Kinetic bounds for nonequilibrium systems

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Measuring and Manipulating Non-equilibrium Systems
Nordita – 17.10.2024

Measuring dissipation in small systems

Ciliberto, PRX (2017).
Seifert, Ann. Rev. Cond. Matter (2019).
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Van Vu, Tuan Vo, Hasegawa, PRE (2020).
Van Vu & K. Saito, PRX (2023).
Di Terlizzi et al, Science (2024)
etc...

In this talk:

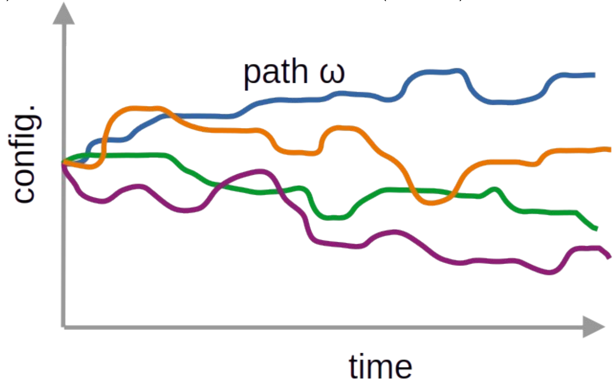
- Life processes uncorrelated with dissipation
- Time-symmetric sector of dynamical fluctuations
- Kinetic Uncertainty Relation (KUR)

... *traffic*

Time-symmetric portion of the path-integral

- **Maes** and van Wieren,
  Time-Symmetric Fluctuations in Nonequilibrium Systems, PRL (2006)
- **Maes**, Netočný and Wynants, Markov Proc.R.F. (2008)
- ...

$$P(\omega) \sim \exp A(\omega) \sim \exp\left[\frac{S(\omega)}{2} - K(\omega)\right]$$



entropy production

Integrated mean jumping rate
= dynamical activity
= ”frenesy”
= “traffic”
= …

Baiesi and Falasco, *Inflow rate, a time-symmetric observable obeying fluctuation relations* (2015)

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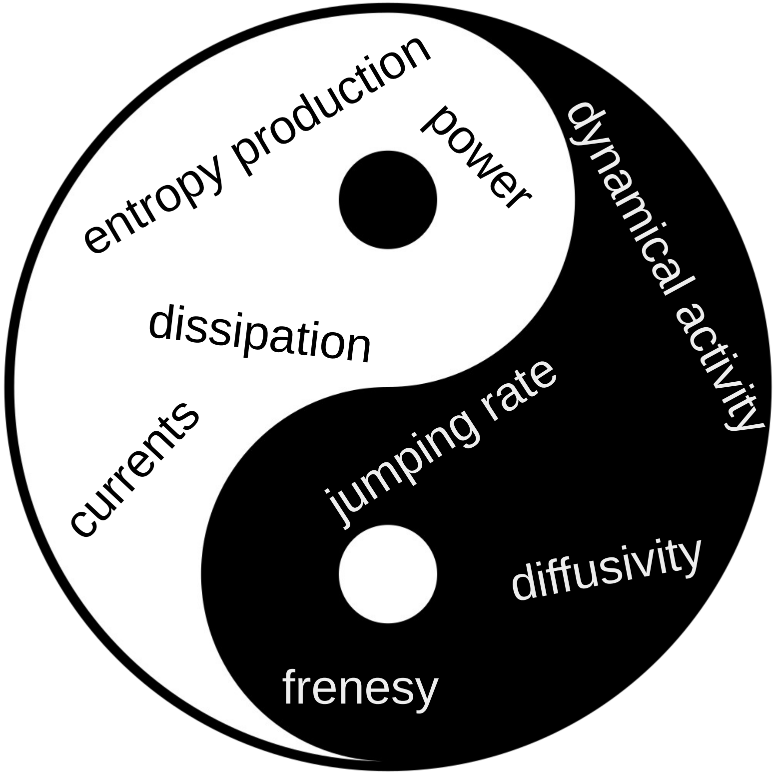
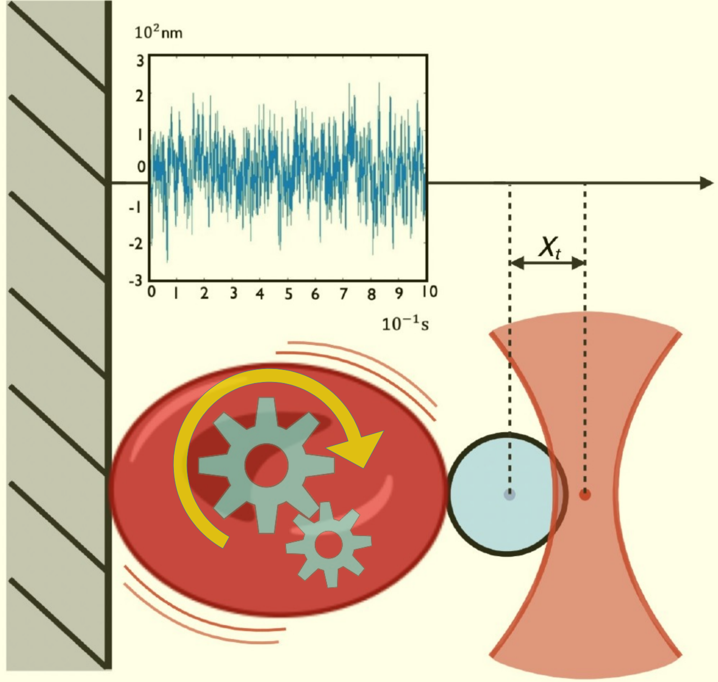
- Time-symmetric sector of dynamical fluctuations
- Kinetic Uncertainty Relation (KUR)



In this talk:

- Life processes uncorrelated with dissipation
- Time-symmetric sector of dynamical fluctuations
- Kinetic Uncertainty Relation (KUR)
- Measure of entropy production in *irreversible* systems

Baiesi, Nishiyama, Falasco, Commun. Phys. 7, 264 (2024)

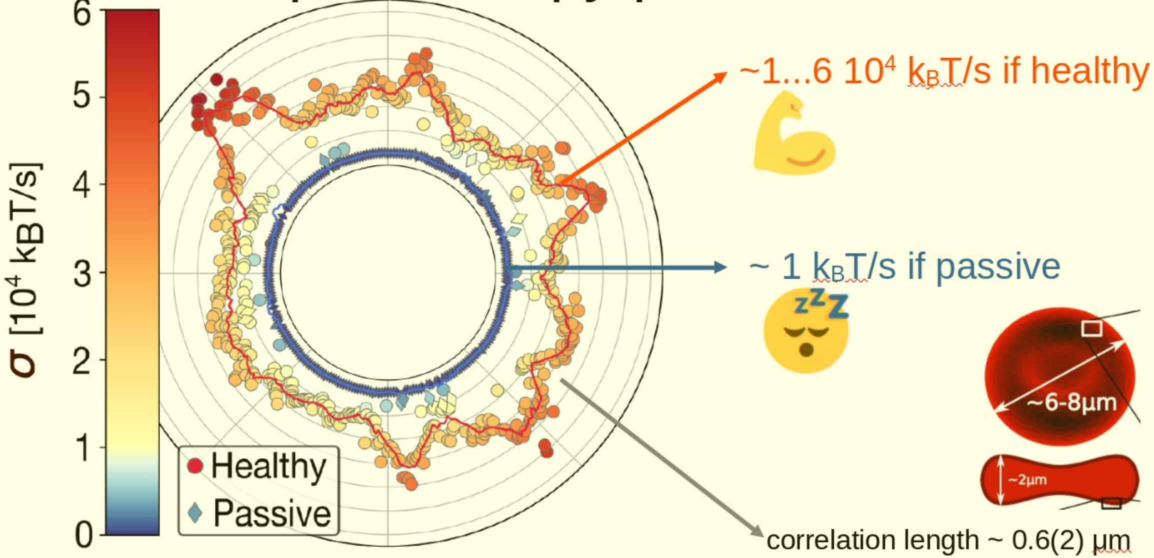


RESEARCH ARTICLE | THERMODYNAMICS

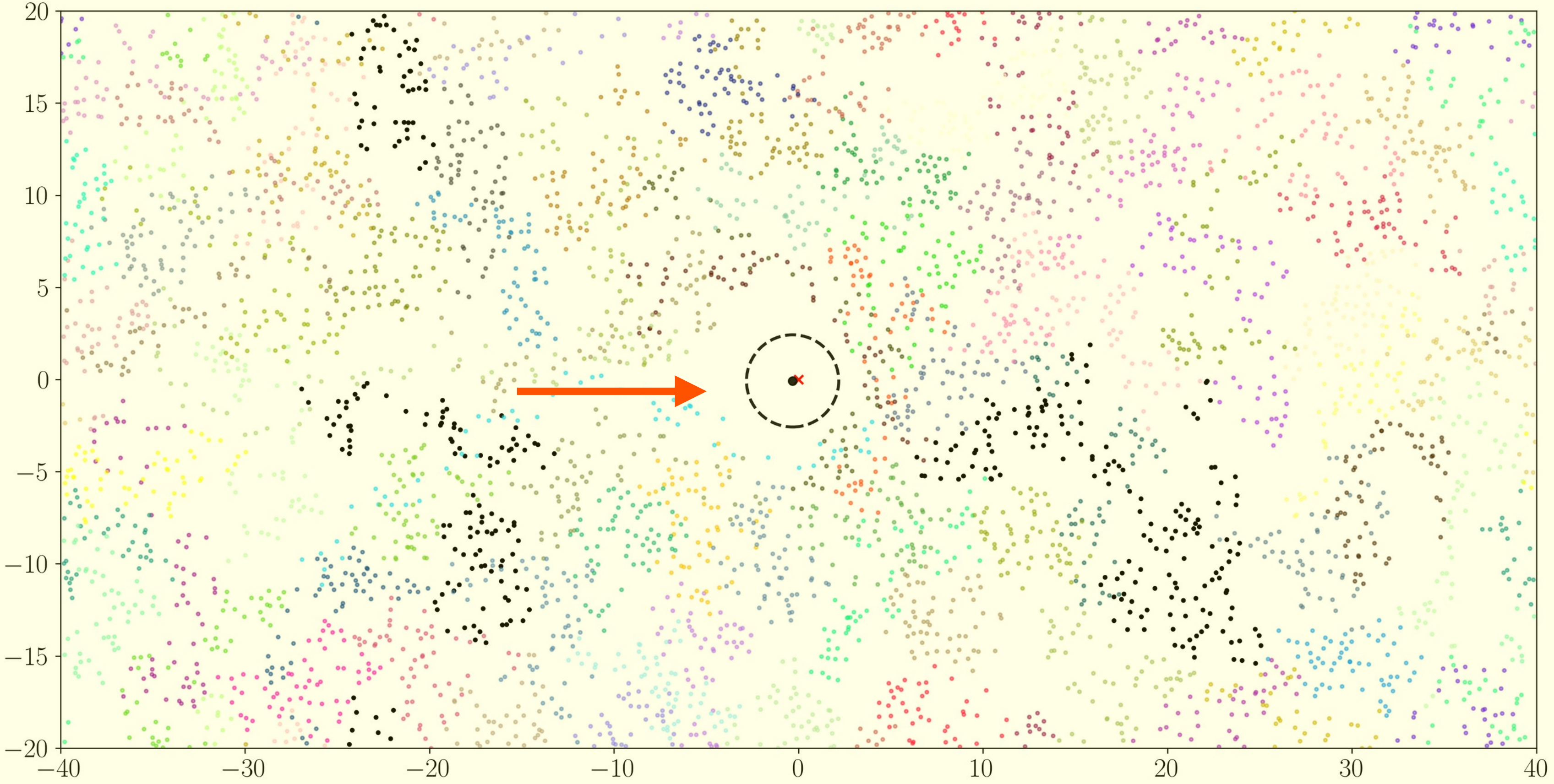
Variance sum rule for entropy production

I. DI TERLIZZI, M. GIRONELLA, D. HERRAEZ-AGUILAR, T. BETZ, F. MONROY, M. BAIESI, AND F. RITORT

Map of entropy production



Inferring nonequilibrium regimes in complex fluids from the probe's variance

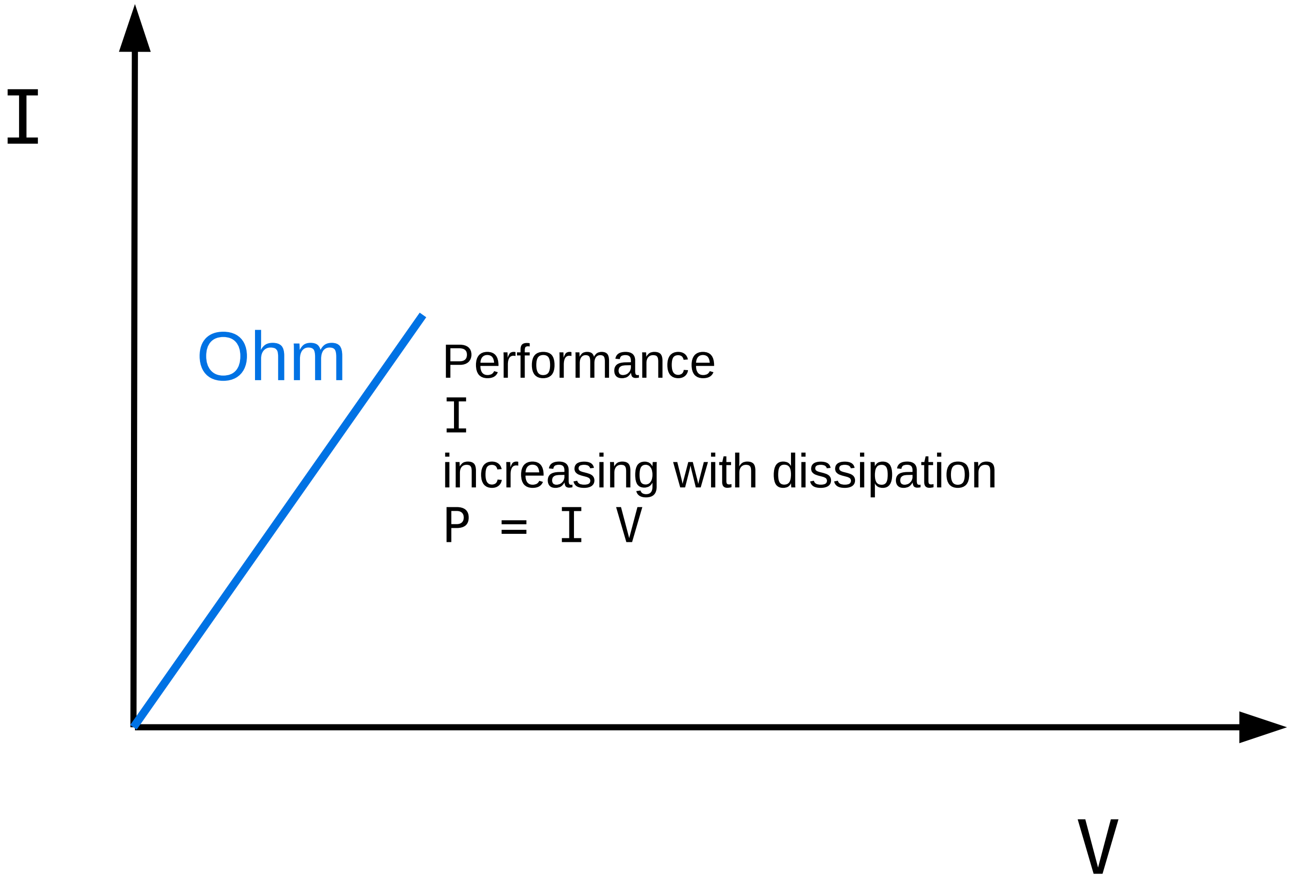


Forastiere, Locatelli, Falasco, Orlandini, Baiesi, *to appear on the arXiv*

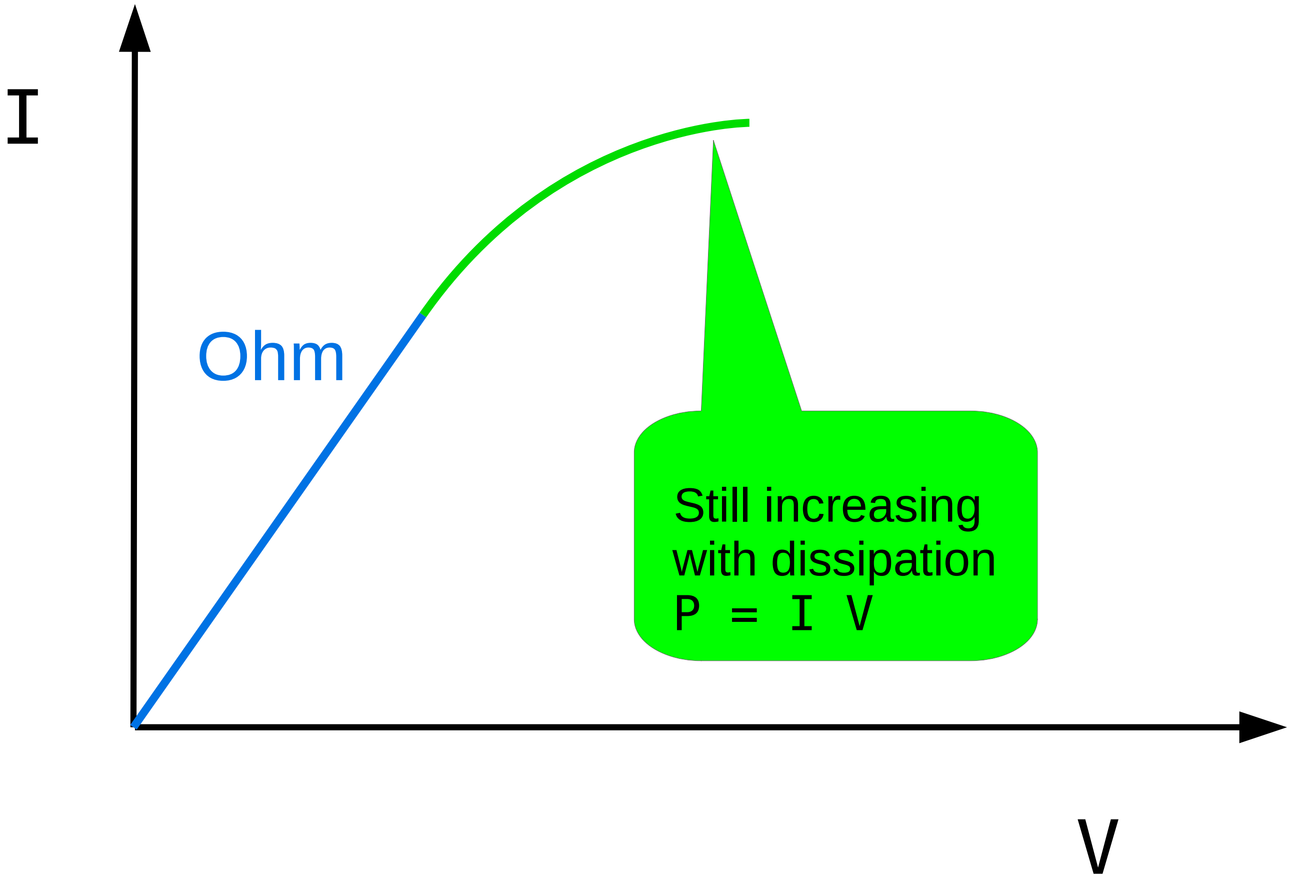
Dissipation = entropy production = irreversibility

- Suffices for understanding nonequilibrium?
- Waste more fuel = better performances?

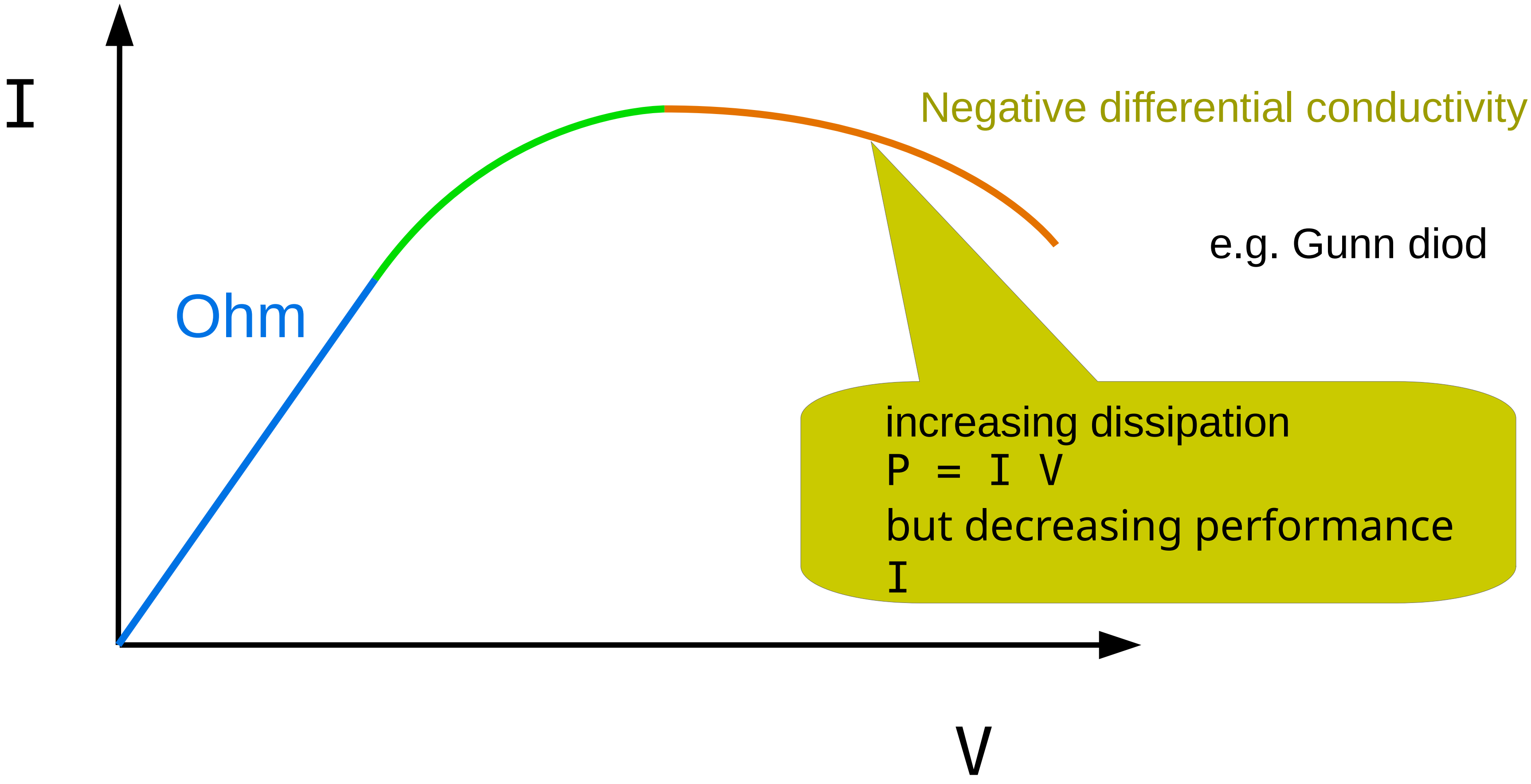
Current-voltage example



Current-voltage example

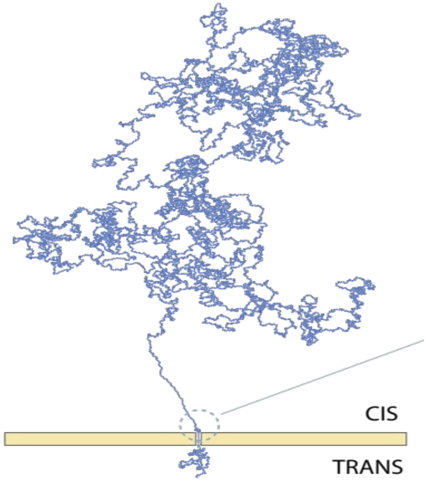


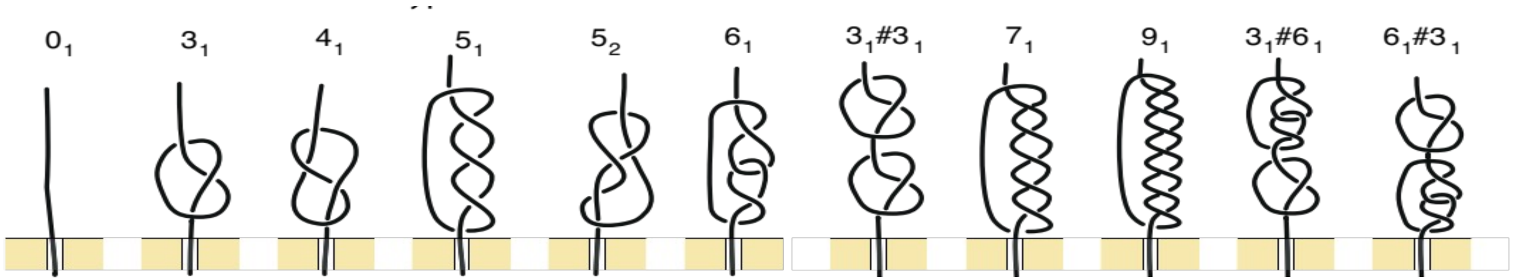
Current-voltage example

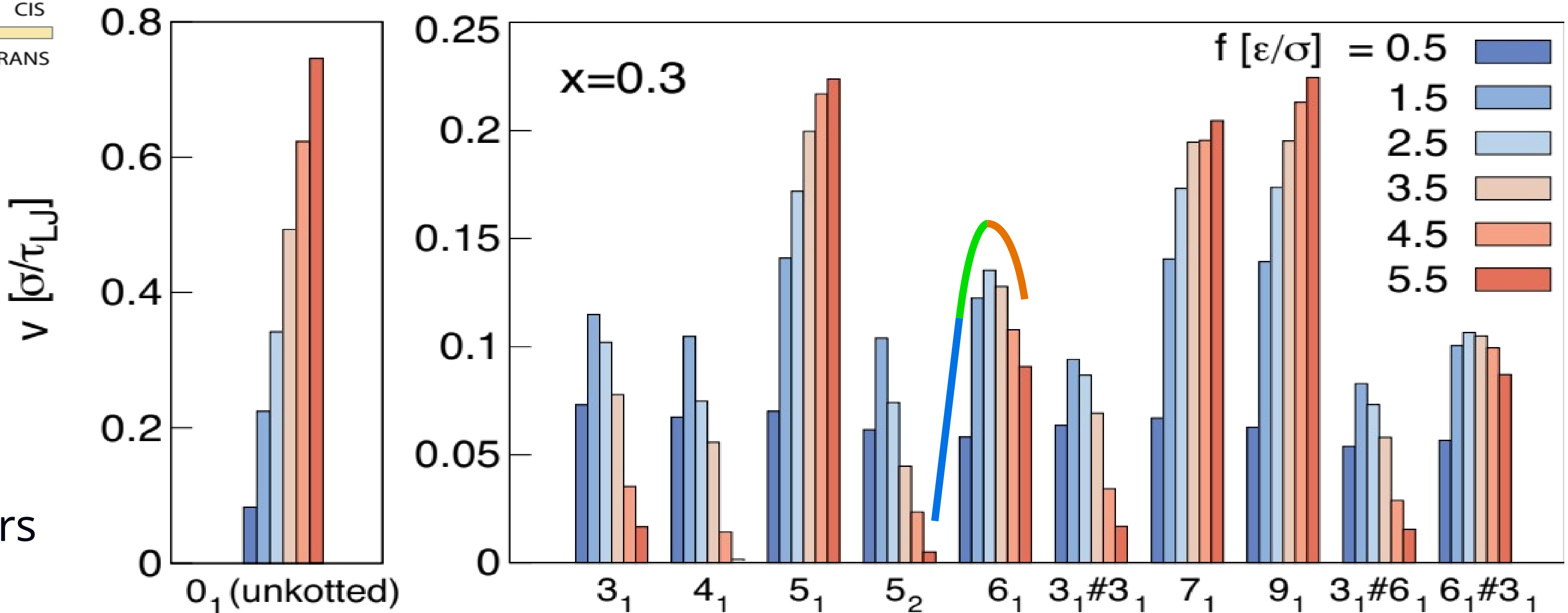


Translocation velocity vs pulling force

from Cristian Micheletti







Suma et al.
ACS Macro Letters
(2015)

When dissipation is not enough: activation

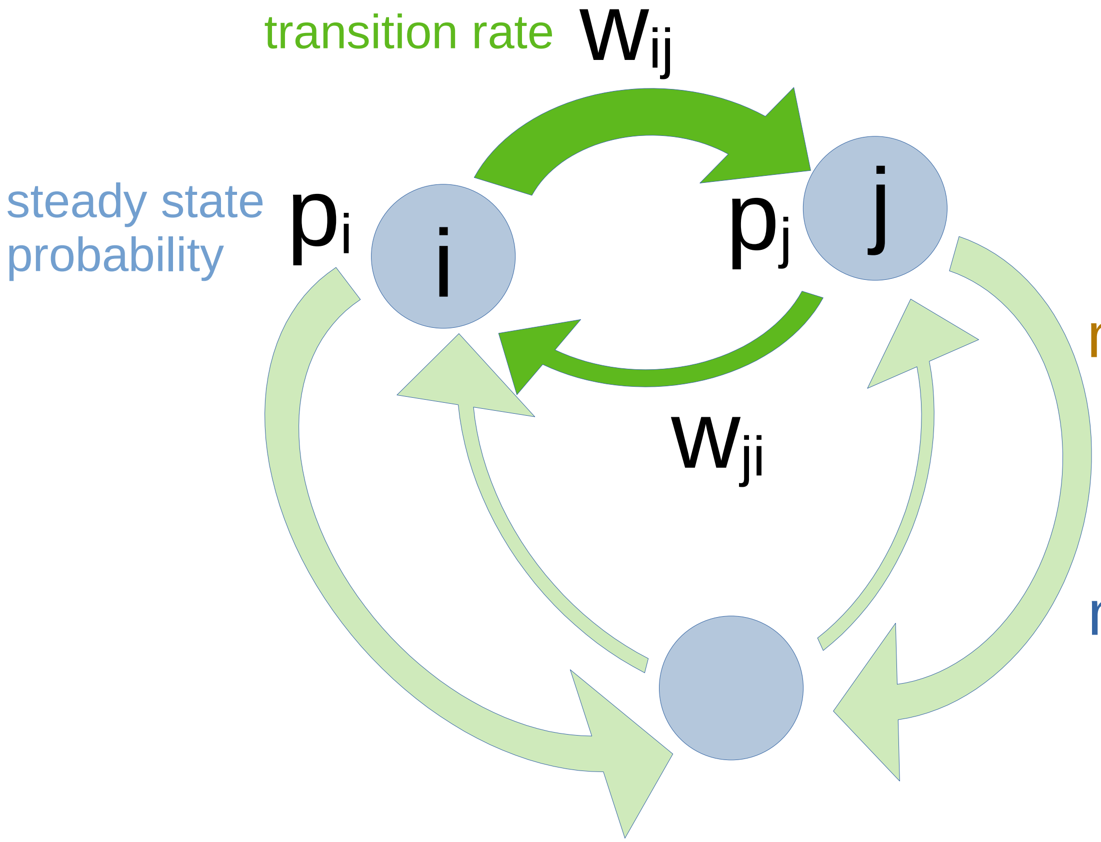
- e.g. in kinetically constrained models of glasses

  (spin can flips only if at least one neighbor is up)

  - Lecomte, Appert-Rolland, van Wijland, Chaotic Properties of Systems with Markov Dynamics, PRL (2005)
  - Merolle, Garrahan, Chandler, Space-time thermodynamics of the glass transition, PNAS (2005)
  - Hedges, Jack, Garrahan, Chandler, Dynamic order-disorder in atomistic models of structural glass formers, Science (2009)
  - ...

- Characterized more by *dynamical activity* (jumping rate of the system) rather than entropy production

Markov jump processes



$$\phi_{ij} = p_i w_{ij}$$

mean entropy production rate

$$\sigma = \sum_{i<j} (\phi_{ij} - \phi_{ji}) \log \frac{\phi_{ij}}{\phi_{ji}}$$

mean jumping rate

$$\kappa = \sum_{i<j} (\phi_{ij} + \phi_{ji})$$

Path weights

$$P(\omega) \sim \exp\left[\frac{S(\omega)}{2} - K(\omega) \right]$$

$$S(\omega) = \ln \rho_{ini} / \rho_{fin} + Q(\omega)/T$$

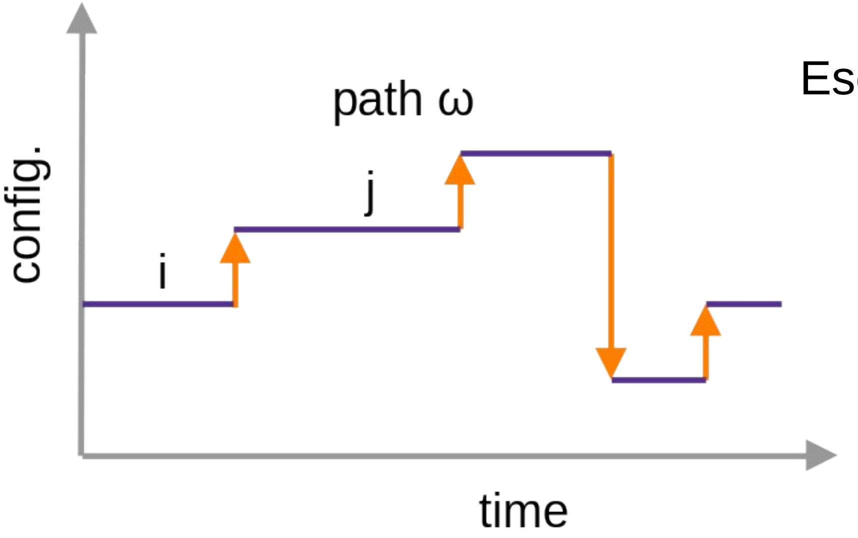
$$\langle S \rangle = t\,\sigma$$

$$K(\omega) = \sum_i \lambda_i t_i$$ Integrated escape rate

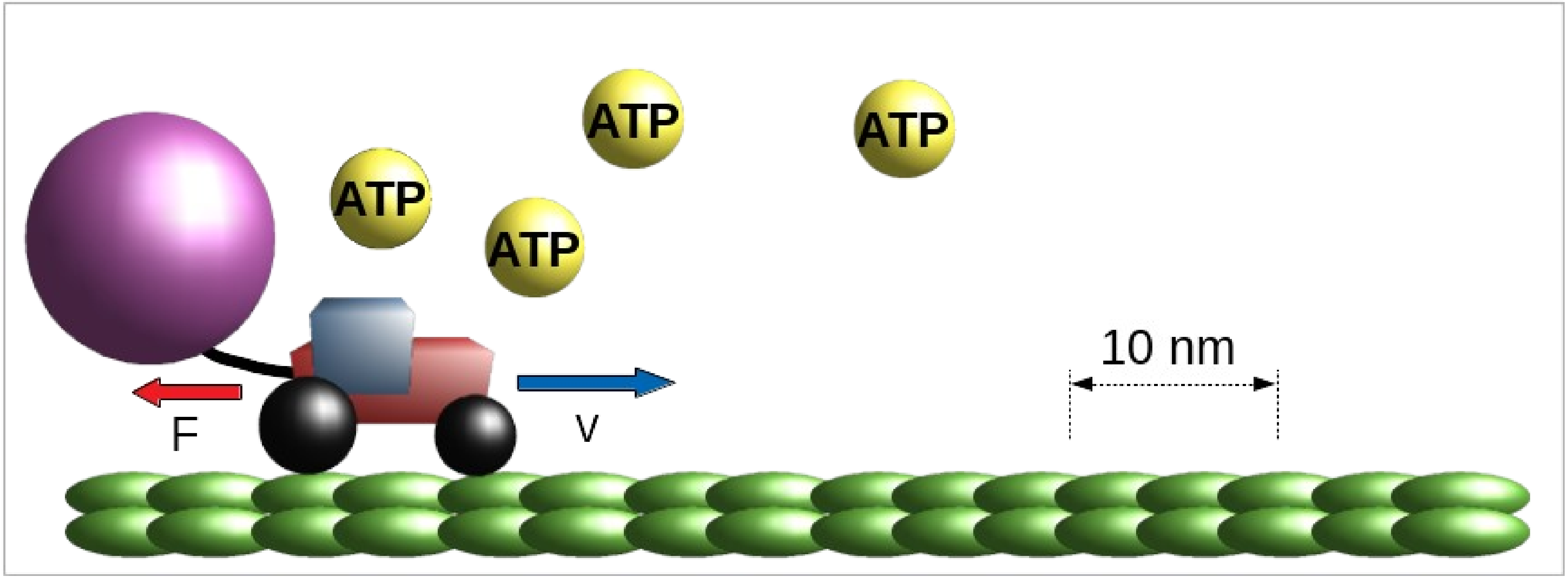
$$\langle K \rangle = t\,\kappa$$

Mean jumping rate

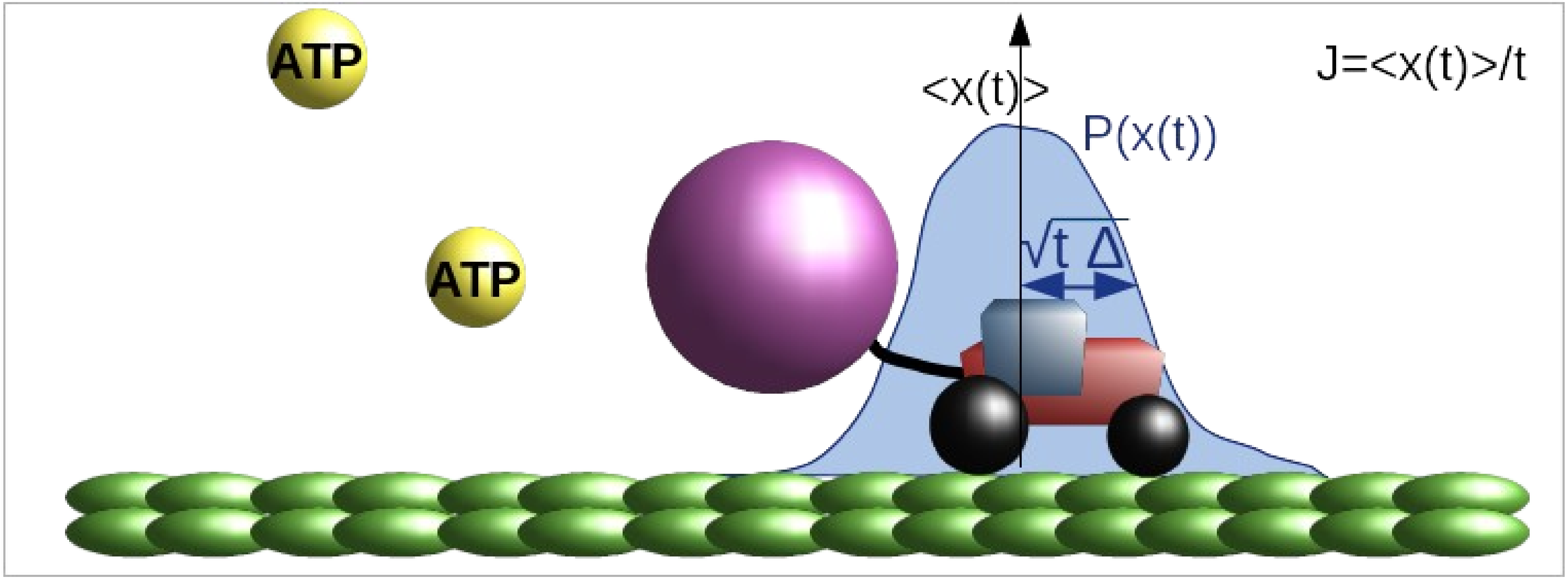
Escape rate $\lambda_i = \sum_j w_{ij}$



Life & nonequilibrium: molecular motor

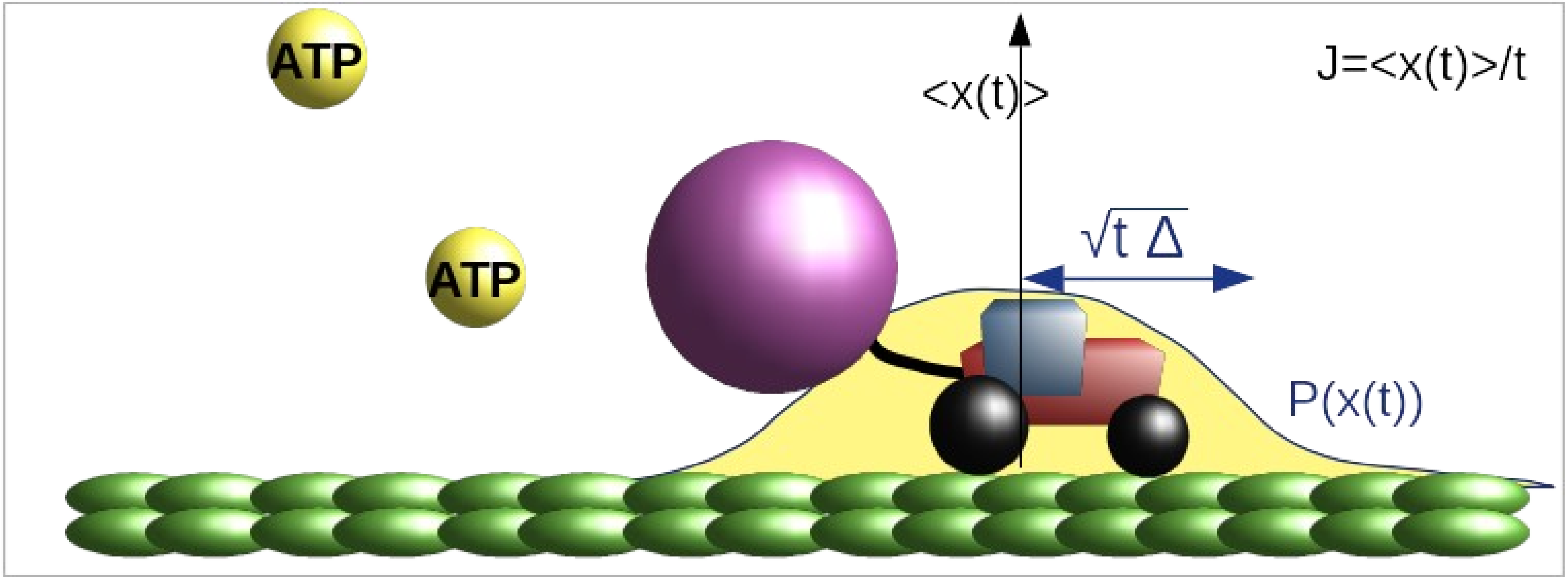


After a time *t*, (a) precision



How does "precision" $g = J^2/\Delta$ depend on resource [ATP] ?

After a time *t*, (a) precision



How does “precision” $g = J^2/\Delta$ depend on resource [ATP] ?

Thermodynamic Uncertainty Relation (TUR)

- $J^2/\Delta \leq \frac{1}{2}\,\sigma$ Barato & Seifert, PRL 2015

σ = mean entropy production rate (natural units, $k_B=1$)

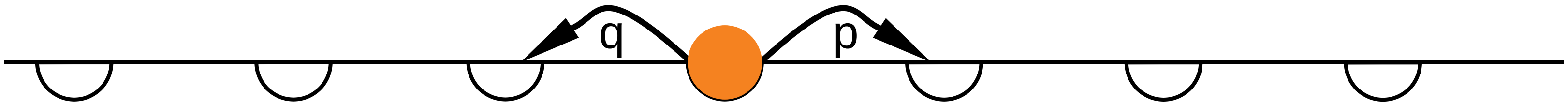
Kinetic Uncertainty Relation (KUR)

- $J^2/\Delta \leq \kappa$ Di Terlizzi & Baiesi, JPA 2019

κ = mean jumping rate

See also: Prech et al, ...clock uncertainty relation..., arXiv:2406.19450

TUR vs KUR: 1d biased random walk



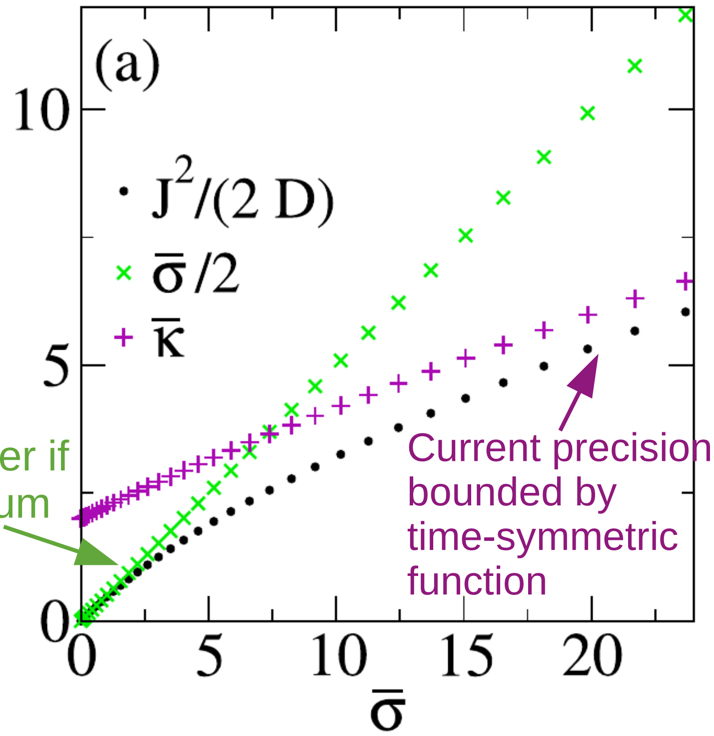
Jumping rate p (right) and q (left)

→ current $J = \langle x \rangle / t = p - q$

→ entropy prod. rate $\sigma = J \log(p/q)$

→ jumping rate $\kappa = p + q$

→ diffusion constant $D = \langle \Delta^2 x \rangle / 2t$

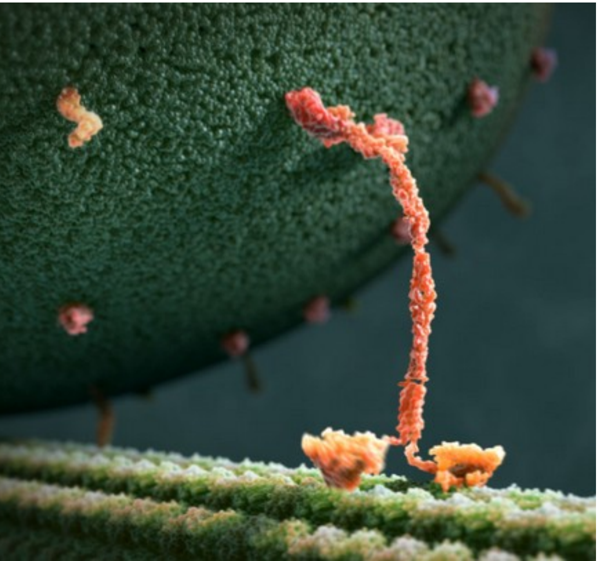


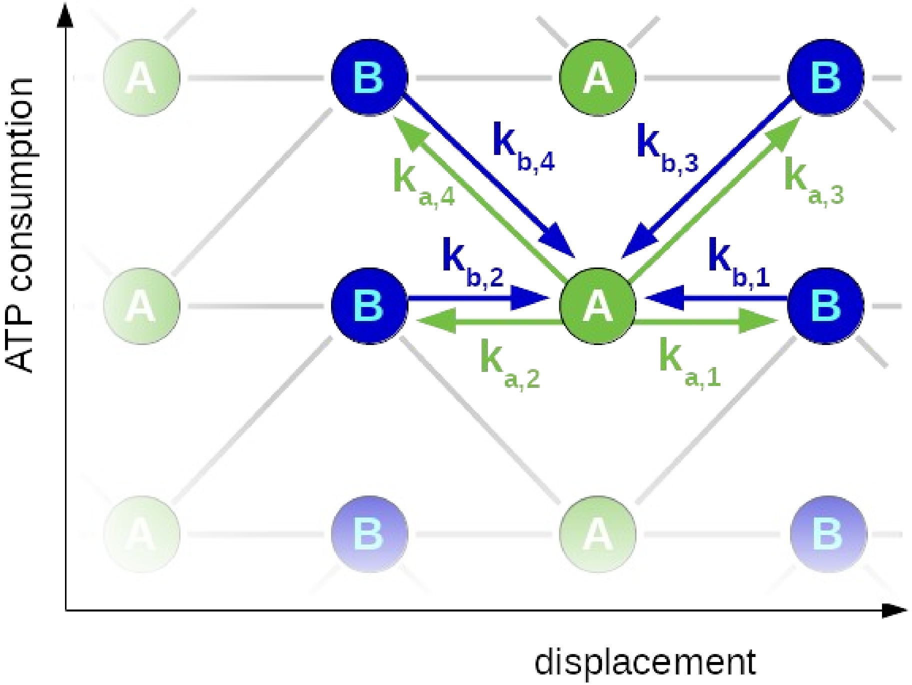
TUR always better if close to equilibrium

Kinesin model

A = both legs down

B = one leg up





Lau, Lacoste and Mallick PRL 2007 & **PRE**

Rates k determined from <u>experiments</u>

Master equation

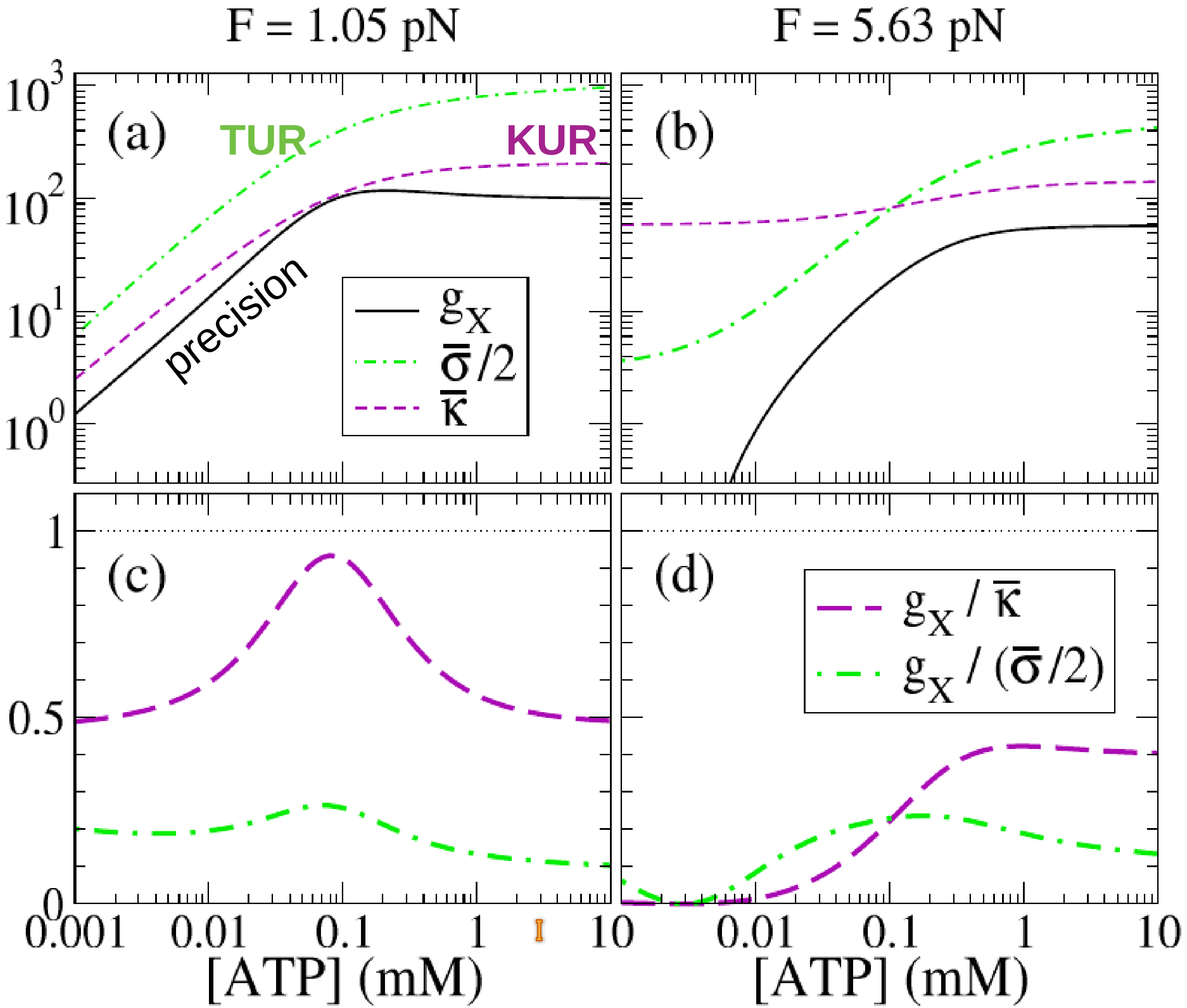
Tilted generator

Cumulants

observing precision

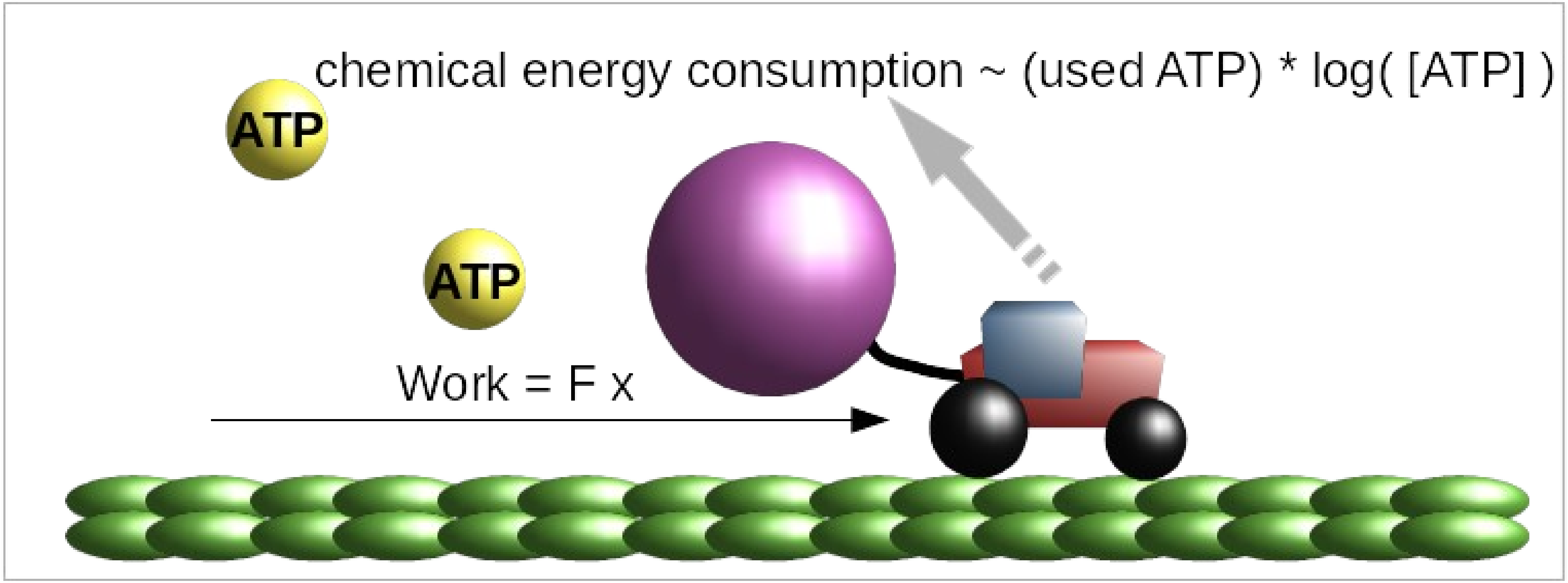
$g=J^2/2D$

of displacement along the tubule



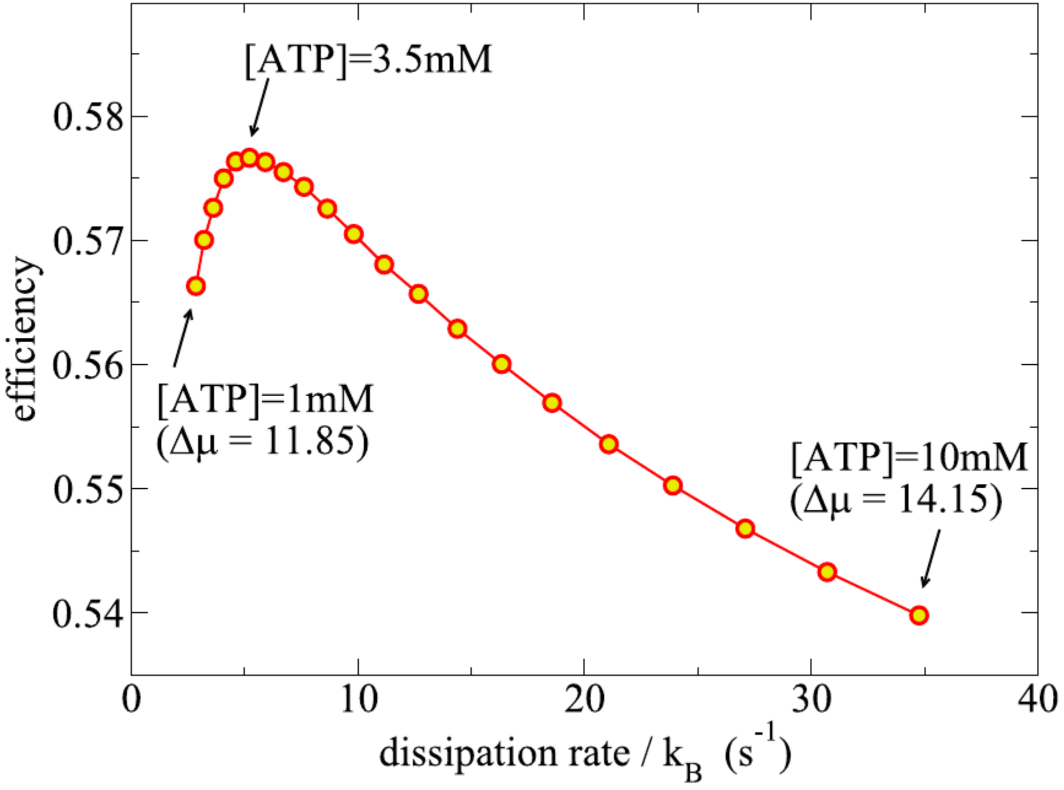
Physiological regime [ATP] > 1 mM

After a time *t*, (b) efficiency



How does **Efficiency = Work / Consumption** depend on resource [ATP] ?

Kinesin efficiency vs dissipation



For force F ~ 4 pN

Baiesi & Maes, J. Phys. Commun (2018)

Performance(s)

- Average speed (absolute performance)
- Efficiency (relative performance)
- Precision
  - $mean^2$ / variance
  - Clock regularity (absolute performance)
- Error minimization
- etc

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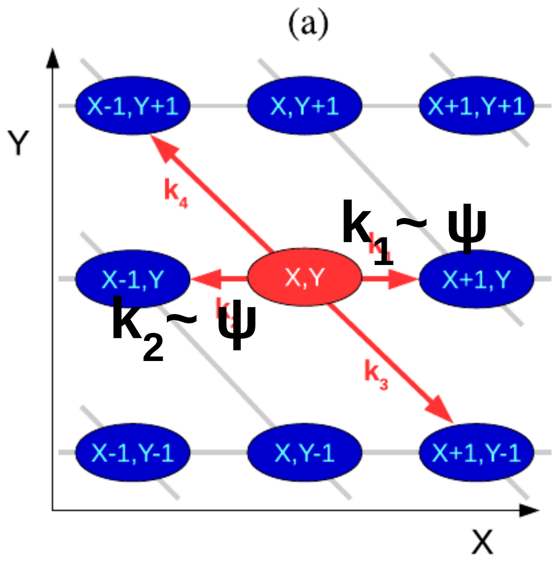
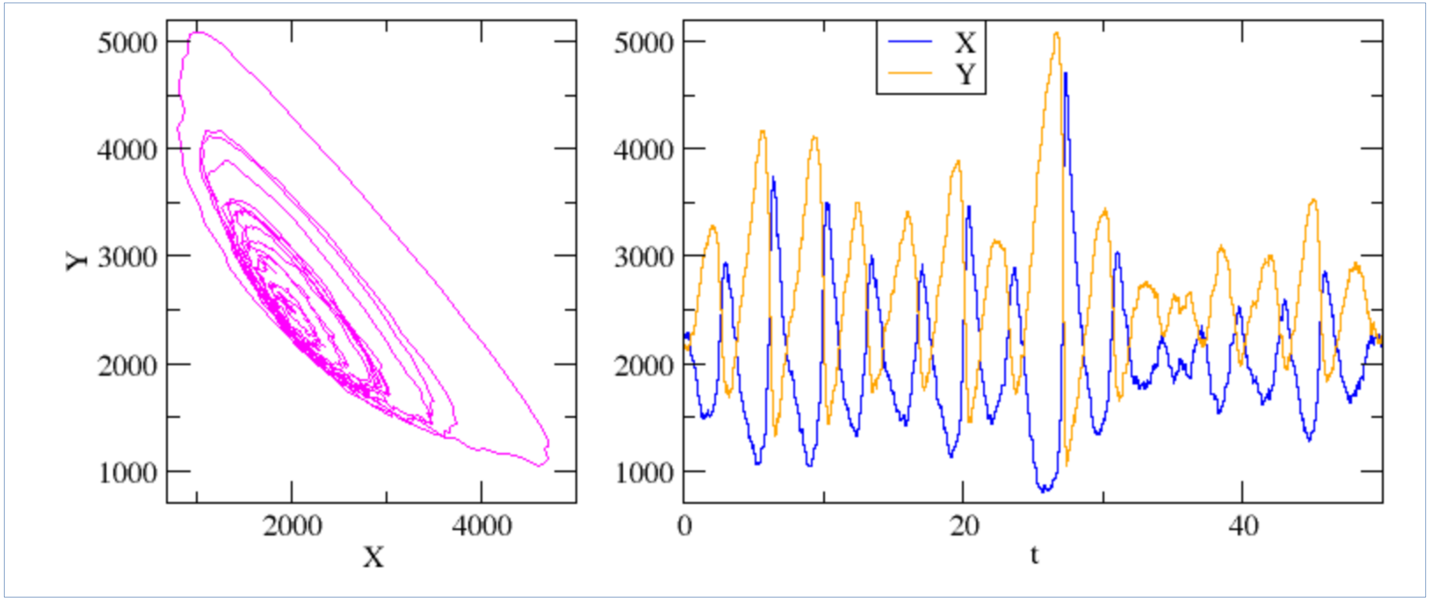
Clock regularity of Brussellator



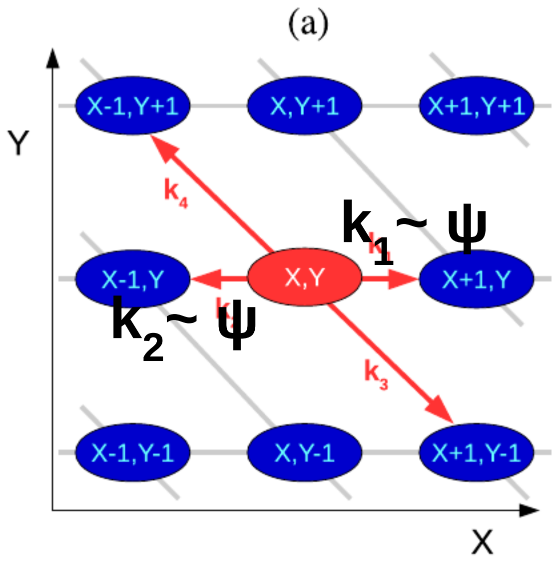
$$k_1(x) = \psi a \Omega$$
$$k_2(x) = \psi X$$
$$k_3(x) = \frac{1}{\Omega^2} X(X-1)Y$$
$$k_4(x) = bX$$

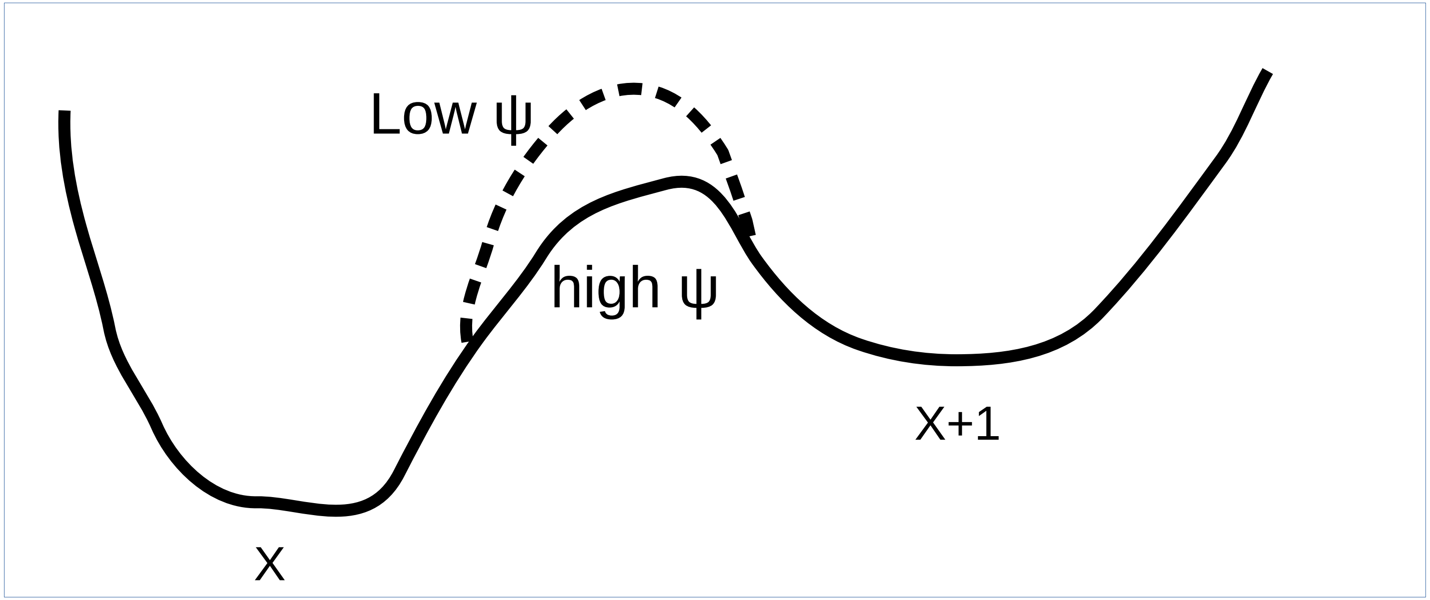


Toy model for a autocatalytic reaction
(Ilya Prigogine's group)

Baiesi & Maes, J. Phys. Commun (2018)

Clock regularity of Brussellator





$$k_1(x) = \psi a \Omega$$ ← just modulating activity via "barrier height" ψ

$$k_2(x) = \psi X$$

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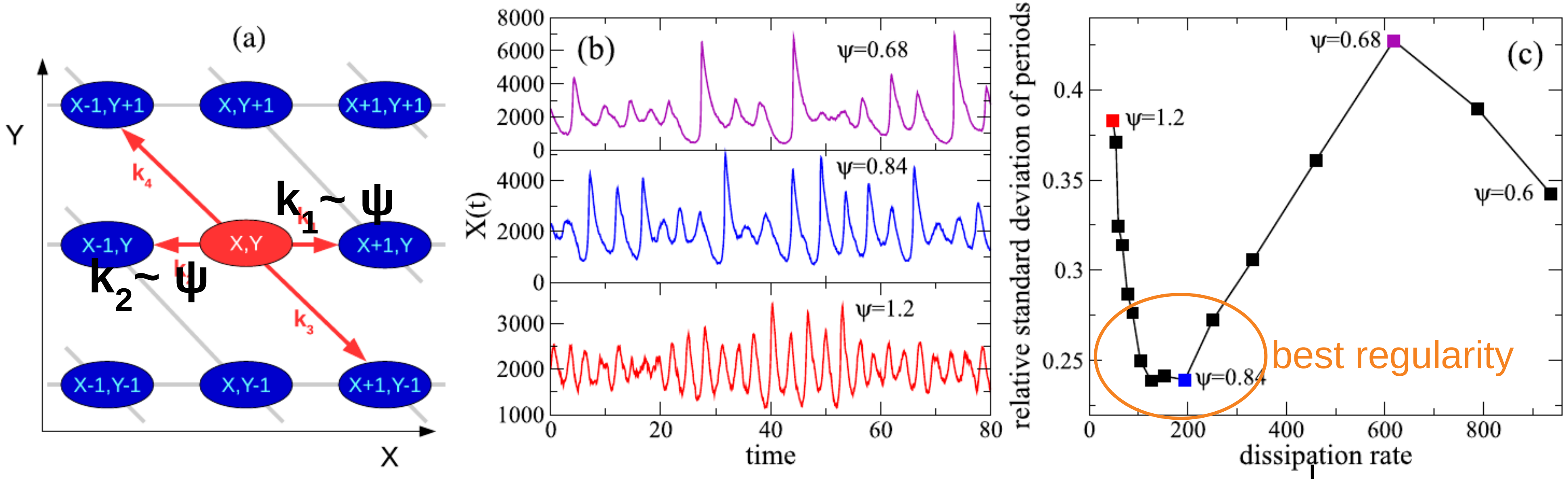
Baiesi & Maes, J. Phys. Commun (2018)

Clock regularity of Brussellator



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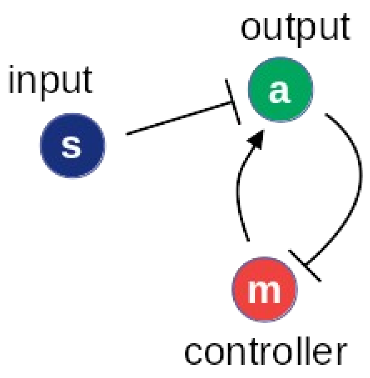
Irreversibility: average
log k(i → j) / k(j → i)
of all transitions “i → j” of the trajectory

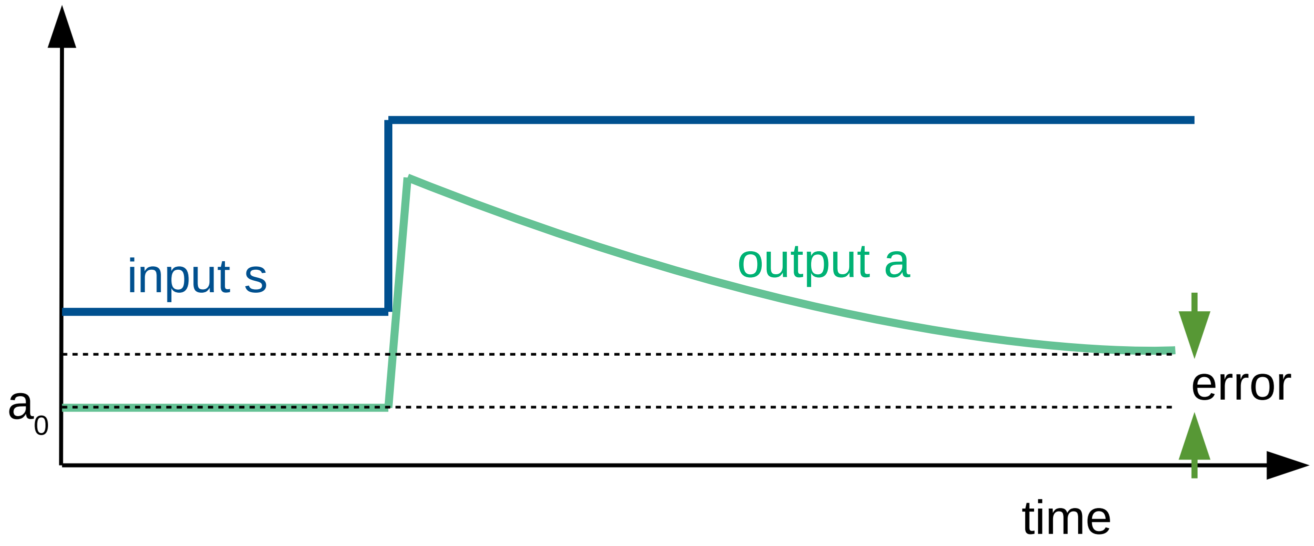
Baiesi & Maes, J. Phys. Commun (2018)

Precision of sensory adaptation

buffer variable **m(t)** reacts to variations of an external stimulus **s(t)** and its feedback keeps **a(t)** close to the optimal a_0.



feedback error = $|\langle a \rangle - a_0|$ = distance from optimum



Baiesi & Maes, J. Phys. Commun. (2018)

Lan, Sartori, Neumann, Sourjik and Tu, Nat. Phys. 2012 ← focus on entropy production

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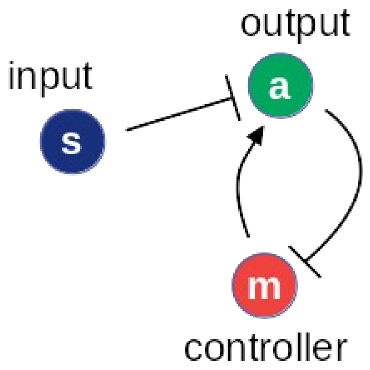

feedback error = **| <a> - a_0 |** = distance from optimum

$$\dot{a} = F_a + \sqrt{2\Delta_a}\,\xi^a(t)$$

$$\dot{m} = F_m + \sqrt{2\Delta_m}\,\xi^m(t)$$

$$F_a = -\omega_a[a - G(s, m)]$$

$$F_m = -\omega_m(a - a_0)[\beta - (1 - \beta)\, C\, \partial_m G(s, m)]$$

$$G(s, m) = (1 + s e^{-2m})^{-1}$$

Baiesi & Maes, J. Phys. Commun. (2018)

Lan, Sartori, Neumann, Sourjik and Tu, Nat. Phys. 2012 ← focus on entropy production

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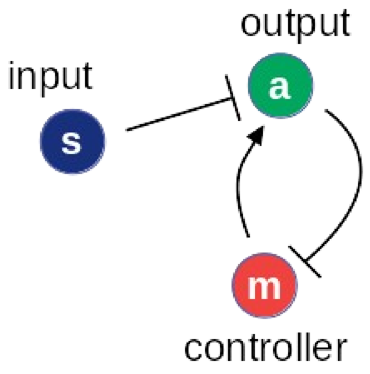
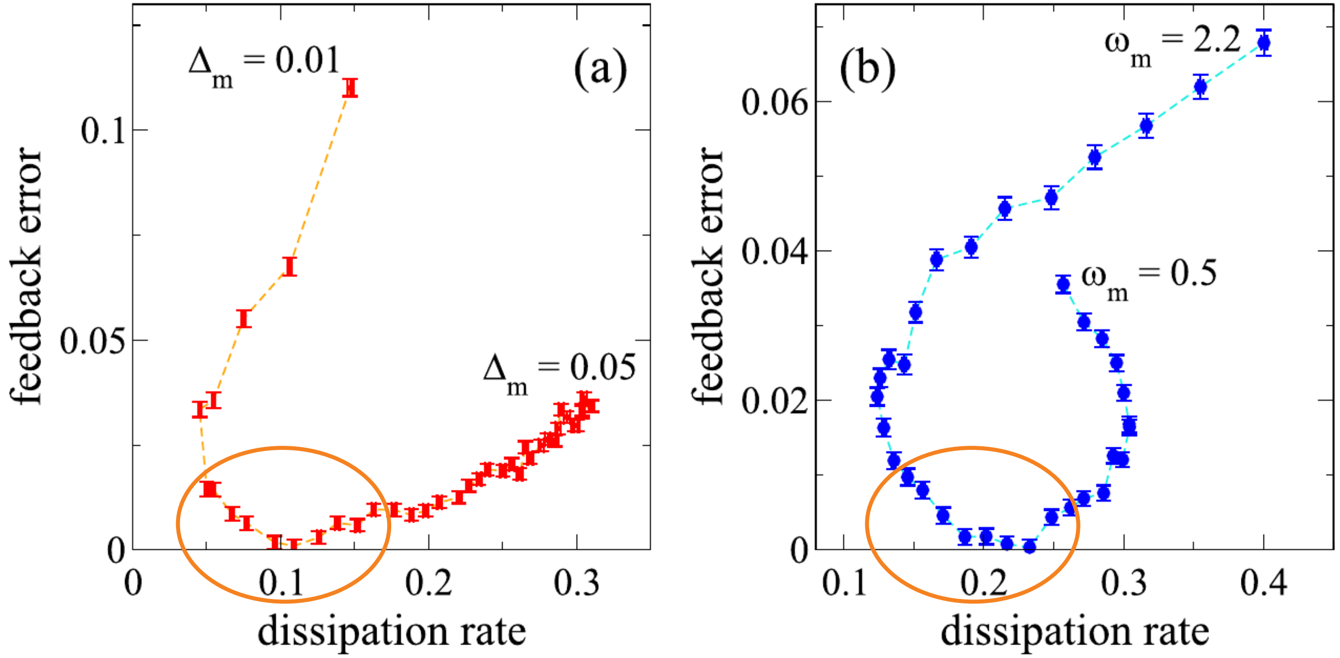


feedback error = **$|\langle a\rangle - a_0|$** = distance from optimum



$$\sigma \equiv \langle F_a \circ da/\Delta_a + F_m \circ dm/\Delta_m \rangle / dt$$

Response theory for nonequilibrium

ω = path

$$P(\omega) \sim \exp A(\omega) \sim \exp[\ \frac{1}{2}S(\omega) - K(\omega)\ ]$$

$$\frac{\partial \langle O(\omega) \rangle_h}{\partial h} = \frac{1}{2}\langle S_h(\omega) O(\omega) \rangle - \langle K_h(\omega) O(\omega) \rangle$$

Susceptibility of observable *O* to perturbation *h*

Unperturbed correlation with entropy produced S_h, in excess by perturbation h

Unperturbed correlation with frenesy (over T) K_h, in excess by perturbation h

One of the many fluctuation-response relations for nonequilibrium systems

Review: Baiesi and Maes, New J. Phys. (2013)

Response theory for ~~non~~equilibrium

ω = trajectory

$$\frac{\partial \langle O(\omega)\rangle_h}{\partial h} = \frac{1}{2}\langle S_h(\omega) O(\omega)\rangle - \langle K_h(\omega) O(\omega)\rangle$$

Susceptibility of observable *O* to perturbation *h*

Unperturbed correlation with entropy produced S_h, in excess by perturbation h

Kubo formula:

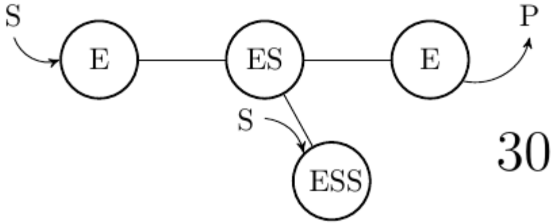
in equilibrium one may consider only entropy production

Negative differential response

in chemical reactions

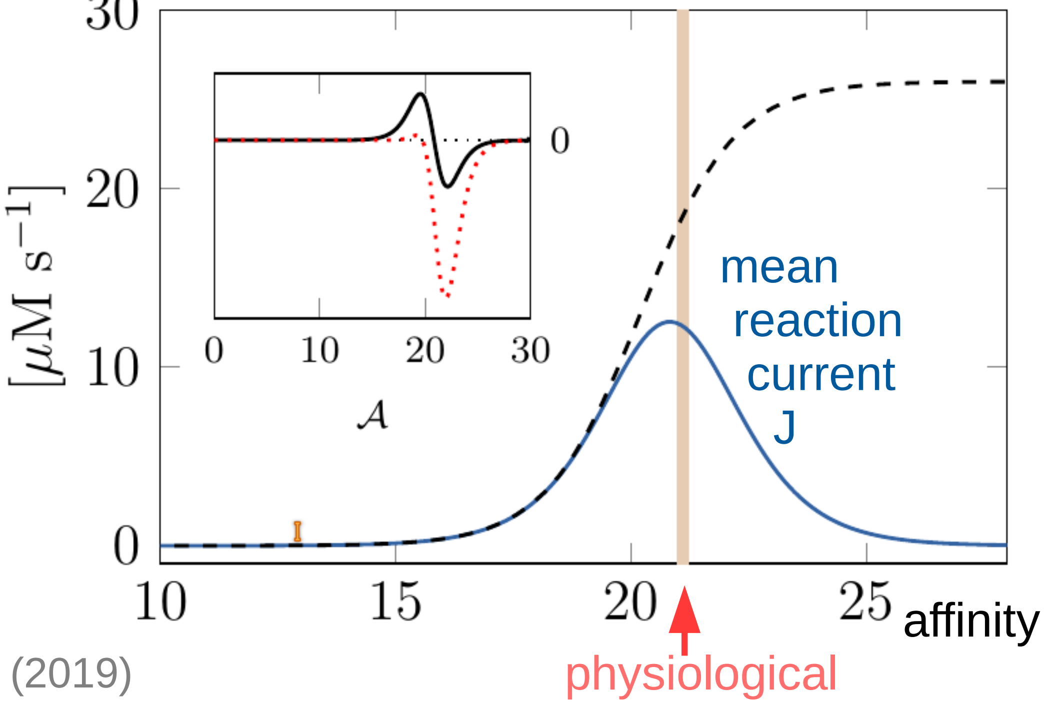
$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \mathrm{ES} \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} \mathrm{E} + \mathrm{P}$$

$$\mathrm{ES} + \mathrm{S} \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} \mathrm{ESS}$$



Substrate inhibition is estimated
to occur in 20% of known enzymes

synthesis of dopamine



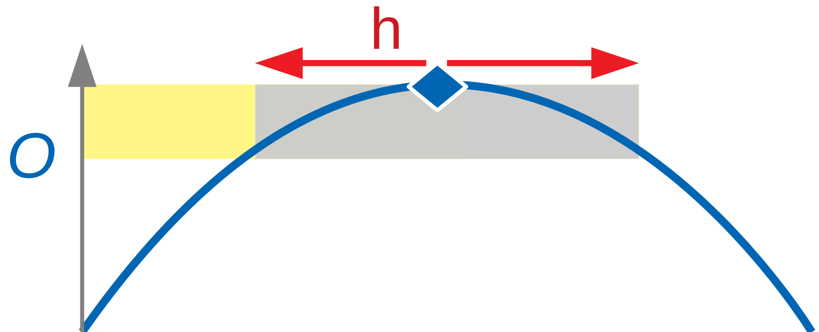
Falasco, Cossetto, Penocchio, Esposito, New J. Phys. (2019)

Omeostasis

- Biological systems may enjoy a better stability where entropic and frenetic terms of linear response cancel each other

synthesis of dopamine.

$$\frac{\partial\langle O(\omega)\rangle}{\partial h} = \frac{1}{2}\langle S_h(\omega)O(\omega)\rangle - \langle K_h(\omega)O(\omega)\rangle$$



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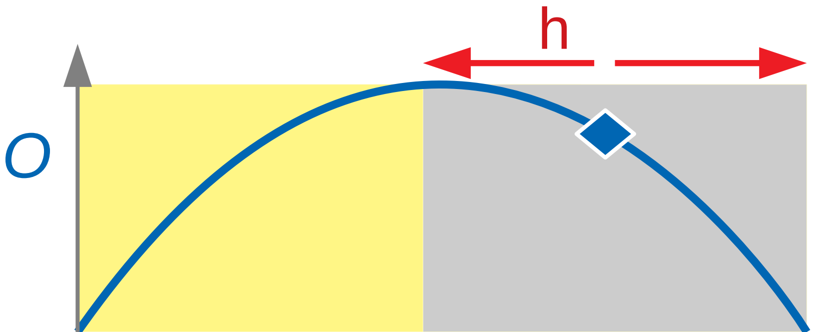
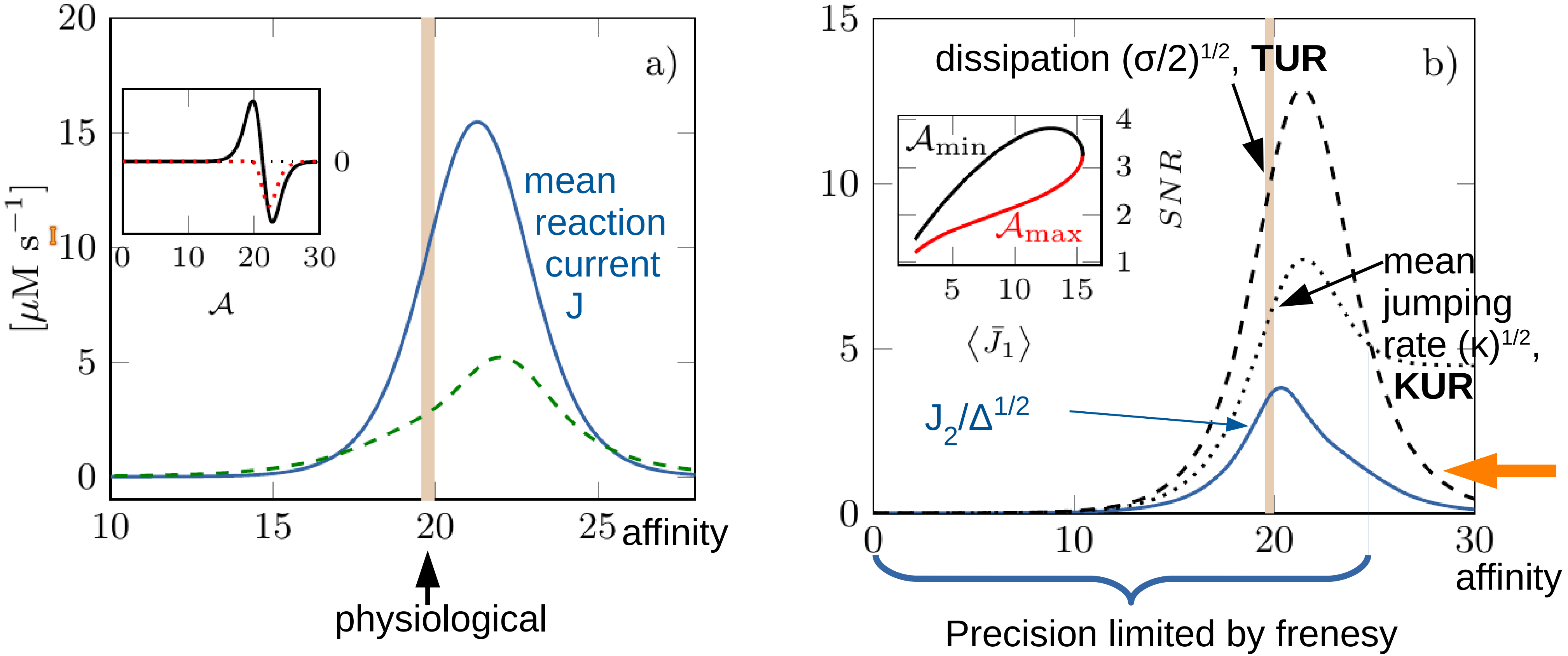


Negative differential response

(in synthesis of serotonin)

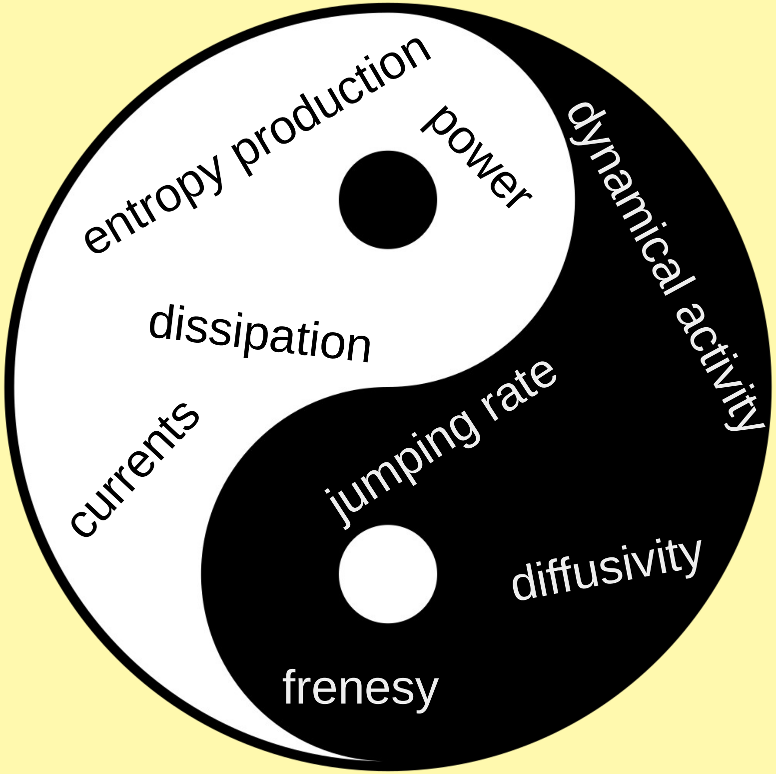


Falasco, Cossetto, Penocchio, Esposito, New J. Phys. (2019)

Summary (1)

- Time-antisymmetric and time-symmetric quantities characterize nonequilibrium systems

Time antisymmetric



Time symmetric

- **Kinetic uncertainty relation**, Ivan Di Terlizzi & Marco Baiesi, J. Phys. A 52 (2019) 02LT03

- **Life efficiency does not always increase with the dissipation rate**, Marco Baiesi & Christian Maes, J. Phys. Commun. 2 (2018) 045017

- **An update on the nonequilibrium linear response**, Baiesi and Maes, New J. Phys. 15 (2013) 013004

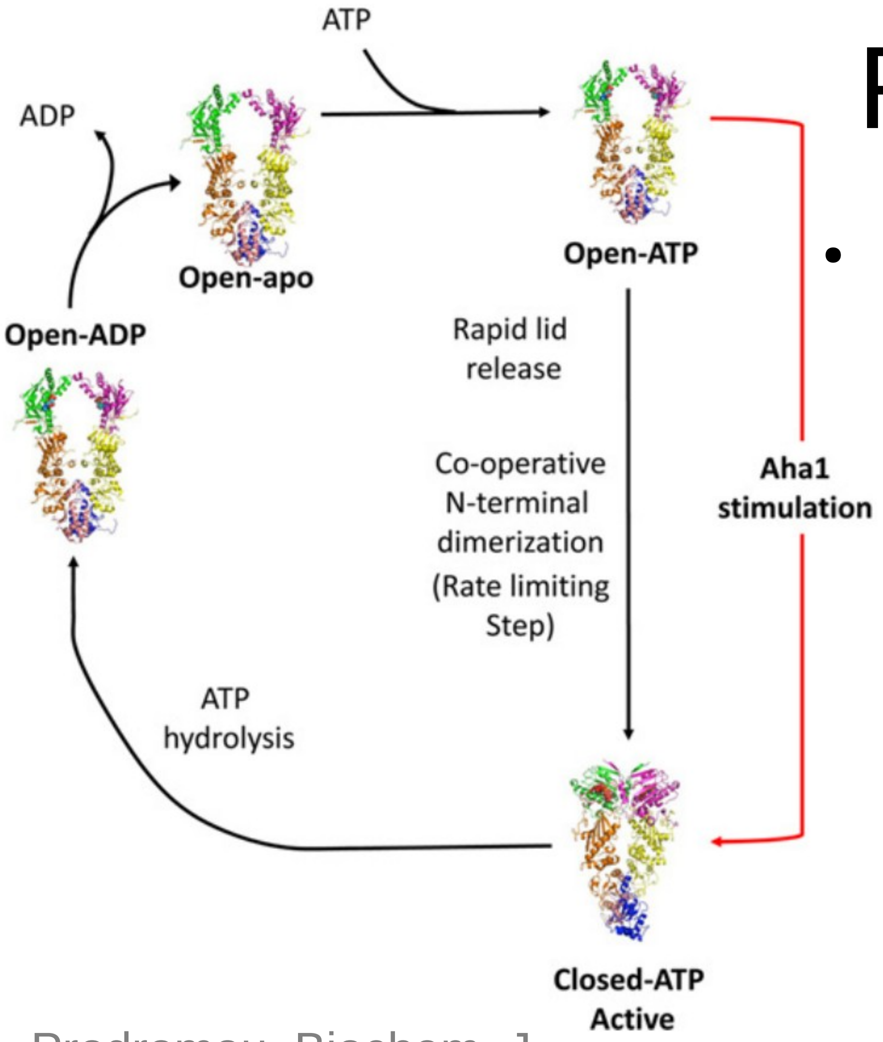
In this talk:

- Life processes uncorrelated with dissipation
- Time-symmetric sector of dynamical fluctuations
- Kinetic Uncertainty Relation (KUR)

→ Measure of entropy production in *irreversible* systems

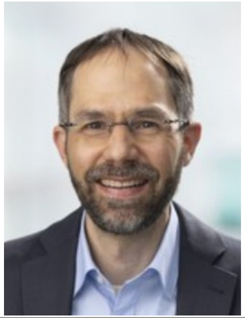
Baiesi, Nishiyama, Falasco,
"*Effective estimation of entropy production with lacking data*"
Commun. Phys. 7, 264 (2024)

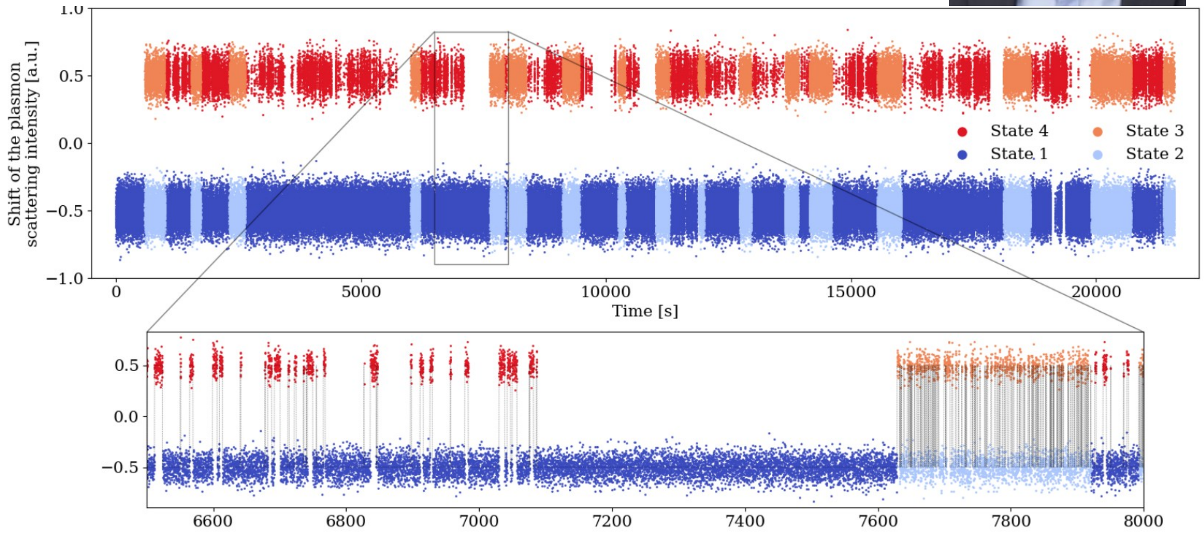
Reconstructing jumping



Prodromou, Biochem. J. (2016)

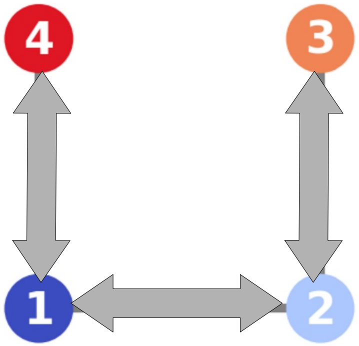
- Hsp90 chaperone, FRET data from Thorsten Hugel (Freiburg)

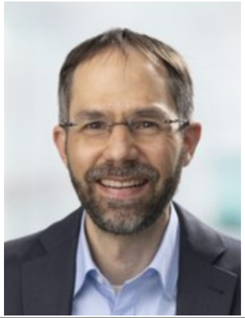


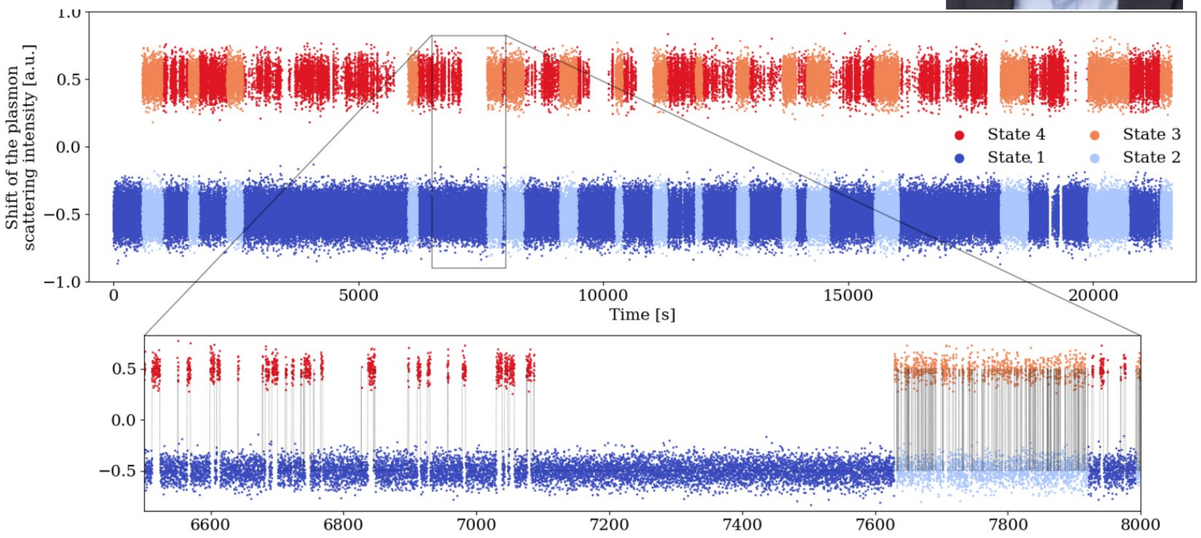


Reconstructing jumping

- Hsp90 chaperone, FRET data from Thorsten Hugel (Freiburg)
- Hidden Markov model reconstruction



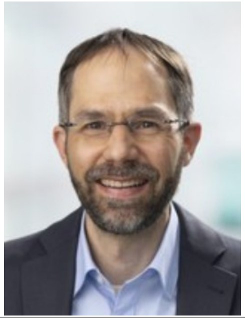




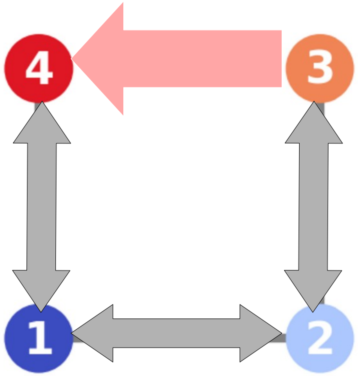
Tancredi et al, New. J. Phys. 2024

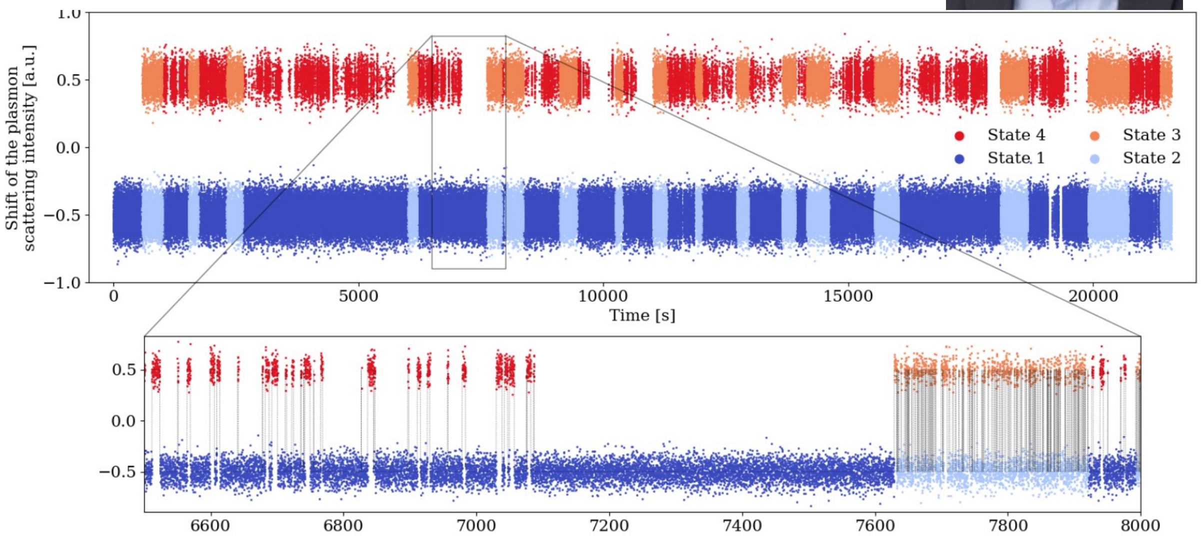
Reconstructing jumping

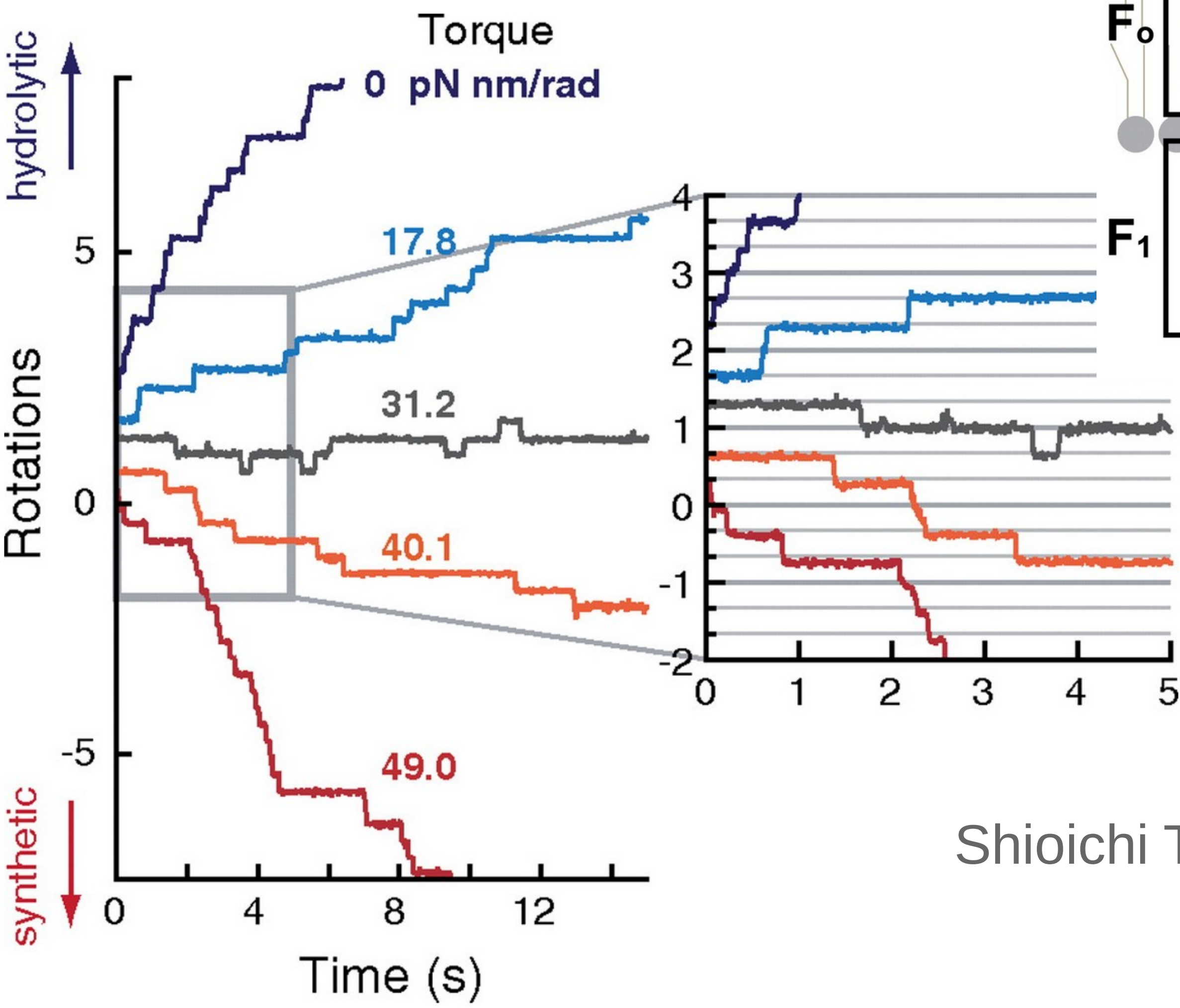
- Hsp90 chaperone, FRET data from Thorsten Hugel (Freiburg)
- Hidden Markov model reconstruction

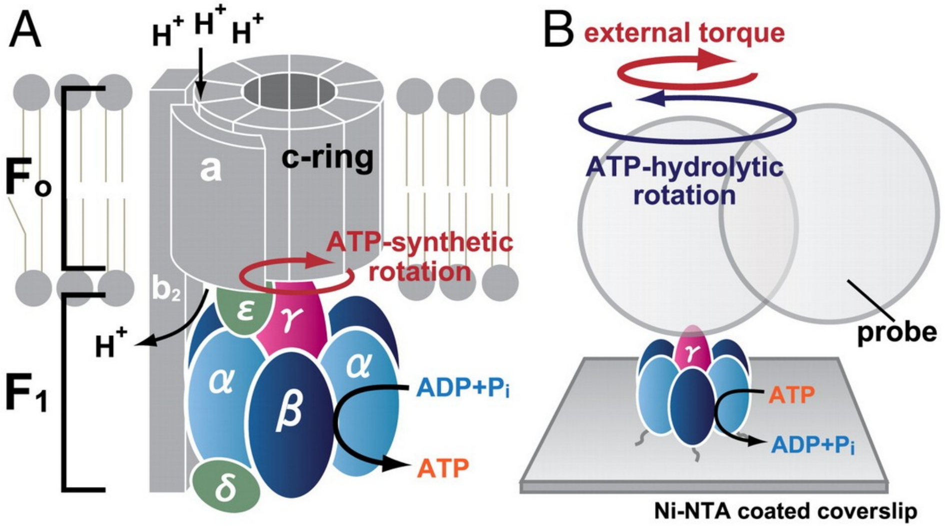


What if unidirectional ?









Shioichi Toyabe et al, PNAS 2011

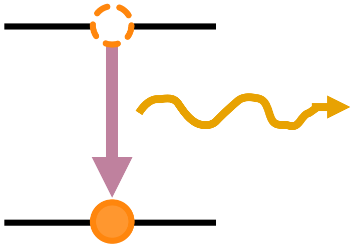
Can we measure entropy production?

- Trajectory: state vs time
- Unknown jumping rates w_{ij}
- Unidirectional jumps

Apparent irreversibility

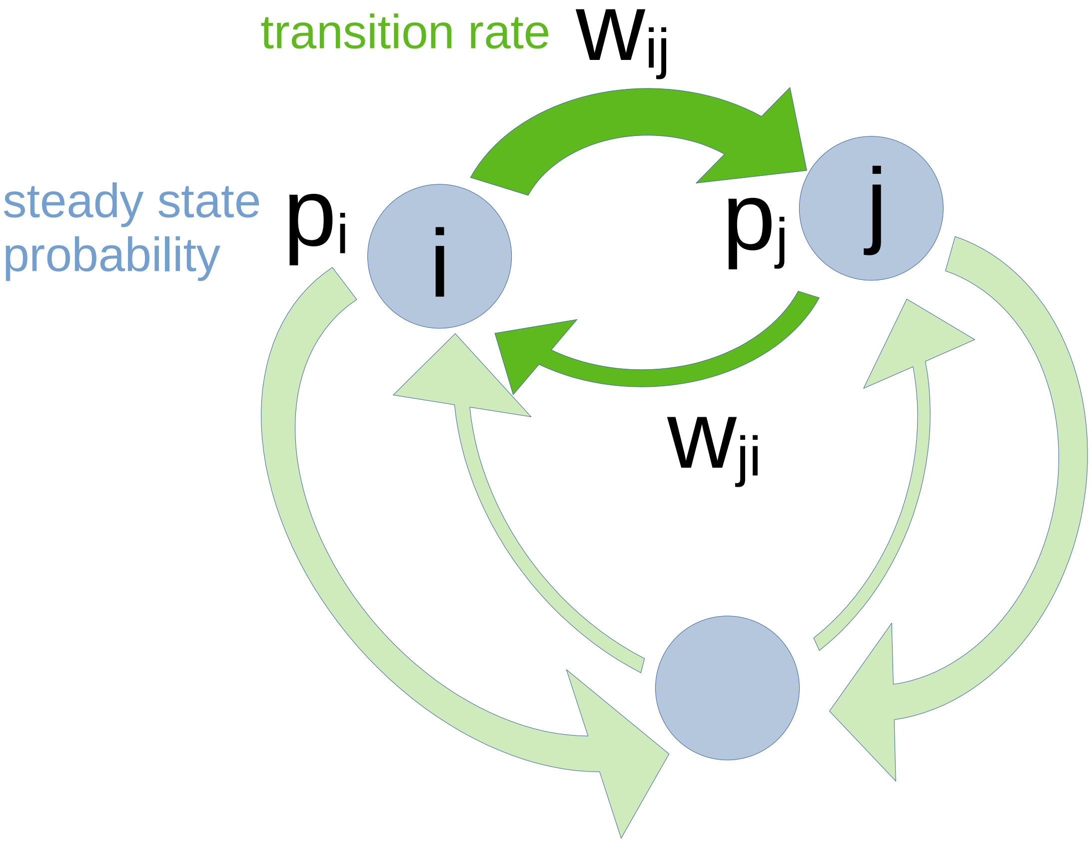
- Chemical reactions

  $X + Y \rightarrow 2X$ if one never observes the reverse
- Photon emissions
- TASEP, ...
- Lacking data: short trajectories



Entropy production, irreversibility $\rightarrow \infty$

Markov jump processes



$$\phi_{ij} = p_i w_{ij}$$

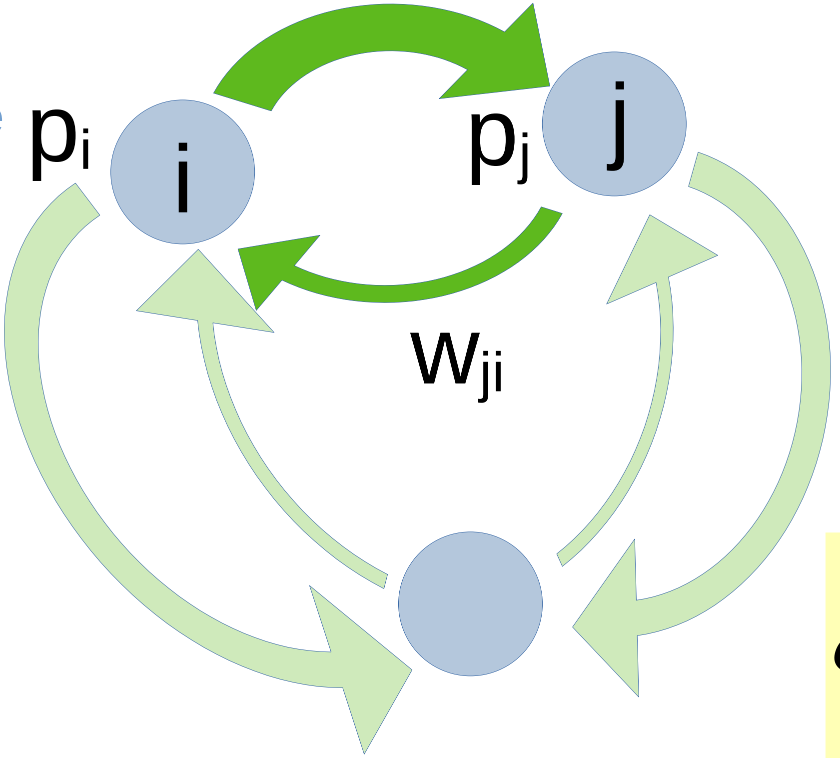
entropy production rate

$$\sigma = \sum_{i<j} \left(\phi_{ij} - \phi_{ji}\right) \log \frac{\phi_{ij}}{\phi_{ji}}$$

Estimating the entropy production rate σ

we do not know the transition rate w_{ij}

steady state probability p_i



$$\phi_{ij} = p_i w_{ij}$$

$$\dot{n}_{ij} = n_{ij} / t$$

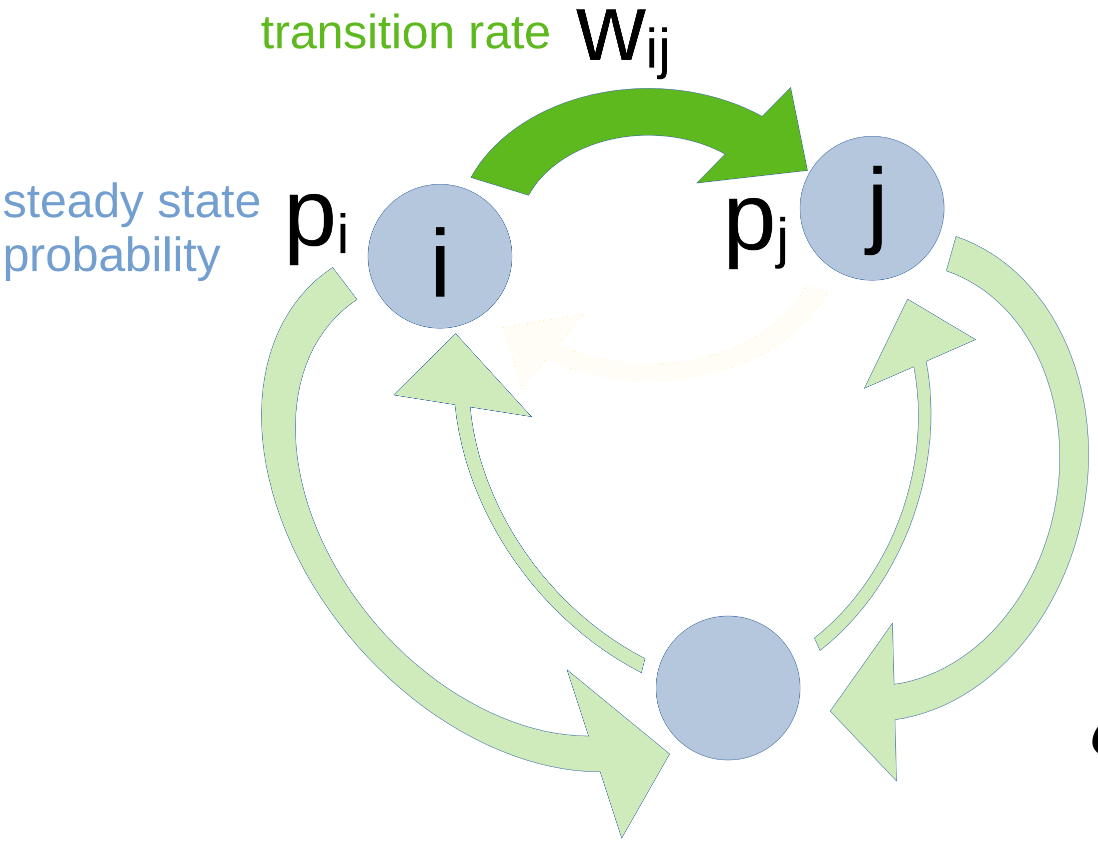
number of jumps $i \rightarrow j$ in a trajectory of duration t: n_{ij}

entropy production rate

$$\sigma = \sum_{i<j} (\phi_{ij} - \phi_{ji}) \log \frac{\phi_{ij}}{\phi_{ji}}$$

$$\sigma_{emp} = \sum_{i<j} (\dot{n}_{ij} - \dot{n}_{ji}) \log \frac{\dot{n}_{ij}}{\dot{n}_{ji}}$$

Problem: missing transitions



some

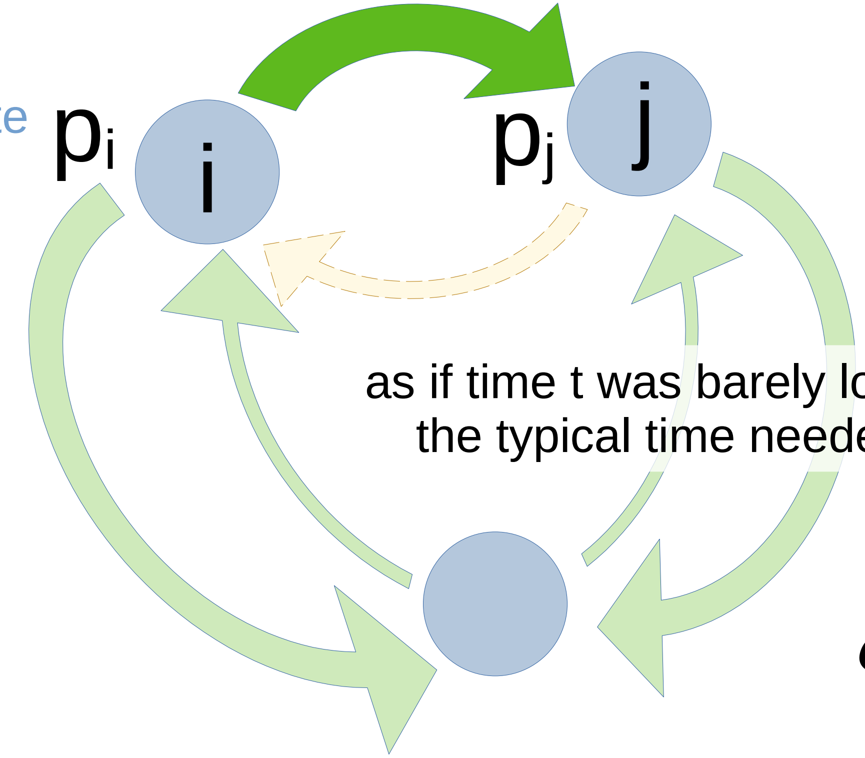
$$\dot{n}_{ij} = n_{ij}/t \neq 0 \quad \text{but} \quad n_{ji} = 0$$

entropy production rate:
singular contributions,
apparent irreversibility

$$\sigma_{emp} = \sum_{i<j} \left(\dot{n}_{ij} - \dot{n}_{ji}\right) \log \frac{\dot{n}_{ij}}{\dot{n}_{ji}}$$

A cure

Zeraati, Jafarpour, Hinrichsen, J.Stat.Mech (2012)



as if time t was barely longer than the typical time needed to jump

some

$$\dot{n}_{ij} = n_{ij}/t \neq 0 \quad \text{but} \quad n_{ji} = 0$$

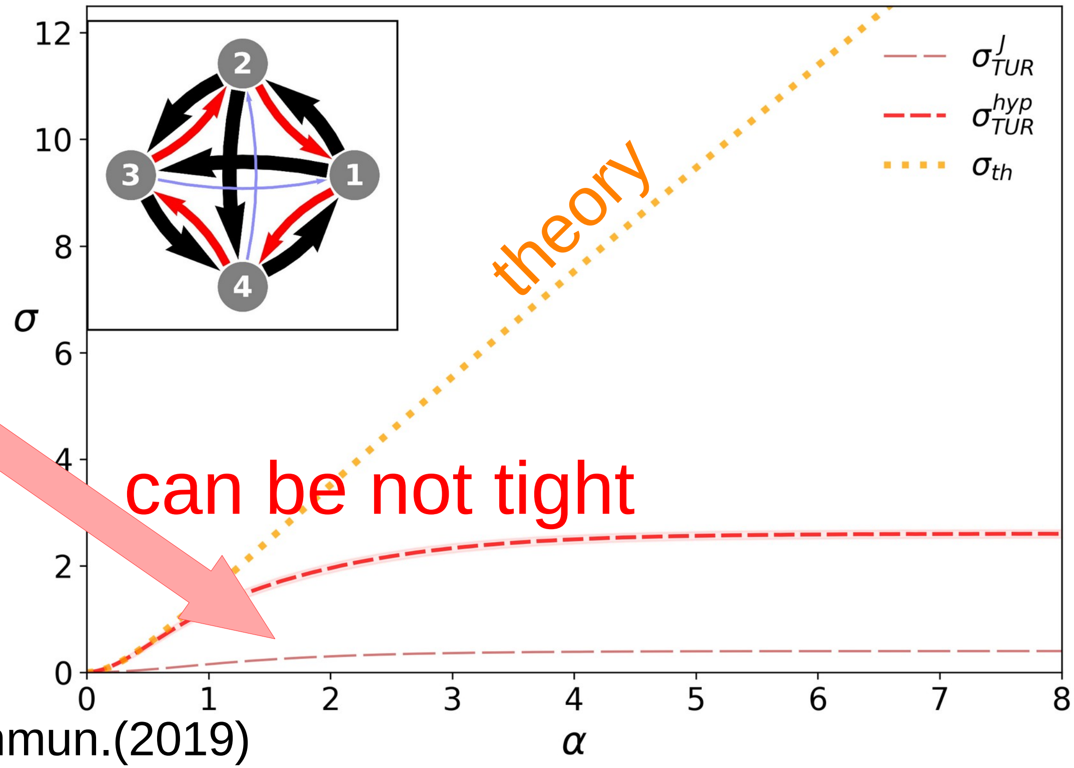
$$\dot{n}_{ji} \equiv \frac{p_i}{p_j} \cdot \frac{1}{t} \sim \frac{1}{t}$$

$$\sigma_{emp} = \sum_{i<j} (\dot{n}_{ij} - \dot{n}_{ji}) \log \frac{\dot{n}_{ij}}{\dot{n}_{ji}}$$

Lower bound estimate?

- Thermodynamic uncertainty relation

$$\sigma \geq 2\frac{\langle J \rangle^2}{var(J)\,\tau}$$



case where TUR works better:
Li, Horowitz, Gingrich, Fakhri, Nature Commun.(2019)

Enhanced lower bound estimate

Baiesi, Nishiyama, Falasco, Commun. Phys. 2024

Optimized:

- J, short time (τ) limit — Manikandan, Gupta, Krishnamurthy, PRL (2020); Otsubo, Ito, Dechant, & Sagawa, PRE (2020)
- hyper accurate current — Busiello & Pigolotti, PRE (2019); Falasco, Esposito & Delvenne, NJP (2020)

  "precision"

$$p^{hyp} = \lim_{\tau \to 0} \frac{\langle J^{hyp} \rangle^2}{var(J^{hyp})\tau} = \sum_{i<j} \frac{(\phi_{ij} - \phi_{ji})^2}{\phi_{ij} + \phi_{ji}}$$

- " $\tanh^{-1}$ " TUR — Tuan Vo, Van Vu, Hasegawa, JPA 55, 405004 (2022)

$$p(J) \le \frac{\sigma^2}{4\kappa f^2(\sigma/2\kappa)}$$

f : inverse of x tanh x

Enhanced lower bound estimate

Baiesi, Nishiyama, Falasco, Commun. Phys. 2024

- Lower bound based on average jumping rate κ

$$\sigma \geq \sigma_{\tanh}^{hyp}$$

if at least one transition *is* reversible

$$\sigma_{\tanh}^{hyp} = 2\sqrt{p^{hyp}\kappa}\ \tanh^{-1}\sqrt{p^{hyp}/\kappa}$$

if **all** transitions *are* irreversible $p^{hyp} = \kappa$ → $\sigma_{\tanh}^{hyp} = 2\kappa \tanh^{-1}\sqrt{1-\frac{4}{\kappa t}}$

assumption that *any* unobserved inverse transition is at most taking place with rate ~ 1/t

Enhanced lower bound estimate

Baiesi, Nishiyama, Falasco, Commun. Phys. 2024

Lower bound on dissipation rate based on jumping rate κ

$$\sigma \geq \sigma_{\mathrm{tanh}}^{hyp}$$

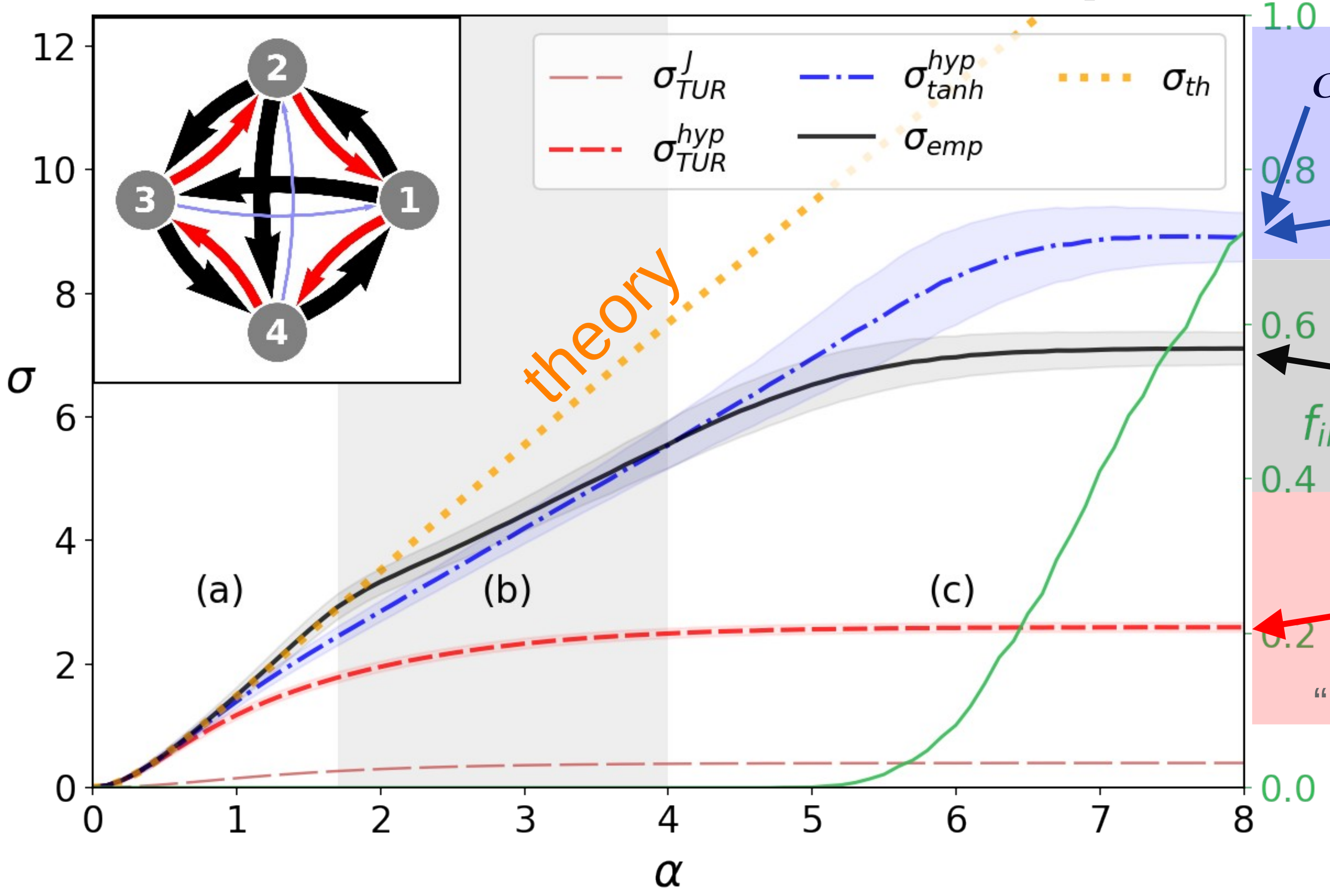
if all transitions *appear* irreversible

$$\sigma \geq \kappa \log \kappa t$$

for $\kappa t \gg 1$

Example

fixed t



strength of nonequilibrium drive

$$\sigma^{hyp}_{\tanh} = 2\sqrt{p^{hyp}\kappa}\ \tanh^{-1}\sqrt{p^{hyp}/\kappa}$$

$$\sigma^{hyp}_{\tanh} = \kappa \log \kappa t$$

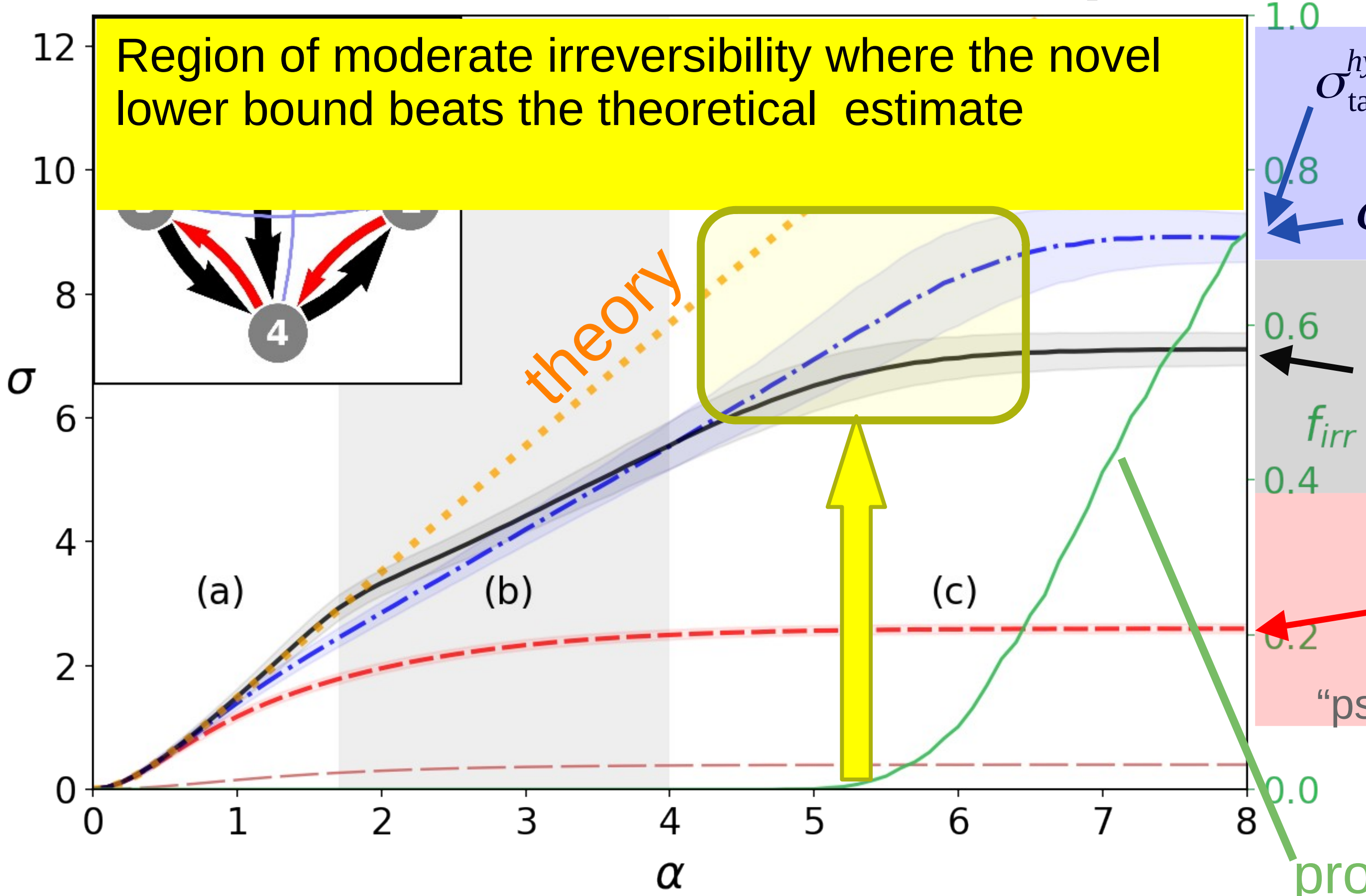
$$\sigma_{emp} = \sum_{i<j} \left(\dot{n}_{ij} - \dot{n}_{ji}\right) \log \frac{\dot{n}_{ij}}{\dot{n}_{ji}}$$

$$\sigma^{PS} = 2\sum_{i<j} \frac{\left(\dot{n}_{ij} - \dot{n}_{ji}\right)^2}{\dot{n}_{ij} + \dot{n}_{ji}}$$

“pseudo-entropy” (Shiraishi JPA 2021)

Example

fixed t



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$$\sigma^{hyp}_{\tanh} = 2\sqrt{p^{hyp}\kappa}\ \tanh^{-1}\sqrt{p^{hyp}/\kappa}$$

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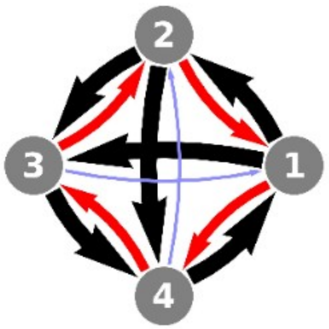
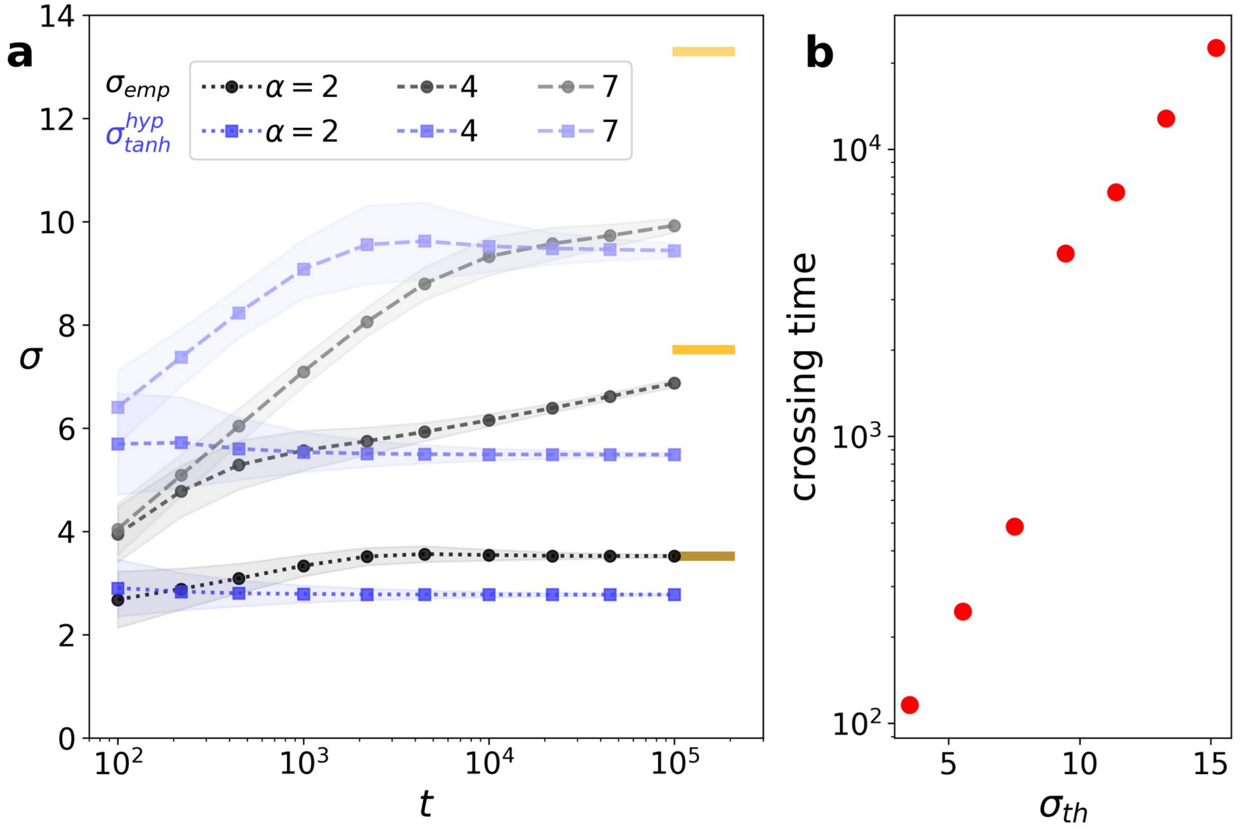
“pseudo-entropy” (Shiraishi JPA 2021)

probability of measuring a totally irreversible path

Example fixed nonequilibrium strength





trajectory duration

2nd Conclusions

- A lower bound can beat the direct estimate of entropy production in regimes lacking data
- Cheap assumption on reversibility
- Further entropy/frenesy interplay

$$\sigma \geq \kappa \log \kappa t$$

$$S \geq K \log K$$

Baiesi, Nishiyama, Falasco,
“Effective estimation of entropy production with lacking data”
Commun. Phys. 7, 264 (2024)