Fluctuation theorems: where do we go from here ?

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Outline of the talk

1. Fluctuation theorems for systems out of equilibrium

2. Modified fluctuation-dissipation theorems out of equilibrium

3. Fluctuations theorems for systems at equilibrium

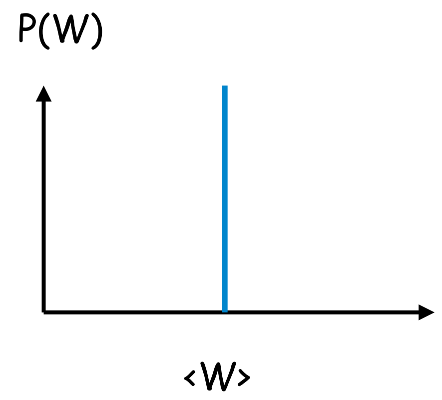
4. Non-invasive estimation of dissipation

Fluctuation theorems
for systems out of equilibrium

What is stochastic thermodynamics ?

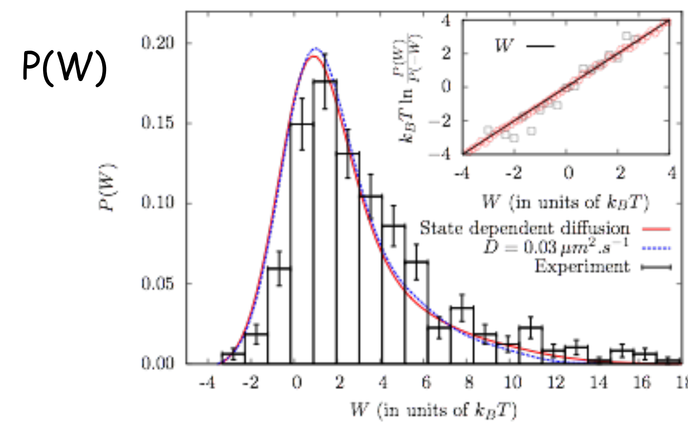
1. <u>Classical Thermodynamics</u>

- First and second law
- Macroscopic systems : fluctuations are gaussian and small
- Absence of time as a parameter



2. <u>Stochastic thermodynamics</u>

- First and second law at the trajectory level
- Small systems : large non-gaussian fluctuations
- Time enters as an essential parameter



Jarzynski relation

Assume system equilibrated by the contact with a reservoir at temperature T at t=0

Then a control parameter λ_t is applied; final state at time t is not in equilibrium

If system is disconnected from heat bath at t=0 $\quad W_t = H(x_t, \lambda_t) - H(x_0, \lambda_0)$

$$\begin{aligned} \langle e^{-\beta W_t} \rangle &= \int dx_0 p_{eq}(x_0) e^{-\beta W_t} \\ &= \frac{1}{Z(\lambda_0)} \int dx_t \left| \frac{\partial x_t}{\partial x_0} \right|^{-1} e^{-\beta H(x_t, \lambda_t)} = \frac{Z(\lambda_t)}{Z(\lambda_0)} = e^{-\beta \Delta F} \end{aligned}$$

- An exponential average over non-equilibrium trajectories leads to equilibrium behavior
- A method to evaluate free energies from non-equilibrium experiments

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

« Violations » of the second law of thermodynamics

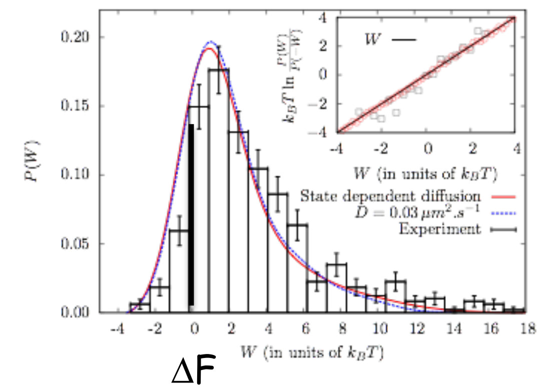
Using Jensen's inequality $\langle \exp(x) \rangle \geq \exp\langle x \rangle$

one obtains the second law (only valid on average) $\langle W \rangle \geq \Delta F$

Second law can be « violated » for particular realizations, but

$$P(W < \Delta F - \xi) = \int_{\infty}^{\beta(\Delta F - \xi)} dW\, P(W)$$

$$\leq \int_{\infty}^{\beta(\Delta F - \xi)} P(W) e^{\beta(\Delta F - \xi - W)} \leq e^{-\beta\xi}$$



- Such « violations » are required for the JE to hold but they are exponentially rare.
- « Violations » are pratically unobservable for macroscopic systems

Systems in contact with a thermostat

Interaction with thermostat now described by a markovian evolution $$\frac{dP_t}{dt} = M_\lambda \cdot P_t$$

Accumulated work up to time t: $$W_t = \int_0^t \dot{\lambda}(\tau) \frac{\partial H_\lambda}{\partial \lambda}(x_t) d\tau$$

Laplace distribution of joint distribution of work and of the fluctuating variable

$$\hat{P}_t(x,\gamma) = \int dW \, P_t(x,W) e^{-\gamma W}$$

satisfies $$\frac{\partial \hat{P}_t}{\partial t} = M_\lambda \cdot \hat{P}_t - \gamma \dot{\lambda} \frac{\partial H_\lambda}{\partial \lambda} \hat{P}_t$$

The solution is $$\hat{P}_t(x,\beta) = \langle \delta(x_t - x) e^{-\beta W_t} \rangle = \frac{1}{Z_A} e^{-\beta H_\lambda(x)}$$

- Jarzynski relation proved by integration over all x: $\langle e^{-\beta W_t} \rangle = e^{-\beta \Delta F}$
- More generally, for any observable A(x): $\langle A(x_t) e^{-\beta W_t} \rangle = A_{eq}(x_t)$

Hatano-Sasa relation

Generalization when initial condition is in a non-equilibrium steady state (NESS)

Work like functional $$Y_t = \int_0^t d\tau \dot{\lambda} \frac{\partial \phi}{\partial \lambda}(x_\tau, \lambda_\tau)$$ where $$\phi(x,\lambda) = -\ln P_{stat}(x,\lambda)$$

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

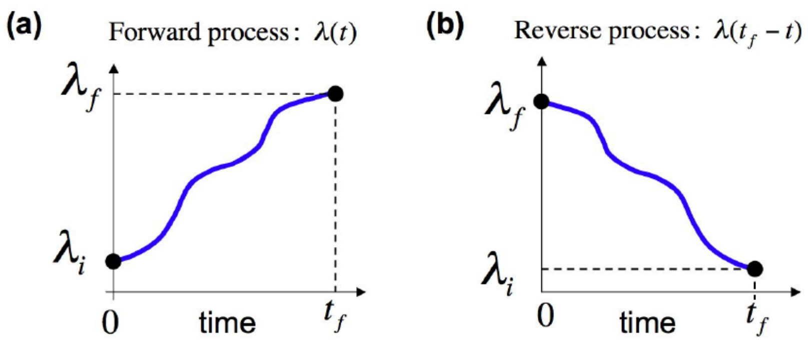
$$\langle e^{-Y_t} \rangle = 1$$

T. Hatano and S. Sasa, (2001)

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

Crooks relation

Let us define forward and reverse processes which both start in an equilibrium with fixed value of λ



Forward trajectory $\gamma_F=\{x_F(t), 0<t<t_f\}$

Reverse trajectory $\gamma_R=\{x_R(t), 0<t<t_f\}$

with $x_R(t) = x_F^*(t_f - t)$

If the reservoir is removed during the process

$$\frac{P_F(\gamma_F)}{P_R(\gamma_R)} = \frac{P_F(x_F(0))}{P_R(x_R(0))} = \frac{e^{-\beta H(x_F(0),\lambda_i)}}{Z(\lambda_i)} \frac{Z(\lambda_f)}{e^{-\beta H(x_F(t_f),\lambda_f)}} = e^{\beta(W_F - \Delta F)}$$

As a particular case, at equilibrium, fluctuations are symmetric under time-reversal

$$P_{eq}(\gamma_F) = P_{eq}(\gamma_R)$$

Same result holds for systems obeying markovian stochastic dynamics provided

$$\frac{M_\lambda(x \to x')}{M_\lambda(x' \to x)} = e^{-\beta\left(H(x',\lambda)-H(x,\lambda)\right)}$$

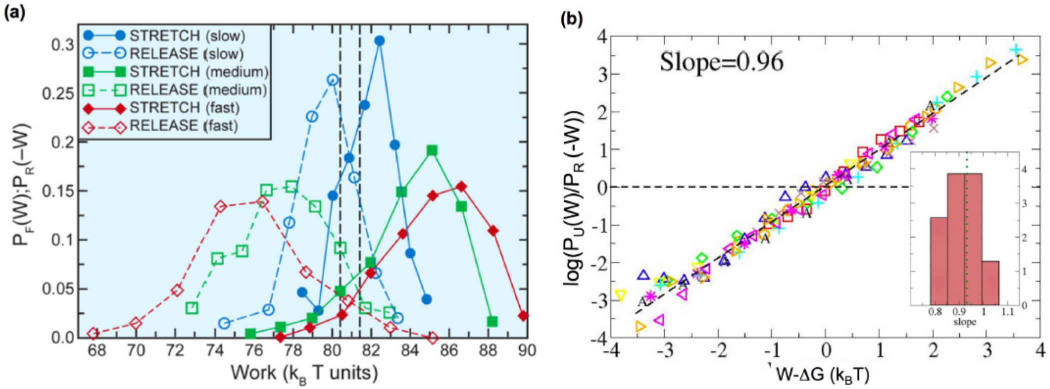
Rk: this detailed balance condtion holds only if the heat bath is ideal

Through integration of trajectories of given value of $W=W_F$

$$\frac{P_F(W)}{P_R(-W)} = e^{\beta(W-\Delta F)}$$

G. Crooks, PRE **61**,2361 (1999)

Experiments : using RNA hairpin pulled by optical tweezers



D. Collin, Nature (2005)

- Introducing KL divergence $D(p|q) = \sum_c p(c) \ln \frac{p(c)}{q(c)} \geq 0$

  - asymmetric character of the measure is crutial

- From $\frac{P_F(\gamma_F)}{P_R(\gamma_R)} = e^{\beta(W_F - \Delta F)}$ by taking the average

$$D(P_F|P_R) = \frac{\langle W \rangle - \Delta F}{k_B T} = \frac{\langle W^{diss} \rangle}{k_B T}$$

- The functional $W_{diss} = W - \Delta F$ leads to the same estimate of dissipation as the KL divergence of path probabilities

- Non-equilibrium fluctuations created by irreversible processes (such as systems presenting hysteresis) are asymmetric with respect to time-reversal

Evans-Searles and Gallavotti-Cohen relation

1. Transient fluctuation theorem of Evans-Searles

- The system is initially at equilibrium and evolves towards a NESS

$$\frac{P_\tau(\Delta S)}{P_\tau(-\Delta S)} = e^{\Delta S/k_B}$$

Evans DJ, Searles DJ, (1994)

- NESS can be created from multiple reservoirs or from time-symmetric driving
- Also holds separetely for parts of entropy production under conditions

2. Fluctuation theorem of Gallavotti-Cohen

- The asymptotic distribution of entropy production rate $\sigma = \Delta S/\tau$ in a NESS

$$\lim_{\tau\to\infty} \frac{1}{\tau} \ln \frac{P_\tau(\sigma)}{P_\tau(-\sigma)} = \frac{\sigma}{k_B T}$$

Gallavotti G., Cohen EGD, (1995)

- Implies relations for distribution of currents in a NESS

Trajectory dependent entropy for a particle or system

1. <u>Within Fokker-Planck equation (markovian)</u> $$\partial_t p_t(x_t) = -\partial_x j_t(x)$$

   - Definition : stochastic entropy $s_t = -\ln p_t(x_t)$ Seifert U., (2005)

2. <u>Second law of thermodynamics</u>

   - Heat dumped into heat bath assumed ideal according to Sekimoto : q

$$\ln \frac{P_F[x_t|x_0]}{P_R[x_t^R|x_0^R]} = \Delta s_m = \frac{q}{T}$$

Then $$\Delta s = \ln p_0(x_0) - \ln p_t(x_t)$$ difference of Shanon entropy

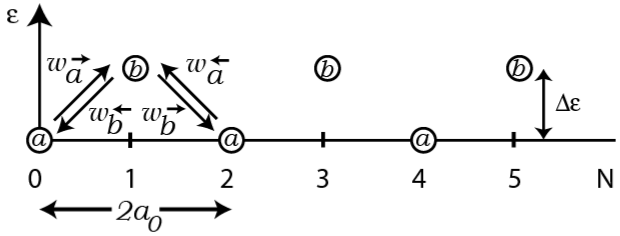
$$\Delta s_{tot} = \ln \frac{P_F[x_t]}{P_R[x_t^R]} = \Delta s_m + \Delta s$$

which satisfies an integral fluctuation theorem by construction $\langle e^{-\Delta s_{tot}} \rangle = 1$

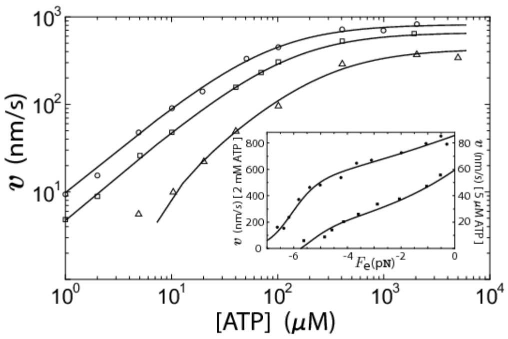
Rk: condtions for a detailed FT for s_{tot} are more restrictive

Fluctuation theorems for molecular motors

• Discrete ratchet model



Velocity data of kinesin K. Vissher et al., (1999)



- Average ATP consumption rate: $\bar{r} = 111 s^{-1}$
- Strong coupling $\ell = \frac{\bar{v}}{\bar{r}} \approx 0.97$

A.W.C. Lau et al., PRL **99**, 158102 (2007); D. L. et al., PRE **78**, 011915 (2008) .

Minimal ratchet: thermodynamics

- Statistics of the displacement n(t) and of the number of ATP molecules consumed y(t) as function of external and chemical loads ?

Velocity (mechanical current)

$$\bar{v}(f,\Delta\mu) = \lim_{t\to\infty} \frac{d\langle n(t)\rangle}{dt}$$

ATP consumption rate (chemical current)

$$\bar{r}(f,\Delta\mu) = \lim_{t\to\infty} \frac{d\langle y(t)\rangle}{dt}$$

- At thermodynamic equilibrium: f=0 and $\Delta\mu$=0 , fluctuations of n(t) and y(t) are gaussian, characterized by two diffusion coefficients D_1 and D_2

- Near equilibrium: for small f and $\Delta\mu=0$, linear response theory holds,

$$\bar{v} = L_{11} f + L_{12}\Delta\mu$$

Einstein relations: $L_{11}=D_1$ and $L_{22}=D_2$

$$\bar{r} = L_{21} f + L_{22}\Delta\mu$$

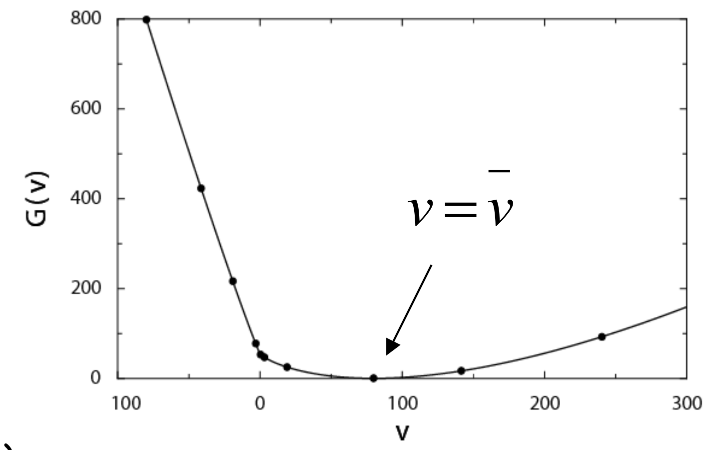
Onsager relations: $L_{12}=L_{21}$

- What happens far from equilibrium ?

Large deviations of the currents

• Long time properties of n(t) and y(t) are embodied in the large deviation function G(v,r)

$$\text{Prob}\left(\frac{n(t)}{t} = v, \frac{y(t)}{t} = r\right) \simeq e^{-tG(v,r)}$$



• Equivalently, one has the cumulant generating function E(λ,γ)

$$\left\langle e^{\lambda n + \gamma y} \right\rangle \simeq e^{tE(\lambda,\gamma)}$$

• In particular $\bar{v}(f, \Delta\mu) = \frac{\partial E}{\partial \lambda}(0,0)$ and $\bar{r}(f, \Delta\mu) = \frac{\partial E}{\partial \gamma}(0,0)$

• The functions G(v,r) and E(λ,γ) are related by Legendre transforms

Gallavotti-Cohen relation for a discrete ratchet model

- The function E(λ,γ) satisfies the Gallavotti-Cohen symmetry :

$$E(\lambda,\gamma) = E(-\lambda - f, -\gamma - \Delta\mu)$$

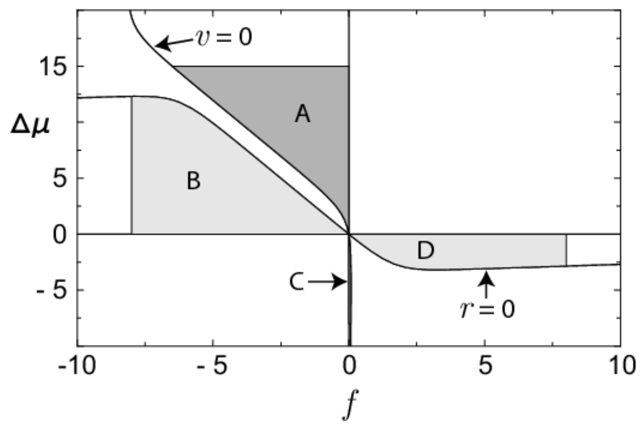
which implies the Fluctuation theorem in the long time limit:

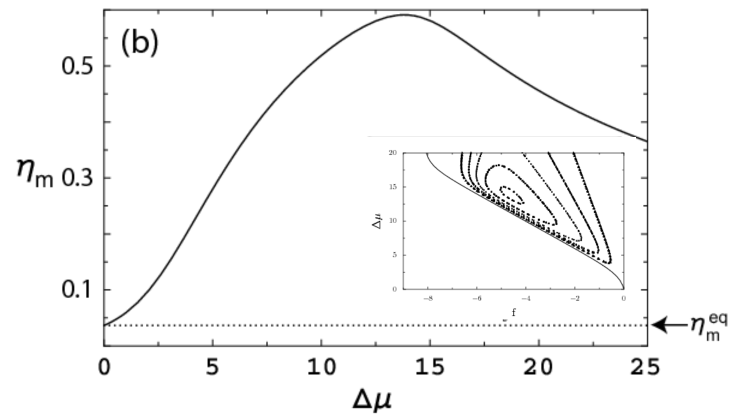
$$\frac{\text{Prob}(\frac{n(t)}{t} = v, \frac{y(t)}{t} = r)}{\text{Prob}(\frac{n(t)}{t} = -v, \frac{y(t)}{t} = -r)} \simeq e^{t(fv + r\Delta\mu)}$$

- Valid arbitrary far from equilibrium
  Linear expansion near equilibrium leads to Einstein and Onsager relations

- Results from local thermodynamic constraints : Generalized Detailed Balance

Phase diagram and thermodynamic efficiency





<u>4 regions of mechano-transduction :</u>

A: ATP in excess -> mechanical work
B: mechanical work -> ATP
C: ADP in excess -> mechanical work
D: mechanical work -> ADP

$$A: \quad f\,\overline{v} < 0 \text{ and } \overline{r}\Delta\mu > 0$$
$$B: \quad f\,\overline{v} > 0 \text{ and } \overline{r}\Delta\mu < 0$$
$$C: \quad f\,\overline{v} < 0 \text{ and } \overline{r}\Delta\mu > 0$$
$$D: \quad f\,\overline{v} < 0 \text{ and } \overline{r}\Delta\mu < 0$$

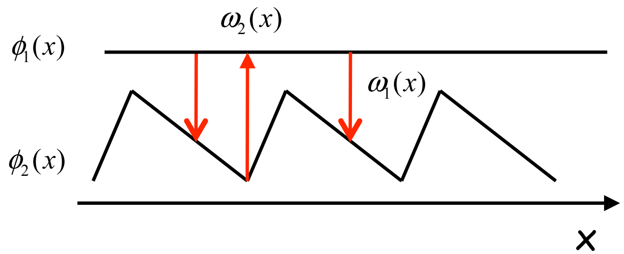
<u>Thermodynamic efficiency</u>

$$\eta = -\frac{f\,\overline{v}}{\overline{r}\Delta\mu}$$

is maximum far from equilibrium
(which is reached on a point in (Δμ,f) plane)

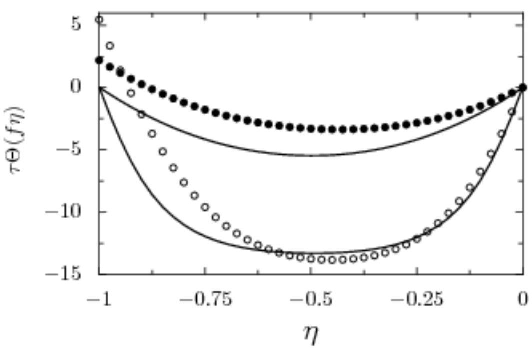
Gallavotti-Cohen relation for a continuous ratchet model

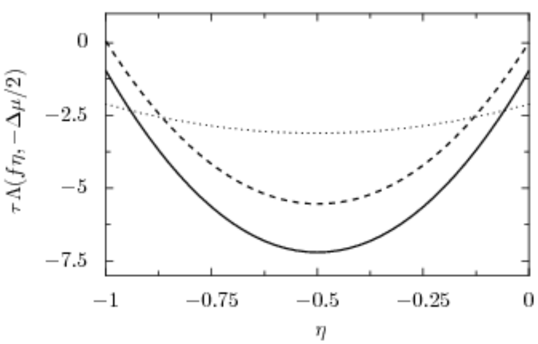
Flashing ratchet model



also obeys the GC symmetry provided both mechanical and chemical variables are included

$E(f-\lambda, \Delta\mu - \gamma) = E(\lambda, \gamma)$ but in general $e(f-\lambda) \neq e(\lambda)$





D. L. et al., PRE **80**, 021923 (2009); Séminaires Poincaré, biological physics (2009)

Modified fluctuation-dissipation theorems out of equilibrium

Standard fluctuation-dissipation theorem (FDT)

Only holds for systems which are close to an equilibrium state

A perturbation : $H_0 -> H_0 - h_{t'} O$ is applied at time t' :

Response function (for t>t')

$$R(t,t') = \left. \frac{\partial \langle A(t) \rangle}{\partial h_{t'}} \right|_{h=0} = \beta \frac{d}{dt'} \langle A(t) O(t') \rangle_{eq}$$

Einstein (1905), Nyquist (1928);
H. Callen and T. Welton (1951), Kubo (1966)

Many attempts to extend the result to non-equilibrium systems

From Jarzynski equality to fluctuation-dissipation theorem (FDT)

- More general form of Jarzynski equality

$$\left\langle A(x_t) e^{-\beta W_{diss}} \right\rangle = \langle A(x_t) \rangle_{eq}$$

- If dissipated work W_{diss} is small with respect to kT

$$\langle A_t(x_t) \rangle_{eq} \simeq \langle A_t(x_t) \rangle + \left\langle A_t(x_t) \int_0^t d\tau' \dot{h}_{\tau'} \partial_h \log p_{eq}(x_{\tau'}, h_{\tau'}) \right\rangle$$

- Take functional derivative with respect to perturbation

$$R(t', t) = \left. \frac{\delta \langle A(x_t) \rangle}{\delta h_{t'}} \right|_{h \to 0} = \frac{d}{dt'} \left\langle A_t(x_t) \frac{\partial \log p_{eq}(c_{t'}, h_{t'})}{\partial h} \right\rangle_{eq}$$

Modified fluctuation-dissipation theorem (MFDT) near NESS

- Variant of Hatano-Sasa (2001) :

$$\left\langle A(x_t) e^{\int_0^\tau dt \dot{h}_t \partial_h \log p_{st}(x_t, h_t)} \right\rangle = \langle A(x_t) \rangle_{st}$$

- Response function near a non-equilibrium steady state for a general observable *A*

$$R(t', t) = \frac{d}{dt'} \left\langle A_t(x_t) \frac{\partial \log p_{st}(c_{t'}, h_{t'})}{\partial h} \right\rangle_{st}$$

- Particular case $$A_{t'}(x_{t'}) = \frac{\partial \log p_{st}(c_{t'}, h_{t'})}{\partial h}$$ J. Prost et al. (2009)

U. Seifert et al. (2010)

- General case G. Verley, K. Mallick, D. L., EPL, **93**, 10002 (2011)

Perturbation near an arbitrary non-stationary state

- Most general MFDT obtained from an Hatano-Sasa like relation:

$$R(t',t) = \frac{d}{dt'} \left\langle A_t(x_t) \frac{\partial \log \pi_t(c_{t'}, h_{t'})}{\partial h} \right\rangle$$

G. Verley et al., J. Stat. Mech. (2011)

- Several alternate formulations:

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

    M. Baiesi et al. (2009); E. Lippiello et al. (2005)

  - In terms of a local velocity/current   R. Chétrite et al. (2008); U. Seifert et al. (2006)

Rk: in all these formulations, markovian dynamics is assumed

Origin of the additive structure of MFDT

- Stochastic trajectory entropy $s_t(c_t,[h]) = -\ln \pi_t(c_t,[h])$
  - Distinct but similar to $\tilde{s}_t(c_t,[h]) = -\ln p_t(c_t,[h])$ U. Seifert, (2005)
  - It can be split 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:

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

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

- Additive structure of the MFDT involving local currents:

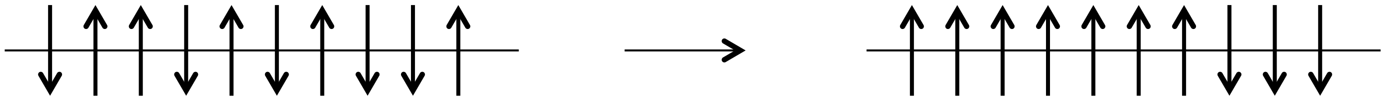
$$R(t,t') = \left\langle \left(j_{t'}(c_{t'}) - \nu(c_{t'})\right) A_t(c_t)\right\rangle$$

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

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

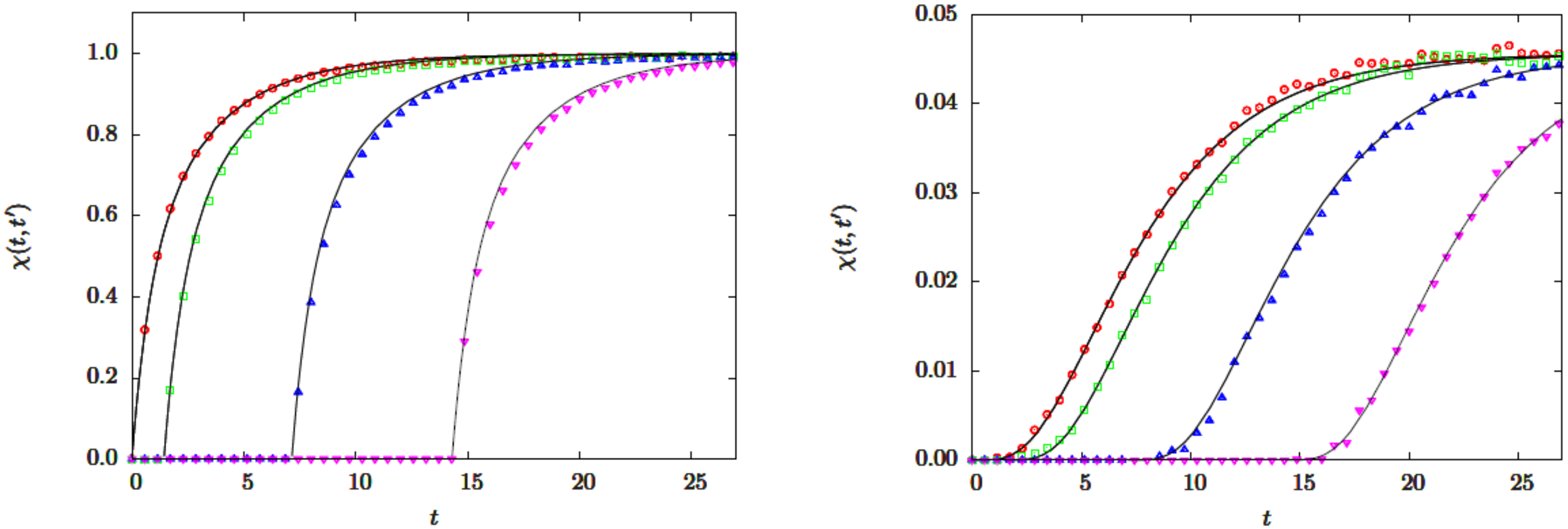
- Analytical verification :

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

  - Analytical form of the response is known

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

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



G. Verley et al., J. Stat. Mech. (2011)

Fluctuation theorems for equilibrium systems

1. For non-equilibrium systems:

- Extension of Gallavotti-Cohen

$$\lim_{\tau\to\infty} \frac{1}{\tau} \ln \frac{P_\tau(\mathbf{J})}{P_\tau(\mathbf{J}')} = \epsilon \cdot (\mathbf{J} - \mathbf{J}')$$

P. Hurtado et al. (2011)

for any pairs of isometric current vectors $|\mathbf{J}| = |\mathbf{J}'|$ and ϵ is related to entropy production

2. For equilibrium systems with discrete broken symmetry

- For an ensemble of N Ising spins in a magnetic field

$$P_B(M) = P_B(-M) e^{2\beta BM}$$

P. Gaspard (2012)

- Equilibrium fluctuations in finite systems are in general non-gaussian

- Non-gaussianity particularly significant near critical points

- Consider N Heisenberg spins in a magnetic field

$$H_N(\sigma;\mathbf{B}) = \mathbf{H_N}(\sigma;\mathbf{0}) - \mathbf{B}\cdot\mathbf{M_N}(\sigma) \quad \text{with} \quad \mathbf{M_N}(\sigma) = \sum_{\mathbf{i=1}}^{\mathbf{N}} \sigma_{\mathbf{i}}$$

- Fluctuations of the magnetization M obey the general relation:

$$P_{\mathbf{B}}(\mathbf{M}) = P_{\mathbf{B}'}(\mathbf{M})\ \mathrm{e}^{\beta(\mathbf{B}-\mathbf{B}')\cdot\mathbf{M}},$$

where $\mathbf{M}' = R_g^{-1}\cdot\mathbf{M}$ thus $|\mathbf{M}| = |\mathbf{M}'|$ (isometric fluctuation theorems)

- This fluctuation theorem expresses a symmetry of the large deviation function defined by

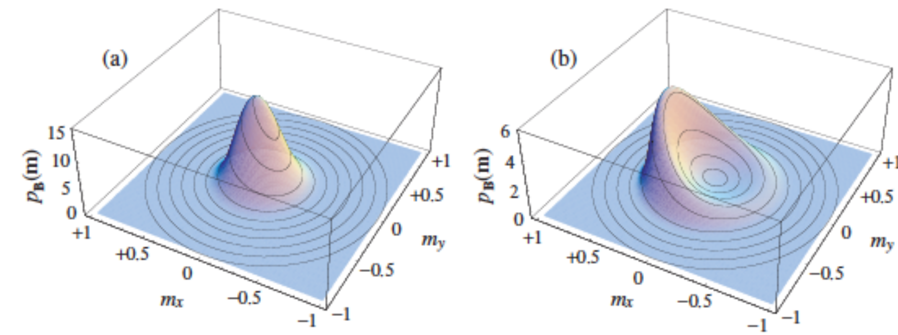
$$P_{\mathbf{B}}(\mathbf{M}) = \mathbf{A_N}(\mathbf{m})\,\mathrm{e}^{-\mathbf{N}\Phi_{\mathbf{B}}(\mathbf{m})}, \quad \text{for } \mathbf{N}\to\infty$$

- These fluctuation theorems quantify the breaking of a symmetry different from time reversal

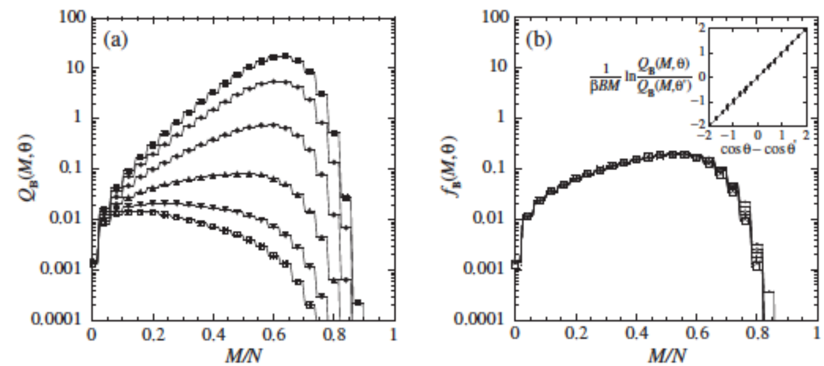
D. L. and P. Gaspard, under review (2014)

Illustrative examples

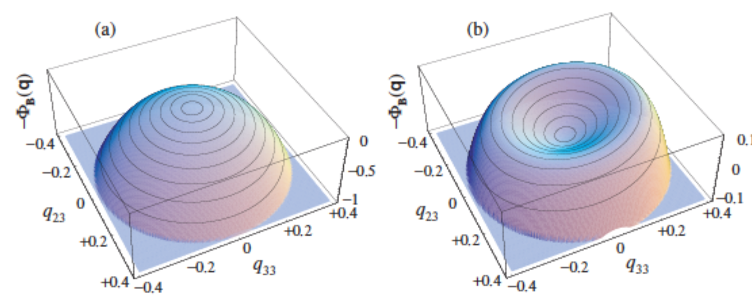
- Curie-Weiss model in a magnetic field: exact evaluation of the large deviation function



- XY model in a magnetic field numerical verification at low and high temperatures



- More complex symmetry breaking with tensorial order parameter in a liquid crystal mean-field model



Non-invasive estimation of dissipation from trajectory information

Irreversibility as time-reversal symmetry breaking

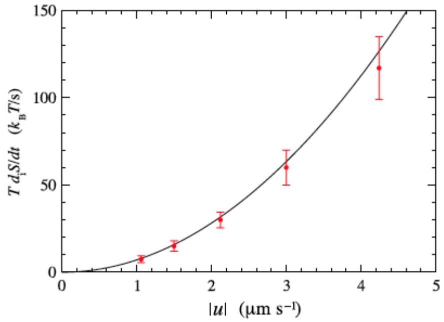
- Direct determination of work or heat is difficult for most complex systems
- Non-equilibrium fluctuations created by irreversible processes have a well-defined arrow of time
- This arrow of time can be « measured » by comparing the statistics of fluctuations forward and backward in time using the KL divergence
- This amounts to enforce fluctuation theorems and exploit them to extract a measurement rather than trying to « verify » them

Estimation of dissipation in a NESS

- Mesure of dynamical randomness associated with direct and reverse path where in the reverse path the driving is reversed

$$\frac{d_i S}{dt} = \lim_{t\to\infty} \frac{k_B}{t} \langle \frac{P_+[z_t|z_0]}{P_-[z_t^R|z_0^R]} \rangle$$

D. Andrieux et al. (2008)



- In other types of NESS, the driving if present is constant and does not need to be reversed -> simpler implementation with a single data series

Simpler implementation with no reversal of the driving

- Probability to observe a block of length m, $(x_1..x_m)$ within a trajectory of total length n in the forward direction $p_F=p(x_1..x_m)$

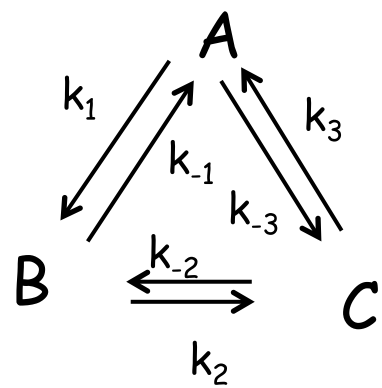
$$D_m(p_F|p_B) = \sum_{x_1..x_m} p(x_1..x_m) \ln \frac{p(x_1..x_m)}{p(x_m..x_1)}$$

- Connection between thermodynamics and information-theoretic estimation

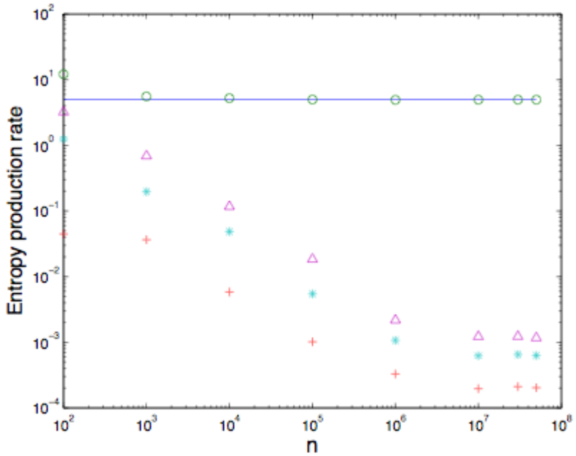
$$\langle \Delta S \rangle \geq d(p_F|p_B) = \lim_{m\to\infty} \frac{1}{m} D_m(p_F|p_B)$$

E. Roldan et al. (2010)

Dissipation in chemical reactions networks



- Equilibrium condition (detailed balance): $k_1 k_2 k_3 = k_{-1} k_{-2} k_{-3}$
- Conservation of the total number of particles: linear dynamics
- Can one detect that the system is out of equilibrium using only information contained in the fluctuations of $\{n_A, n_B\}$ or n_A ?



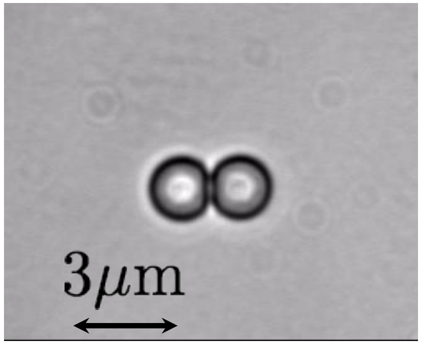
with full information $\{n_A, n_B\}$ trajectory

with partial information $\{n_A\}$ trajectory

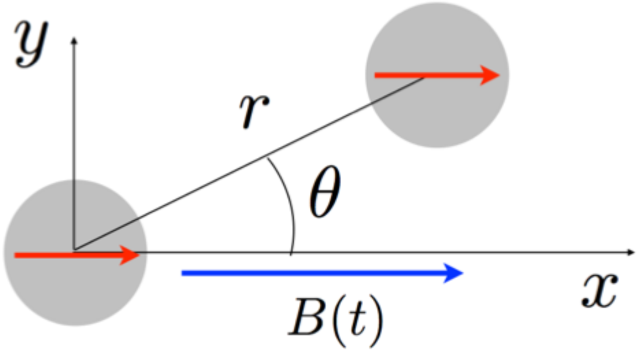
- Possibility to distinguish equilibrium from non-equilibrium fluctuations in a non-invasive way, even when only partial information is available
- Method works for arbitrary number of non-linear chemical reactions
- The quality of the estimate depends primarily on the resolution, i.e. on the degree of coarse-graining of the input data

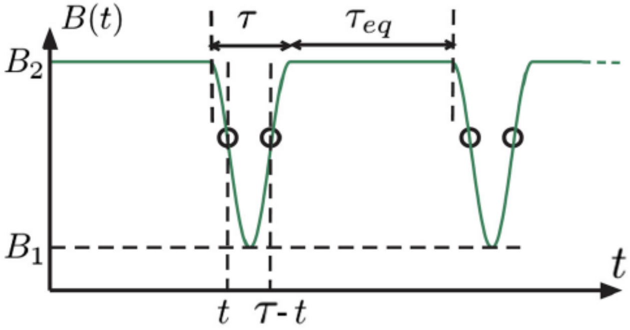
S. Muy et al., J. Chem. Phys. (2013)

Estimating dissipation in systems with time-dependent driving



S. Tush et al., PRL, (2014)





Stochastic work and heat on a cycle:

$$W(\tau) = \int_0^\tau dt\ \dot{B}(t)\partial_B U(\mathbf{r}(t), B(t))$$

$$Q(\tau) = \int_0^\tau dt \nabla_{\mathbf{r}} U(\mathbf{r}(t), B(t)) \circ \dot{\mathbf{r}}.$$

Energy vs. information based estimation of dissipation

For information based estimation:

a) compare forward/backward probability distributions

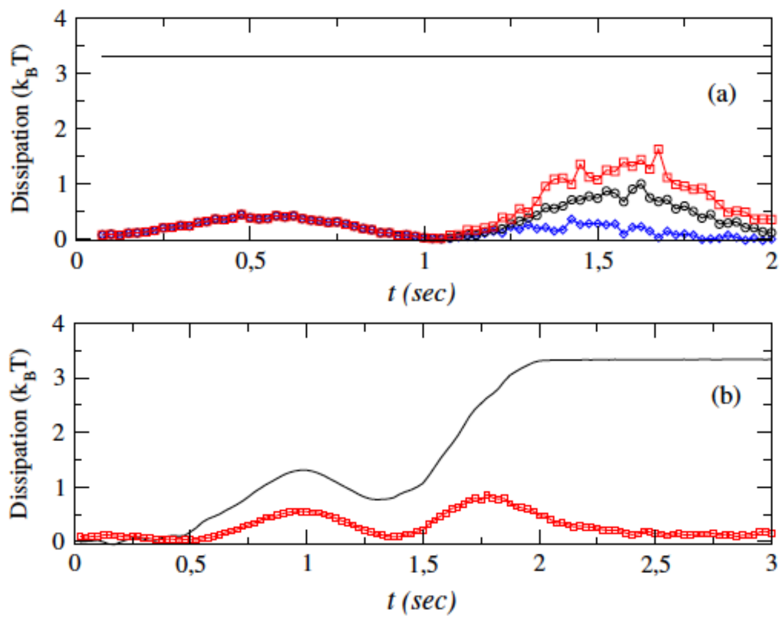
b) compare equilibrium/non-equilibrium probability distributions

$$\beta\langle W_{diss}(\tau)\rangle \geq D(p_F(t)||p_R(\tau - t))$$

R. Kawai et al. (2007)

$$\beta\langle W_{\text{diss}}(t)\rangle \geq D(p_{\text{neq}}(t)\|p_{\text{eq}}(t)),$$

S. Vaikuntanathan et al. (2009)



Acknowledgements

1. Fluctuation theorems for systems out of equilibrium
   K. Mallick, A. Lau

2. Fluctuations theorems for systems at equilibrium
   P. Gaspard

3. Modified fluctuation-dissipation theorems out of equilibrium
   R. Chétrite, G. Verley

4. Non-invasive estimation of dissipation from trajectory information
   Theory: A. Kundu, G. Verley
   Experiments with manipulated colloids: S. Tush, J. Baudry