The Second Fluctuation–Dissipation Theorem for probe dynamics in a nonequilibrium bath

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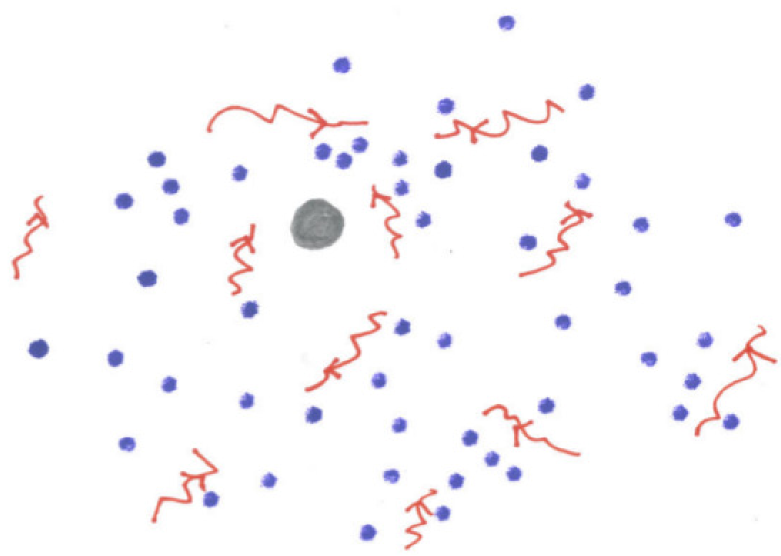
Cambridge, 30 October 2013

On three levels:
Probe interacting with driven particles in a heat reservoir.



Main questions:

I. nature of reduced dynamics..?

II. nature of statistical forces...?

Practical questions:

I. how to model... what is physical ?

II. how to compute statistical forces...?

How to do it for particles in contact with equilibrium bath?

to be specific: 1dim. Langevin dynamics,

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = v_t$$

$$\frac{\mathrm{d}v_t}{\mathrm{d}t} = -\int_{-\infty}^{t} \mathrm{d}s\, \gamma(t-s) v_s + F_t(x_t) + \eta_t$$

$\gamma(s)$: memory kernel.

F_t : possibly time-dependent forcing.

η_t : mean zero stationary Gaussian noise.

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = v_t$$
$$\frac{\mathrm{d}v_t}{\mathrm{d}t} = -\int_{-\infty}^{t} \mathrm{d}s\, \gamma(t-s) v_s + F_t(x_t) + \eta_t$$

What is the relation between $\gamma(t-s)$ and the noise covariance $\langle \eta_s \eta_t \rangle$?

The (usual) second fluctuation–dissipation relation,

or Einstein relation,

for probes in contact with equilibrium bath:

- from equipartition;
- from local detailed balance;
- from the first fluctuation–dissipation relation.

For example, from **local** detailed balance,

$$\frac{\text{Prob}[\omega]}{\widetilde{\text{Prob}}[\theta\omega]} = \exp\left(\frac{1}{k_B}\text{ total entropy flux in }\omega\right)$$

for every system path ω with $\theta\omega$ its time-reversal, and where $\widetilde{\text{Prob}}$ is the probability under reversed protocol of the dynamics.

Total entropy flux is the time-integrated entropy flux in all equilibrium reservoirs as seen from the path ω of the probe.

Assuming equilibrium medium at uniform temperature T,

the entropy flux per k_B is

$$\frac{1}{k_B T}\{-\int \mathrm{d}s\, \dot{v}_s\, v_s + \int \mathrm{d}s\, F_s(x_s)\, v_s\}$$

and time-reversal are

$$\theta x_t = x_{-t}, \quad \theta v_t = -v_{-t} \quad F_t \to F_{-t}$$

Local detailed balance is verified whenever

$$\langle \eta_s \eta_t \rangle = k_B T\, \gamma(|t-s|)$$

That Einstein relation can also be derived from the first fluctuation–dissipation relation:

E.g. coupled equations of motion

$$
\begin{aligned}
M\frac{\mathrm{d}^2 q_t}{\mathrm{d}t^2} &= -V'(q_t) + \sum_j \lambda_j \varepsilon_j \,[q_t^j - \varepsilon_j\, q_t], \qquad q_0 = y, V'(y) = 0 \\
\frac{\mathrm{d}q_t^j}{\mathrm{d}t} &= -\sum_{j'\neq j} \Phi'(q_t^j - q_t^{j'}) - \lambda_j\,[q_t^j - \varepsilon_j\, q_t] + \sqrt{2k_B T}\,\xi_t^j
\end{aligned}
$$

First Fluctuation–Dissipation Theorem

Suppose at $t = 0$ equilibrium system at β^{-1}. Add perturbation $-h_t V$, $t > 0$ to potential. Look at linear response:

$$\langle A(t) \rangle^h = \langle A(t) \rangle + \int_0^t \mathrm{d}s \, h_s R_{AV}(t,s) + o(h)$$

In equilibrium:

$$R_{AV}(t,s) = \beta \frac{\mathrm{d}}{\mathrm{d}s} \langle V(s) A(t) \rangle$$

What if the medium is active/driven/in nonequilibrium itself?

For example, probe=silica bead attached to the cytoskeleton of a living cell pushed and carried around by molecular motors and with a thermal bath as background medium.
Or, probe=balloon in atmospheric layer subject to vortices/wind that are in contact with other equilibrium layers...

Example: **oscillator model** for the probe $q_t \in S^1$ and driven medium $Q_t = \{q_t^j \in S^1\}$;

half of medium is driven clockwise and half is driven counter clockwise by external field $F^j = (-1)^j F$, $j = 1, \ldots, N$:

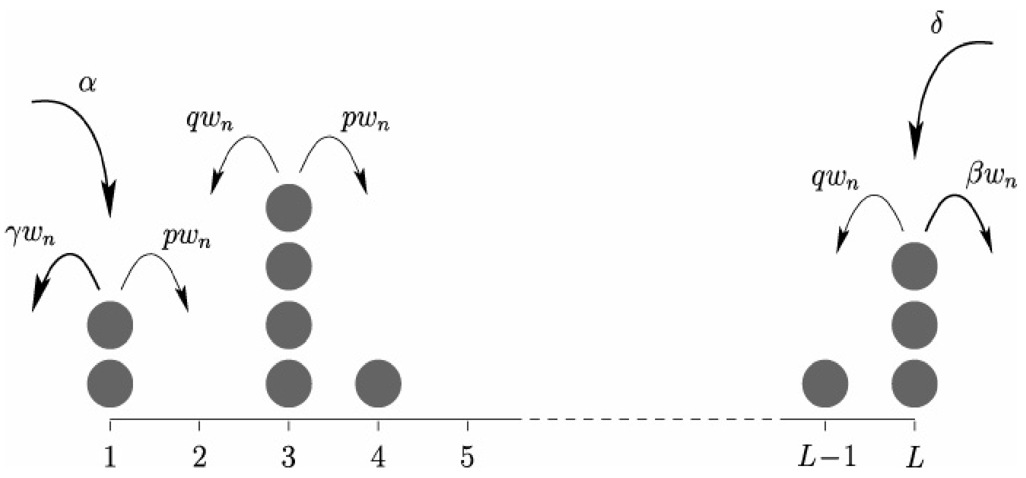
$$\Gamma \frac{\mathrm{d}q_t}{\mathrm{d}t} + V'(q_t) = -\lambda \sum_j \sin[q_t^j - q_t], \qquad q_0 = 0$$
$$\dot{q}_t^j = F^j + a \sin q_t^j + \lambda \sin[q_t^j - q_t] + \sqrt{2T}\,\xi_t^j$$

Position $q_0 = 0$ is the preferred probe direction, with $V'(0) = 0$ and Γ is large to damp the oscillations.
Weak coupling makes $q_t = O(\lambda)$, $\lambda \propto 1/\sqrt{N}$, $N \uparrow \infty$.

We now need NONEQUILIBRIUM RESPONSE.

How does the driven medium react to a repositioning of the probe?

ANSWER: both via
entropic and frenetic effects.



e.g. Perturbation $w_n(i) \to (1+h)\, w_n(i)$ for some i (where the probe is sitting).

The nonequilibrium formula takes the form

$$\langle A(t)\rangle^h - \langle A(t)\rangle = \frac{1}{2}\langle \text{ENT}^{[0,t]}\, A(t)\rangle + \langle \text{ESC}^{[0,t]}\, A(t)\rangle$$

where

$\text{ESC}^{[0,t]}$ is the excess in dynamical activity due to the decay of the perturbation over time-interval $[0,t]$ = frenetic contribution

More specifically, let us assume a Markov jump process with rates

$$k(x,y) = \psi(x,y)\, e^{s(x,y)/2}, \quad \psi(x,y) = \psi(y,x), \quad s(x,y) = -s(y,x)$$

satisfying local detailed balance so that $s(x,y)$ is the entropy flux during $x \rightarrow y$,
and $\psi(x,y)$ is a time-symmetric reactivity, also contributing to the escape rate

$$\xi(x) = \sum_y k(x,y)$$

all possibly changing under a perturbation.

For a Markov jump process with rates

$$k(x,y) = \psi(x,y)\, e^{s(x,y)/2}, \quad \psi(x,y) = \psi(y,x), \quad s(x,y) = -s(y,x)$$

we have response determined by

$$\mathrm{ENT}^{[0,t]} = \frac{\mathrm{d}}{\mathrm{d}h} \sum_i s(x_{s_i}, x_{s_{i+1}})$$

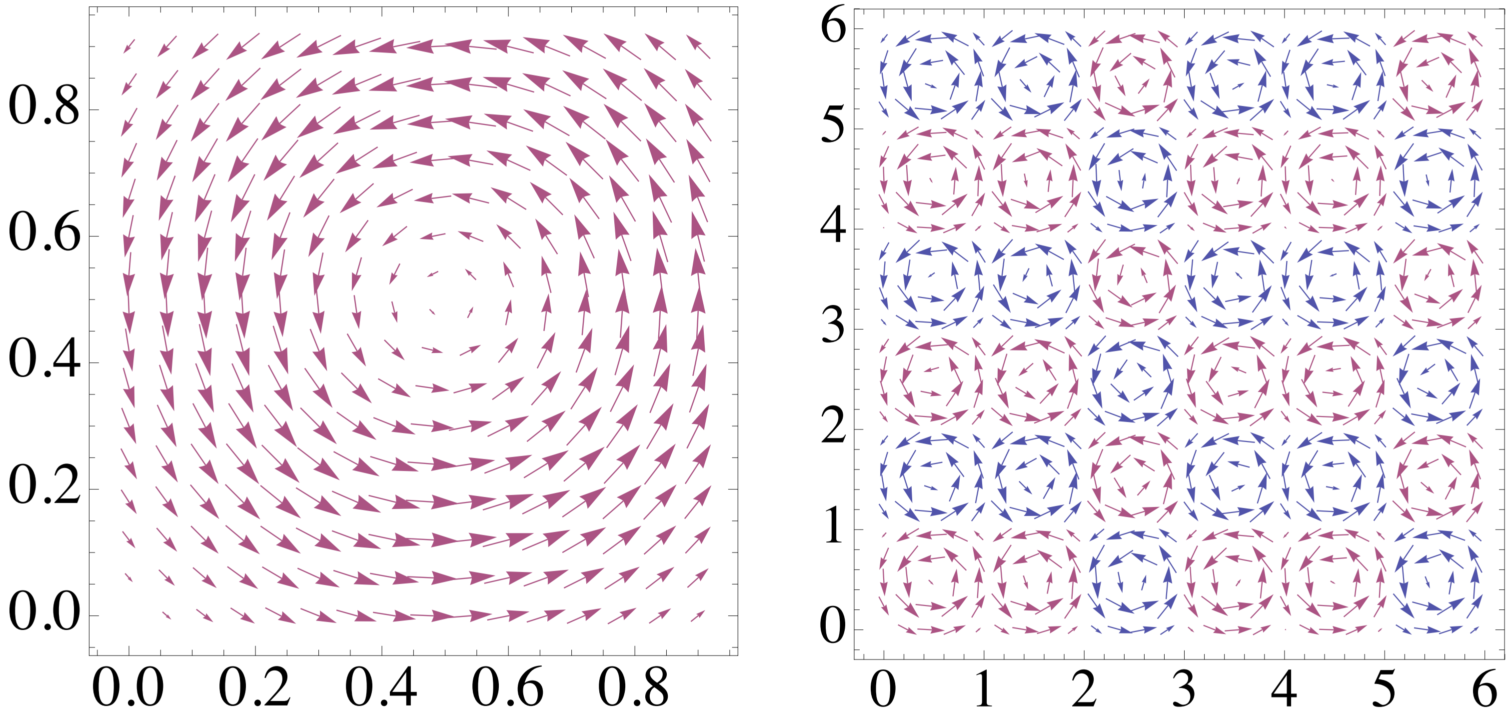
$$\mathrm{ESC}^{[0,t]} = \frac{\mathrm{d}}{\mathrm{d}h} [\int_0^t \mathrm{d}s\, \xi(x_s) - \sum_i \log \psi(x_{s_i}, x_{s_{i+1}})]$$

Modification of Sutherland-Einstein relation between diffusion and mobility.

EXAMPLE in 2 dimensions:

$$\begin{aligned} m\dot{v}_{x,t} &= F_x(x_t, y_t) - \gamma v_{x,t} + \sqrt{2m\gamma T}\,\xi_{x,t} \\ m\dot{v}_{y,t} &= F_y(x_t, y_t) - \gamma v_{y,t} + \sqrt{2m\gamma T}\,\xi_{y,t} \end{aligned}$$

Forcing $\vec{F} = A\vec{f}$, with A some constant and $\vec{f}$ rotational:

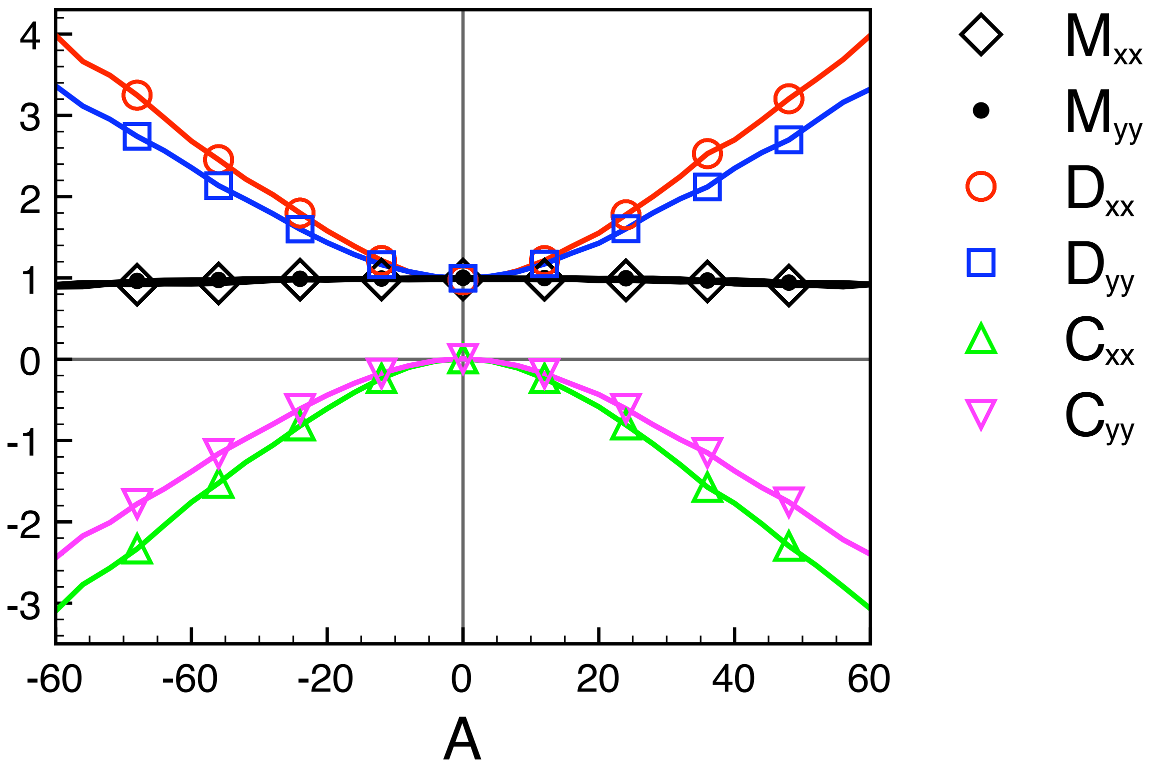

0.0
0.2
0.4
0.6
0.8
0
1
2
3
4
5
6

Response is quantified by the differential mobility,

$$\mu(E) = \lim_{t\to\infty} \frac{\partial}{\partial E} \langle v_x(t) \rangle^E$$

The diffusion constant measures the fluctuation in the position of the particle,

$$D(E) = \lim_{t\to\infty} \frac{1}{2t} [\langle (x_t - x_0)^2 \rangle - \langle (x_t - x_0) \rangle^2]$$


4
3
2
1
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-1
-2
-3
-60
-60
-20
0
20
40
60
A
Mxx
Myy
Dxx
Dyy
Cxx
Cyy

Back to the problem of the

modified second fluctuation–dissipation theorem:

oscillator model

$$
\begin{aligned}
\Gamma \frac{\mathrm{d}q_t}{\mathrm{d}t} + V'(q_t) &= -\lambda \sum_j \sin[q_t^j - q_t], \qquad q_0 = 0 \\
\dot{q}_t^j &= F^j + a \sin q_t^j + \lambda \sin[q_t^j - q_t] + \sqrt{2T}\,\xi_t^j
\end{aligned}
$$

First approximation: infinite time-scale separation

Use stationary density $\rho_{q_t}(q^j)$ of the medium for *fixed* q_t to take the averaged probe dynamics

$$\Gamma \frac{\mathrm{d}q_t}{\mathrm{d}t} + V'(q_t) = G(q_t)$$

with statistical force

$$G(q) = -\lambda \frac{N}{2}\Big[\langle \sin(\theta - q)\rangle_F^q + \langle \sin(\theta - q)\rangle_{-F}^q\Big]$$

where $\langle \cdot \rangle_{\pm F}^q$ is the stationary expectation for the dynamics

$$\dot{\theta}_t = \pm F + a \sin\theta_t + \lambda \sin(\theta_t - q) + \sqrt{2T}\,\xi_t, \qquad \theta_t \in S^1$$

Second order approximation: use modified first FDR

$$\Gamma \frac{dq_t}{dt} + V'(q_t) = G(q_t) - \int_0^t \gamma_s \, \dot{q}_s \, ds + \eta_t, \qquad q_0 = 0$$

with friction kernel to order λ^2,

$$\begin{aligned}\gamma(s) \quad &= \frac{\beta\,\lambda^2 N}{2}\Big[\langle \sin\theta_0\,;\,\sin\theta_s\rangle_F^0 \\ &- \int_{-\infty}^0 du\,\{F\,\langle\cos\theta_u\,;\,\sin\theta_s\rangle_F^0 + \\ &\frac{a}{2}\langle\sin 2\theta_u\,;\,\sin\theta_s\rangle_F^0 - T\,\langle\sin\theta_u\,;\,\sin\theta_s\rangle_F^0\}\Big]\end{aligned}$$

where the connected time-correlations are in the stationary process for the decoupled driven dynamics

$$\dot{\theta}_t = F + a\,\sin\theta_t + \sqrt{2T}\,\xi_t$$

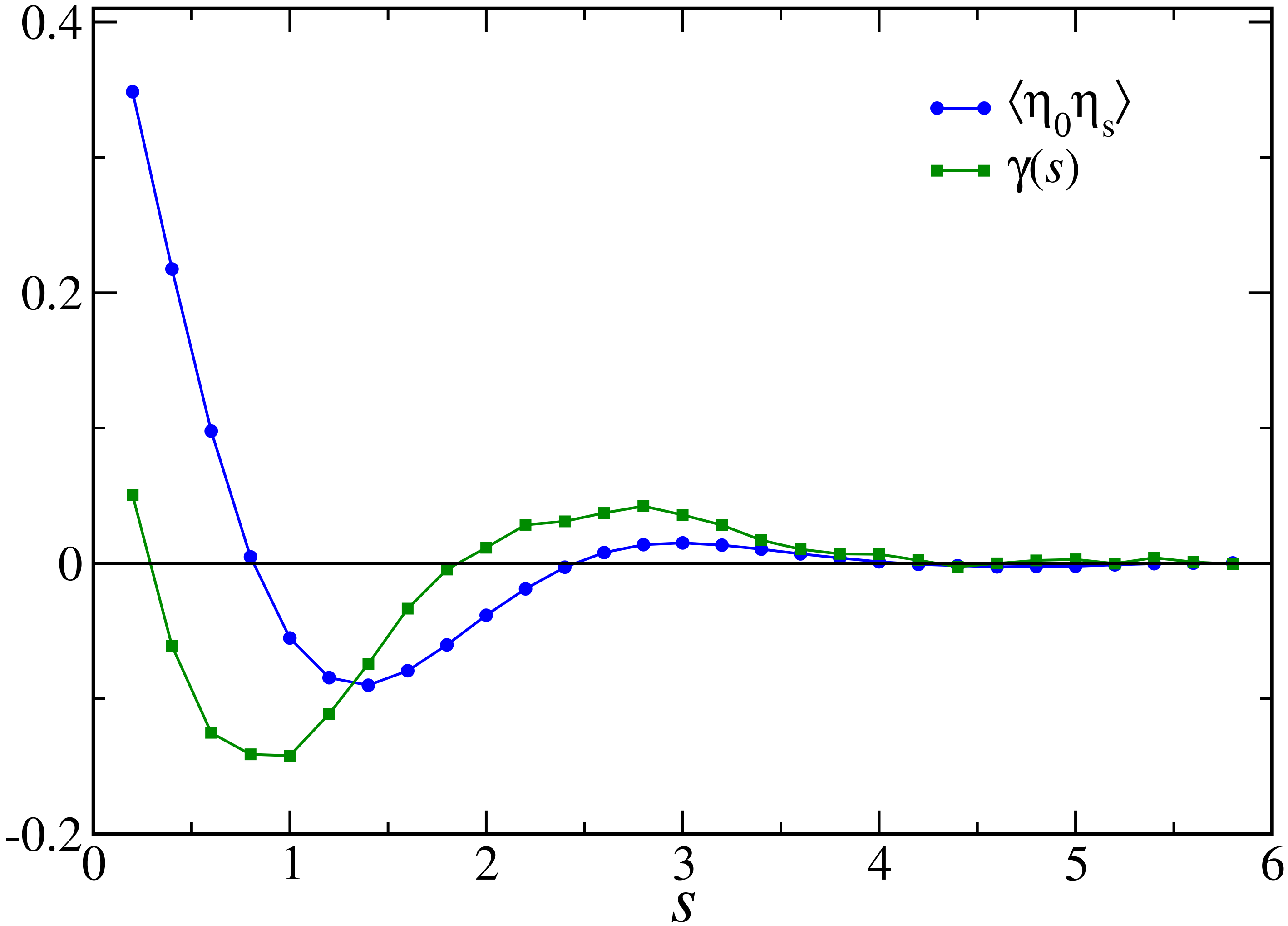
with ξ_t standard white noise.

$$\Gamma \frac{\mathrm{d}q_t}{\mathrm{d}t} + V'(q_t) = G(q_t) - \int_0^t \gamma_s\, \dot{q}_s\, \mathrm{d}s + \eta_t, \qquad q_0 = 0$$

Noise η_t has mean zero and stationary covariance

$$\langle \eta_0 \eta_s \rangle = \beta\, \lambda^2 N\, \langle \sin\theta_0\, ;\, \sin\theta_s \rangle_F^0$$

For detailed balance, $F = 0$, we get $\beta\, \gamma^{\mathrm{eq}}(s) = \langle \eta_0 \eta_s \rangle$;
For nonequilibrium there is a correction: even in the Markov limit and while the staionary probe dynamics q_t appears time-reversible, the effective temperature for the fluctuations around $q = 0$ is not T when $F \neq 0$.



Noise covariance and friction memory kernel.

Nonequilibrium theory cannot be...
just nonequilibrium thermodynamics.

and nonequilibrium concepts will be based on **more than** energy–entropy considerations, **more than** work and heat and entropy production only.

Nonequilibrium phenomena also and crucially depend on kinetics.

For example, population statistics (like in population inversion) depends on reactivities.
cf. e.g. Landauer (1975) in the blowtorch theorem writing *against* entropy production principles.

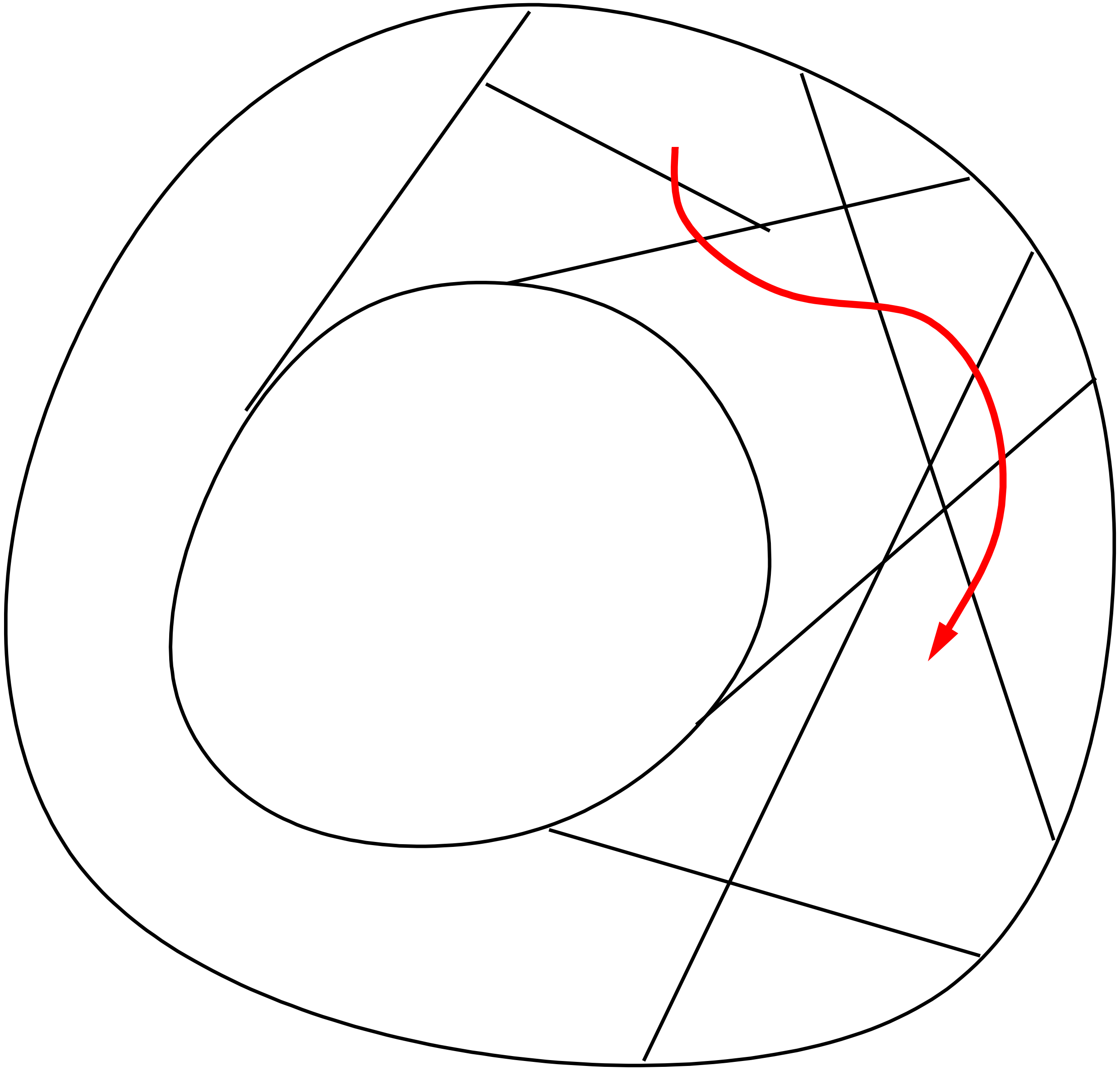
Example: random walker on $N-$ring, $N > 2$
for $x \in \{1 = N+1, 2, 3, \ldots, N\}$, transition rates:

$$k(x, x+1) = a_x \, e^{\beta Q/2}, \quad k(x+1, x) = a_x \, e^{-\beta Q/2}, \qquad \beta Q > 0$$

has a low-temperature steady population law

$$\rho(x) \sim \frac{1}{a_x}$$

depending on the reactivities a_x.



Given that we agree on the *obvious*
"that kinetics matters for nonequilibrium, beyond energy-entropy considerations",

is it then still possible to make
unifying or systematic considerations that enable both qualitatively useful and quantitatively precise estimates?

this talk: about the modification of the second fluctuation–dissipation relation

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