Entropy production in Non-equilibrium Processes

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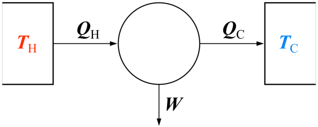
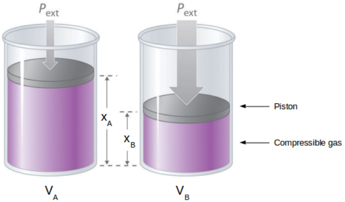
Entropy versus Entropy production

$$S = k_B \log \Omega = -K_B \Sigma_s P_s \log P_s \quad (1)$$

- **Entropy** determines thermodynamic properties of a system in **equilibrium**
- Entropy production rate σ is **zero** at equilibrium conditions





- $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$

Equilibrium systems

Entropy versus Entropy production

$$S = k_B \log \Omega = -K_B \Sigma_s P_s \log P_s \tag{1}$$

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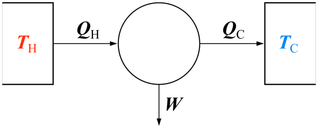
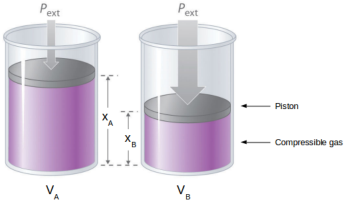
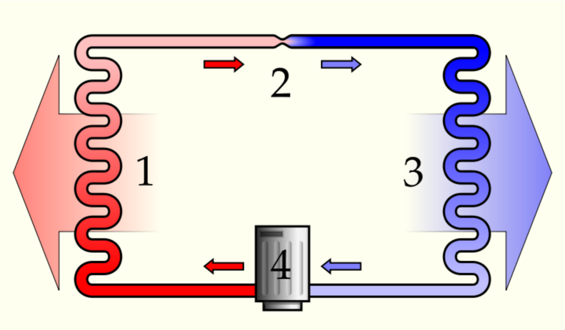




- $\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$

- What happens however **before** a system reaches equilibrium ? Or if it is **maintained** out-of-equilibrium ?

Out-of-equilibrium systems: Macroscopic



Out-of-equilibrium systems $\Rightarrow$ entropy production

- Nonequilibrium systems $\rightarrow$ Entropy production > 0
- Entropy production gives us useful quantitative information about the system $\longrightarrow$ dissipation, efficiencies, transport coefficients, cost of information erasure ....

Out-of-equilibrium systems ⇒ entropy production

- Nonequilibrium systems → Entropy production > 0
- Entropy production gives us useful quantitative information about the system ⟶ dissipation, efficiencies, transport coefficients, cost of information erasure ....
- Fluctuations are important on the **microscopic** scale so even entropy production is fluctuating!

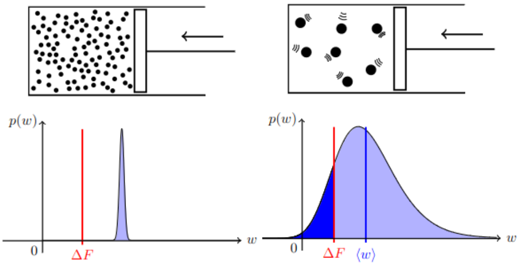
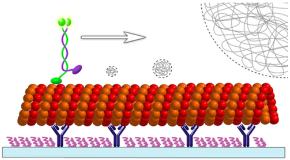
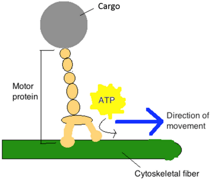


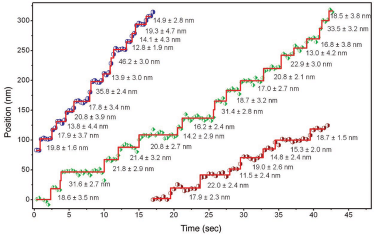
Figure taken from Phd Thesis, Jannik Ehrich (2020)

Out-of-equilibrium systems: Microscopic

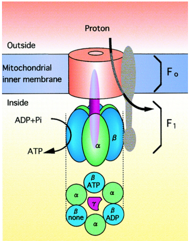
- Kinesin (8 nm for every ATP)

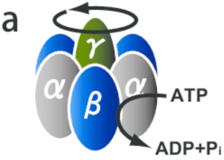


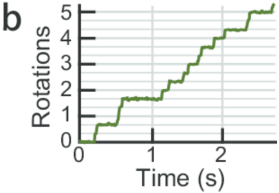




- F1-ATPase (120^{deg} for every ATP)



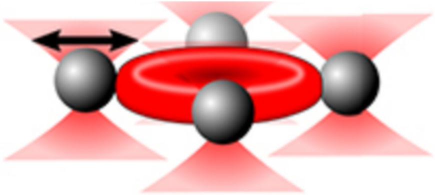


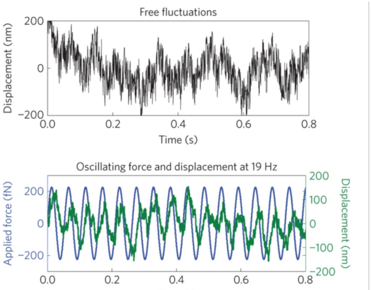


A. Yildiz *et al* Science (2004), K. Kinosita *et al* Cell (1998), K. Sozanski ıet al PRL (2015)

Out-of-equilibrium systems: Microscopic

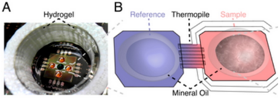
- RBC [1]



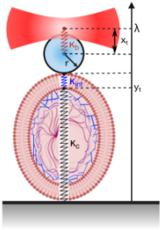


[1] H. Turlier *et al*, Nature Physics (2016)

How to estimate Entropy production?



Pico Calorimetry
P. J. Foster *et al* PNAS **120** (2023)



Model for an RBC
I. Di Terlizzi *et al* Science **383** (2024)

Chlamydomonas
C. Battle et al, Science, (2016)

- Model-free methods ?

(In the context of Markovian continuous-time) Models $\rightarrow$ Stochastic Thermodynamics

- Master Equations:

$$\frac{d\mathbf{P}}{dt} = \sum \left[P_i \, \omega_{ij} - P_j \, \omega_{ji}\right].$$

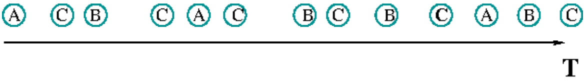
- Overdamped Langevin Equations:

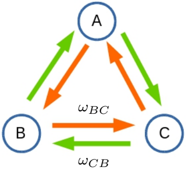
$$\gamma \dot{x}(t) = A(x(t), t) + B(x(t), t) \cdot \eta(t).$$

- Underdamped Langevin Equations:

$$m\ddot{x}(t) = A(x(t), t) - \gamma \dot{x}(t) + B(x(t), t) \cdot \eta(t).$$

$$\langle \eta(t) \eta(t') \rangle = \delta(t - t')$$

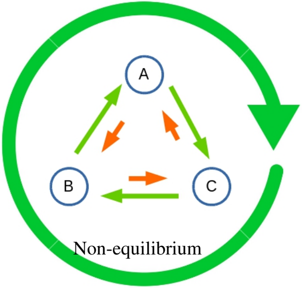




Equilibrium

$$P_B\ \omega_{BC} = P_C\ \omega_{CB}$$

$$\frac{\omega_{BC}}{\omega_{CB}} = \frac{P_C}{P_B} = e^{-\beta\ \Delta E}$$

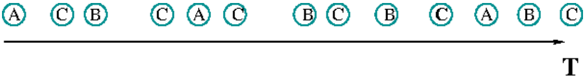


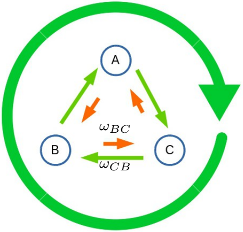
Non-equilibrium

$$P_B\ \omega_{BC} \neq P_C\ \omega_{CB}$$

$$\frac{P_B\ \omega_{BC}}{P_C\ \omega_{CB}} = e^{\beta\ q + \Delta s}$$

Entropy production in finite state-space systems



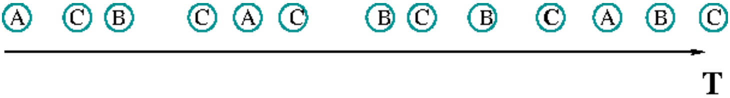


Entropy production in the link BC $= [\, \beta q + \Delta s \,]_{BC} \equiv \mathrm{F}_{BC}$

Total no. of transitions in BC / time $= \hat{j}_{BC} = P_B\, \omega_{BC} - P_C\, \omega_{CB}$

Rate of total entropy production $\equiv \sigma = \sum_{\text{links}} \hat{j}_{BC}\, \mathrm{F}_{BC} \geq 0$

Entropy Production ⇒ Irreversibility



$$\textbf{Entropy production} \equiv \log \frac{P_{\text{forward}}}{P_{\text{backward}}}$$

$$S_{\text{Total}} = \log\left(\frac{\mathcal{P}[x(\tau)]}{\mathcal{P}[x(t-\tau)]}\right)$$

$$\langle S_{\text{Total}} \rangle \geq 0$$

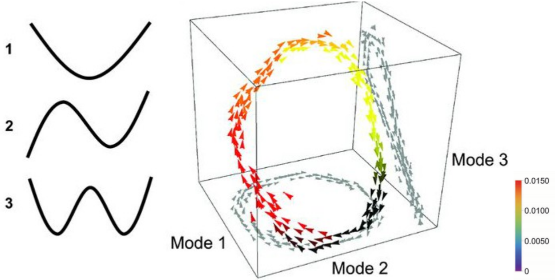
$$\sigma \equiv \frac{\langle S_{\text{Total}} \rangle}{T} \geq 0$$

- If not all degrees of freedom are observed, at best **lower bound**

Building a model from data

Entropy Production ⇒ Currents in Phase Space

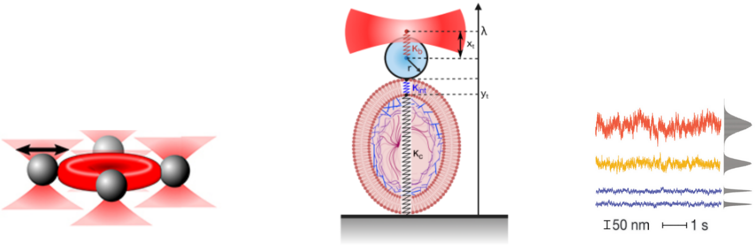
Chlamydomonas



First three bending modes and the probability density (color) and flux map (arrows)[2].

[2] C. Battle et al, Science, (2016)

Fitting data to a model: active flickering of RBC cell membrane[3]



$$\dot{x}_t = \mu_x\left(-k_b x_t - k_{\rm int}(x_t - y_t) + C_1\right) + \sqrt{2D_x}\eta_t^x$$
$$\dot{y}_t = \mu_y\left(-k_c y_t + k_{\rm int}(x_t - y_t) + f_t^a + C_2\right) + \sqrt{2D_y}\eta_t^y$$

$$\dot{f}_t^a = -f_t^a/\tau_a + \sqrt{2\epsilon^2/\tau_a}\,\eta_t^f\ ,$$

[3] I. Di Terlizzi *et al* Science **383** (2024)

Overdamped Langevin Equations

$$\dot{x}(t) = A(x(t), t) + \sqrt{2D}\eta(t).$$

$$A(x(t), t) = -\gamma \frac{\partial}{\partial x} U(x, \lambda) + f$$

$$\gamma = \frac{D}{k_b T}$$

$$\langle \eta(t)\eta(t') \rangle = \delta(t - t')$$

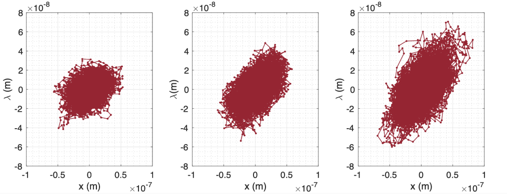
Probability currents

$$\partial_t p(x, t) = -\frac{\partial}{\partial x}\, j(x, t),$$
$$j(x, t) = A(x, t)p(x, t) - D\frac{\partial}{\partial x} p(x, t),$$

Overdamped Langevin Equations

- Trajectories

$$\overline{x} \equiv \{x_t\}_0^{\tau}$$



Overdamped Langevin Equations

- Can define Heat, Work and Entropy production for each trajectory

$$\sigma(t) = \int \mathrm{d}x \; \frac{j^2(x,t)}{D(x,t)p(x,t)}$$

- Consistent with log-ratio of probabilities for forward and reverse paths.

The thermodynamic uncertainty relation (TUR): Placing bounds on Entropy Production via "Model-free" methods

The finite-time thermodynamic uncertainty relation[4] relates the fluctuations of any arbitrary steady-state current $\mathcal{J}$ to entropy production rate σ as,

$$\frac{\text{Var}\left(\mathcal{J}\right)}{\left\langle\mathcal{J}\right\rangle^2} \times \sigma \times \tau \geq 2, \qquad \mathcal{J} = W, Q_1, Q_2..., \qquad k_B = 1.$$

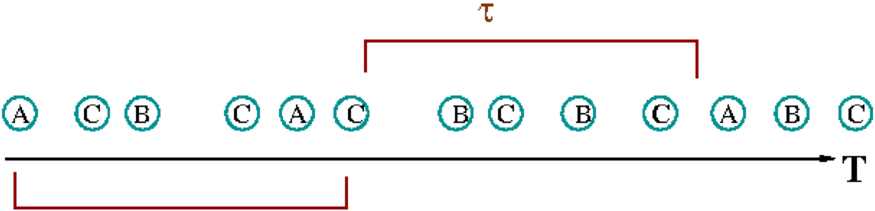
- Can be alternatively[5] used to bound steady-state value of σ by steady-state fluctuations of $\mathcal{J}$ as,

$$\sigma \geq \sigma_L \equiv \frac{2\left\langle\mathcal{J}\right\rangle^2}{\tau\text{Var}(\mathcal{J})}.$$

[4] **Pietzonka**; **Ritort and Seifert**; **PRE (2017)**.

[5] **J. M. Horowitz and T. R. Gingrich**; **PRE (2017)**.

Inferring σ using TUR



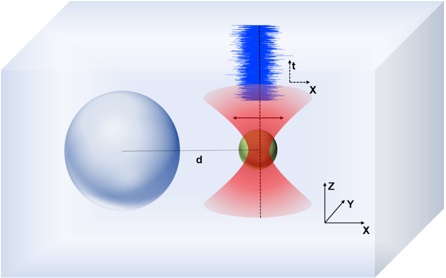
- Calculate average and variance of current J over segments τ to compute σ_L.
- The smaller the τ the better the bound![6]

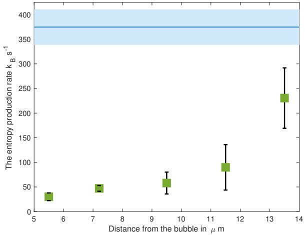
$$\sigma = \max\left\{ \lim_{\tau \to 0} \sigma_L \right\}.$$

[6] **Manikandan et al PRL (2020)**.

Predicting entropy production from Experimental data

Inferring σ [7] from experimental data on SSP + Bubble

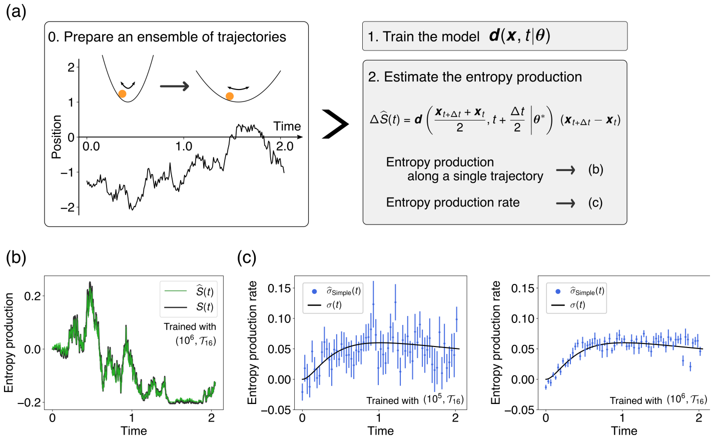




[7] S. K. Manikandan *et al* Commun Phys **4**, 258 (2021)

Entropy production along single trajectories

Inferring entropy production along a single trajectory [8] for transient data

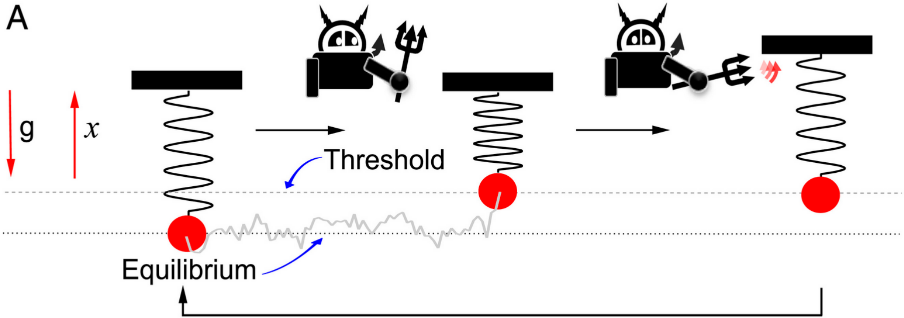


[8] Shun Otsubo *et al* , Commun Phys **4**, 11 (2022)

Information engines[9]

- Information as fuel!

- We can extract work on average, proportional to the information acquired in the measurement.



[9] T. K. Saha *et al*, PNAS (2021)

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