Entropic fluctuations in classical (and quantum) statistical mechanics

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joint work with

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mostly based on works by

Cohen, Evans, Gallavotti, Kurchan, Lebowitz, Morriss, Searles, Spohn, . . .

Overview

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- And what about quantum dynamics ?

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Measurable dynamical system with decent metric properties $(M, \mathcal{F}, \phi^t, \mu)$

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Notation: For $\nu \in \mathcal{P}$, $f \in \mathcal{B}$ and $t \in \mathbb{R}$

$$\nu(f) = \int_M f d\nu$$

$$f^t = f \circ \phi^t, \qquad \nu^t(f) = \nu(f^t)$$

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Notation:

$$\mathcal{P}_I = \{\nu \in \mathcal{P} \,|\, \forall t \in \mathbb{R}, \nu^t = \nu\} \quad \text{(steady states)}$$

$$\mathcal{P}_\mu = \{\nu \in \mathcal{P} \,|\, \nu \ll \mu\} \quad \text{(μ-normal states)}$$

$$\text{For } \nu \in \mathcal{P}_\mu : \Delta_{\nu|\mu} = \frac{d\nu}{d\mu}, \qquad \ell_{\nu|\mu} = \log \Delta_{\nu|\mu}$$

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Relative entropy: For $\omega, \nu \in \mathcal{P}$

$$0 \geq \mathrm{Ent}(\omega|\nu) = -\sup_{\mathrm{f}\in\mathcal{B}} \Big(\omega(\mathrm{f}) - \log \nu(\mathrm{e}^{\mathrm{f}})\Big) = \begin{cases} -\infty & \text{if } \omega \notin \mathcal{P}_\nu \\ -\omega(\ell_{\omega|\nu}) & \text{if } \omega \in \mathcal{P}_\nu \end{cases}$$

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Basic assumptions:

(REG) $\quad \forall t \in \mathbb{R}, \mu^t \in \mathcal{P}_\mu$ and $\sigma = \left.\frac{d}{dt}\ell_{\mu^t|\mu}\right|_{t=0}$ is continuous on M

$$(TRI) \qquad \forall f \in \mathcal{B}, \mu(f \circ \vartheta) = \mu(f)$$

1. Entropy production

Proposition. (The cocycle property) For all $s, t \in \mathbb{R}$ one has

$$\ell_{\mu^{t+s}|\mu} = \ell_{\mu^t|\mu} + \ell_{\mu^s|\mu} \circ \phi^{-t}$$

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Corollary. Under ou basic assumption (REG)

$$\ell_{\mu^t|\mu} = \int_0^t \sigma^{-s} \, ds$$

and hence one has the entropy balance equation

$$\mathrm{Ent}(\mu^{\mathrm{t}}|\mu) - \mathrm{Ent}(\mu|\mu) = -\mu^{\mathrm{t}}(\ell_{\mu^{\mathrm{t}}|\mu}) = -\int_0^{\mathrm{t}} \mu(\sigma^{\mathrm{s}}) \, \mathrm{ds}$$

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$$\downarrow$$

Mean entropy production rate over the period $[0, t]$

$$-\frac{1}{t}\,\mathrm{Ent}(\mu^{\mathrm{t}}|\mu) = \frac{1}{\mathrm{t}}\int_0^{\mathrm{t}} \mu(\sigma^{\mathrm{s}})\,\mathrm{ds} \geq 0$$

2. Entropic fluctuations: The Evans-Searles theorem

$$\mathcal{S}_t = \frac{1}{t}\int_0^t \sigma^s \, ds = \frac{1}{t}\ell_{\mu^t|\mu} \circ \phi^t$$

(mean entropy production rate observable)

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$$P^t(f) = \mu(f(\mathcal{S}_t)) \qquad \overline{P}^t(f) = \mu(f(-\mathcal{S}_t))$$ (distributions of $\mathcal{S}_t$ and $-\mathcal{S}_t$)

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Theorem. (Evans-Searles [1994] or transient fluctuation theorem) Under assumptions (REG) and (TRI) negative values of $\mathcal{S}_t$ become exponentially rare as $t \to \infty$ (dynamical form of 2nd law !). More precisely one has

$$\frac{d\overline{P}^t}{dP^t}(s) = e^{-ts}$$

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Proof. (TRI) $\Rightarrow \mu^t(f \circ \vartheta) = \mu^{-t}(f) \Rightarrow \sigma \circ \vartheta = -\sigma \Rightarrow \ell_{\mu^t|\mu} \circ \vartheta = -\mathcal{S}_t$

$$\overline{P}^t(f) = \mu\left(f\left(-\frac{1}{t}\ell_{\mu^t|\mu} \circ \phi^t\right)\right) = \mu^t\left(f\left(-\frac{1}{t}\ell_{\mu^t|\mu}\right)\right) = \mu\left(f\left(-\frac{1}{t}\ell_{\mu^t|\mu}\right)e^{\ell_{\mu^t|\mu}}\right)$$

$$= \mu\left(f\left(-\frac{1}{t}\ell_{\mu^t|\mu} \circ \vartheta\right)e^{\ell_{\mu^t|\mu} \circ \vartheta}\right) = \mu\left(f\left(\mathcal{S}_t\right)e^{-t\mathcal{S}_t}\right) = P^t(fe^{-ts})$$

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Alternative formulation of the ES theorem: the ES symmetry

$$e^t(1-\alpha) = e^t(\alpha)$$

3. Entropic fluctuations: The generalized ES theorem

Assume we have some contol of our dynamical system

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- $X \mapsto \sigma_X$ is C^1 near $X = 0$, then

$$\sigma_X = X \cdot \Phi_X = \sum_{j=1}^{n} X_j \Phi_X^{(j)}$$

and $\Phi_X = (\Phi_X^{(1)}, \ldots, \Phi_X^{(n)})$ is the vector of current observables, the current $\Phi_X^{(j)}$ being associated to the force X_j.

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- ϑ is idependant of X, then

$$\Phi_X \circ \vartheta = -\Phi_X \qquad \mu_0(\Phi_0) = 0$$

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$$P_X^t(f) = \mu\left(f\left(\frac{1}{t}\int_0^t \Phi_X^s\, ds\right)\right) \qquad \overline{P}_X^t(f) = \mu\left(f\left(-\frac{1}{t}\int_0^t \Phi_X^s\, ds\right)\right)$$

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Theorem. (Generalized ES fluctuation theorem) Under our assumptions, as $t \to \infty$ the currents flow mostly in definite directions

$$\frac{d\overline{P}_X^t}{dP_X^t}(\Phi^{(1)}, \ldots, \Phi^{(n)}) = \exp\left(-t\sum_{j=1}^n X_j \Phi^{(j)}\right)$$

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satisfies the generalized ES symmetry

$$g^t(X, X-Y) = g^t(X,Y)$$

4. Linear response: Finite time

If

$$X \mapsto \langle \Phi_X \rangle^t = \frac{1}{t} \int_0^t \mu_X(\Phi_X^s)\, ds$$

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Theorem. (Finite time Green-Kubo formula and Onsager reciprocity relations) Assume that $(X, Y) \mapsto g^t(X, Y)$ is C^2 near $(0, 0)$. Then

$$L_{jk}^t = \frac{1}{2} \int_{-t}^t \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s} \right) \left(1 - \frac{|s|}{t} \right) ds$$

and in particular the finite time transport matrix is symmetric (Onsager Reciprocity).

4. Linear response: Finite time

Remark. The following shows that the transport matrix is non-negative.

$$0 \leq \langle \sigma_X \rangle^t = \sum_{j=1}^{n} X_j \langle \Phi_X^{(j)} \rangle^t = \sum_{j,k=1}^{n} L_{jk}^t X_j X_k + o(|X|^2)$$

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Proof of the theorem. One has

$$L_{jk}^t = \partial_{X_k} \langle \Phi_X^{(j)} \rangle^t \Big|_{X=0} = -\frac{1}{t}\, \partial_{X_k} \partial_{Y_j} g^t(X,Y) \Big|_{X=Y=0}$$

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As a consequence of the generalized ES symmetry one also has

$$-\partial_{X_k} \partial_{Y_j} g^t(X,Y) \Big|_{X=Y=0} = \frac{1}{2}\, \partial_{Y_k} \partial_{Y_j} g^t(X,Y) \Big|_{X=Y=0}$$

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(note that the symmetry of L^t already follows from this formula!) Thus we can write

$$L_{jk}^t = \frac{1}{2t} \int_0^t \int_0^t \mu_0 \left(\Phi_0^{(k)s_1} \Phi_0^{(j)s_2} \right) ds_1 ds_2 = \frac{1}{2t} \int_0^t \int_0^t \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s_2 - s_1} \right) ds_1 ds_2$$

4. Linear response: Finite time

Remark. The following shows that the transport matrix is non-negative.

$$0 \le \langle \sigma_X \rangle^t = \sum_{j=1}^{n} X_j \langle \Phi_X^{(j)} \rangle^t = \sum_{j,k=1}^{n} L_{jk}^t X_j X_k + o(|X|^2)$$

Proof of the theorem. One has

$$L_{jk}^t = \partial_{X_k} \langle \Phi_X^{(j)} \rangle^t \Big|_{X=0} = -\frac{1}{t}\, \partial_{X_k} \partial_{Y_j} g^t(X,Y) \Big|_{X=Y=0}$$

As a consequence of the generalized ES symmetry one also has

$$-\partial_{X_k} \partial_{Y_j} g^t(X,Y) \Big|_{X=Y=0} = \frac{1}{2}\, \partial_{Y_k} \partial_{Y_j} g^t(X,Y) \Big|_{X=Y=0}$$

(note that the symmetry of L^t already follows from this formula!) Thus we can write

$$L_{jk}^t = \frac{1}{2t} \int_0^t \int_0^t \mu_0 \left(\Phi_0^{(k)s_1} \Phi_0^{(j)s_2} \right) ds_1 ds_2 = \frac{1}{2t} \int_0^t \int_0^t \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s_2 - s_1} \right) ds_1 ds_2$$

and the result follows by a simple change of integration variables.

5. Nonequilibrium Steady States

Definition. $\mu^+ \in \mathcal{P}$ is the **NESS** of $(M, \mathcal{F}, \phi^t, \mu)$ if

$$\lim_{t\to\infty} \frac{1}{t} \int_0^t \mu^s(f)\, ds = \mu^+(f)$$

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QuasiTheorem. The NESS μ_+ of $(M, \mathcal{F}, \phi^t, \mu)$ is entropically non-trivial if and only if $\mu^+ \notin \mathcal{P}_\mu$, i.e., μ^+ is singular w.r.t. μ.

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Entropic non-triviality is the signature of non-equilibrium

Theorem.(i) If $\nu \in \mathcal{P}_I \cap \mathcal{P}_\mu$ then $\nu(\sigma) = 0$.
(ii). If $\mu^+(\sigma) - \mu^t(\sigma) = O(t^{-1})$ then $\mu^+(\sigma) = 0$ implies $\mu^+ \in \mathcal{P}_I \cap \mathcal{P}_\mu$.

6. Linear response: The large time limit

Assume that for small $X \in \mathbb{R}^n$ the controlled system $(M, \mathcal{F}, \phi_X^t, \mu_X)$ has a NESS μ_X

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If the limit and derivative can be exchanged

$$L_{jk} = \lim_{t\to\infty} L_{jk}^t = \lim_{t\to\infty} \frac{1}{2} \int_{-t}^{t} \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s} \right) \left(1 - \frac{|s|}{t} \right) ds$$

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If the equilibrium current-current correlation function $s \mapsto \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s} \right)$ is integrable one gets the Green-Kubo formula and the Onsager reciprocity relations

$$L_{jk} = \frac{1}{2} \int_{-\infty}^{\infty} \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s} \right) ds, \qquad L_{jk} = L_{kj}$$

7. The Central Limit Theorem – Fluctuation-Dissipation

The Central Limit Theorem holds for the currents if there is a positive definite matrix D s.t., for all bounded continuous function $f : \mathbb{R}^n \to \mathbb{R}$,

$$\lim_{t\to\infty} \mu_0 \left(f\left(\frac{1}{\sqrt{t}} \int_0^t \Phi_0^s \, ds \right) \right) = \frac{1}{\sqrt{(2\pi)^n \det D}} \int_{\mathbb{R}^n} f(\Phi) e^{-\frac{1}{2}\Phi \cdot D^{-1}\Phi} \, d\Phi$$

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Einstein's relation

$$D_{jk} = 2L_{jk}$$

together with the Green-Kubo formula

$$L_{jk} = \frac{1}{2} \int_{-\infty}^{\infty} \mu_0 \left(\Phi_0^{(k)} \Phi_0^{(j)s} \right) \, ds$$

and the Onsager reciprocity relations $L_{jk} = L_{kj}$ complete the Fluctuation-Dissipation theorem for the system $(M, \mathcal{F}, \phi_X^t, \mu_X)$ near equilibrium ($X = 0$).

8. Entropic fluctuations: The limiting ES symmetry

Recall the ES function

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exists and is differentiable for all $\alpha \in \mathbb{R}$.

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So what ?

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$$\mu\left(\left\{x \in M \,\middle|\, \left|\frac{1}{t}\int_0^t \sigma^t(x)\,dt - \mu^+(\sigma)\right| \geq \epsilon\right\}\right) \leq e^{-ta(\epsilon)}$$

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Similar conclusions hold for individual currents $\Phi_X^{(j)}$ if one assumes that the limiting generalized ES function

$$g(X,Y) = \lim_{t\to\infty} \frac{1}{t} \log g^t(X,Y) = \lim_{t\to\infty} \frac{1}{t} \log \mu_X \left(e^{-Y\cdot\int_0^t \Phi_X^s \, ds} \right)$$

exists and is a C^1 function of $Y \in \mathbb{R}^n$.

9. The Gallavotti-Cohen symmetry

Let μ^+ be a NESS of $(M, \mathcal{F}, \phi^t, \mu)$ and assume that the Gallavotti-Cohen function

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Remark. In general, unlke the ES function $e^t(\alpha)$, the finite time GC function

$$e^{+t}(\alpha) = \mu^+ \left(e^{-\alpha \int_0^t \sigma^s \, ds} \right)$$

does not satisfy "the symmetry", i.e. $e^{+t}(1-\alpha) \neq e^{+t}(\alpha)$.

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- 1999: Maes relates the GC symmetry to the Gibbs property of μ^+.

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- The generalized GC-symmetry $g^+(X, X-Y) = g^+(X,Y)$ yields the fluctuation-dissipation theorem if $g^+(X,Y)$ is $C^{1,2}$.

10. The principle of regular entropic fluctuations

Remark. Since, for entropically non-trivial systems, μ and μ^+ are mutually singular, the ES-symmetry and the GC-symmetry are two very different statements. The ES symmetry is a mathematical triviality (even though it has deep consequences) while the GC-symmetry is a true mathematical finesse containing a lot of interesting information about the NESS μ^+.

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Our main contribution to the subject (as far as classical systems are concerned) is the following

Principle of regular entropic fluctuations. In all systems known to exhibit the GC-symmetry, respectively the generalized GC-symmetry, one has

$$e^+(\alpha) = e(\alpha), \qquad \text{respectively} \qquad g^+(X, Y) = g(X, Y),$$

which is equivalent to

$$\lim_{t\to\infty} \lim_{s\to\infty} \frac{1}{t} \log \mu^s \left(e^{-\alpha \int_0^t \sigma^\tau \, d\tau} \right) = \lim_{s\to\infty} \lim_{t\to\infty} \frac{1}{t} \log \mu^s \left(e^{-\alpha \int_0^t \sigma^\tau \, d\tau} \right)$$

11. A list of example

- A shift. The left shift on the sequences $x = (x_i)_{i\in\mathbb{Z}} \in \mathbb{R}^{\mathbb{Z}}$ with the measure

$$d\mu(x) = \left(\prod_{i\le 0} F(-x_i)dx_i\right)\left(\prod_{i>0} F(x_i)dx_i\right)$$

  Time revesal is $\vartheta(x)_i = -x_{-i}$ and $d\mu^+(x) = \prod_{i\in\mathbb{Z}} F(x_i)dx_i$. A simple calculation yields

$$e(\alpha) = e^+(\alpha) = \log\int\left(\frac{F(-x)}{F(x)}\right)^{\alpha} F(x)dx$$

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$$d\mu(x) = \left(\prod_{i \leq 0} F(-x_i) dx_i \right) \left(\prod_{i > 0} F(x_i) dx_i \right)$$

  Time revesal is $\vartheta(x)_i = -x_{-i}$ and $d\mu^+(x) = \prod_{i \in \mathbb{Z}} F(x_i) dx_i$. A simple calculation yields

$$e(\alpha) = e^+(\alpha) = \log \int \left(\frac{F(-x)}{F(x)} \right)^\alpha F(x) dx$$

  and one immediately checks that $e(1 - \alpha) = e(\alpha)$.
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