Second-law like inequalities for transitions between non-stationary states

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Outline of the talk

I. Preliminaries on fluctuation theorems

II. Modified Fluctuation-dissipation theorem off-equilibrium

III. Second-law like inequalities for transitions between non-stationary states

Acknowlegments:

G. Verley, ESPCI, Paris
R. Chétrite, Univ. Nice, France

Jarzynski relation

Stochastic definition of work

$$W_t = \int_0^t d\tau \, \dot{h}_\tau \frac{\partial H}{\partial h}(c_\tau, h_\tau)$$

• Average over non-equilibrium trajectories leads to equilibrium behavior :

$$\left\langle e^{-\beta W_t} \right\rangle = e^{-\beta \Delta F}$$

C. Jarzynski, PRL **78**, 2690 (1997)

This leads to a formulation of the second-law for macroscopic systems :

$$\left\langle W_t \right\rangle \geq \left\langle \Delta F \right\rangle$$

• Derivation using Feyman-Kac relation :

Hummer G and Szabo, PNAS **98**, 3658 (2001)

$$\left\langle \delta(c - c_t) e^{-\beta W_t} \right\rangle = \frac{1}{Z_A} e^{-\beta H(c, h_t)}$$

Hatano-Sasa relation

Work like functional $Y_t = \int_0^t d\tau \, \dot{h}_\tau \frac{\partial \phi}{\partial h}(c_\tau, h_\tau)$ where $\phi(c,h) = -\ln P_{st}(c,h)$

- Average over non-equilibrium trajectories leads to steady-state behavior

$$\left\langle e^{-Y_t} \right\rangle = 1$$

T. Hatano and S. Sasa, PRL **86**, 3463 (2001)

Now $\left\langle Y_t \right\rangle \geq 0$ where the equality holds for a quasi-stationary process

- Initial condition in a non-equilibrium steady state (NESS)

- Expansion of the relation to first order in the perturbation leads to a modified FDT near a NESS

II. The three routes to modified Fluctuation-dissipation theorems (MFDT)

- In terms of an additive correction (the asymmetry) which vanishes at equilibrium

  valid near any non-equilibrium state

  M. Baiesi et al. (2009); E. Lippiello et al. (2005)
  G. Diezemann (2005); L. Cugliandolo et al. (1994)

- In terms of a local velocity/current

  valid near any non-equilibrium state

  R. Chétrite et al. (2008); U. Seifert et al. (2006)

- In terms of a new observable constructed from the non-equilibrium stationary distribution

  valid near a NESS

  J. Prost et al. (2009);
  G. Verley, K. Mallick, D. L., EPL 93, 10002 (2011)

Rk: in all 3 cases, markovian dynamics is assumed

> Is it possible to extend the third route for a general observable and a general non-equilibrium state ?

Three relevant probability distributions

- Probability distribution $\rho_t(c)$ solution of unperturbed master equation :

$$\frac{\partial \rho_t(c)}{\partial t} = \sum_{c'} \left[w_t(c',c)\rho_t(c') - w_t(c,c')\rho_t(c) \right] = \sum_{c'} \rho_t(c') L_t(c',c)$$

- Probability $P_t(c,[h_t])$ has a functional dependence on a perturbation $[h_t]$,

$$\frac{\partial P_t(c,[h_t])}{\partial t} = \sum_{c'} \left[w_t^{h_t}(c',c) P_t(c',[h_t]) - w_t^{h_t}(c,c') P_t(c,[h_t]) \right] = \sum_{c'} P_t(c',[h_t]) L_t^{h_t}(c',c)$$

- Probability $\pi_t(c,h)$ defined for a constant time independent perturbation h,

$$\frac{\partial \pi_t(c,h)}{\partial t} = \sum_{c'} \left[w_t^{h}(c',c)\pi_t(c',h) - w_t^{h}(c,c')\pi_t(c,h) \right] = \sum_{c'} \pi_t(c',h) L_t^{h}(c',h)$$

- Trajectory dependent quantity of interest constructed from $\pi_t(c,h)$:

$$\psi_t(c_t,h_t) = -\ln \pi_t(c_t,h_t)$$

A particle obeying Langevin dynamics and submitted to a temperature quench

- Model: $\dot{x}_t = -\frac{k_t}{\gamma} x_t + \frac{h_t}{\gamma} + \eta_t,$ with $\langle \eta_t \rangle = 0$, and $\langle \eta_t \eta_{t'} \rangle = \frac{2T_t}{\gamma} \delta(t-t')$

- Response function is $$R(t,t') = \left.\frac{\partial \langle x_t \rangle_{[h]}}{\partial h_{t'}}\right|_{h\to 0} = \frac{1}{\gamma} \exp\left(-\int_{t'}^{t} d\tau \frac{k_\tau}{\gamma} \right),$$

- Alternatively, one has

$$P_t(x,[h_t]) = \frac{1}{\left(2\pi\sigma_t^2\right)^{1/2}} \exp\left(-\frac{1}{2\sigma_t^2} \left(x - \int_0^t d\tau \frac{h_\tau}{\gamma} \exp\left(-\int_\tau^t d\tau' \frac{k_{\tau'}}{\gamma} \right) \right)^2 \right),$$

and thus for a constant protocol h

$$\pi_t(x,h) = \frac{1}{\left(2\pi\sigma_t^2\right)^{1/2}} \exp\left(-\frac{1}{2\sigma_t^2} \left(x - \frac{h}{\gamma} \int_0^t d\tau \exp\left(-\int_\tau^t d\tau' \frac{k_{\tau'}}{\gamma} \right) \right)^2 \right),$$

- Using this together with the MFDT, the same response is recovered

Our work like path functional $$Y = \int_0^t d\tau \, \dot{h}_\tau \partial_h \psi_\tau(c_\tau, h_\tau)$$

The Feyman-Kac approach : $$\left\langle A_t(c_t, h_t) e^{-Y} \right\rangle_{[h]} = \int dc \, \pi(c, h_t) A_t(c, h_t) = \left\langle A_t(c_t, h_t) \right\rangle_{[\pi_t]}$$

Generalized Hatano-Sasa relation $$\left\langle e^{-Y} \right\rangle_{[h]} = 1$$

Through linear expansion, one obtains for t>t'>0,

$$R(t,t') = \left. \frac{\partial \left\langle A_t(c_t, h_t) \right\rangle_{[h]}}{\partial h_{t'}} \right|_{h \to 0} = -\frac{d}{dt'} \left\langle \left. \partial_h \psi_{t'}(c_{t'}, h) \right|_{h \to 0} A_t(c_t, h_t) \right\rangle$$

- This generalized Hatano-Sasa relation does not require any thermodynamic structure nor stationary reference process

- It contains a very general modified Fluctuation-dissipation theorem which can be also obtained directly from linear response theory

G. Verley, R. Chétrite, D. L., J.Stat. Mech., P10025 (2011)

Stochastic trajectory entropy

- Stochastic trajectory entropy $s_t(c_t,[h]) = -\ln \pi_t(c_t,h) = \psi_t(c_t,h)$
  - Distinct from Kolmogorov-Sinai entropy
  - Distinct from $\tilde{s}_t(c_t,[h]) = -\ln p_t(c_t,h)$ U. Seifert PRL **95**,040602 (2005)
  - It can be decomposed into -Reservoir entropy + Total entropy production

$$\Delta s_t(c_t,[h]) = -\Delta s_r(c_t,[h]) + \Delta s_{tot}(c_t,[h])$$

- Consequence of this decomposition for MFDT:

$$R_{eq}(t,t') = \frac{d}{dt'}\left\langle \partial_h \Delta s^r_{t'}(c_{t'},h)\Big|_{h\to 0} A_t(c_t)\right\rangle = \left\langle j_{t'}(c_{t'}) A_t(c_t)\right\rangle$$

$$R_{neq}(t,t') = \frac{d}{dt'}\left\langle \partial_h \Delta s^{tot}_{t'}(c_{t'},h)\Big|_{h\to 0} A_t(c_t)\right\rangle = \left\langle v_{t'}(c_{t'}) A_t(c_t)\right\rangle$$

- Additive structure of the MFDT involving local currents:

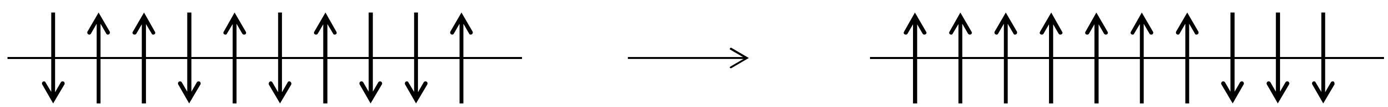
$$R(t,t') = \left\langle (j_{t'}(c_{t'}) - v(c_{t'})) A_t(c_t)\right\rangle$$

The 1D Ising model with Glauber dynamics

• Classical model of coarsening : L Ising spins in 1D described by the hamiltonian

$$H(\{\sigma\}) = -J\sum_{i=1}^{L}\sigma_i\sigma_{i+1} - H_m\sigma_m,$$

• System intially at equilibrium at $T=\infty$ is quenched at time t=0 to a final temperature T.



• At the time t'>0, a magnetic field H_m is turned on:

$$H_m(t) = H_m\theta(t-t'),$$

• The dynamics is controlled by time-dependent (via H_m) Glauber rates

$$w^{H_m}(\{\sigma\},\{\sigma\}^i) = \frac{\alpha}{2}\Big(1-\sigma_i \tanh\big(\beta J\left(\sigma_{i-1}+\sigma_{i+1}\right)+\beta H_m\delta_{im}\big)\Big),$$

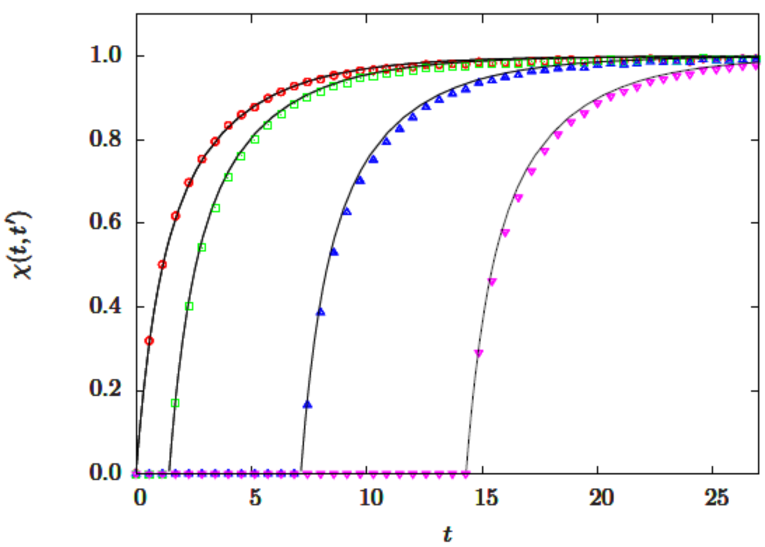
- Analytical verification :

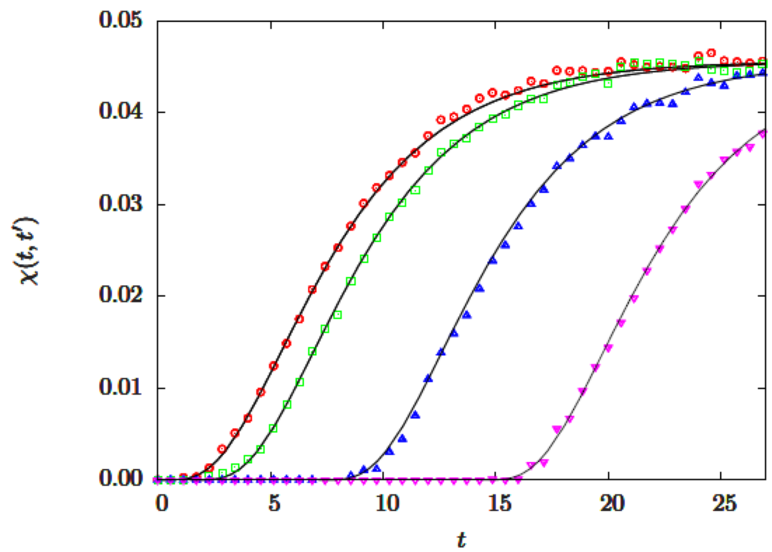
  - MFDT can be verified although the distributions $\pi_t(\{\sigma\},H_m)$ even for a zero magnetic field are not analytically calculable

  - Analytical form of the response is known   C. Godrèche et al. (2000)

- Numerical verification : the distributions $\pi_t(\{\sigma\},H_m)$ can be obtained numerically for a small system size (L=14); and the MFDT verified:

  Integrated response function $\chi_{n-m}(t,t') = \int_{t'}^{t} d\tau R_{n-m}(t,\tau)$





III. Inequalities generalizing the second law of thermodynamics for transitions between non-stationary states

Particular case: Transitions between periodically driven states

- Vibrated granular medium
- Electric circuits
- Oscillations in biological systems
- Manipulated colloids

Does a form of second law holds for such transitions ?

G. Verley, R. Chétrite, D. L., Phys. Rev. Lett., 108, 120601 (2012)

The three faces of the second law

• Two different mechanisms to put a system into non-equilibrium state :

- from the breaking of detailed balance via non-equilibrium boundary conditions
- from an external driving

• This leads to a splitting of the total entropy production into

$$\Delta S_{tot} = \Delta S_a + \Delta S_{na}$$

M. Esposito et al., PRL **104**, 090601 (2010)

where each part satisfies, each separately, a detailed and an integral FT:

$$\frac{P(\Delta S_{tot})}{\overline{P}(-\Delta S_{tot})} = \exp(\Delta S_{tot})$$

$$\frac{P(\Delta S_{na})}{\overline{P}^{+}(-\Delta S_{na})} = \exp(\Delta S_{na}) \qquad \frac{P(\Delta S_{a})}{P^{+}(-\Delta S_{a})} = \exp(\Delta S_{a})$$

leading to a splitting of the second law into $\langle \Delta S_{tot} \rangle \geq 0,\ \langle \Delta S_{a} \rangle \geq 0,\ \langle \Delta S_{na} \rangle \geq 0,$

Is it possible to generalize this decomposition using a non-stationary distribution as reference ?

• Now Duality transformation (^) with respect to a non-stationary distribution :

$$\hat{w}_t^h(c,c') = \pi_t^{-1}(c,h)\, w_t(c',c)\, \pi_t(c',h)$$

• Second term is a difference of traffic between the direct and dual dynamics,

$$\lambda_t^{h_t}(c') = \sum_{c \neq c'} w_t^{h_t}(c',c),$$

C. Maes et al., PRL **96**, 240601 (2006)

Traffic is the time-integrated escape rate

$$\Delta \mathrm{T}[c] = \int_0^T dt \left[\lambda_t^{h_t}(c_t) - \hat{\lambda}_t^{h_t}(c_t) \right] = -\int_0^T dt \left(\partial_t \ln \pi_t \right)(c_t, h_t),$$

It is symmetric with respect to time-reversal: $\Delta T[c] = \Delta \overline{T}\left[\overline{c}\right]$, unlike the entropy

• When $(\tilde{\ }) = (\overline{\wedge})$ and $(^{*}) = (\overline{\ })$, the action A is called non-adiabatic : $\Delta A_{na} = \ln \dfrac{P[\Delta A_{na}]}{\hat{\overline{P}}[-\Delta A_{na}]}$,

• When $(\tilde{\ }) = (\wedge)$ and $(^{*}) = \mathrm{Id}$, the action A is called adiabatic : $\Delta B_a = \ln \dfrac{P[\Delta B_a]}{\hat{P}[-\Delta B_a]}$,

similar but different from the 3FTs of

- Fast relaxation of the accompagnying distribution towards a stationary distribution, then $\Delta T = 0$, and one recovers the 3 FTs.

- For transitions between non-stationary states, the generalized Hatano-Sasa relation follows

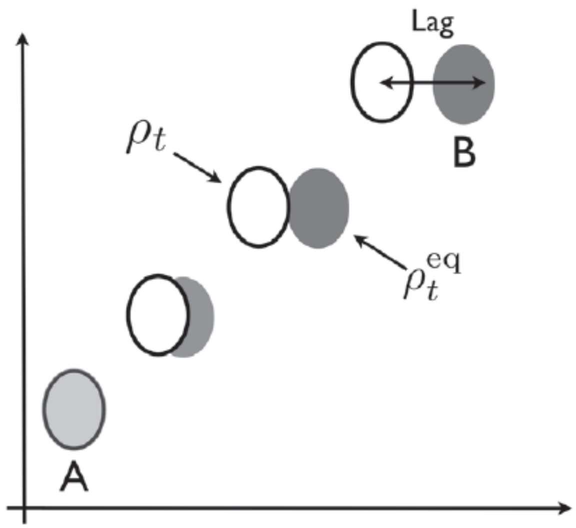
$$\left\langle \exp(-Y) \right\rangle = 1,$$

- Modified second law (Clausius type inequality)

$$\left\langle \Delta S \right\rangle \geq -\left\langle \Delta S_{ex} \right\rangle + \left\langle \Delta T \right\rangle \quad \text{or} \quad \left\langle Y \right\rangle \geq -\left\langle \Delta S_b \right\rangle = D(p_T \,\|\, \pi_T) \geq 0$$

- Equality corresponds to the adiabatic limit (slow driving) :

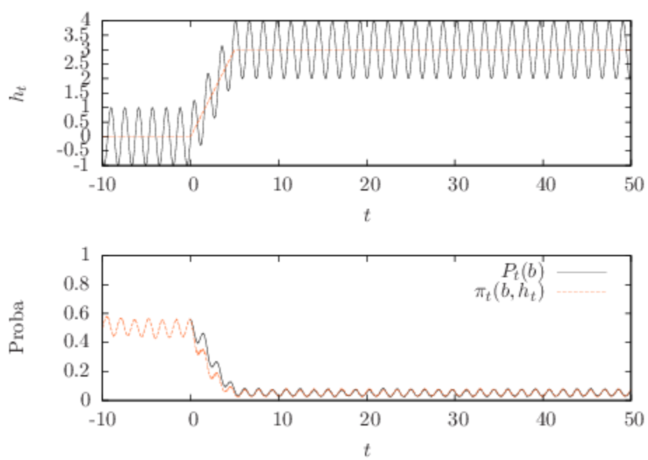
  where $\left\langle \Delta S_b \right\rangle = 0$ and $\Delta A_{na} = \Delta T = 0$



For an initial equilibrium state,
« Dissipated work dictates the maximum extend to which equilibrium can be broken
– equivalently the maximum amount of lag
– at a given instant during the process. »

$$\langle W_{diss} \rangle \geq \beta^{-1} D(p_T \parallel p_T^{eq})$$

S. Vaikunanathan and C. Jarzynski (2009)



For an arbitrary non-stationary initial state, the lag between P_T and π_T distributions provides a bound for

$$\langle Y_T \rangle \geq D(p_T \parallel \pi_T) \geq 0$$

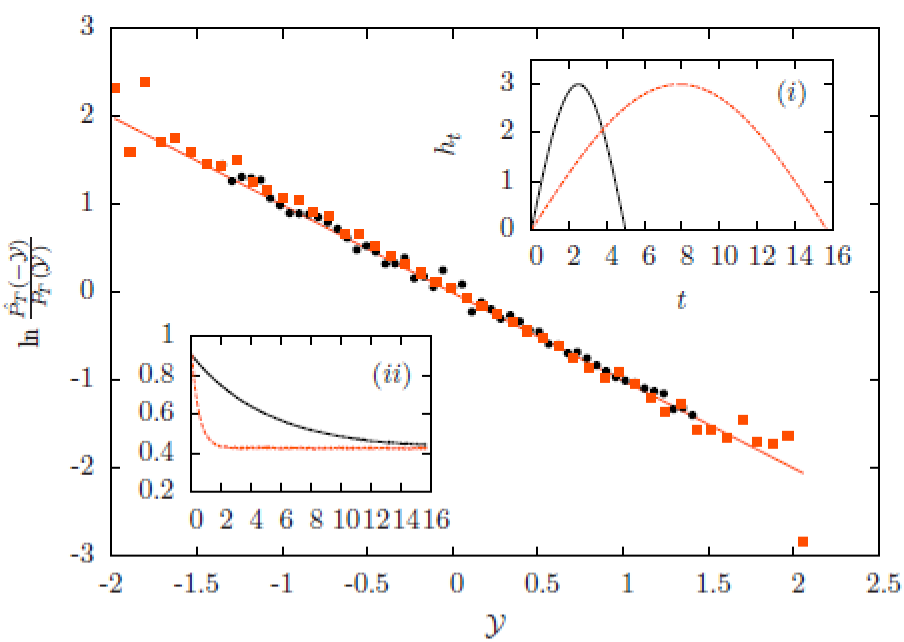
Non-stationarity due to relaxation

- A reference dynamics is created by some initial conditions different from steady state values
- The model (with two states dynamics) is further driven

$$w^{h_t}(a,b) = w(a,b)e^{-h_t/2}\,;\; w^{h_t}(b,a) = w(b,a)e^{h_t/2}$$

- Direct simulation of trajectories from which distributions $\ln \pi_t$ and of Y are obtained

- DFT holds independently of the relaxation time of π_t



Non-stationarity from periodic driving

- A sinusoidally driven two states model is further perturbed using

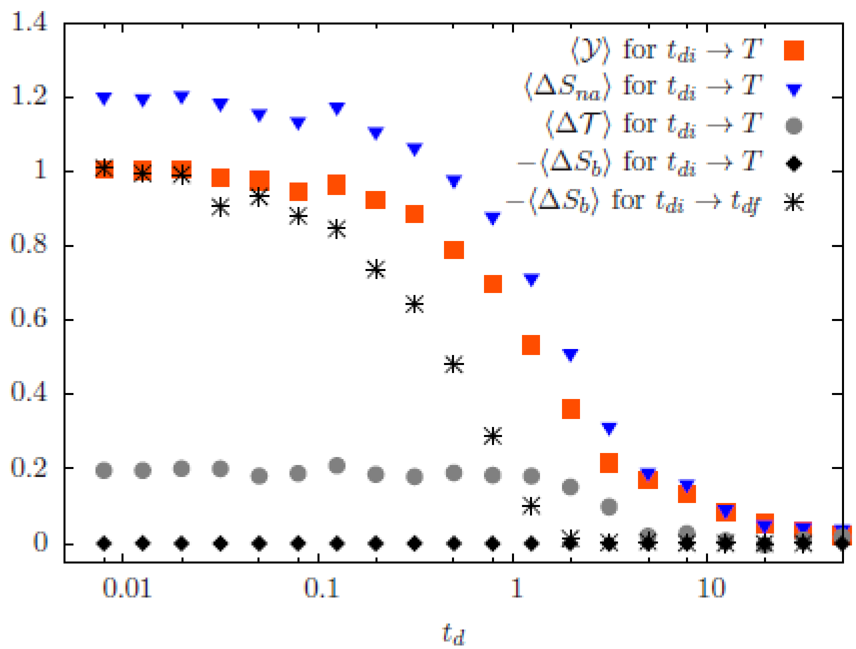
$$w^{h}(a,b)=w(a,b)e^{-h-\sin(\omega_0 t)}\ ;\ w^{h_t}(b,a)=w(b,a)e^{h+\sin(\omega_0 t)}$$

- As expected $\langle Y_T \rangle \geq 0$ and

$$\langle \Delta S_{na} \rangle - \langle \Delta T \rangle = \langle Y_T \rangle$$

in the quasi-static limit

$$\langle \Delta T \rangle = \langle Y_T \rangle = \langle \Delta S_{na} \rangle = 0$$



Conclusions

• A formalism based on fluctuation relations leads to a modified fluctuation-dissipation theorem and modified second law of thermodynamics off equilibrium.

•Such a formalism could be useful for studying transitions between periodically driven states, or between states which are undergoing relaxation due to coarseing or aging.