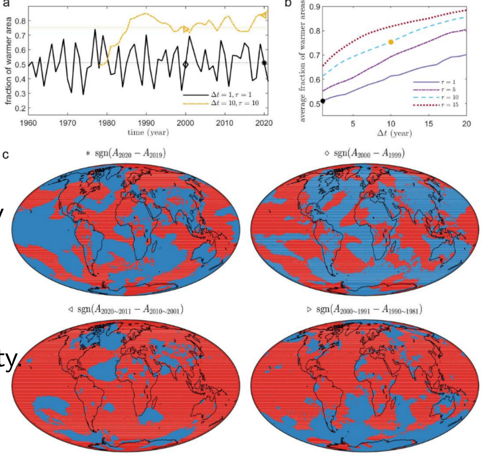
More than derivations suggest: global climate as... **a small system!**

Climate change more evident in long timescale.

Temperature fluctuations, precipitation extremes vary erratically hiding process.

Mean annual temperature may be deceiving due to strong space-time variability.

Year 2020, one of hottest on record – 49.1 % of Earth colder than previous.



(a) Earth's surface fraction with annual temperatures higher than previous year (black solid) or decade-average temperatures higher than previous decade (yellow dash-dot). (b) Average fraction of warmer areas with varying time difference and averaging windows. (c) Geographical distributions of warmer (red) and colder (blue) regions with different averaging windows and time differences.

Temperature anomaly $a =$ deviation from average temperature over 1959-2014. Local anomaly: average over time window:

$$A(t;\tau) = \frac{1}{\tau}\int_{t-\tau}^{t} a(s)ds\,; \quad \Delta A(t;\tau;\Delta t) = A(t;\tau) - A(t-\Delta t;\tau)$$

PDF of A and ΔA robust when changing τ and Δt: double exponential tails more evident for longer τ:

$$f(x,m;\beta_1,\beta_2) = \begin{cases} \beta_0 \exp\big(-(x-m)/\beta_1\big) & x > m \\ \beta_0 \exp\big((x-m)/\beta_2\big) & x < m \end{cases} \qquad \beta_0 = \frac{1}{\beta_1+\beta_2}$$

PDF gradually turns anticlockwise, producing positive skewness in the more recent years: warming trend toward more extreme events, as well as acceleration of global warming

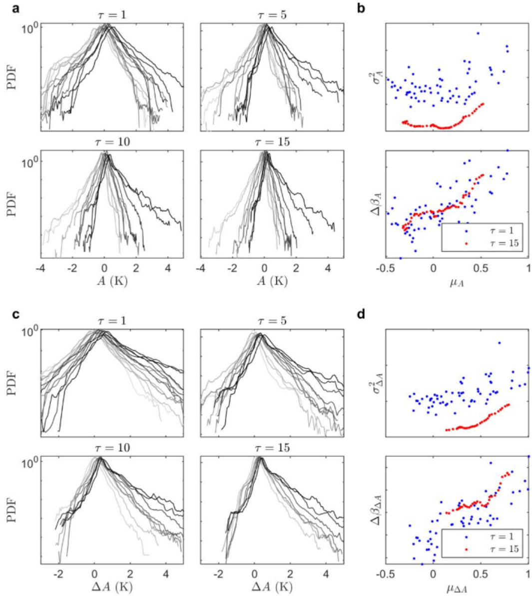
Lighter color as earlier year (or shorter time differences); darker color for later years (or longer time differences)

$\mu =$ mean

$\sigma^2 =$ variance

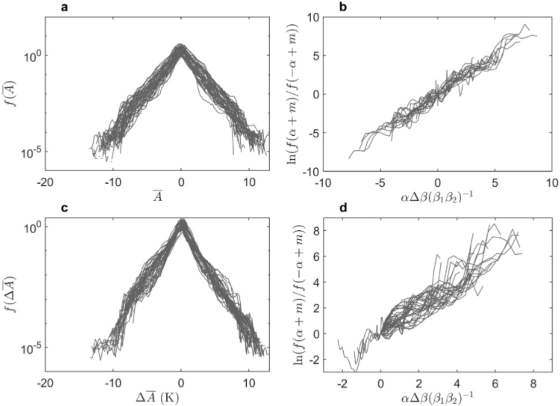
$\Delta\beta =$ asymmetry.

Data 1959 - 2021.



Rescale and get universal large deviation functional verifying Fluctuation Relation:

$$\ln\left[\frac{f(\alpha+m)}{f(-\alpha+m)}\right] = \frac{\alpha\Delta\beta}{\beta_1\beta_2}$$



Asymptotics: kind of large deviation functional, captures not only growth of mean, but also growing skewness in favour of hotter T.

Idea of correlations decay for response

New property concerning initial (equilibrium) distribution $f^{(0)}$ and nonequilibrium dynamics S^t, **t-mixing**:

$$\lim_{t\to\infty}\left[\left\langle\left(\mathcal{O}\circ S^t\right)\mathcal{P}\right\rangle^{(0)}-\left\langle\mathcal{O}\circ S^t\right\rangle^{(0)}\langle\mathcal{P}\rangle^{(0)}\right]=0$$

Taking $\mathcal{P}=\Omega^{(0)}$ and observing that $\langle\Omega^{(0)}\rangle^{(0)}=0$, the previous condition means $\left\langle\left(\mathcal{O}\circ S^t\right)\Omega^{(0)}\right\rangle^{(0)}\to 0.$

For steady state FR need less, but simple algebra leads to

Response Relation

$$\langle\mathcal{O}\rangle^{(t)}=\langle\mathcal{O}\rangle^{(0)}+\int_0^t \mathrm{d}s\left\langle\left(\mathcal{O}\circ S^s\right)\Omega^{(0)}\right\rangle^{(0)}$$

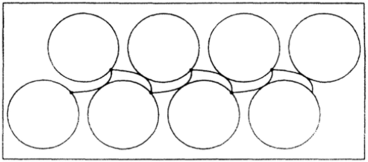
Response amounts to **convergence to steady state** in standard, *i.e.* ensemble, sense. Works even for convergence to equilibrium.

Per se, this kind of relaxation does not speak of the irreversibility of a given macroscopic system.

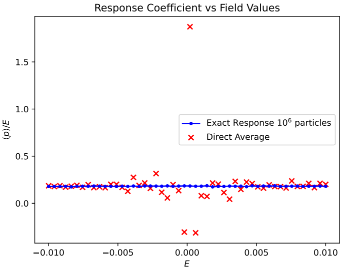
Conditions can be given for single system relaxation.

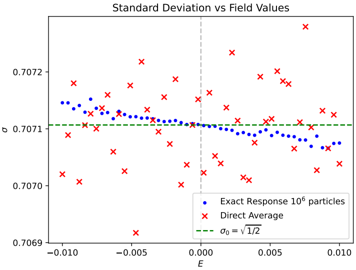
Nonequilibrium Lorentz gas: very simple, complex under parameters variations. Does it have a (sensible) linear regime?

$$\dot{x} = p_x \,; \qquad \dot{p}_x = F_x + E - \alpha p_x$$
$$\dot{y} = p_y \,; \qquad \dot{p}_y = F_y - \alpha p_y$$



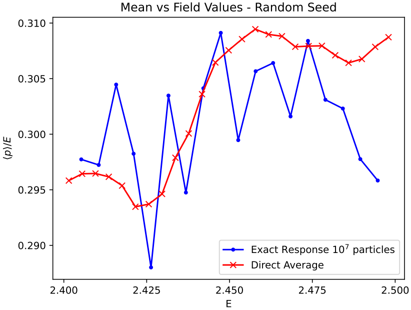
At small fields, signal to noise ratio is very poor.
Compare direct average and exact response formula.

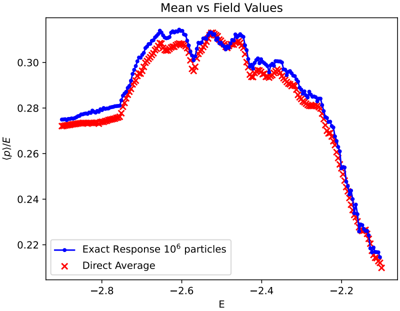


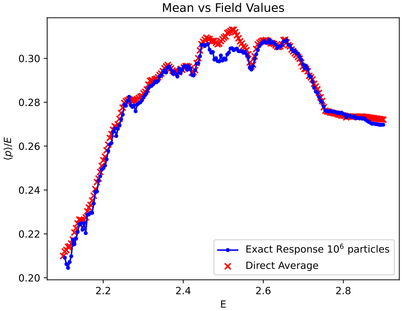


Can detect phase transitions

Increasing field, it goes from chaotic, through phase transitions, eventually collappses on periodic orbit. While formula remains valid, efficiency is reduced with simple dynamics: decay of correlations must be in initial ensmble, that needs to be very well approximated.







Kuramoto synchronization

$N \geq 1$ oscillators, rotating in unit circle of complex plane.
Dynamics defined on torus $\mathcal{T}^N = (\mathbb{R}/(2\pi\mathbb{Z}))^N$, for phases $\theta_i(t)$:

$$\dot{\theta}_i = \omega_i + \frac{K}{N} \sum_{j=1}^{N} \sin(\theta_j - \theta_i) \qquad i = 1, \ldots, N \; ,$$

$K > 0$ constant; natural frequencies $\omega_i \in \mathbb{R}$ drawn from given distribution $g(\omega)$. With polar coordinates for the center of mass:

$$Re^{i\Phi} = \frac{1}{N} \sum_{j=1}^{N} e^{i\theta_j} \; ; \quad R \in (0, 1] \, , \quad \Phi \in \mathbb{R}$$

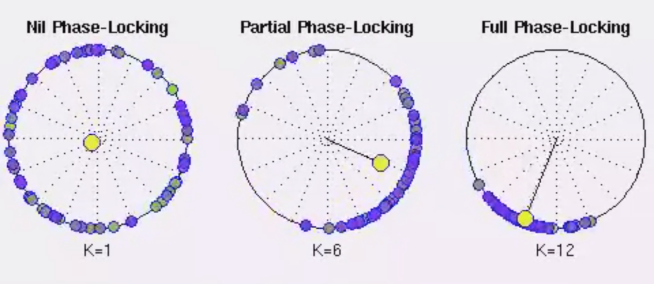
one gets:

$$\dot{\theta}_i = \omega_i + KR \sin(\Phi - \theta_i) \, , \qquad i = 1, \ldots, N$$

with $R = R(\theta(t))$ the **order parameter** and $\Phi = \Phi(\theta(t))$ the **collective phase**, with $\theta = (\theta_1, ..., \theta_N)$.

Definition

A *complete frequency synchronization* occurs when the differences $\theta_i(t) - \theta_j(t)$ tend to a constant for all i and j, and $R(t)$ tends to a given $\overline{R} \in (0, 1]$, as $t \to +\infty$. In case $\overline{R} = 1$ the Kuramoto system undergoes *phase synchronization*.



Nil, partial and full phase synchronization in the Kuramoto model for different coupling strengths K (from wikipedia).

Benedetto, Caglioti, Montemagno, 2014: case of **identical oscillators**, i.e. $\omega_i = \omega$ for $i = 1, \ldots, N$. unperturbed vector field $V_0(\theta) = W = (\omega, \ldots, \omega)$ (decoupled oscillators); $\mathrm{div}_\theta V_0 = 0$,

$$f_0(\theta) = (2\pi)^{-N}$$

Perturbation implies dissipation, and:

$$\begin{aligned} \Omega^{f_0,V} &= -(\mathrm{div}_\theta V + V \cdot \nabla \log f_0) = K\left(NR^2 - 1\right) \\ &= \frac{K}{N} \sum_{i,j=1}^{N} \cos(\theta_j - \theta_i) - K \end{aligned}$$

and the density evolves as:

$$f_t(\theta) = \exp\left\{\Omega^{(0)}_{-t,0}(\theta)\right\} f^{(0)}(\theta) = \frac{1}{(2\pi)^N} \exp\left[-K\left(t - NR^2_{-t,0}(\theta)\right)\right]$$

where $R_{-t,0}$ denotes the integral of R from time $-t$ to 0

Synchronization can be understood considering the observable $\mathcal{O} = \Omega^{f_0,V}$:

$$\langle \Omega^{f_0,V} \rangle_t = \langle \Omega^{f_0,V} \rangle_0 + \int_0^t \langle (\Omega^{f_0,V} \circ S^\tau) \Omega^{f_0,V} \rangle_0 \, d\tau$$

Take now $N \geq 2$ and $\omega = 0$.
The following lemma holds (Amadori, Colangeli, Correa, R, 2022):

Lemma

For every $t > 0$, the time derivative of the expectation of the Dissipation Function obeys:

$$\frac{d}{dt}\left(\Omega^{f_0,V}(S^t\theta)\right) \geq 0 \quad \textit{and} \quad \frac{d}{dt}\left\langle \Omega^{f_0,V} \right\rangle_t = \left\langle (\Omega^{f_0,V} \circ S^t)\Omega^{f_0,V} \right\rangle_0 \geq 0$$

Stationary solutions. Synchronization understood with Dissipation Function.

Lemma

(Synchronization): *Irrespective of the initial condition $\theta \in \mathcal{T}$, the Dissipation Function obeys:*

$$\lim_{t\to\infty} \Omega^{f_0,V}(S^t\theta) = \begin{cases} K\,(N-1)\,, & \text{for } \theta \neq \Theta^\dagger \\ K\,(N-1)\left(\frac{N-4}{N}\right) & \text{for } \theta = \Theta^\dagger \end{cases}$$

where $K(N-1)$, the maximum of $\Omega^{f_0,V}$ in $\mathcal{T}^N$, corresponds to $(N,0)$ synchronization.

The phase function $\Omega^{f_0,V}(\cdot)$, computed along **a single trajectory**, reaches an asymptotic value corresponding to a synchronized state.

Remark

$$\lim_{N\to\infty}\lim_{t\to\infty}\frac{\Omega_V^{f_0}(S^t\theta)}{N} = K\,.$$

In the large t and N limits the coupling constant K equals the average Dissipation per oscillator.

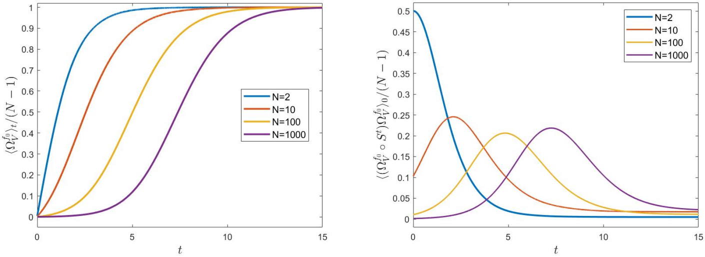


Figure: Behavior of $\langle\Omega^{f_0,V}\rangle_t$ (left panel) and $\langle(\Omega^{f_0,V}\circ S^t)\Omega^{f_0,V}\rangle_0$ (right panel) as functions of time, for $K=1$, $\omega=0$ and for different values of N.

Compare exact response with linear response.

$$V_\varepsilon(\theta) = V_0(\theta) + \varepsilon R \sin(\Phi - \theta)$$

S_ε^t and S_0^t perturbed and unperturbed flows.

$$\Omega^{f_0,V_\varepsilon} = \Omega^{f_0,V_0} + \varepsilon\Omega^{f_0,V_p} = \varepsilon\Omega^{f_0,V_p} = \varepsilon\frac{1}{N}\sum_{i,j=1}^{N}\cos\left(\theta_j - \theta_i\right) - 1$$

We get:

$$\langle\mathcal{O}\rangle_{t,\varepsilon} - \overline{\langle\mathcal{O}\rangle}_{t,\varepsilon} = \varepsilon\int_0^t \left\langle \Big[(\mathcal{O}\circ S_\varepsilon^\tau) - (\mathcal{O}\circ S_0^\tau) \Big] \Omega^{f_0,V_p} \right\rangle_0 \, d\tau$$

at fixed t, identify in small ε limit. Take *e.g.* $V_0 = \omega = 0$ and $N = 2$:

$$\left\langle \left(\Omega^{f_0,V_\varepsilon}\circ S_\varepsilon^\tau\right)\Omega^{f_0,V_\varepsilon}\right\rangle_0 = \frac{\varepsilon^2}{1+\cosh\left(\varepsilon\tau\right)} \ ,$$

which leads to:

$$\langle\Omega^{f_0,V_\varepsilon}\rangle_{t,\varepsilon} = \varepsilon\tanh\left(\frac{\varepsilon t}{2}\right), \quad \text{and} \quad \overline{\langle\Omega^{f_0,V_\varepsilon}\rangle}_{t,\varepsilon} = \frac{\varepsilon^2 t}{2} \ ,$$

so that

$$\langle\Omega^{f_0,V_\varepsilon}\rangle_{t,\varepsilon} = \overline{\langle\Omega^{f_0,V_\varepsilon}\rangle}_{t,\varepsilon} + o(\varepsilon^2)t \ .$$

At fixed $\varepsilon > 0$, difference small at small t, but increase linearly with time.

There are specific approaches, but this looks **speedy and general.**

Time dependent perturbations

Given $\dot{\Gamma} = G(\Gamma)$ on $\mathcal{M}$, consider time dependent perturbation:

$$\dot{\Gamma} = \widehat{G}(\Gamma, t) = G(\Gamma) + \mathcal{F}\widehat{w}(t) \,, \quad \text{for} \quad t \in [0, T] \,, \quad T \ \text{ large}$$

Eliminate time dependence with new variables (θ, ϕ):

$$\dot{\theta} = \phi \, ; \qquad \dot{\phi} = -\theta \quad \text{and}$$

$\mathcal{F}\widehat{w}(t) =$

$$\mathcal{F} \sum_{n=-\infty}^{\infty} \alpha_n e^{i\beta_n t} = \sum_{n=-\infty}^{\infty} \alpha_n \mathcal{F}^{1-\beta_n} \Big(\theta(t) - i\phi(t)\Big)^{\beta_n} \sum_{n=-\infty}^{\infty} \alpha_n w_n(\theta, \phi)$$

$$\dot{\widetilde{\Gamma}} = \widetilde{G}(\Gamma, \theta, \phi) = \begin{pmatrix} G(\Gamma) + w(\theta, \phi) \\ \phi \\ -\theta \end{pmatrix} \quad \widetilde{\Gamma} \in \mathcal{M} \times \mathcal{M}_{\theta\phi} \subset \mathcal{M} \times \mathbb{R}^2$$

autonomous, $\widetilde{\Lambda} = \widetilde{\Lambda}(\Gamma, \theta, \phi) = \Lambda(\Gamma)$.

Given $\widetilde{f}_0 = f_0(\Gamma) g_0(\theta, \phi)$,

$$\begin{aligned} \widetilde{\Omega}_{\widetilde{f}_0}(\Gamma, \theta, \phi) &= \Omega_{f_0}(\Gamma) - \frac{1}{f_0(\Gamma)} \sum_{n=-\infty}^{\infty} w_n(\theta, \phi) \sum_{k=1}^{N} \alpha_{nk} \frac{\partial f_0}{\partial \Gamma_k}(\Gamma) \\ &- \frac{1}{g_0(\theta, \phi)} \left(\phi \, \frac{\partial g_0}{\partial \theta}(\theta, \phi) - \theta \, \frac{\partial g_0}{\partial \phi}(\theta, \phi) \right) \end{aligned}$$

For observables $\widetilde{\mathcal{O}}$ not depending on (θ, ϕ):

$$\left\langle \widetilde{\Omega}_{\widetilde{f}_0} \left(\widetilde{\mathcal{O}} \circ \widetilde{S}^s \right) \right\rangle_{\widetilde{f}_0} = \left\langle \widetilde{\mathcal{O}} \right\rangle_{f_0}$$

$$+ \int_0^t ds \int_{\mathcal{M}_{\theta\phi}} d\theta d\phi \, g_0(\theta, \phi) \int_{\mathcal{M}} d\Gamma \, \widetilde{\Omega}_{\widetilde{f}_0}(\Gamma, \theta, \phi) \widetilde{\mathcal{O}} \left(\widetilde{S}^s \, \widetilde{\Gamma} \right) f_0(\Gamma)$$

Interesting by itself, and for what follows

Stochastic perurbations

THM[Karhunen–Loève]: Let X_t, $t \in [a,b]$ square-integrable process, zero mean, on probability space (Θ, F, P), continuous covariance $K_X(s,t)$; e_k orthonormal basis on $\mathcal{L}^2([a,b])$ formed by eigenfunctions of T_{K_X} with eigenvalues λ_k, X_t. Then:

$$X_t = \sum_{k=1}^{\infty} Z_k e_k(t)\,; \quad Z_k = \int_a^b X_t e_k(t) dt$$

convergence in $\mathcal{L}^2$, uniform in t. Furthermore, random variables Z_k have a zero mean, are uncorrelated, and have variance λ_k:

$$\langle Z_k \rangle = 0, \quad \forall k \in \mathbb{N} \qquad \textit{and} \qquad \langle Z_i Z_j \rangle = \delta_{ij}\lambda_j, \quad \forall i,j \in \mathbb{N}$$

Representation of the Wiener process in interval $[0,T]$:

$$w_t = \frac{\sqrt{2T}}{\pi} \sum_{k=1}^{\infty} Z_k \frac{\sin\left[(k-\frac{1}{2})\pi \frac{t}{T}\right]}{(k-\frac{1}{2})}$$

$\{Z_k\}_{k=1}^{\infty}$ sequence of independent Gaussian random variables, each of zero mean and unit variance. Valid in $[0,T]$ for any $T>0$; convergence in the $\mathcal{L}^2$ norm and uniform in t.

More possibilities arise: can

average over initial conditions in $\mathcal{M}$, at fixed stochastic realization;
average over stochastic realizations, at fixed initial condition in $\mathcal{M}$;
average over both;
average over distribution of initial conditions in angular variables.
Useful especially at finite times and finite size.

Simple example: harmonic oscillator in 1D

$$H_0 = \frac{p^2}{2} + \frac{\omega^2 q^2}{2} \, ; \quad H_p = -w(t) q = -\epsilon Z \sin(\gamma t) q \, ; \quad H = H_0 + H_p$$

Z, w stochastic in general, deterministic as a special case, with:

$$\widetilde{G}(\Gamma, \theta, \phi) = \begin{pmatrix} \dot{q} \\ \dot{p} \\ \dot{\theta} \\ \dot{\phi} \end{pmatrix} = \begin{pmatrix} p \\ w(\theta, \phi) - \omega^2 q \\ \phi \\ -\gamma^2 \theta \end{pmatrix} \; ; \quad w(t) = -\epsilon Z \phi(t)$$

Take $\widetilde{f}_0(\Gamma, \theta, \phi) = e^{-\beta H_0}/\sigma Z_0$, σ circumference of (θ, ϕ), then

$$\widetilde{\Omega}^{f_0}(\Gamma, \theta, \phi) = \beta \omega^2 pq + \beta w(\theta, \phi) p - \beta \omega^2 qp = \beta w(\theta, \phi) p$$

$\mathcal{O} = q$. Linear response for single realization *i.e.* given value Z:

$$\langle q \rangle_t^{(st)} = \frac{Z}{2\omega} \left(\frac{\sin[(\omega - \gamma)t]}{(\omega - \gamma)} - \frac{\sin[(\omega + \gamma)t]}{(\omega + \gamma)} \right)$$

under present conditions differs from exact response:

$$\langle q \rangle_{\widetilde{f}_t}^{(st)} = -\frac{Z}{\sigma\gamma} \int_0^t ds \frac{\sin(\omega s)}{\omega} \iint d\theta d\phi (-\gamma\theta \sin(\gamma s) + \phi \cos(\gamma s)) = 0$$

For $\widetilde{f}_0(\Gamma, \theta, \phi) = \delta(\theta_0 - 1)\delta(\phi_0) e^{-\beta H_0}/Z_0$ linear response does not change, while exact response coincides with linear response.

Special case: *e.g.* $\mathcal{O} = qp$, linear response is $\langle q \rangle_{f_t}^{(st)} = 0$, exact is:

$$\langle qp \rangle_{\widetilde{f}_t}^{(st)} = -\frac{2\mathcal{F}^2 Z^2}{\omega(\omega^2 - \gamma^2)} \times \left[\frac{(\gamma - 2\omega)\sin(\gamma t + 2\omega t)}{4\gamma^2 - 16\omega^2} - \frac{(\gamma + 2\omega)\sin(\gamma t - 2\omega t)}{4\gamma^2 - 16\omega^2} + \frac{\sin^2 \gamma t}{4\gamma} \right]$$

even with last $\widetilde{f}_0$

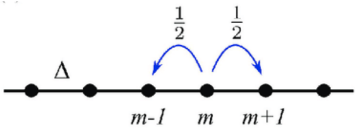
Not just time dependence, also relevant observables

Not all functions fit use of probabilities, even if "correct".

Standard ensembles need negligible finite size effects.

For instance, random walk: 1/2 and 1/2 jump probability; velocity $v = \pm 1$; step $\tau = 1$

Central Limit THM



$$f_t(x) = \frac{1}{\sqrt{2\pi t}}\ e^{-x^2/2t}\ ,\ |x| \lesssim \sqrt{t}$$

meaningless for $|x| > t$ (physically even if density too small).

But averages of $\mathcal{O}(x) = x^{2n}$ for full and truncated Gaussian

$$\langle \mathcal{O} \rangle_\infty = \int_{-\infty}^{\infty} \frac{e^{-x^2/2t}}{\sqrt{2\pi t}}\ x^{2n} dx = c_n\, t^n$$

$$\langle \mathcal{O} \rangle_t = \int_{-t}^{t} \frac{e^{-x^2/2t}\ x^{2n}}{\mathrm{erf}\left(\sqrt{t/2}\right)\sqrt{2\pi t}} dx = c_n\, t^n + O\left(t^{2n-1/2} e^{-t/2}\right)$$

agree at large t: density close to CLT prediction.

What if $\mathcal{P}(x) = \exp(x)$?

$$\langle \mathcal{P} \rangle_\infty = \int_{-\infty}^{\infty} \frac{e^{-x^2/2t}}{\sqrt{2\pi t}} \; e^x dx = e^{t/2}$$

$$\langle \mathcal{P} \rangle_t = \int_{-t}^{t} \frac{e^{-x^2/2t} \; e^x}{\mathrm{erf}\left(\sqrt{t/2}\right) \sqrt{2\pi t}} dx = \frac{1}{2} \; \frac{\mathrm{erf}\left(\sqrt{2t}\right)}{\mathrm{erf}\left(\sqrt{t/2}\right)} \; e^{t/2}$$

Even asymptotically there is factor 2. More:

exact distribution: $P_t(x) = \dfrac{t!}{j!(t-j)!2^t} \,, \quad x = 2j - t \,, \quad j = 0, ..., t$

$$\langle \mathcal{P} \rangle_{E,t} = \sum_{j=0}^{t} \frac{t! e^{2j-t}}{j!(t-j)!2^t} = \left(\frac{1+e^2}{2e} \right)^t = e^{at} \,, \quad a \approx 0.434 < 1/2 \,!$$

Larger t makes it worse, not better!

Difference between $\mathcal{O}$ and $\mathcal{P}$? $\langle \mathcal{O} \rangle$ determined by bulk, $\langle \mathcal{P} \rangle$ by tail of distribution. Average of exponentials can lead into total error.

Baths large, but finite; short times do not allow full exploration; fast trajectories get trapped.

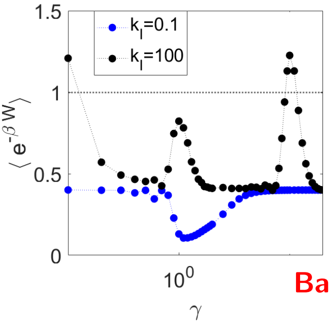
Other toy model: let $\lambda(t) = \sin \gamma t$, and

$$\mathcal{H}(\mathbf{x}, \mathbf{v}; t) =$$

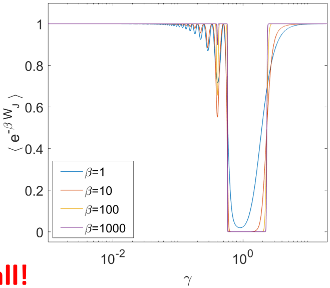
$$\frac{p_E^2}{2m_E} + \frac{k_E}{2} x_E^2 + \frac{p_S^2}{2m_S} + \frac{k_S}{2} x_S^2 + \frac{k_D}{2} (\lambda - x_S)^2 + \frac{k_I}{2} (x_E - x_S)^2$$

JE yields canonical ensemble result. What if canonical ensemble is truncated as in the RW example? Finite size bath, too short τ etc.

Quite unpredictable protocol dependence, even in such trivial case



Bad? Not at all!



Exactly solvable stochastic model of billiard dynamics

Modify Ehrenfest urn model: crowding reduces transition rates by factor $\varepsilon \in (0,1]$. For $T < N/2$, take:

$$p_{n,n+1} = \frac{N-n}{N}\varepsilon \quad \text{and} \quad p_{n,n-1} = \frac{n}{N}\,, \quad \text{for } n \le T,$$

$$p_{n,n+1} = \frac{N-n}{N}\varepsilon \quad \text{and} \quad p_{n,n-1} = \frac{n}{N}\varepsilon\,, \quad \text{for } T < n < N-T,$$

$$p_{n,n+1} = \frac{N-n}{N} \quad \text{and} \quad p_{n,n-1} = \frac{n}{N}\varepsilon\,, \quad \text{for } n \ge N-T$$

For $T > N/2$, take:

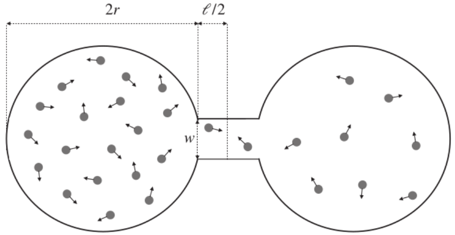
$$p_{n,n+1} = \frac{N-n}{N}\varepsilon \quad \text{and} \quad p_{n,n-1} = \frac{n}{N}\,, \quad \text{for } n \le N-T,$$

$$p_{n,n+1} = \frac{N-n}{N} \quad \text{and} \quad p_{n,n-1} = \frac{n}{N}\,, \quad \text{for } N-T < n < T,$$

$$p_{n,n+1} = \frac{N-n}{N} \quad \text{and} \quad p_{n,n-1} = \frac{n}{N}\varepsilon\,, \quad \text{for } n \ge T$$

Ehrenfest urn model recovered for $\varepsilon = 1$.

Exactly solvable stochastic model of billiard dynamics



N particles, two urns. At each step, one urn is chosen with probability proportional to number of particles it contains, $n(t)$ or $N - n(t)$, and one of its particles is moved to the other urn. If number of particles exceeds threshold, it bounces back with some probability (clogging).

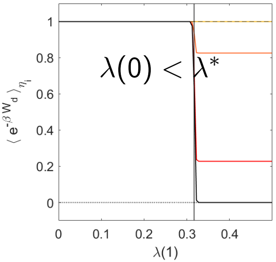
Order parameter

$$\chi = \left| \frac{2\langle n \rangle}{N} - 1 \right| = \begin{cases} 0 & \text{if} \quad \lambda < \lambda^* \\ \dfrac{1-\epsilon}{1+\epsilon} & \text{if} \quad \lambda > \lambda^* \end{cases}$$ phase transition

Jarzynski Equality for single time step: $\lambda(0) \to \lambda(1)$

$$\left\langle e^{-\beta W_d} \right\rangle = 1 \, , \quad W_d = W_J - \Delta F$$

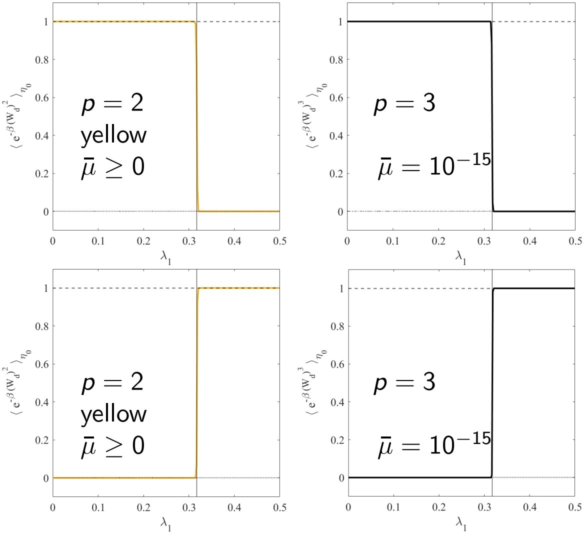
Homogeneous initial state; homogeneous or inhomogeneous final state. Compute $\left\langle e^{-\beta W_d} \right\rangle_i$ as functions of $\lambda(1)$ for full and truncated averages: Yellow, orange, red, black: cutoff $\bar{\mu} = 0,\ 10^{-60},\ 10^{-50},\ 10^{-20}$.



JE verified by full distribution, not by truncated ones.

Good! "Bad" statistic for "bad" variable reveals phase transition! and much more. "Good" statistic can't.
Useful: time could be too short to explore wide fraction of canonical; bath could be large, but... finite!.

Take $\exp\{-\beta\,(W_d)^p\}$. W_d^2 only non-negative values, while negative values fundamental for usual relations. Higher odd powers of make negative values computationally prohibitive. Sharp transition at $\lambda = \lambda^*$ even for $\bar{\mu} \geq 0$.



$\langle e^{-\beta (W_d)^p} \rangle_{\eta_0}$
as function of λ_1

start homogeneous

start inhomogeneous

Discussion

- Transient (ensemble) FR for *"entropy production"* led to dissipation function (1994 - 2000):

$$\Omega^{(0)} = -G \cdot \partial_\Gamma \ln f^{(0)} - \Lambda$$

  present in all relations, determining relaxation of observables.
- Transient FRs: require only reversibility a symmetric $f^{(0)}$. Close circle with Fluctutation Dissipation Relations: nonequilibrium dynamics reveals equilibrium properties.
- Steady state FR holds if t-mixing does and, most importantly:

$$\langle \mathcal{O} \rangle^{(\infty)} = \langle \mathcal{O} \rangle^{(0)} + \int_0^\infty \mathrm{d}s \left\langle (\mathcal{O} \circ S^s) \, \Omega^{(0)} \right\rangle^{(0)}$$

  but... a lot to do!
- **Time dependent deterministic and stochastic, single system response.**
- W_d^p with $p \neq 1$ indicates that approach may result effective with variables of quite different nature.