Fluctuation and response of time-symmetric current around nonequilibrium stationary states

Naoto Shiraishi (Univ. of Tokyo)

N. Shiraishi, Phys. Rev. Lett. 129, 020602 (2022)
N. Shiraishi, arXiv:2211.11437

Outline

Review of stochastic thermodynamics

Fluctuation-response relation for stall states

Fluctuation-response relation for general NESS

Outline

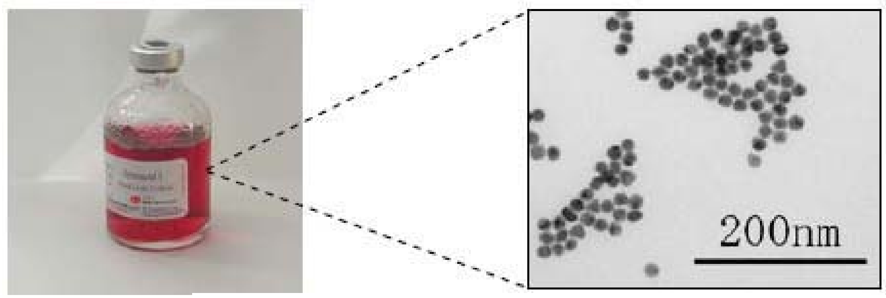
Review of stochastic thermodynamics

Fluctuation-response relation for stall states

Fluctuation-response relation for general NESS

Stage: stochastic thermodynamics

System follows stochastic process due to thermal noise.

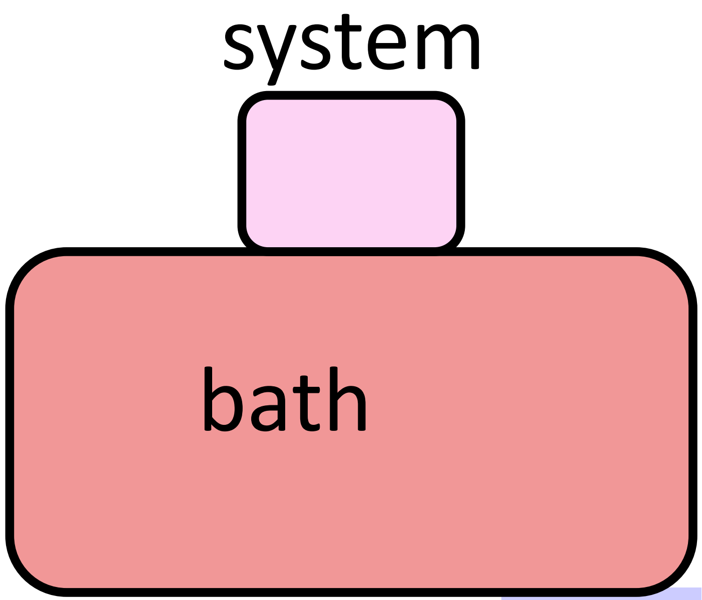


Colloidal particle

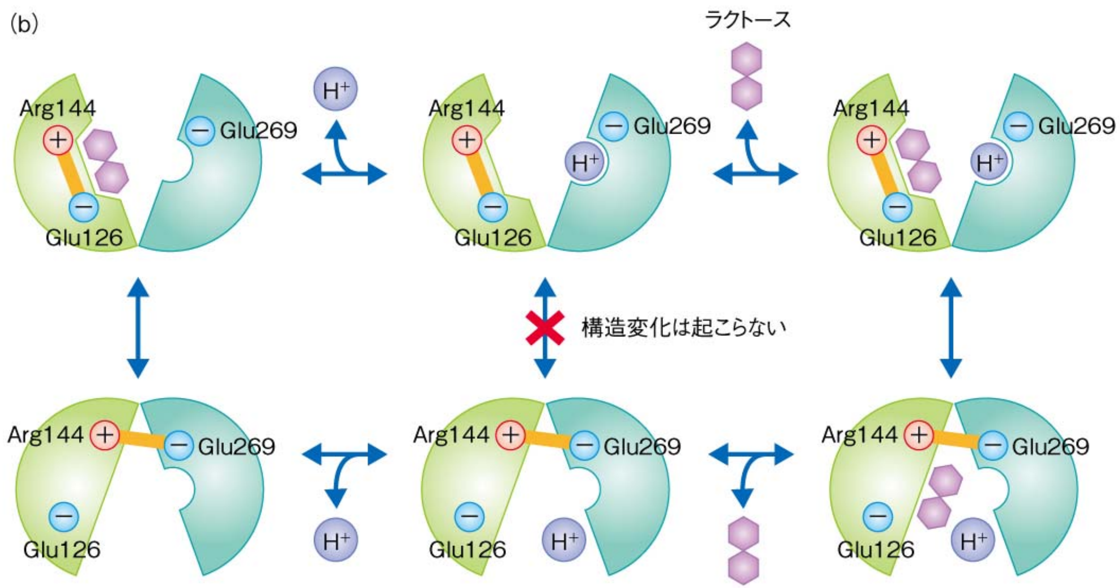
<u>Throughout this talk</u>

- We treat classical systems.
- Heat bath is always in equilibrium

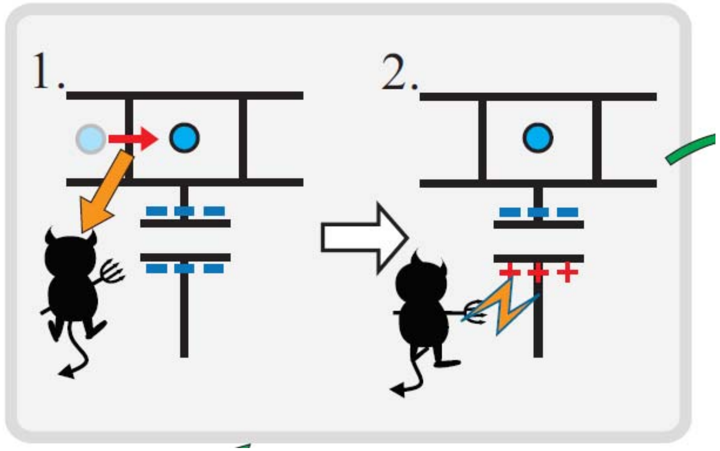
  →We use **Markov processes**.



Situation (examples)



(http://leading.lifesciencedb.jp/2-e009)



(https://phys.org/news/2016-01-maxwell-demon-self-contained-information-powered-refrigerator.html)

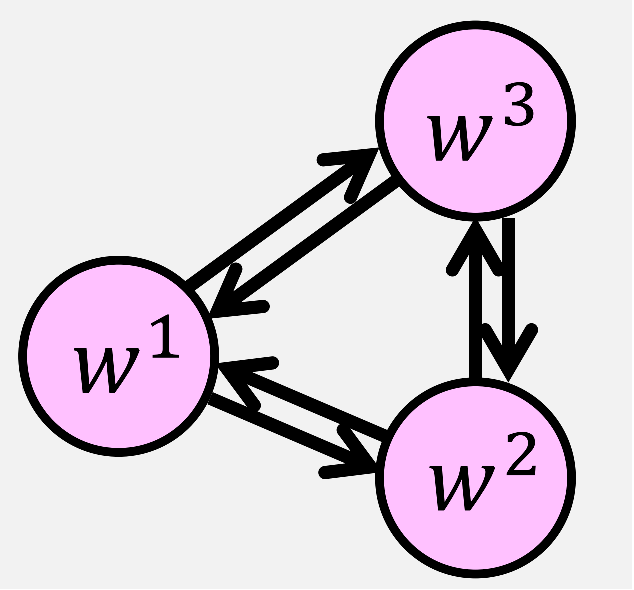
We employ Markov jump processes on discrete states.

Time-evolution equation

Time evolution of **probability distribution** $\boldsymbol{p}$ is given by **master equation**.

$$\frac{d}{dt} p_{w,t} = \sum_{w'} R_{ww'} p_{w',t}$$

transition matrix



normalization condition $\sum_{\boldsymbol{w}} \boldsymbol{R}_{\boldsymbol{ww'}} = \boldsymbol{0}$

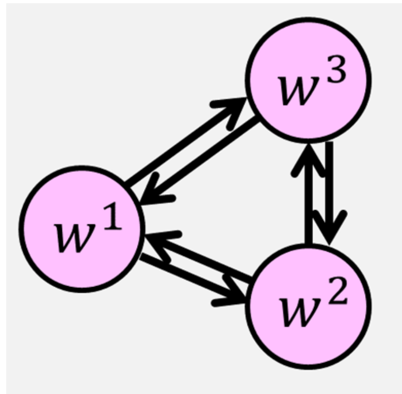
(Diagonal elements $R_{w'w'}$ are negative. Off-diagonals are nonnegative)

Local detailed-balance

Local detailed-balance

In canonical distribution, no microscopic probability current occurs.

$$\frac{R_{ww'}}{R_{w'w}} = e^{-\beta(E_w - E_{w'})}$$



(If a system is attached to multiple baths, we apply local detailed-balance for each bath)

Average entropy production rate

Average entropy production rate is defined as

$$\langle \dot{\sigma} \rangle = -\sum_w \beta E_w \frac{dp_w}{dt} + \frac{d}{dt}\left(-\sum_w p_w \ln p_w\right)$$

Entropy increase in baths (dQ/T)

(Shannon) entropy increase in the system

Average entropy production

Average entropy production rate is defined as

$$\langle \dot{\sigma} \rangle = -\sum_w \beta E_w \frac{dp_w}{dt} + \frac{d}{dt}\left(-\sum_w p_w \ln p_w \right)$$

$$= \sum_{w,w'} R_{w'w} p_w \ln \frac{R_{w'w} p_w}{R_{ww'} p_{w'}}$$

Assuming local detailed-balance

Second law

Entropy production is time-integration of entropy production rate:

$$\langle \sigma \rangle = \int_0^\tau dt\, \langle \dot{\sigma} \rangle$$

$\langle \dot{\sigma} \rangle \geq 0$ implies $\langle \sigma \rangle \geq 0$.
(Both inequalities are called the second law.)

Stochastic entropy production

Define entropy production for each single trajectory.

<u>(stochastic) entropy production σ</u>

For each single transition $w \to w'$, we count

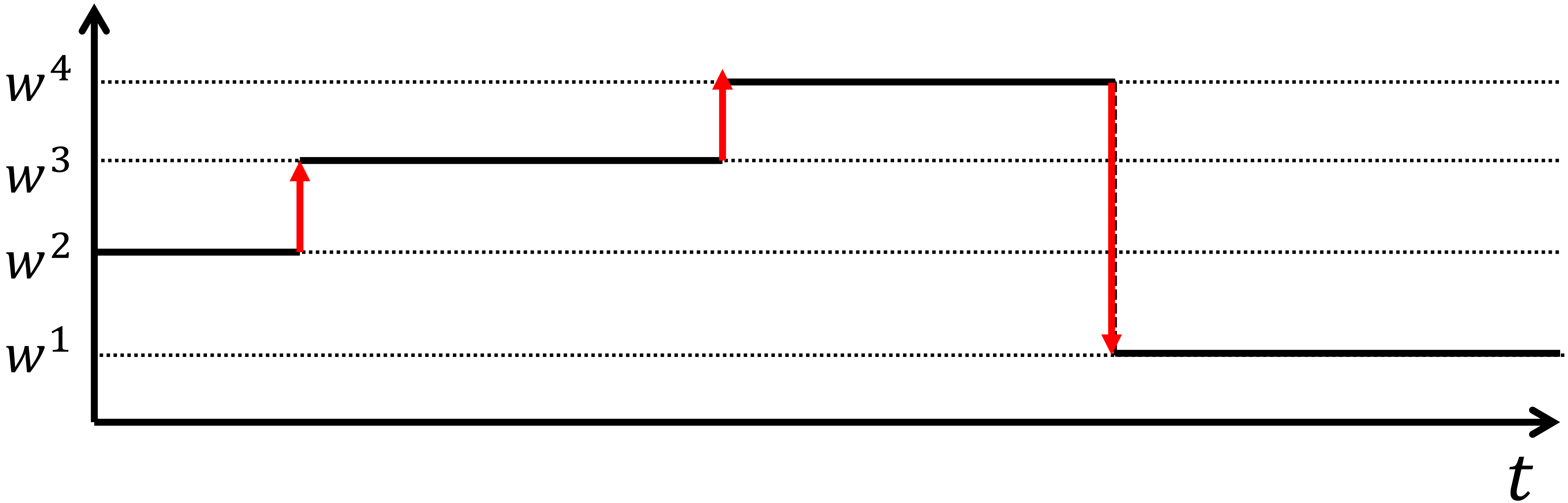
$$\boldsymbol{\beta}(\boldsymbol{E}_{\boldsymbol{w}} - \boldsymbol{E}_{\boldsymbol{w}'}) + \mathbf{ln}\frac{\boldsymbol{p}_{\boldsymbol{w}}}{\boldsymbol{p}_{\boldsymbol{w}'}} = \mathbf{ln}\frac{\boldsymbol{R}_{\boldsymbol{w}'\boldsymbol{w}}\boldsymbol{p}_{\boldsymbol{w}}}{\boldsymbol{R}_{\boldsymbol{w}\boldsymbol{w}'}\boldsymbol{p}_{\boldsymbol{w}'}}$$

(We assumed local detailed-balance condition)

The second term corresponds to stochastic entropy (c.f., Shannon entropy as its averaged version)

Example of entropy production

Consider a stationary system.



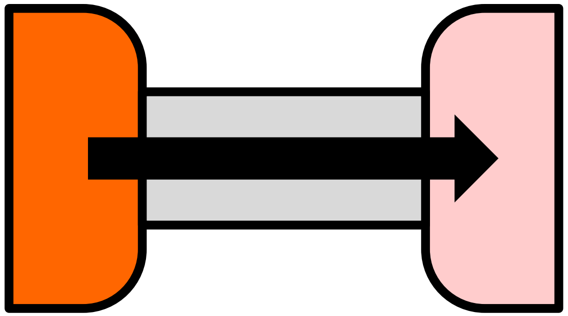
$$\sigma = \ln \frac{R_{32} p_2}{R_{23} p_3} + \ln \frac{R_{43} p_3}{R_{34} p_4} + \ln \frac{R_{14} p_4}{R_{41} p_1}$$

Ex) stationary systems

Case: stationary and long-time

For cumulative current $\mathcal{J} = \int J(t)dt$, affinity h

$$\sigma = h\mathcal{J}$$



Ex) $\mathcal{J} = \int J_Q(t)dt$ (heat current), $h = \Delta\beta$ (inverse temperature difference)

Fluctuation theorem

second law : $\langle \sigma \rangle \geq 0$

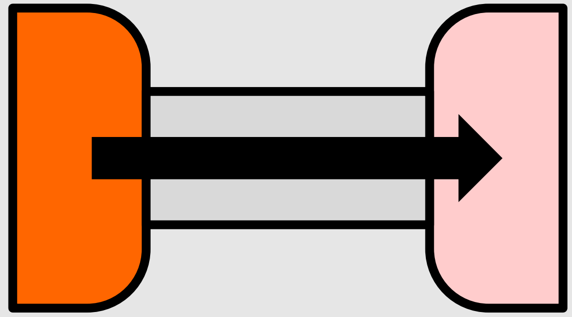
fluctuation theorem : $\langle \boldsymbol{e^{-\sigma}} \rangle = \mathbf{1}$

(D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. 71, 2401 (1993), C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997), J. Kurchan, J. Phys. A: Math. Gen. 31, 3719 (1998).)

From fluctuation theorem, we can derive various relations including the second law and the fluctuation-response relation (FRR).

Derivation of FRR

$$1 = \langle e^{-h\mathcal{J}} \rangle$$
$$= 1 - h\langle \mathcal{J} \rangle + \frac{h^2}{2}\langle \mathcal{J}^2 \rangle + O(h^3)$$



$h = \Delta\beta$ is small.

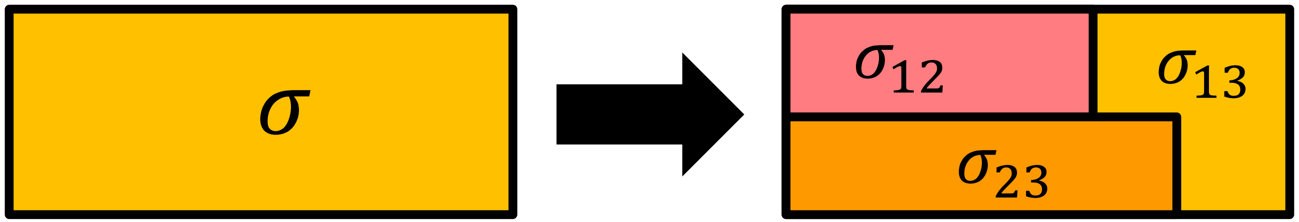
Since the ensemble $\langle \cdot \rangle$ also depends on h, we have

$$\langle \mathcal{J} \rangle = \langle \mathcal{J} \rangle_0 + \left.\frac{d\langle \mathcal{J} \rangle_h}{dh}\right|_{h=0} h + O(h^2)$$

Comparing coefficient of h^2, $\frac{1}{2}\langle \mathcal{J}^2 \rangle_0 = \left.\frac{\partial \langle \mathcal{J} \rangle_h}{\partial h}\right|_{h=0}$

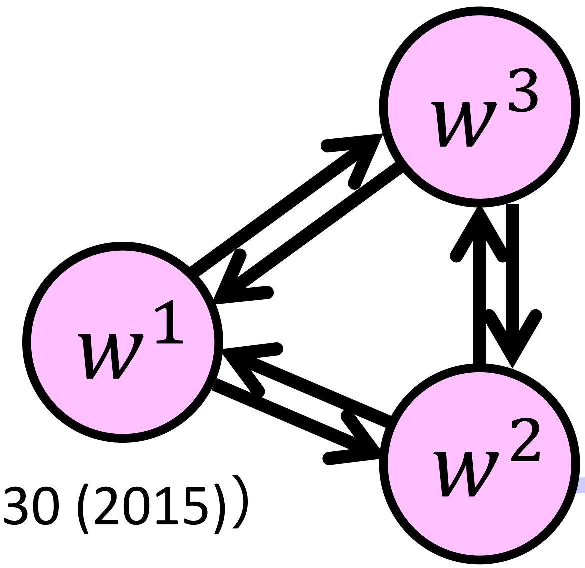
Partial entropy production

Partial entropy production：Decomposing entropy production to single transitions with keeping thermodynamic properties.



second law：$\langle \sigma_{12} \rangle \geq 0$

fluctuation theorem：$\langle e^{-\sigma_{12}} \rangle = 1$

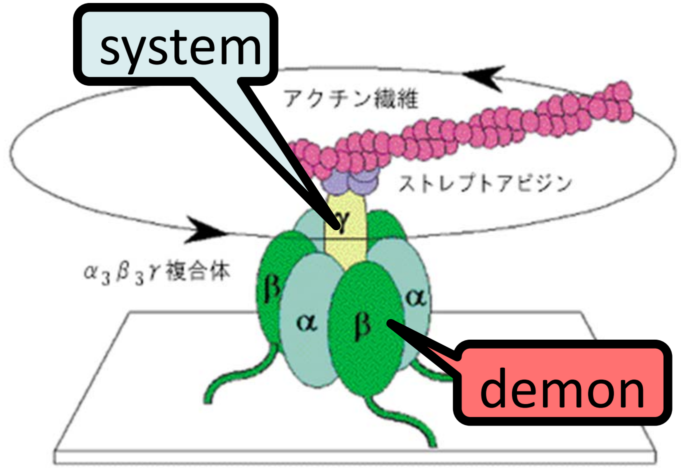


（NS and T. Sagawa, PRE 91. 012130 (2015)）

Application of partial entropy production

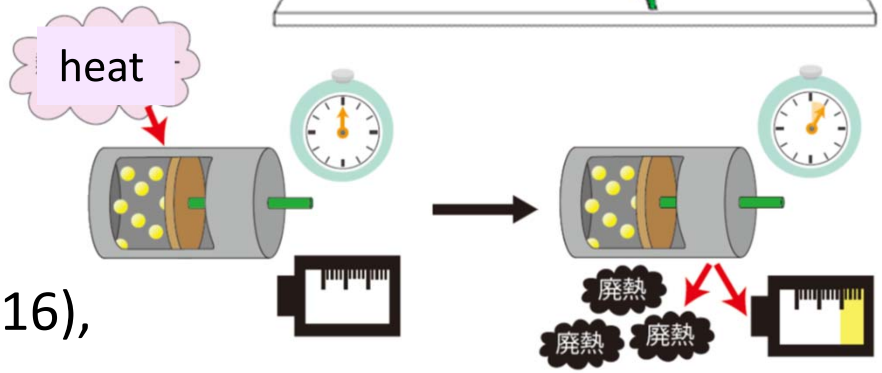
Information thermodynamics (autonomous Maxwell's demon).

(NS, *et.al.*, NJP. 17, 045012 (2015),
NS, *et.al.*, NJP 18, 013044 (2016))



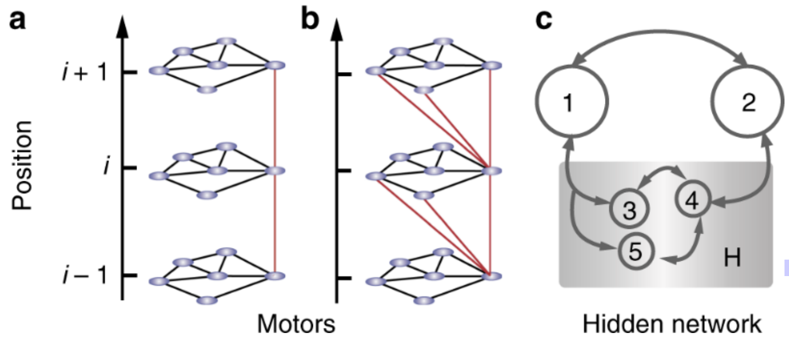
Trade-off between efficiency and power.

(NS, K. Saito, and H. Tasaki, PRL 117, 190601 (2016),
NS and K. Saito, JSP 174, 433 (2019))



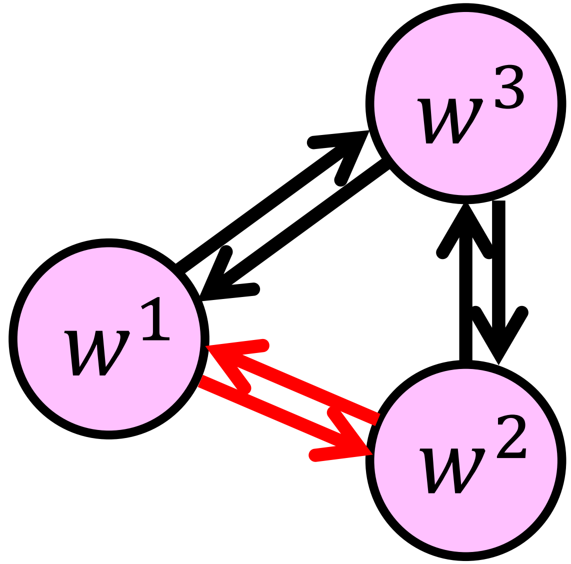
Estimating dissipation

(G. Bisker, *et al.*, J. Stat. Mech. 093210 (2017),
I. A. Martinez, *et a*l., Nat. Comm.10, 3542 (2019))



Definition of partial entropy production

Partial entropy production σ_{12} is defined as the following accumulation.



- If transition 12 occurs, count $\pm \ln \frac{R_{12} p_2}{R_{21} p_1}$.
- If the state is 1, integrate $\int \frac{J_{12}}{p_1} dt$ (similarly to 2).

Another partial entropy production

There is another definition of partial entropy production if we do not require it as decomposition of total entropy production.

We define I-partial entropy production σ_{12}^{I} as

- If transition 12 occurs, count $\pm \ln \frac{R_{12} p_2^*}{R_{21} p_1^*}$.

  (p_i^*: stationary distribution of a system constructed by removing transition 12)

It also satisfies fluctuation theorem $\langle e^{-\sigma_{12}^{I}} \rangle = 1$.

(M. Polettini and M. Esposito, PRL 119, 240601 (2017).)

Outline

Review of stochastic thermodynamics

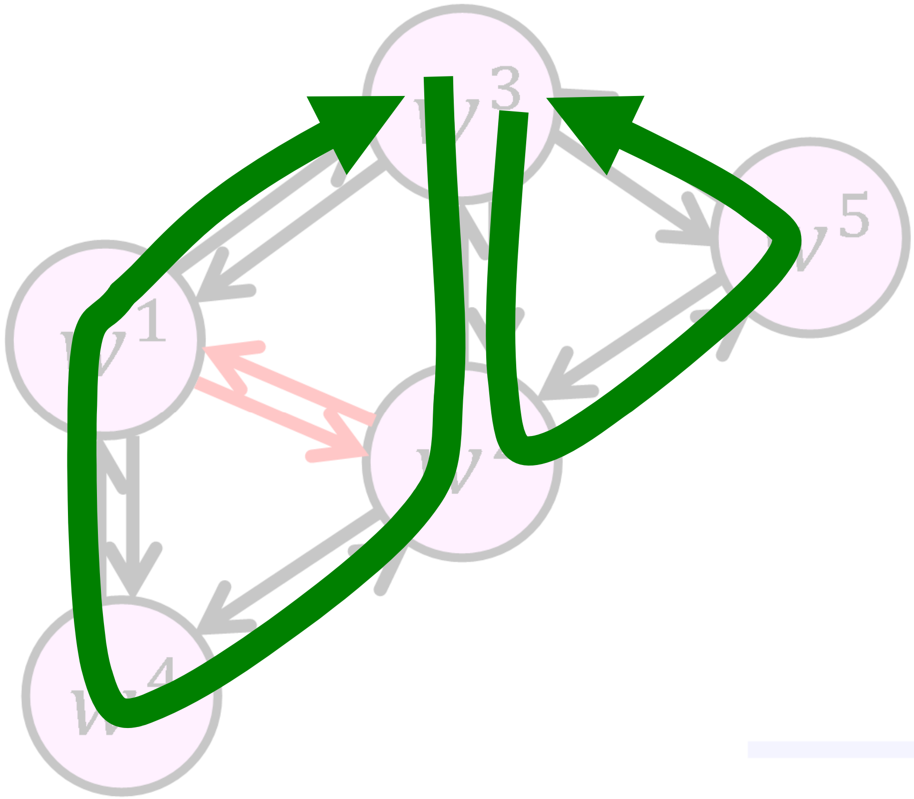
Fluctuation-response relation for stall states

Fluctuation-response relation for general NESS

Stall state

A **stall state** is a nonequilibrium stationary state where the edge in interest (12 in the figure) has zero probability current.

For a while, we discuss the edge in a stall state.



Fluctuation-response relation (FRR) in stall state

I-partial entropy production σ_{12}^{I} for edge 12 reads

$$\boldsymbol{\sigma_{12}^{I} = \ln \frac{R_{12} p_2^*}{R_{21} p_1^*} \mathcal{J}_{12} = (x_{12} - x_{12}^*) \mathcal{J}_{12}}$$

($x_{12} := \ln \frac{R_{12}}{R_{21}}$ is the conjugated affinity)

(x_{12}^*: The parameter at stall state)

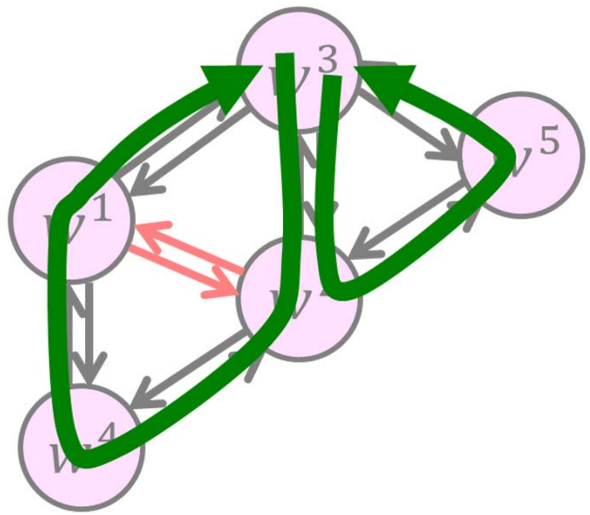
Expanding $\langle e^{-\sigma_{12}^{I}} \rangle = 1$ with $\Delta x_{12} := x_{12} - x_{12}^*$,

$$\boldsymbol{\frac{1}{2} \left\langle \mathcal{J}_{12}^2 \right\rangle_{x=x^*} = \left. \frac{\partial \langle \mathcal{J}_{12} \rangle_x}{\partial x_{12}} \right|_{x=x^*}}$$

(B. Altaner, M. Polettini and M. Esposito, PRL 117, 180601 (2016).)

Meaning of stall FRR

$$\frac{1}{2}\left\langle \mathcal{J}_{12}^2 \right\rangle_{x=x^*} = \left.\frac{\partial \langle \mathcal{J}_{12} \rangle_x}{\partial x_{12}}\right|_{x=x^*}$$



- FRR holds on the stalling edge (zero probability current), whose form is the same as the equilibrium FRR.
- Except the edge in interest, strong stationary current may flow.

Time-symmetric current

Current $\mathcal{J}$ changes its sign under time-reversal:

$$\mathcal{J}(\Gamma^\dagger) = -\mathcal{J}(\Gamma).$$

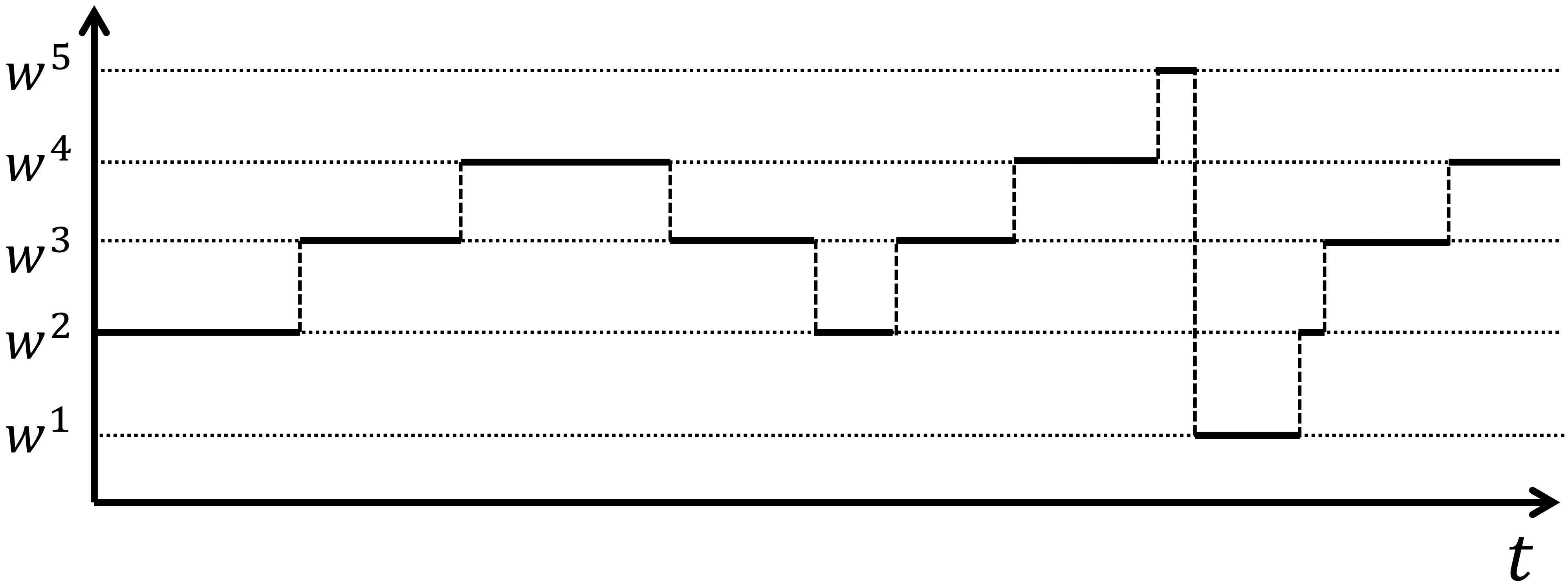
We investigate current-like but time-symmetric quantity, i.e.,

$$\boldsymbol{I}(\boldsymbol{\Gamma}^\dagger) = \boldsymbol{I}(\boldsymbol{\Gamma}) \text{ and } \langle \boldsymbol{\mathcal{J}} \rangle = \langle \boldsymbol{I} \rangle$$

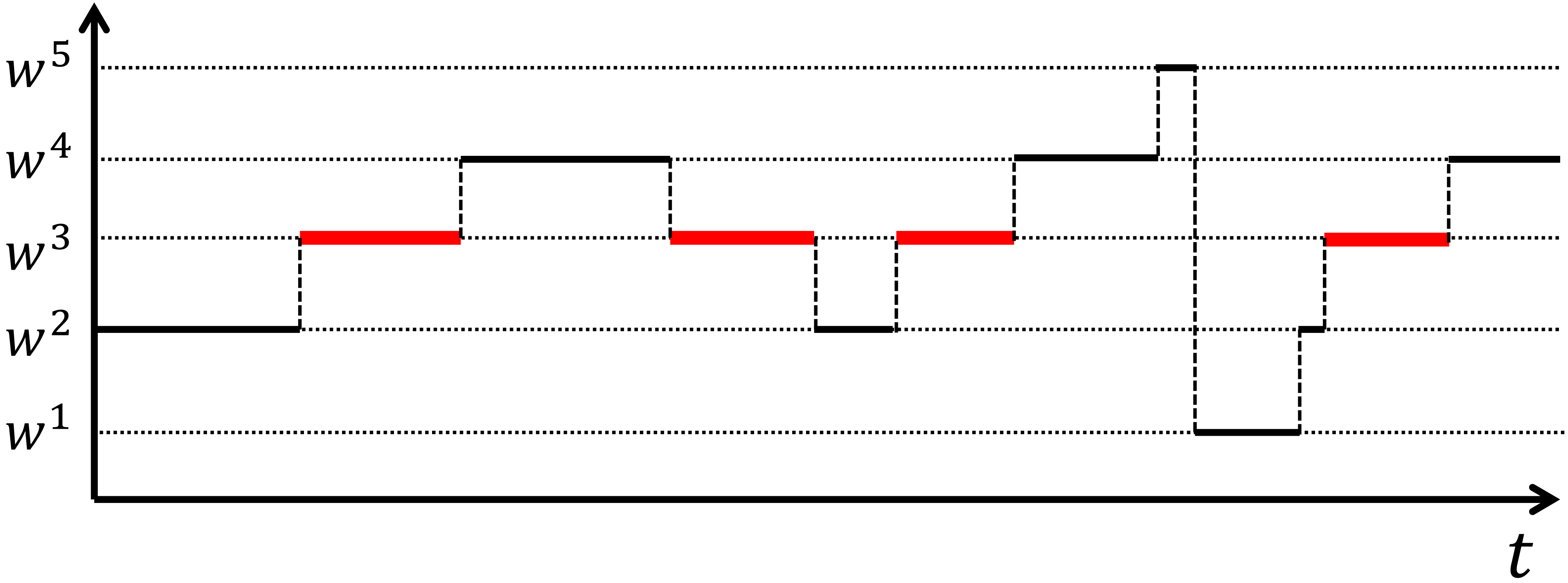
Time-symmetric quantities are considered to be important in nonequilibrium physics.

(J. P. Garrahan, *et al.*, PRL 98, 195702 (2007). M. Baiesi, C. Maes, and B. Wynants, PRL 103, 010602 (2009), T. Bodineau and C. Toninelli, CMP 311, 357 (2012).)

Ex) empirical measure

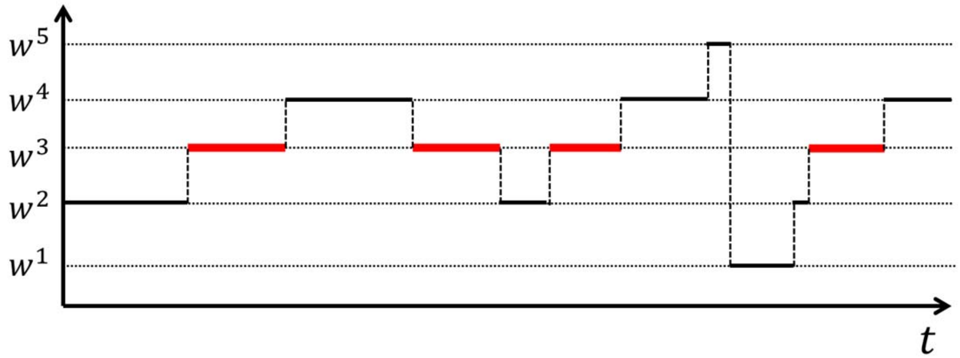


Ex) empirical measure



Empirical measure τ_3

Definition of time-symmetric current



Using empirical measure τ, time-symmetric current I_{ij} is defined as

$$\boldsymbol{I_{ij} := R_{ij}\tau_j - R_{ji}\tau_i}$$

By construction, $I_{ij}(\Gamma^\dagger) = I_{ij}(\Gamma)$ and $\langle \mathcal{J}_{ij} \rangle = \langle I_{ij} \rangle$

(Note: I_{ij} itself has x_{ij} dependence through R)

FRR for time-symmetric current

In stall states, the time-symmetric current satisfies

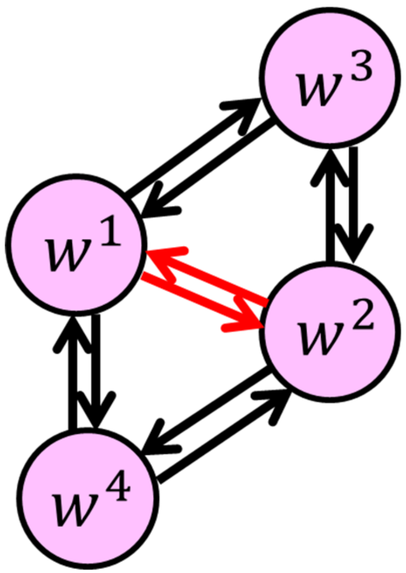
$$\frac{1}{2}\left\langle I_{ij}^2 \right\rangle_{x=x^*} = -\left.\frac{\partial \left\langle I_{ij,x^*} \right\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$

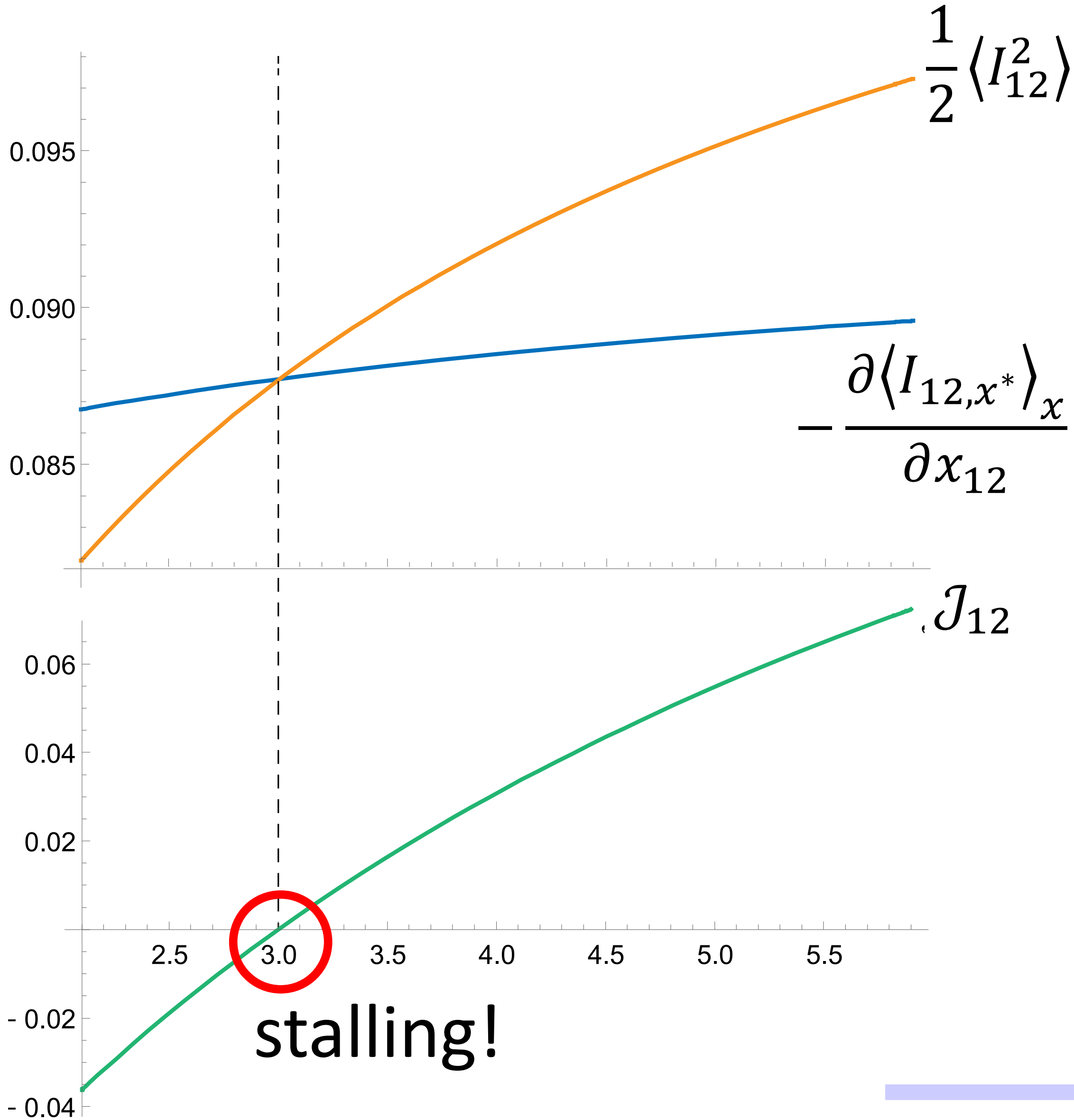
(NS, Phys. Rev. Lett. 129, 020602 (2022))

(Note: In the derivative of the r.h.s., we fix the function of I_{ij}(i.e., R in $I_{ij} := R_{ij}\tau_j - R_{ji}\tau_i$) and perturb the path probability)

Numerical demonstration

$$\frac{1}{2}\left\langle I_{ij}^2 \right\rangle_{x=x^*} = -\left.\frac{\partial \left\langle I_{ij,x^*} \right\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$





Above FRR holds only when $\mathcal{J}_{12} = 0$ (stall).

Before proof… Twisted empirical measure

Twisted empirical measure is defined as

$$\boldsymbol{C_{ij,x}} := \frac{\boldsymbol{\tau_j}}{\boldsymbol{p_j^{ss}(x)}} - \frac{\boldsymbol{\tau_i}}{\boldsymbol{p_i^{ss}(x)}}$$

- For any x, average is zero: $\left\langle C_{ij,x} \right\rangle_x = 0$
- In stall states, $\boldsymbol{I_{ij,x^*} = R_{ij} p_j^{ss}(x^*) C_{ij,x^*}}$
- Its derivative satisfies $\left.\frac{\partial \langle \boldsymbol{C_{ij,x^*}} \rangle_x}{\partial x_{ij}}\right|_{x=x^*} = \frac{\partial}{\partial x} \ln \frac{p_j^{ss}}{p_i^{ss}}$

Proof : expanding $\langle e^{-\sigma_{ij}} \rangle = 1$

Partial entropy production for edge ij reads

$$\boldsymbol{\sigma_{ij} = a_{ij}\mathcal{J}_{ij} - \langle J_{ij} \rangle C_{ij,x} = (\mathcal{J}_{ij} - I_{ij})a_{ij} + O(a_{ij}^2)},$$

where $a_{ij} := \ln \frac{R_{ij}p_j}{R_{ji}p_i}$ is total thermodynamic force.

Since $a_{ij} = 0$ in stall states, the expansion of $\langle e^{-\sigma_{ij}} \rangle = 1$ with a_{ij} implies

$$\frac{1}{2}\left\langle \left(\mathcal{J}_{ij} - I_{ij}\right)^2 \right\rangle_{x=x^*} = -\left.\frac{\partial \langle \mathcal{J}_{ij} \rangle_x}{\partial a_{ij}}\right|_{a=0}$$

Proof: two technical relations

$$\frac{1}{2}\left\langle \left(\mathcal{J}_{ij} - I_{ij}\right)^2 \right\rangle_{x=x^*} = \left.\frac{\partial \langle \mathcal{J}_{ij} \rangle_x}{\partial a_{ij}}\right|_{a=0}$$

We use the following two relations

$$\langle \boldsymbol{\mathcal{J}_{ij} I_{ij}} \rangle = \mathbf{0}$$

(This relation is trivial for equilibrium. For nonequilibrium stall states, we need the method with counting field.)

$$\left.\frac{\partial \langle \mathcal{J}_{ij} \rangle_x}{\partial a_{ij}}\right|_{a=0} = \left.\frac{\partial \langle \mathcal{J}_{ij} \rangle_x}{\partial x_{ij}}\right|_{x=x^*} - \left.\frac{\partial \left\langle I_{ij,x^*} \right\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$

Proof: difference between two FRR for two partial entropy production

FRR derived from σ_{ij}:

$$\frac{1}{2}\left\langle \mathcal{J}_{ij}^2 \right\rangle_{x=x^*} + \frac{1}{2}\left\langle I_{ij}^2 \right\rangle_{x=x^*} = \left.\frac{\partial \left\langle \mathcal{J}_{ij} \right\rangle_x}{\partial x_{ij}}\right|_{x=x^*} - \left.\frac{\partial \left\langle I_{ij,x^*} \right\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$

FRR derived from σ_{ij}^I:

$$\frac{1}{2}\left\langle \mathcal{J}_{ij}^2 \right\rangle_{x=x^*} = \left.\frac{\partial \left\langle \mathcal{J}_{ij} \right\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$

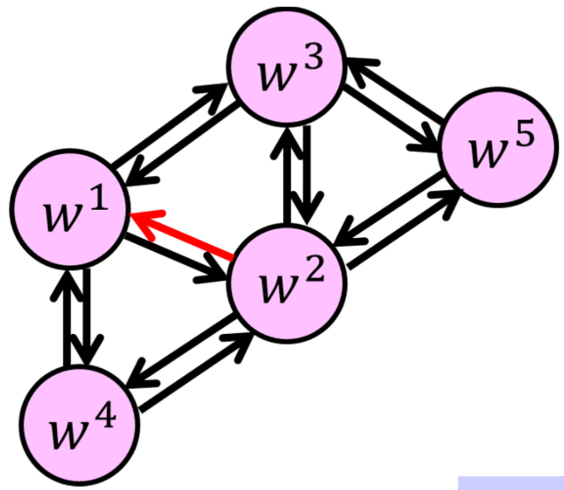
The difference between these two equals FRR for time-symmetric current (Proof end).

Applications for experiments

(Since time-symmetric current I_{ij} and twisted empirical measure C_{ij} are connected as $I_{ij} = R_{ij} p_j^{ss} C_{ij}$, we shall consider the role of C_{ij} in the following)

Time-symmetric current and twisted empirical measure are useful for estimating **a bare transition rate R_{ij}.**

(We keep in mind the situation that time-resolution is low and only time-cumulative quantity is measurable)



Evaluation of R_{ij} (1)

Rewriting FRR for time-symmetric current in terms of C_{ij}, we have

$$\boldsymbol{R_{ij} = -\frac{2}{\left\langle C_{ij,x^*}^2 \right\rangle_{x^*} p_j^{ss}} \frac{\partial \langle C_{ij,x^*} \rangle_x}{\partial x_{ij}} \Bigg|_{x=x^*}}$$

Only empirical measure appears.
(No current appears.)

$$\boldsymbol{C_{ij,x} := \frac{\tau_j}{p_j^{ss}(x)} - \frac{\tau_i}{p_i^{ss}(x)}}$$

Evaluation of R_{ij} (2)

Calculating from the definition of time-symmetric current, we have

$$\boldsymbol{R_{ij}} = \frac{\left.\dfrac{\partial \langle \mathcal{J}_{ij} \rangle_x}{\partial x_{ij}}\right|_{x=x^*}}{p_j^{ss}\left(\tau + \left.\dfrac{\partial \langle C_{ij,x^*} \rangle_x}{\partial x_{ij}}\right|_{x=x^*}\right)}$$

(τ : measurement time length)

Fluctuation term does not appear.

Evaluation of R_{ij} (3)

$$\boldsymbol{2R_{ij}p_j^{ss}} = \left.\frac{\partial\langle\mathcal{J}_{ij}\rangle_x}{\partial x_{ij}}\right|_{x=x^*} - \left.\frac{\partial\langle I_{ij,x^*}\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$

$$= \langle\mathcal{J}_{ij}^2\rangle_{x^*} + \langle I_{ij,x^*}^2\rangle_{x^*}$$

$$= \langle\boldsymbol{\mathcal{J}_{ij}^2}\rangle_{\boldsymbol{x^*}} + \left(\boldsymbol{R_{ij}p_j^{ss}}\right)^{\boldsymbol{2}}\langle\boldsymbol{C_{ij,x^*}^2}\rangle_{\boldsymbol{x^*}}$$

By solving $R_{ij}p_j^{ss}$, we have an expression of R_{ij} only with **fluctuation terms (response terms do not appear)**

Note: Certainty relation

The condition for the quadratic equation for $R_{ij}p_j^{ss}$

$$2R_{ij}p_j^{ss} = \langle \mathcal{J}_{ij}^2 \rangle_{x^*} + \left(R_{ij}p_j^{ss}\right)^2 \langle C_{ij,x^*}^2 \rangle_{x^*}$$

having real solution (discriminant$\geq$ 0) leads to

$$\boldsymbol{\langle \mathcal{J}_{ij}^2 \rangle_{x^*} \langle C_{ij,x^*}^2 \rangle_{x^*} \leq 1}.$$

In stall states, both the current and twisted empirical measure cannot have large fluctuation simultaneously.

Outline

Review of stochastic thermodynamics

Fluctuation-response relation for stall states

Fluctuation-response relation for general NESS

Result: FRR for general NESS

Around general NESS with $x = x'$, current, time-symmetric current and twisted empirical measure satisfy

$$\frac{2}{\left\langle C_{ij,x'}^2 \right\rangle_{x'}} = \frac{\frac{d\left\langle I_{ij,x'} \right\rangle_x}{dx_{ij}} - \frac{d\left\langle \mathcal{J}_{ij} \right\rangle_x}{dx_{ij}}}{\frac{d\left\langle C_{ij,x'} \right\rangle_x}{dx_{ij}}}$$

Fluctuation term

Response terms

(N. Shiraishi, arXiv:2211.11437)

Remark: Situation beyond stall state

Two key quantities:

Time-symmetric current

$$\boldsymbol{I_{ij,x^*} := R_{ij}\tau_j - R_{ji}\tau_i}$$

Twisted empirical measure

$$\boldsymbol{C_{ij,x^*} := \frac{\tau_j}{p_j^{ss}} - \frac{\tau_i}{p_i^{ss}}}$$

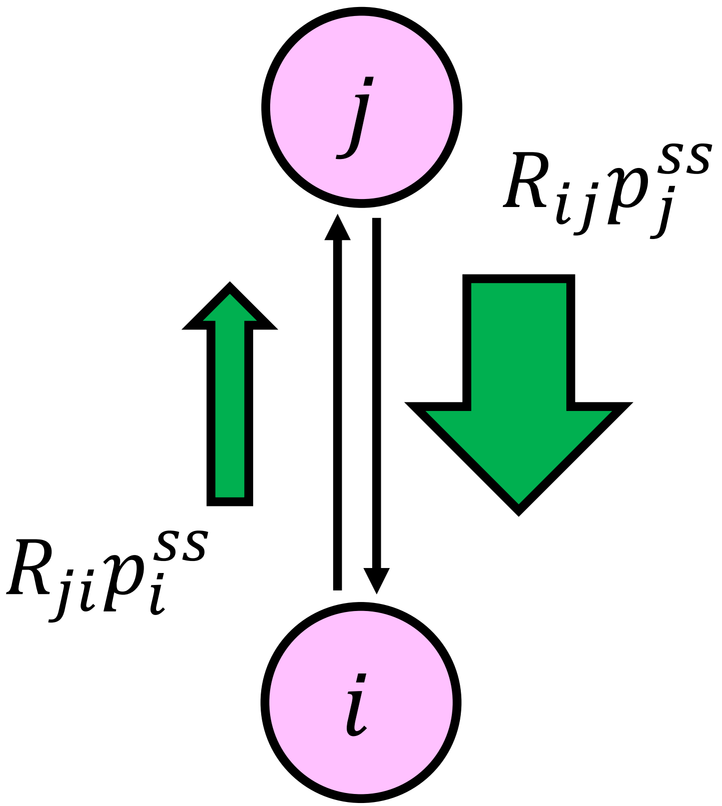
In stall states, these two are connected via

$$\boldsymbol{R_{ij} p_j^{ss} C_{ij,x^*} = I_{ij,x^*}}.$$

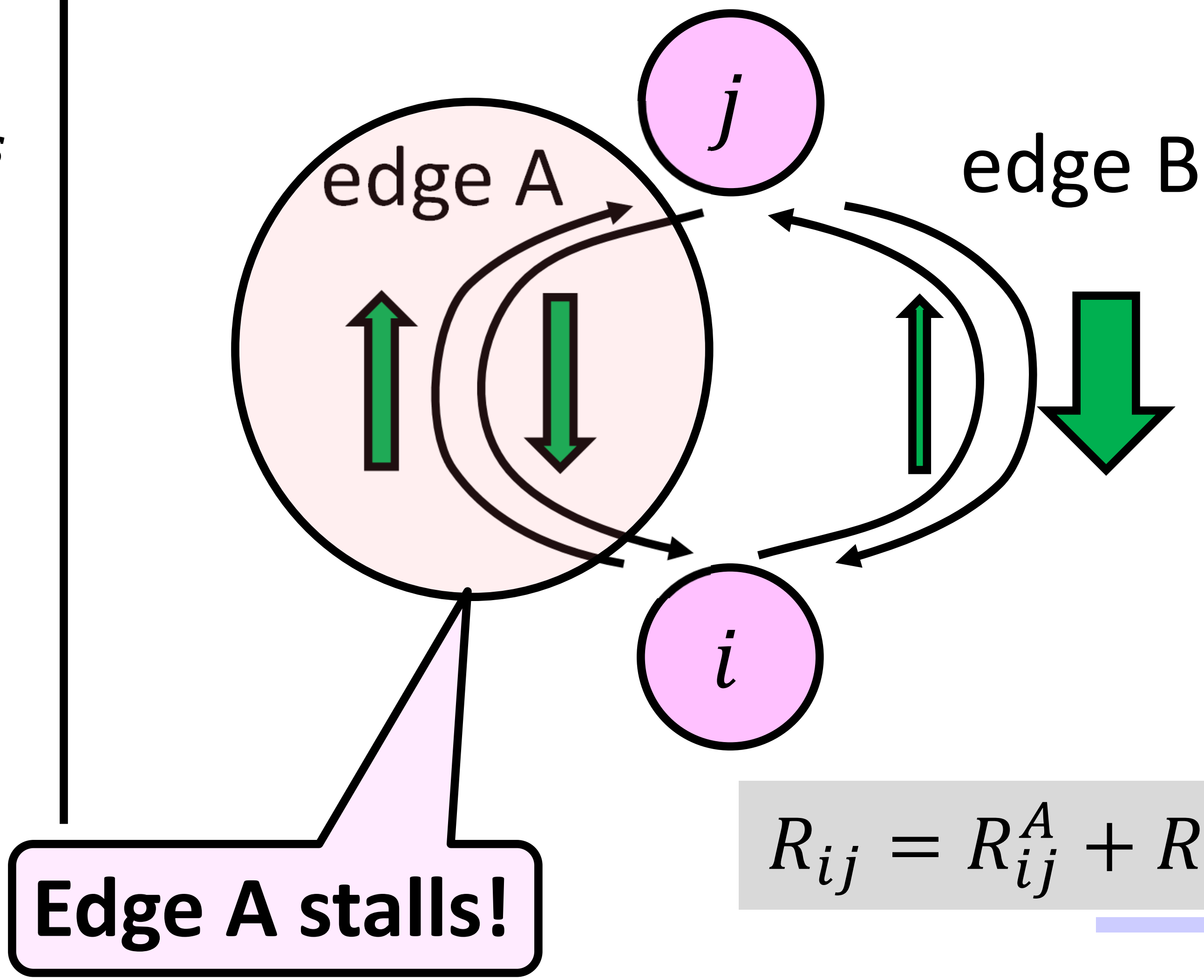
In general nonequilibrium stationary states (NESS), no simple connection exists.

Proof idea: decomposing transition

<u>Original</u>



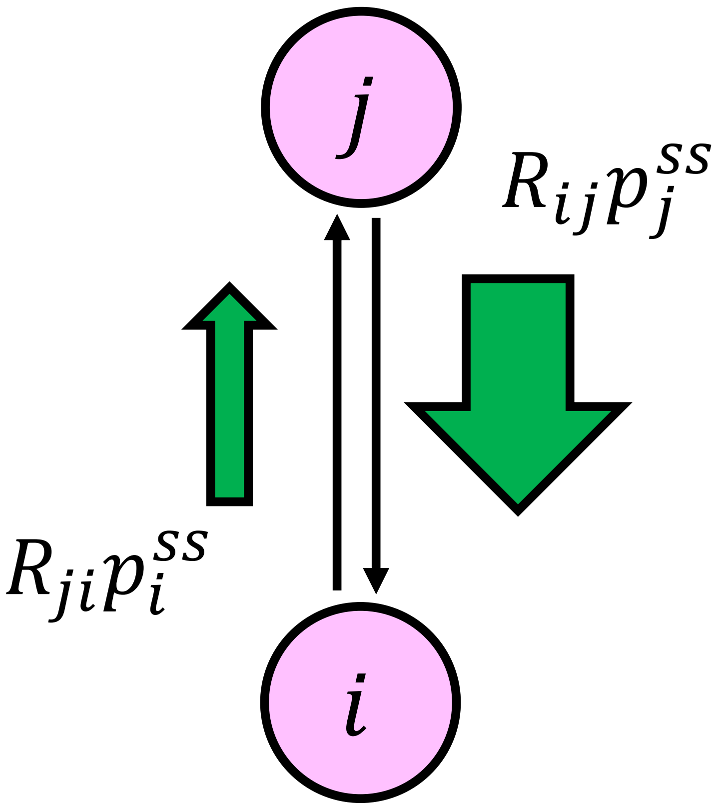
<u>Edge decomposed</u>



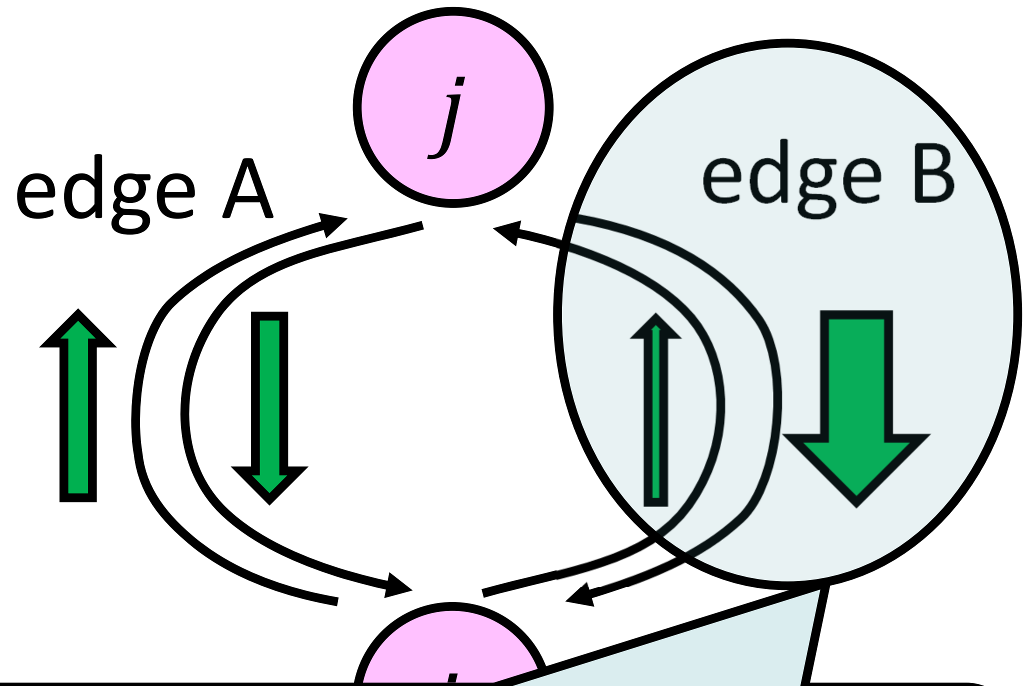
$$R_{ij} = R_{ij}^A + R_{ij}^B$$

Proof idea: decomposing transition

Original



Edge decomposed



R_{ij}^B and R_{ji}^B are fixed.
(unchange under perturbation)

Parameter dependence under decomposition

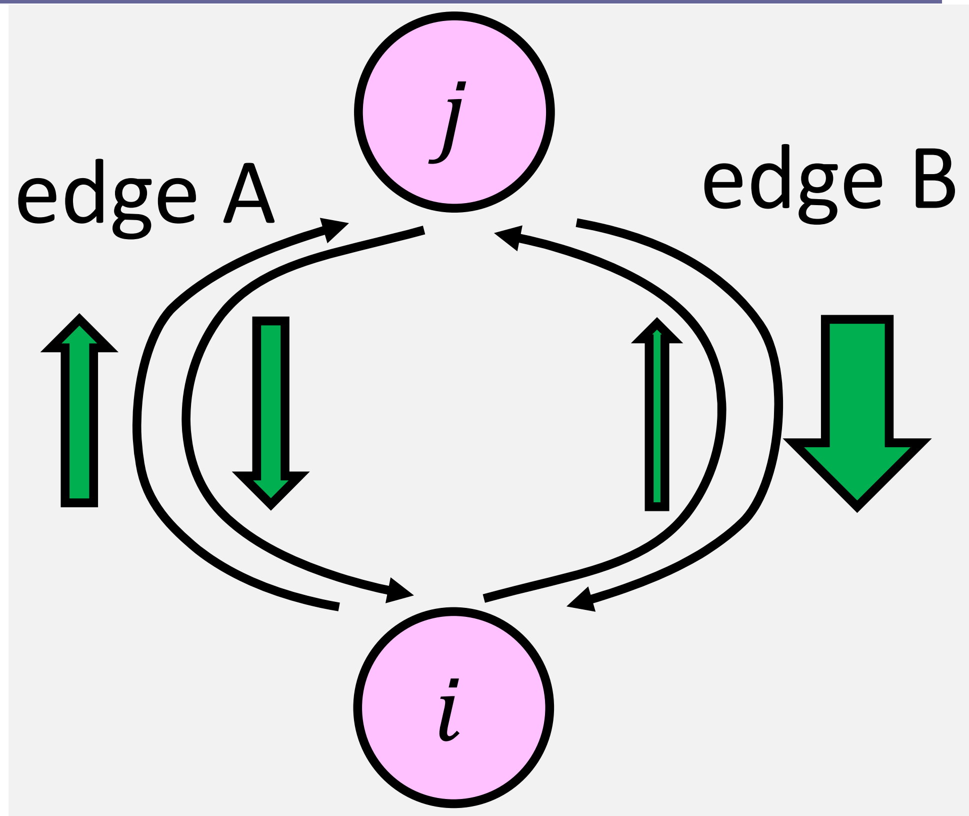
$$x_{ij} = \ln \frac{R_{ij}}{R_{ji}}, \qquad x_{ij}^A = \ln \frac{R_{ij}^A}{R_{ji}^A}$$

Since edge B is fixed, $\boldsymbol{\Delta R_{ij} = \Delta R_{ij}^A, \Delta R_{ji} = \Delta R_{ji}^A}$.

Direct calculation shows the Jacobian relation:

$$\frac{dx_{ij}^A}{dx_{ij}} = \frac{1}{R_{ij}^A p_j^{ss}} \left(\frac{d\langle \mathcal{J}_{ij} \rangle_x}{dx_{ij}} - \frac{d\langle I_{ij,x'} \rangle_x}{dx_{ij}} \right)$$

FRR for stalling edge A



Since edge A stalls, we have

$$\frac{1}{2} R_{ij}^{A} p_{j}^{ss} \left\langle C_{ij,x'}^{2} \right\rangle_{x'} = -\frac{d\langle C_{ij,x'} \rangle_{x}}{dx_{ij}^{A}}$$

Deriving FRR for NESS

FRR for edge A: $\frac{1}{2}R_{ij}^{A}p_{j}^{ss}\left\langle C_{ij,x'}^{2}\right\rangle_{x'} = -\frac{d\langle C_{ij,x'}\rangle_{x}}{dx_{ij}^{A}}$

Jacobian relation: $\frac{dx_{ij}^{A}}{dx_{ij}} = \frac{1}{R_{ij}^{A}p_{j}^{ss}}\left(\frac{d\langle \mathcal{J}_{ij}\rangle_{x}}{dx_{ij}} - \frac{d\left\langle I_{ij,x'}\right\rangle_{x}}{dx_{ij}}\right)$

Combining these two, we arrive at FRR for NESS.

$$\frac{2}{\left\langle C_{ij,x'}^{2}\right\rangle_{x'}} = \frac{\frac{d\left\langle I_{ij,x'}\right\rangle_{x}}{dx_{ij}} - \frac{d\left\langle \mathcal{J}_{ij}\right\rangle_{x}}{dx_{ij}}}{\frac{d\langle C_{ij,x'}\rangle_{x}}{dx_{ij}}}$$

Summary

- We introduced time-symmetric current $I_{ij,x}$ and twisted empirical measure $C_{ij,x}$.
- We showed the FRR around stall states:

$$\frac{1}{2}\left\langle I_{ij}^{2}\right\rangle_{x=x^*} = -\left.\frac{\partial\left\langle I_{ij,x^*}\right\rangle_x}{\partial x_{ij}}\right|_{x=x^*}$$

- We showed the FRR around general NESS:

$$\frac{2}{\left\langle C_{ij,x'}^{2}\right\rangle_{x'}} = \frac{\frac{d\left\langle I_{ij,x'}\right\rangle_x}{dx_{ij}} - \frac{d\left\langle \mathcal{J}_{ij}\right\rangle_x}{dx_{ij}}}{\frac{d\left\langle C_{ij,x'}\right\rangle_x}{dx_{ij}}}$$