



Nonequilibrium response, relaxation and the t-mixing condition

L. Rondoni, Politecnico Torino

Denis J. Evans (ANU), O.G. Jepps (Griffith), Debra J. Searles (UQ)

S. Williams (ANU), P. Adamo (PoliTO)

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J. Stat. Phys. 2007; Nonlinearity 2007; Phys. Rep. (2008)

J. Phys. A (2010); J. Chem. Phys. (2012)

Outline

- 1 Concise history
 - Dissipation Function Ω
- 2 Fluctuation Relations
 - Transient Fluctuation Relations and General Response
 - Steady State Fluctuation Relations
 - t-mixing
- 3 Discussion

In brief, we are going to see:

- The dissipation function Ω , a kind of nonequilibrium thermodynamic potential
- Transient fluctuation relations

$$\frac{\mu^{(0)}(\overline{\mathcal{O}} \sim -A)}{\mu^{(0)}(\overline{\mathcal{O}} \sim A)} = \left\langle e^{-\Omega} \right\rangle_{\overline{\mathcal{O}} \sim A}^{(0)}$$

- Steady state fluctuation relations

$$\frac{1}{\tau} \ln \frac{\mu^{(\infty)}(\overline{\Omega} \sim A)}{\mu^{(\infty)}(\overline{\Omega} \sim -A)} = A + \epsilon + O\left(\frac{1}{\tau}\right)$$

- t-mixing and nonequilibrium response

$$\langle \mathcal{O} \rangle^{(\infty)} = \langle \mathcal{O} \rangle^{(0)} + \int_0^\infty ds \langle \mathcal{O}(s) \Omega(0) \rangle^{(0)}$$

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General form of field-driven thermostatted nonequilibrium system:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i \mathbf{F}_e ; \quad \dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i \mathbf{F}_e - \alpha \mathbf{p}_i$$

\mathbf{F}_e = field applied via \mathbf{C}_i , \mathbf{D}_i (which may depend on $\Gamma = (\mathbf{q}_i, \mathbf{p}_i)$).
 $-\alpha \mathbf{p}_i$ = deterministic time reversible term to add or remove energy.

Dissipative flux, \mathbf{J} , obtained from adiabatic time-derivative of internal energy

$$H_0 = \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} + \Phi(\mathbf{q})$$

and, by definition:

$$\dot{H}_0^{ad} = \sum_{i=1}^N \left(\mathbf{D}_i \frac{\mathbf{p}_i}{m} - \mathbf{C}_i \mathbf{F}_i \right) \cdot \mathbf{F}_e := \mathbf{J} \mathbf{V} \cdot \mathbf{F}_e ,$$

For isoenergetic SLLOD, Evans-Cohen-Morriss (20 years ago!)

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

proposed and tested this Fluctuation Relation (FR):

$$\frac{\mu_i}{\mu_{i^*}} = \frac{\exp \left[-\sum_n^+ \lambda_{i,n} \tau \right]}{\exp \left[-\sum_n^+ \lambda_{i^*,n} \tau \right]} = \exp \left[Nd \bar{\alpha}_i^T \tau \right]$$

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

Because for SLLOD

$$\begin{aligned} \bar{\alpha}_i^T &\propto \text{phase space contraction rate} = -\sum_n \lambda_{i,n} \\ &\propto \text{average "entropy production rate"} \end{aligned}$$

*Model chosen because phase space volumes contraction rate of **this particular time reversible** model can be related to SRB measures of Anosov systems, as made explicit in Gallavotti-Cohen '95.*

Charming (because rigorous) mathematical theory, but hard to advance and facing some conceptual and some practical difficulties.

Problems arise with time scales and near equilibrium states.

Phase space contraction rate fluctuations not associated with energy dissipation, except in (unnatural) isoenergetic case.

Although FR for **energy dissipation** commonly verified.

Change point of view

Q.: if FR holds, what mechanisms are responsible for that?

Search for necessary conditions and physical structure;

find out what surely happens in physically relevant situations.

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$\dot{\Gamma} = G(\Gamma)$ 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.:

$\Lambda =$ phase space volume variation rate $= \text{div} G$, $\langle \Lambda \rangle < 0$

Let $f^{(0)}$ = initial distribution.

Dissipation function:

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

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

It looks like mysterious, but...

For equilibrium $f^{(0)}$: $\Omega^{(0)} =$ **dissipation rate !!**

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Note: $\Omega^{(0)}$ is **odd** under i : $\Omega^{(0)}(i\Gamma) = -\Omega^{(0)}(\Gamma)$.

Isoenergetic case: equilibrium density is constant along trajectory:

$$\Omega_{t,t+\tau}^{(0)}(\Gamma) = \ln \frac{f^{(0)}(S^t\Gamma)}{f^{(0)}(S^{t+\tau}\Gamma)} - \Lambda_{t,t+\tau}(\Gamma) = -\Lambda_{t,t+\tau}(\Gamma)$$

as in the original case.

Isokinetic case:

$$\Lambda(\Gamma) \propto \beta \left[\dot{\Phi}(\Gamma) + \mathbf{J}(\Gamma) \mathbf{V} \cdot \mathbf{F}_e \right]$$

$$f^{(0)}(\Gamma) \sim e^{-\beta\Phi} \delta(K(\Gamma) - K_0), \quad \frac{f^{(0)}(S^t\Gamma)}{f^{(0)}(S^{t+\tau}\Gamma)} = \exp \beta \int_t^{t+\tau} \dot{\Phi}(S^s\Gamma) ds$$

$$\overline{\Omega}_{t,t+\tau}^{(0)}(\Gamma) = \beta \frac{1}{\tau} \int_t^{t+\tau} \dot{H}_0(S^s\Gamma) ds - \overline{\Lambda}_{t,t+\tau}(\Gamma) \propto \overline{(\mathbf{J} \cdot \mathbf{F}_e)}_{t,t+\tau} V \beta$$

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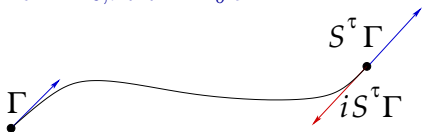
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Transient FRs and Response

Let $A_\delta^+ = (A - \delta, A + \delta)$ $A_\delta^- = (-A - \delta, -A + \delta)$

Observe that $\{\Gamma : \bar{\Omega}_{0,\tau}^{(0)}(\Gamma) \in A_\delta^-\} = iS^\tau \{\Gamma : \bar{\Omega}_{0,\tau}^{(0)}(\Gamma) \in A_\delta^+\}$



Consider

$$\frac{\mu^{(0)}(\bar{\Omega}_{0,\tau}^{(0)} \in A_\delta^+)}{\mu^{(0)}(\bar{\Omega}_{0,\tau}^{(0)} \in A_\delta^-)} = \frac{\int_{A_\delta^+} f^{(0)}(\Gamma) d\Gamma}{\int_{A_\delta^-} f^{(0)}(\Gamma) d\Gamma}$$

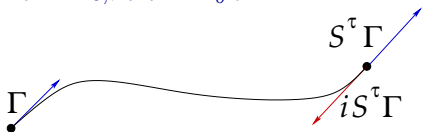
and introduce $\Gamma = iS^\tau X$, with jacobian

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

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$$\int_{A_\delta^-} f^{(0)}(\Gamma) d\Gamma = \int_{A_\delta^+} f^{(0)}(iS^\tau X) e^{\Lambda_{0,\tau}(X)} dX =$$

$$\int_{A_\delta^+} f^{(0)}(X) e^{-\Omega_{0,\tau}^{(0)}(X)} dX = e^{-[A + \epsilon(A, \delta, \tau)]\tau} \int_{A_\delta^+} f^{(0)}(X) dX$$

which leads to

$$\frac{\mu^{(0)}(\overline{\Omega}_{0,\tau}^{(0)} \in A_\delta^+)}{\mu^{(0)}(\overline{\Omega}_{0,\tau}^{(0)} \in A_\delta^-)} = \exp \{ \tau [A + \epsilon(A, \delta, \tau)] \} ; \quad \epsilon(A, \delta, \tau) \leq \delta$$

Transient Ω -FR: (unbreakable) identity for a property of $f^{(0)}$, holding $\forall \tau$, due only to time reversibility and symmetry of $f^{(0)}$.

Ubiquitous $\Omega^{(0)}$:

$$\begin{aligned} f^{(t)}(\Gamma) &= \exp\{-\Lambda_{-t,0}(\Gamma)\} f^{(0)}(S^{-t}\Gamma) \\ &= \exp\left\{\Omega_{-t,0}^{(0)}(\Gamma)\right\} f^{(0)}(\Gamma) \end{aligned}$$

meaning that a density $f^{(0)}$ evolves, unless $\Omega^{(0)} \equiv 0$.
If $\mathcal{O}(i\Gamma) = -\mathcal{O}(\Gamma)$; then $\forall \delta, \tau > 0$

$$\frac{\mu^{(0)}(\overline{\mathcal{O}}_{0,\tau} \in A_{\delta}^{-})}{\mu^{(0)}(\overline{\mathcal{O}}_{0,\tau} \in A_{\delta}^{+})} = \left\langle e^{-\Omega_{0,\tau}^{(0)}} \right\rangle_{\overline{\mathcal{O}}_{0,\tau} \in A_{\delta}^{+}}^{(0)}$$

$$1 = \frac{\mu^{(0)}(\overline{\mathcal{O}}_{0,\tau} \in (-\delta, \delta))}{\mu^{(0)}(\overline{\mathcal{O}}_{0,\tau} \in (-\delta, \delta))} = \left\langle e^{-\Omega_{0,\tau}^{(0)}} \right\rangle_{\overline{\mathcal{O}}_{0,\tau} \in (-\delta, \delta)}^{(0)} \implies \left\langle e^{-\Omega_{0,\tau}^{(0)}} \right\rangle^{(0)} = 1$$

What kind of relations are these?

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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. Revealed (for instance) deterioration of lubricant in
this microscope.

Indirect access to non-accessible
quantities.

What about steady state FRs?
What about statistics of fluctuations
along single, long evolution?

Move from statistics of $\mu^{(0)}$ to
statistics of steady state μ_∞ ,
provided it exists.



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) Coherent Compass 4000M Laser, (5) BEOC Laser Stabiliser, (6) MTI IFG CCD Camera, (7) Physik Instrumente Piezo Translator, (8) replacement control computer with custom written Labview software, (9) Sample Cell built in-house.



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Steady state FRs

Consider probability at time t

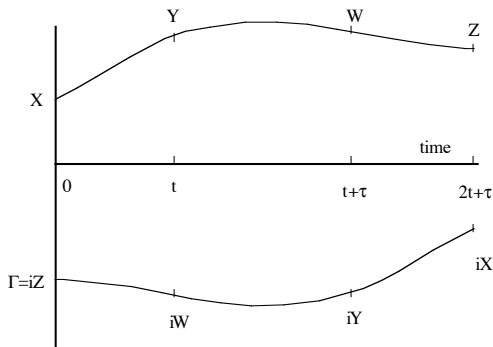
$$\frac{\mu^{(t)}(\overline{\Omega}_{0,\tau}^{(0)} \in A_{\delta}^{+})}{\mu^{(t)}(\overline{\Omega}_{0,\tau}^{(0)} \in A_{\delta}^{-})}$$

Move evolution from sets to probabilities:

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

which yields

$$\frac{\mu^{(0)}(\overline{\Omega}_{t,t+\tau}^{(0)} \in A_{\delta}^{+})}{\mu^{(0)}(\overline{\Omega}_{t,t+\tau}^{(0)} \in A_{\delta}^{-})}$$



Split trajectory as $t + \tau + t$.

$$\{\Gamma : \overline{\Omega}_{t,t+\tau}^{(0)}(\Gamma) \in A_{\delta}^{-}\} = iS^{t+\tau+t}\{X : \overline{\Omega}_{t,t+\tau}^{(0)}(X) \in A_{\delta}^{+}\} \quad \text{Then:}$$

$$\frac{1}{\tau} \ln \frac{\mu^{(t)}(\bar{\Omega}_{0,\tau}^{(0)} \in A_{\delta}^{+})}{\mu^{(t)}(\bar{\Omega}_{0,\tau}^{(0)} \in A_{\delta}^{-})} = -\frac{1}{\tau} \ln \left\langle e^{-\Omega_{0,t}^{(0)}} \cdot e^{-\Omega_{t,t+\tau}^{(0)}} \cdot e^{-\Omega_{t+\tau,2t+\tau}^{(0)}} \right\rangle_{\bar{\Omega}_{t,t+\tau}^{(0)} \in A_{\delta}^{+}}^{(0)}$$

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

Take $t \rightarrow \infty$ to let $\mu_t \rightarrow \mu_{\infty}$. But then $\Omega_{0,t}^{(0)}$, hence $\ln \langle \dots \rangle_{\bar{\Omega}_{t,t+\tau}^{(0)} \in A_{\delta}^{+}}^{(0)}$

may diverge; in which case steady state FR cannot hold at A .

That's fine: for instance, systems having no fluctuations.

Necessary that $\ln \langle \dots \rangle_{\bar{\Omega}_{t,t+\tau}^{(0)} \in A_{\delta}^{+}}^{(0)}$ does not diverge for some $A \neq 0$, in order to have:

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

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What kind of condition is this?

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

$$\begin{aligned} \left\langle e^{-\Omega_{0,t}^{(0)}} \cdot e^{-\Omega_{t+\tau,2t+\tau}^{(0)}} \right\rangle_{\bar{\Omega}_{t,t+\tau}^{(0)} \in A_{\delta}^+}^{(0)} &= \left\langle e^{-\Omega_{0,t}^{(0)}} \cdot e^{-\Omega_{t+\tau,2t+\tau}^{(0)}} \right\rangle^{(0)} \\ &= \left\langle e^{-\Omega_{0,t}^{(0)}} \cdot \left(e^{-\Omega_{0,t}^{(0)}} \circ S^{t+\tau} \right) \right\rangle^{(0)} = \left\langle e^{-\Omega_{0,t}^{(0)}} \right\rangle^{(0)} \left\langle e^{-\Omega_{0,t}^{(0)}} \right\rangle^{(0)} = 1 \end{aligned}$$

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

Then steady state (ensemble) FR immediately verified, in observation time τ . More generally, $O(1/\tau)$ correction.

t-mixing

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

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

Taking $\mathcal{P} = \Omega^{(0)}$ and observing that $\langle \Omega^{(0)} \rangle^{(0)} = 0$ for time even $f^{(0)}$, this means:

$$\langle \Omega^{(0)}(\mathcal{O} \circ S^t) \rangle^{(0)} \rightarrow 0$$

We call **t-mixing** the situation in which the above decays faster than $1/t$, so that:

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$$\frac{d}{dt} \langle \mathcal{O} \rangle^{(t)} = \langle \Omega^{(0)} (\mathcal{O} \circ S^t) \rangle^{(0)} \quad \text{which implies:}$$

$$\left. \frac{d}{dt} \langle \Omega^{(0)} \rangle^{(t)} \right|_{t=0} \geq 0, \quad \text{with " = " only if } \Omega^{(0)} \equiv 0 \quad \text{and}$$

Response
 Relation

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

This provides a general response relation which, in the $t \rightarrow \infty$ limit amounts to **convergence to some (ensemble) steady state!**
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What does t-mixing precisely mean?

It means that $f^{(0)}$ – correlations of observables with **dissipation** decay sufficiently fast,
i.e. correlations decay sufficiently fast with respect to initial **macrostate** $f^{(0)}$.

Then convergence to steady state may follow.

This is quite different from decay of **microscopic** correlations within **steady state** of mixing!

Keep in mind: one cannot (experimentally) start in steady state. Typically, one starts in equilibrium state, and is then driven towards the steady state.

Discussion

- FRs: parameter free; thought to extend beyond Local Thermodynamic Equilibrium; hence relevant for nonequilibrium phenomena and small systems.
- Transient (ensemble) FRs: require only reversibility, concern $f^{(0)}$. Nonequilibrium dynamics reveals equilibrium properties, closing circle with Fluctuation Dissipation Relations.
- In minimal framework for steady state FRs, **t-mixing** arises as condition of decay of **macroscopic** correlations.
- t-mixing implies relaxation to (ensemble) steady state and, indeed, that is the minimal requirement for steady state FRs.
- All relations (which include identities, inequalities, response formulae, further FRs) involve **Dissipation Function** $\Omega^{(0)}$: kind of thermodynamic potential for nonequilibrium states.
- Kind of Green-Kubo relation; More general even in linear regime. But at finite t , only ensemble relation, in general.