# Stochastic Thermodynamics and Thermodynamics of Information

## Thermodynamic uncertainty relations

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# Motivation

- Fluctuation relations discussed so far are *static*
- There is analogy with classical thermodynamics (e.g., efficiency of Carnot engines): optimal efficiency reached for infinitely slow transformations
- Some old results for efficiency at maximum power:

$$\eta_{\max P} \simeq 1 - \sqrt{\frac{T_{\mathrm{c}}}{T_{\mathrm{h}}}}$$

CURZON AND AHLBORN, 1975

- Can we obtain results involving time, speed, power?

# A toy model

Asymmetric random walk as a toy model of a molecular motor

- Position of the molecule: $n \in \mathbb{Z}$, $x = n\,d$
- Transition rates: $R_{\pm} = R_{n\pm1,n}$
- Steps are tightly bound to ATP hydrolysis: Chemical ATP imbalance: $\Delta\mu$
- There is an applied force $f$: Work against the force: $-fd$
- Thermodynamic consistency:

$$\frac{R_+}{R_-} = \mathrm{e}^{(\Delta\mu - fd)/k_\mathrm{B}T} = \mathrm{e}^{A/k_\mathrm{B}}$$

# Master equation

- Equation for $p_{n_+,n_-}(t)$, $n_\pm$: # steps in $\pm$ direction:

$$\frac{\mathrm{d}}{\mathrm{d}t} p_{n_+,n_-}(t) = R_+ p_{n_+-1,n_-}(t) + R_- p_{n_+,n_--1}(t) - (R_+ + R_-)\, p_{n_+,n_-}(t)$$

- Solution: $\pm$ steps are independent Poisson processes:

$$p_{n_+,n_-}(t) = \frac{(R_+ t)^{n_+}}{n_+!} \frac{(R_- t)^{n_-}}{n_-!} \, \mathrm{e}^{-(R_+ + R_-)t}$$

- Therefore

$$\langle n \rangle = \langle n_+ \rangle - \langle n_- \rangle = (R_+ - R_-)\, t = J\, t$$
$$\left\langle (n - \langle n \rangle)^2 \right\rangle = \langle n_+ \rangle + \langle n_- \rangle = (R_+ + R_-)\, t = 2Dt$$

- Mean rate of entropy production:

$$\dot{S}_\mathrm{i} = k_\mathrm{B}\, (R_+ - R_-) \log \frac{R_+}{R_-} = J\, A$$

# Large deviations

- For large values of $t$

$$p_{n_+,n_-}(t) \asymp \mathrm{e}^{-t\,\omega(\nu_+,\nu_-)}$$

  where

$$\nu_\pm = \frac{n_\pm}{t}$$

  and

$$\omega(\nu_+,\nu_-) = \nu_+ \log\frac{\nu_+}{R_+} - \nu_+ + R_+ + \nu_- \log\frac{\nu_-}{R_-} - \nu_- + R_-$$

- Uncertainty in $n$: since $\langle n^2\rangle - \langle n\rangle^2 \propto t \propto \langle n\rangle$ we can use the Fano factor

$$F = \lim_{t\to\infty} \frac{\langle n^2\rangle - \langle n\rangle^2}{\langle n\rangle} = \frac{2D}{J} = \frac{R_+ + R_-}{R_+ - R_-} = \coth\left(\frac{A}{2k_\mathrm{B}}\right)$$

  from which it follows

$$F \geq \frac{2k_\mathrm{B}}{A}$$

- The Fano factor is directly observable…

# Entropy production

- On the other hand we have for the *relative uncertainty*

$$\epsilon^2 = \frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle^2} = \frac{2D}{J^2 t}$$

- Total entropy produced:

$$C = \dot{S}_\mathrm{i}\, t$$

- Therefore

$$C\epsilon^2 = \frac{\dot{S}_\mathrm{i} 2D}{J^2} = \frac{J A\, 2D}{J^2} = A \coth\left(\frac{A}{2k_\mathrm{B}}\right) \geq 2k_\mathrm{B}$$

- $\dot{S}_\mathrm{i}$ is harder to observe...
- The inequality is saturated close to equilibrium and close to the stall force ($f \simeq \Delta\mu/d$), when $A \to 0$

# Observables

- Markov chain $X(t) \in \{x\}$, transition rates $R = (R_{xx'})$
- Observe for duration $t$: empirical density $\bar{p} = (\bar{p}_x)$

$$\bar{p}_x = \frac{\tau_x}{t} = \frac{1}{t}\int_0^t \mathrm{d}t' \; \delta_{xX(t')}$$

- We have $\langle \bar{p}_x \rangle = p_x^{\mathrm{ss}}$ if $R$ is $t$-independent
- Empirical current: $n_{xx'} = \#(x' \longrightarrow x)$ $n = (n_{xx'})$

$$\mathcal{J}_{xx'} = \frac{n_{xx'} - n_{x'x}}{t}$$

- Note that by probability conservation the current $\mathcal{J}$ must be defined to satisfy $\sum_x \mathcal{J}_{xx'} = 0 \; \forall x'$, by adding $n_{x(0)x(t)}$
- Traffic:

$$\mathcal{T}_{xx'} = \frac{1}{t}\left(n_{xx'} + n_{x'x}\right)$$

- We have

$$J_{xx'} = \langle \mathcal{J}_{xx'} \rangle = R_{xx'} p_{x'}^{\mathrm{ss}} - R_{x'x} p_x^{\mathrm{ss}}$$
$$T_{xx'} = \langle \mathcal{T}_{xx'} \rangle = R_{xx'} p_{x'}^{\mathrm{ss}} + R_{x'x} p_x^{\mathrm{ss}}$$

# Observables

- Distances: define $(d^\alpha_{xx'})$ with $d^\alpha_{x'x} = -d^\alpha_{xx'}$
- Then one gets the generalized current

$$\mathcal{J}^\alpha = \frac{1}{t} \sum_{xx'} n_{xx'} d^\alpha_{xx'}$$

- In particular: Fluctuating entropy production rate:

$$d^\sigma_{xx'} = k_\mathrm{B} \log \frac{R_{xx'}}{R_{x'x}} = A_{xx'} \qquad \langle \mathcal{J}^\sigma \rangle = \dot{S}_\mathrm{i}$$

# Rate functions

For Markov processes, one cannot *directly* evaluate the Cramér function for $\bar{p}$ in general

- Look at the joint pdf $P(\bar{p}, n, t | R, p_0)$
- Define the *auxiliary rates* $\hat{R} = (\hat{R}_{xx'})$, $\hat{R}_{xx'} = n_{xx'}/\bar{p}_{x'}$, such that $\bar{p} = p^{\mathrm{ss}}(\hat{R})$ and $\langle n_{xx'} \rangle_{\hat{R}} = n_{xx'}$
- Define $\hat{\gamma}_x = \sum_{x'} \hat{R}_{x'x}$
- Then

$$\frac{P(\tau, n, t | R, x_0)}{P(\tau, n, t | \hat{R}, x_0)} = \exp\left( -\sum_x \tau_x \left(\gamma_x - \hat{\gamma}_x\right) + \sum_{xx'} n_{xx'} \log \frac{R_{xx'}}{\hat{R}_{xx'}} \right)$$

- By multiplying by $P(\tau, n, t | \hat{R}, x_0) / P(p^{\mathrm{ss}} t, R\, p^{\mathrm{ss}} t, t | R, x_0)$ and averaging over $x_0$ we get

$$\frac{P(\tau, n, t | R)}{P(p^{\mathrm{ss}} t, R\, p^{\mathrm{ss}}, t | R)} = \exp\left( -\sum_x \tau_x \left(\gamma_x - \hat{\gamma}_x\right) + \sum_{xx'} n_{xx'} \log \frac{R_{xx'}}{\hat{R}_{xx'}} \right)$$

$$\times \frac{\sum_{x_0} P(\tau, n, t | \hat{R}, x_0) p_{x_0}(t_0)}{\sum_{x_0} P(p^{\mathrm{ss}} t, R\, p^{\mathrm{ss}}, t | R, x_0) p_{x_0}(t_0)} \quad \text{(tends to const!)}$$

# Rate functions

- Thus
$$P(\tau, n, t|R) \asymp \mathrm{e}^{-t\omega(\tau/t, n/t)}$$
with
$$\omega\left(\frac{\tau}{t}, \frac{n}{t}\right) = \frac{1}{t}\left[\sum_x -(\gamma_x - \hat{\gamma}_x)\tau_x + \sum_{xx'} n_{xx'} \log \frac{R_{xx'}}{\hat{R}_{xx'}}\right]$$
- Translate back into $\bar{p}$, $\mathcal{J}$, $\mathcal{T}$:
$$\omega\left(\bar{p}, \mathcal{J}, \mathcal{T}\right) = \sum_{xx'}\left[\frac{\mathcal{J}_{xx'} + \mathcal{T}_{xx'}}{2}\left(\log \frac{\mathcal{J}_{xx'} + \mathcal{T}_{xx'}}{2R_{xx'}\bar{p}_{x'}} - 1\right) + R_{xx'}p^{\mathrm{ss}}_{x'}\right]$$

# Contractions

The contraction principle:

- Given $P_n(x,y) \asymp \mathrm{e}^{-n\omega(x,y)}$:

$$P_n(x) \asymp E^{-n\omega(x)} \qquad \omega(x) = \min_y \omega(x,y)$$

"Any large deviation is done in the least unlikely of all the unlikely ways! " Ellis, 1985

Thus, since $\mathcal{J}_{x'x} = -\mathcal{J}_{xx'}$ and $\mathcal{T}_{x'x} = \mathcal{T}_{xx'}$ we obtain

$$\omega(\bar{p}, \mathcal{J}) = \min_{\mathcal{T}} \omega(\bar{p}, \mathcal{J}, \mathcal{T}) = \omega(\bar{p}, \mathcal{J}, \mathcal{T}^*)$$

with

$${\mathcal{T}^*_{xx'}}^2 = \mathcal{J}^2_{xx'} + 4R_{xx'}R_{x'x}\bar{p}_x\bar{p}_{x'}$$

Gallavotti-Cohen symmetry:

$$\omega(\bar{p}, \mathcal{J}) - \omega(\bar{p}, -\mathcal{J}) = -\sum_{xx'} \mathcal{J}_{xx'} \log \frac{R_{xx'}\bar{p}_{x'}}{R_{x'x}\bar{p}_x} = -\dot{S}_\mathrm{i}(\mathcal{J})/k_\mathrm{B}$$

# Bounds on current fluctuations

- Hard to get rid of $\bar{p}$...
- Bound on the rate function: $\bar{p} \longrightarrow p^{\mathrm{ss}}$:

$$\omega(\bar{p}, \mathcal{J}) \leq \omega(p^{\mathrm{ss}}, \mathcal{J}) = \sum_{x'<x} \Bigg[ \mathcal{J}_{xx'} \log \frac{\mathcal{J}_{xx'} + \sqrt{\mathcal{J}_{xx'}^2 + {\mathcal{T}_{xx'}^*}^2 - {\mathcal{J}_{xx'}^{\mathrm{ss}}}^2}}{\mathcal{J}_{xx'}^{\mathrm{ss}} + \mathcal{T}_{xx'}^{\mathrm{ss}}} - \sqrt{\mathcal{J}_{xx'}^2 + {\mathcal{T}_{xx'}^*}^2 - {\mathcal{J}_{xx'}^{\mathrm{ss}}}^2} + \mathcal{T}_{xx'}^{\mathrm{ss}} \Bigg]$$

- The bound satisfies the symmetry

$$\omega(p^{\mathrm{ss}}, \mathcal{J}) - \omega(p^{\mathrm{ss}}, -\mathcal{J}) = -\sum_{x'<x} \mathcal{J}_{xx'} \underbrace{\log \frac{\mathcal{T}_{xx'}^{\mathrm{ss}} + \mathcal{J}_{xx'}^{\mathrm{ss}}}{\mathcal{T}_{xx'}^{\mathrm{ss}} - \mathcal{J}_{xx'}^{\mathrm{ss}}}}_{\dot{S}_{xx'}^{\mathrm{ss}} / \mathcal{J}_{xx'}^{\mathrm{ss}}} = -\dot{S}_{\mathrm{i}}(\mathcal{J}) / k_{\mathrm{B}}$$

# Bounds on current fluctuations

- Remember that an *upper* bound on $\omega$ means a *lower* bound on the fluctuations
- *Universal* global bound (Gingrich et al., 2016):

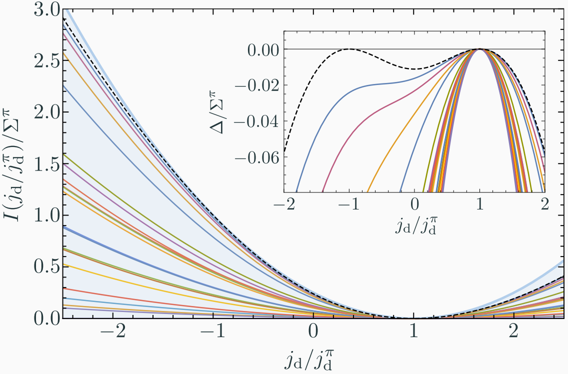
$$k_\mathrm{B}\omega(\mathcal{J}) \leq \sum_{x'<x} \frac{\dot{S}^{\mathrm{ss}}_{xx'}\left(\mathcal{J}_{xx'} - \mathcal{J}^{\mathrm{ss}}_{xx'}\right)^2}{4{\mathcal{J}^{\mathrm{ss}}_{xx'}}^2}$$

- For the general current: choose $\mathcal{J}_{xx'} = \mathcal{J}^{\mathrm{ss}}_{xx'}\mathcal{J}^{\alpha}/\mathcal{J}^{\alpha,\mathrm{ss}}$, then

$$k_\mathrm{B}\omega(\mathcal{J}^\alpha) \leq \frac{\dot{S}_\mathrm{i}(\mathcal{J}^\alpha - \mathcal{J}^{\alpha,\mathrm{ss}})^2}{4{\mathcal{J}^{\alpha,\mathrm{ss}}}^2}$$

- Similar bounds hold for $\bar{p}$

# Examples

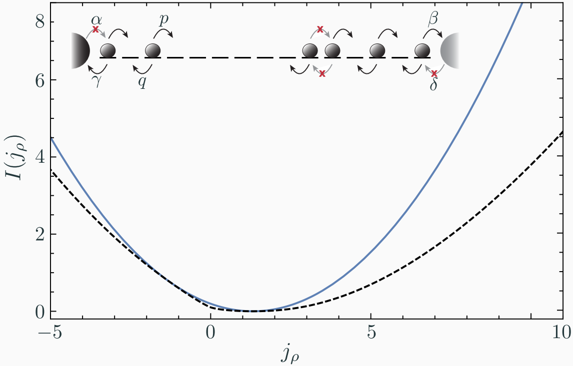



Rate functions for currents $j_d$ in a 4-state model with distances $d$ randomly chosen in $[-1, 1]$ (colored) and for the entropy production (dashed black)

Inset: Distance from bound

GINGRICH ET AL., 2016

# Examples




Current fluctuations in the ASEP model with $L = 15$: $\alpha = 1.25$, $\beta = 0.5$, $\gamma = 0.5$, $\delta = 1.5$, $p = 1$, $q = 0.5$
(Exact solution in the steady state via a matrix technique)

GINGRICH ET AL., 2016

# Thermodynamic uncertainty relations

- Reading off the rate function: uncertainty for the current $\mathcal{J}^\alpha = X^\alpha/t$:

$$\epsilon_\alpha^2 = \frac{\left\langle \left(X^\alpha - J^{\alpha,\mathrm{ss}} t\right)^2 \right\rangle}{(J^{\mathrm{ss},\alpha} t)^2} \simeq \frac{2D_\alpha}{{J^{\mathrm{ss},\alpha}}^2 t}$$

  and thus, since $\Delta S_\mathrm{i} = \dot{S}_\mathrm{i} t$,

$$\Delta S_\mathrm{i} \epsilon_\alpha^2 = \frac{2\dot{S}_\mathrm{i} D_\alpha}{{J^{\mathrm{ss},\alpha}}^2} \geq 2k_\mathrm{B}$$

- $\Delta S_\mathrm{i}$ is hard to measure…

# Thermodynamic uncertainty relations

- Molecular motors:
  - Out-power: $p^{\mathrm{out}} = f\,v = \sum_{xx'} f\,\mathcal{J}_{xx'}\,d_{xx'}$
  - In-power: $p^{\mathrm{in}} = \Delta\mu_{\mathsf{ATP}}\,n_{\mathsf{ATP}}/t$
- Entropy production:

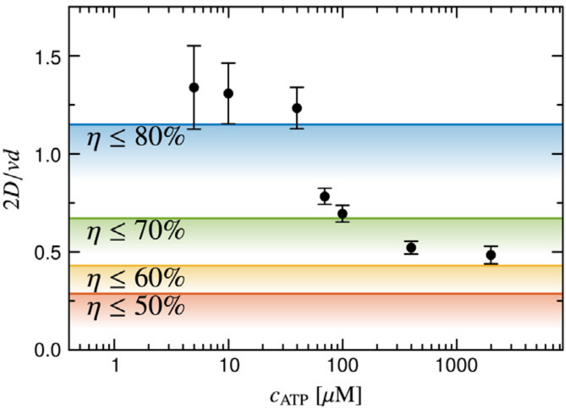
$$\dot{S}_{\mathrm{i}} = \frac{1}{T}\left(p^{\mathrm{in}} - p^{\mathrm{out}}\right)$$

- Efficiency:

$$\eta = \frac{p^{\mathrm{out}}}{p^{\mathrm{in}}} = \frac{p^{\mathrm{out}}}{p^{\mathrm{out}} + \dot{S}_{\mathrm{i}}/T} = \frac{f\,v}{f\,v + \dot{S}_{\mathrm{i}}/T} \leq \underbrace{\frac{1}{1 + k_{\mathrm{B}}T\,v/(D\,f)}}_{\text{observable!}}$$

- Bound independent on microscopic details...

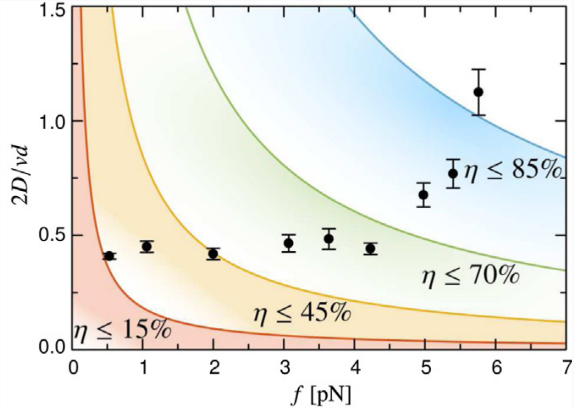
# Kinesin




Randomness parameter $r = 2D/vd$ for kinesin as a function of ATP-concentration (for a fixed force $f = 3.59\,\mathrm{pN}$)

SEIFERT, 2018 Data from VISSCHER ET AL., 1999

# Kinesin




Randomness parameter $r = 2D/vd$ for kinesin for fixed ATP concentration $2\,\mathrm{mM}$

SEIFERT, 2018 Data from VISSCHER ET AL., 1999

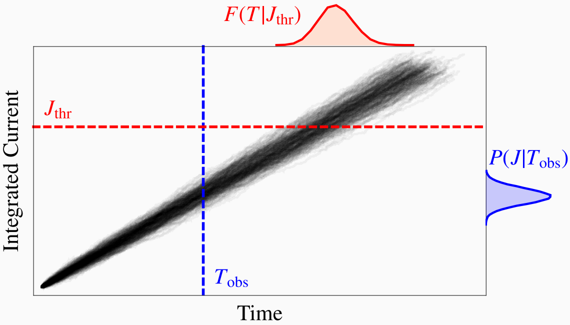
# Fluctuations of the first-passage time

- Current statistics: fix $\mathcal{T}_{\rm obs}$, measure $\mathcal{J}$ (*integrated* current):

$$\dot{S}_i \mathcal{T}_{\rm obs} \frac{\langle \Delta \mathcal{J}^2 \rangle}{\langle \mathcal{J} \rangle^2} \geq 2k_{\rm B}$$

- First-passage time $\mathcal{T}$: fix $J_{\rm thr}$, measure $\mathcal{T}$: $\mathcal{J}(\mathcal{T}) = J_{\rm thr}$

$$\dot{S}_{\rm i} \frac{\langle \Delta \mathcal{T}^2 \rangle}{\langle \mathcal{T} \rangle} \geq 2k_{\rm B}$$



# Fluctuations of the first-passage time

- Large-deviation functions: for the current $\mathcal{J} = j\,\mathcal{T}_{\text{obs}}$

$$P(\mathcal{J}|\mathcal{T}_{\text{obs}}) \asymp \mathrm{e}^{-\mathcal{T}_{\text{obs}}\omega(\mathcal{J}/\mathcal{T}_{\text{obs}})}$$

$$\psi(\lambda) = \lim_{\mathcal{T}_{\text{obs}}\to\infty} \frac{1}{\mathcal{T}_{\text{obs}}} \log \left\langle \mathrm{e}^{-\lambda\,\mathcal{J}} \right\rangle = -\min_{j} \left(\lambda\, j + \omega(j)\right)$$

- Define $\psi_+(\lambda) : \psi'(\lambda) > 0$, $\psi_-(\lambda) : \psi'(\lambda) < 0$
- For the first-passage time $\mathcal{T} = |J_{\text{thr}}|\ t$: distinguish $J_{\text{thr}} > 0$ $(+)$ from $J_{\text{thr}} < 0$ $(-)$

$$\mathcal{F}(\mathcal{T}|J_{\text{thr}}) \asymp \begin{cases} \mathrm{e}^{-J_{\text{thr}}\phi_+(\mathcal{T}/J_{\text{thr}})}, & (+) \\ \mathrm{e}^{J_{\text{thr}}\phi_-(\mathcal{T}/|J_{\text{thr}}|)}, & (-) \end{cases}$$

$$g_\pm(\mu) = -\lim_{J_{\text{thr}}\to\pm\infty} \frac{1}{J_{\text{thr}}} \log \left\langle \mathrm{e}^{-\mu\mathcal{T}} \right\rangle$$

# Results

- Large-deviation function for $t = \mathcal{T} / |J_{\rm thr}|$:

$$\phi_\pm(t) = t\,\omega\left(j = \pm\,\frac{1}{t}\right) \qquad g_\pm(\mu) = \psi_\pm^{-1}(\mu)$$

- **Heuristic argument:** For large $J$ the most likely first-passage time is just given by the condition $\mathcal{J}(\mathcal{T}) = J_{\rm thr}$
- Now for any large $J$

$$\begin{aligned} P(\mathcal{T}{=}t\,J) &= \int \mathcal{D}\boldsymbol{x}\;\delta(\mathcal{T} - t\,J)\,\mathcal{P}(\boldsymbol{x}) \\ &\asymp \int \mathrm{d}J\;\delta(\mathcal{T} - t\,J)\,\mathrm{e}^{-\mathcal{T}\,\omega(J/\mathcal{T})} \simeq \mathrm{e}^{-Jt\,\omega(1/t)} \end{aligned}$$

# Results

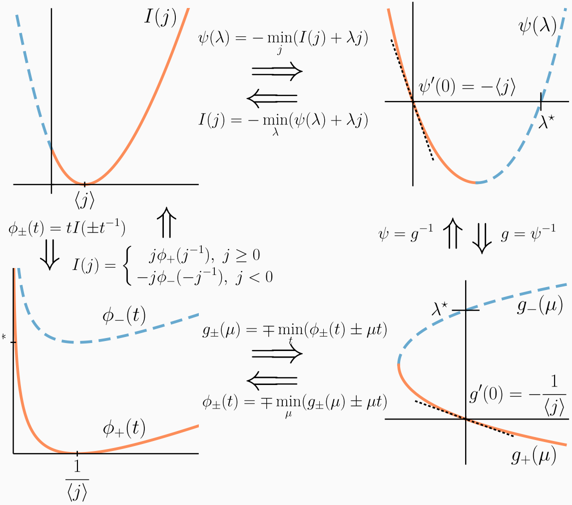
- Generating function: by saddle-point integration

$$g_{\pm}(\mu) = -\min_{t}\left(\mu\, t + \phi_{\pm}(t)\right)$$
$$\psi_{\pm}(\lambda) = -\min_{j \gtrless 0}\left(\lambda\, j + \psi_{\pm}(j)\right)$$

- Denote by $j^*$ the value of $j$ corresponding to minimum and set $t^* = 1/j^*$, then, e.g.,

$$\begin{aligned} g_{+}(\psi_{+}(\lambda)) &= -\left[-\left(\lambda\, j^* + \omega_{+}(j^*)\right) t^* + \phi_{+}(t^*)\right] \\ &= -\left[-\lambda - t^*\,\omega_{+}\left(\frac{1}{t^*}\right) + t^*\omega_{+}\left(\frac{1}{t^*}\right)\right] = \lambda \end{aligned}$$

# Results




Dictionary: $I \longrightarrow \omega$

Gingrich and Horowitz, 2017

# Implications

- Since $\forall j$ one has

$$\omega(j) \leq \frac{(j - \langle j \rangle)^2}{4 \langle j \rangle^2} \dot{S}_{\mathrm{i}} / k_{\mathrm{B}} = \omega_{\mathrm{bnd}}(j)$$

  we have

$$\phi_+(t) \leq \frac{(t - \langle t \rangle)^2}{4t} \dot{S}_{\mathrm{i}} / k_{\mathrm{B}}$$

- By evaluating the variance via

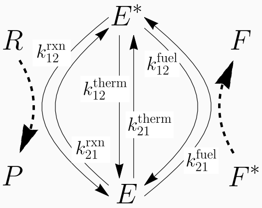
$$\left\langle \Delta \mathcal{T}^2 \right\rangle = \frac{J_{\mathrm{thr}}}{\phi''(\langle t \rangle)}$$

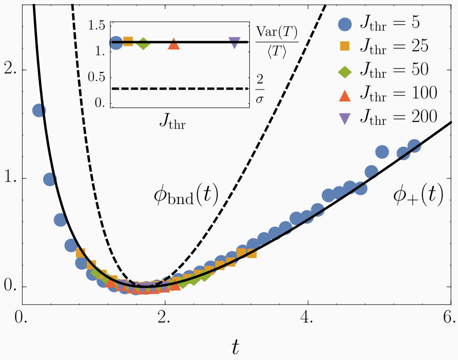
  we obtain a bound for the Fano factor:

$$\frac{\langle \Delta \mathcal{T} \rangle^2}{\langle \mathcal{T} \rangle} \geq \frac{2 k_{\mathrm{B}}}{\dot{S}_{\mathrm{i}}}$$

# Implications

Toy model for an assisted isomerization: $R \leftrightharpoons E^* \leftrightharpoons P$, $E \leftrightharpoons E^*$



# Sketch of a proof

- Basic results can be derived in the simple asymmetric random walk

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = R_+ p_{n-1} + R_- p_{n+1} - (R_+ + R_-)p_n = (\mathcal{L}\, p)_n$$

- $F_n(t)$: probability of reaching $n$ *for the first time* on $t$ if starting from 0 at time 0
- Then, if $t'$ is the last time the walker visited the origin,

$$p_n(t) = \delta_{0n}\delta(t) + \int_0^t \mathrm{d}t'\ F_n(t-t')\, p_0(t')$$

and, defining $\Psi(\lambda, t) = \left\langle \mathrm{e}^{-\lambda J} \right\rangle$

$$\frac{\mathrm{d}}{\mathrm{d}t}\Psi(\lambda, t) = -\psi(\lambda)\,\Psi(\lambda, t)$$

$$\psi(\lambda) = R_+ \mathrm{e}^{\lambda} + R_- \mathrm{e}^{-\lambda} - (R_+ + R_-)$$

(In general, a matrix equation...)

# Sketch of a proof

- Taking the Laplace transform wrt time:

$$\tilde{F}_n(\mu) = \frac{\tilde{p}_n(\mu)}{\tilde{p}_0(\mu)}$$
$$\tilde{\Psi}(\lambda, \mu) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\mu t}\, \Psi(\lambda, t) = \frac{1}{\psi(\lambda) - \mu}$$

- Now

$$\mathrm{e}^{-n g_\pm(\mu)} \asymp \left\langle \mathrm{e}^{-\mu \mathcal{T}} \right\rangle = \tilde{F}(\mu|n) \asymp \tilde{p}_n(\mu)$$

and

$$\tilde{p}_n(\mu) = \int_{-\mathrm{i}\infty}^{+\mathrm{i}\infty} \frac{\mathrm{d}z}{2\pi\mathrm{i}}\, \mathrm{e}^{zn}\, \tilde{\Psi}(z, \mu) = \mathrm{e}^{-\lambda^* n}$$

where

$$\psi(\lambda^*) = \mu$$

# Evaluation of large-deviation functions

- Large fluctuations are *rare*: How to evaluate their probability?
- In Statistical Mechanics one uses *biased ensembles*:

$$p_x^* = \mathrm{e}^{(\Delta F - \Delta E_x)/k_\mathrm{B}T} p_x^\mathrm{eq} \qquad \underbrace{\Delta F = -k_\mathrm{B}T \left\langle \mathrm{e}^{-\Delta E_x/k_\mathrm{B}T} \right\rangle^\mathrm{eq}}_{\text{hard!}}$$

- In dynamics one typically has *biased Liouvillians* $\mathcal{L}_\mu$ that to not conserve normalization:

$$\mathrm{e}^{t\mathcal{L}_\mu}\Psi \sim \mathrm{e}^{-t\psi(\mu)}\Psi^*$$

- One can exploit lack of normalization to evaluate $\psi(\mu)$

GIARDINÀ ET AL., 2006

# The setting

We consider a *Markov chain in discrete time*:

$$\boldsymbol{x} = (x_0, x_1, \ldots, x_t, \ldots)$$

Master equation:

$$p_x(t+1) = \sum_{x'} U_{xx'} p_{x'}(t) = (\mathcal{L}\, p)_x \qquad \sum_{x'} U_{x'x} = 1 \; \forall x$$

Observables:

- Empirical frequencies:

$$\bar{p}_x(\mathcal{T}) = \frac{1}{\mathcal{T}} \sum_{t=0}^{\mathcal{T}-1} \delta_{x x_t}$$

- Currents:

$$J(\mathcal{T}) = \sum_{t=0}^{\mathcal{T}-1} d_{x_{t+1} x_t}$$

# Large-deviation functions

For large values of $\mathcal{T}$:

$$P\left(\frac{J}{\mathcal{T}} = j\right) = \left\langle \delta\left(d_{x_\mathcal{T} x_{\mathcal{T}-1}} + \cdots + d_{x_1 x_0} - j\,\mathcal{T}\right)\right\rangle$$
$$= \int_{-\mathrm{i}\infty}^{+\mathrm{i}\infty} \frac{\mathrm{d}\lambda}{2\pi\mathrm{i}}\ \mathrm{e}^{-\mathcal{T}(\psi(\lambda)+\lambda\, j)}$$

where

$$\psi(\lambda) = -\lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \log\left\langle \mathrm{e}^{\lambda\, J}\right\rangle$$

Therefore

$$P\left(J, \mathcal{T}\right) \asymp \mathrm{e}^{-\mathcal{T}\,\omega(j)} \qquad \omega = -\min_{\lambda}\left(\psi(\lambda) + \lambda\, j\right)$$

# Biased dynamics

Define

$$\tilde{U}_{x'x} = \mathrm{e}^{\lambda d_{x'x}} U_{x'x}$$
$$\Psi_x(\lambda) = \left\langle \delta_{x x(\mathcal{T})}\, \mathrm{e}^{\lambda\, J} \right\rangle$$

then $\Psi$ satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t} \Psi_x = \sum_{x'} \tilde{U}_{xx'} \Psi_{x'} = \left(\mathcal{L}_\lambda\, \Psi\right)_x$$

and we expect

$$\Psi_x(\mathcal{T}) \sim \mathrm{e}^{-\mathcal{T}\, \psi(\lambda)} \Psi^*_x$$

# Birth-death process

Define

$$\gamma_x = \sum_{x'} \tilde{U}_{x'x} \qquad U'_{x'x} = \tilde{U}_{x'x}/\gamma_x$$

then

$$\left(\mathrm{e}^{\mathcal{T}\,\mathcal{L}_\lambda}\right)_{x'x} = \sum_{x_{\mathcal{T}-1},\ldots,x_1} U'_{xx_{\mathcal{T}-1}}\gamma_{x_{\mathcal{T}-1}} \cdots U'_{x_1x_0}\gamma_{x_0}$$

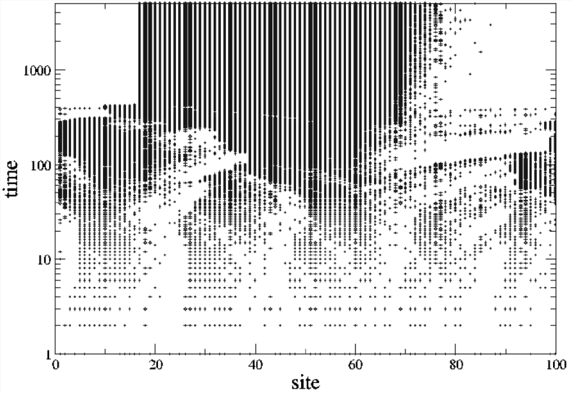
Define a population of $L$ *clones* undergoing a birth-death process:
At each time step:

- *Cloning* step: $p_x(T+\frac{1}{2}) = \gamma_x\, p_x(t)$ by reproducing (or killing) copies of $x$: population goes from $L$ to $(L+G)$
- *Displacement*: $p_x(t+1) = \sum_{x'} U'_{xx'} p_{x'}(t+\frac{1}{2})$
- *Population control:* clone *all* individuals with rate $M_t = L/(L+G)$

Then

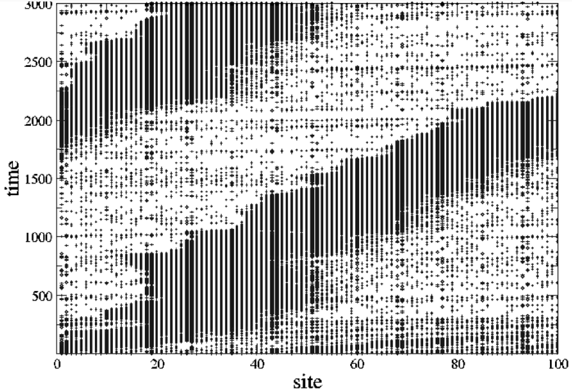
$$\log\left(M_{\mathcal{T}} M_{\mathcal{T}-1} \cdots M_1\right) \simeq \mathcal{T}\,\psi(\lambda)$$

# Results: TASEP



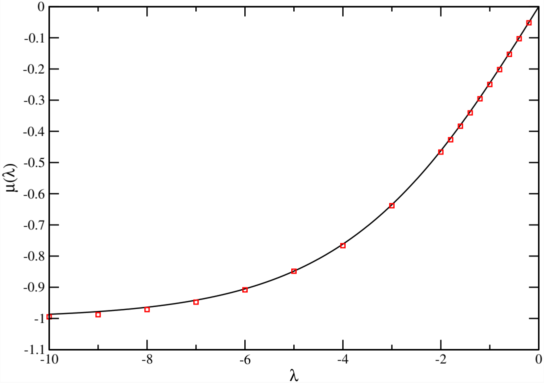

$\lambda = -50$, $\rho = 0.5$

# Results: TASEP




$\lambda = -30$, $\rho = 0.3$

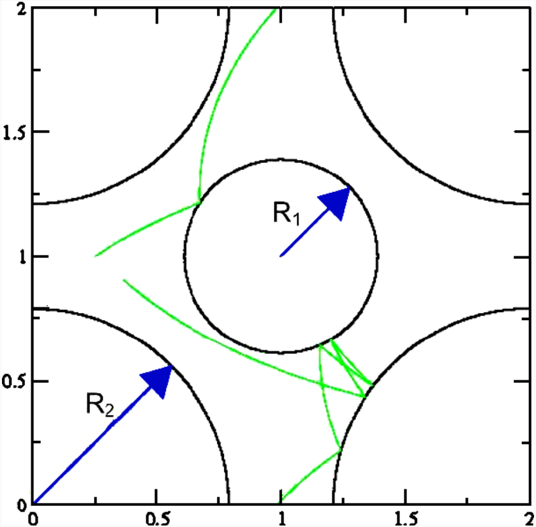
# Results: TASEP



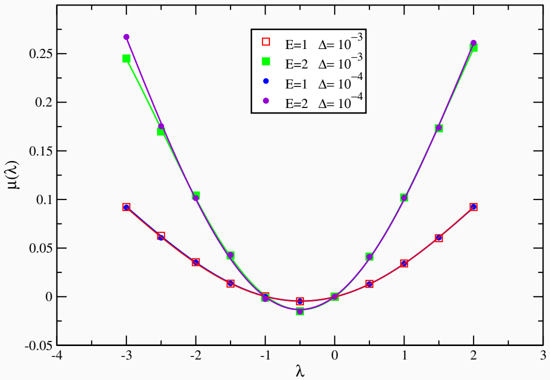

Dictionary: $\mu(\lambda) \longrightarrow -\psi(\lambda)$, $\rho = 0.5$

There is absolute irreversibility (no GC symmetry)

# Results: Lorenz gas



# Results: Lorenz gas




Two values of external field $\boldsymbol{E} = (E, 0)$ with $E = 1, 2$ and different noise intensities

## Summary

- Several results involving fluctuations, dissipation, and speed
- Largely *independent* of system details
- It is essential to maintain thermodynamic consistency

Aspect not discussed in these lectures:

- Quantum systems
- Complex reaction networks
- Generalizations (evolution, finance,...)

... to be continued...

Thank you!

F. Curzon and B. Ahlborn.
**Efficiency of a Carnot engine at maximum power output.**
*American Journal of Physics*, 43(1):22–24, 1975.

R. S. Ellis.
***Entropy, Large Deviations and Statistical Mechanics.***
Springer, Berlin, 1985.

J. P. Garrahan.
**Simple bounds on fluctuations and uncertainty relations for first-passage times of counting observables.**
*Physical Review E*, 95(3):032134, 2017.

C. Giardinà, J. Kurchan, and L. Peliti.
**Direct evaluation of large-deviation functions.**
*Physical Review Letters*, 96:120603, Mar 2006.

T. R. Gingrich and J. M. Horowitz.
**Fundamental bounds on first passage time fluctuations for currents.**
*Physical Review Letters*, 119(17):170601, 2017.

T. R. Gingrich, J. M. Horowitz, N. Perunov, and J. L. England.
**Dissipation bounds all steady-state current fluctuations.**
*Physical Review Letters*, 116(12):120601, 2016.

C. Maes and K. Netočný.
**Canonical structure of dynamical fluctuations in mesoscopic nonequilibrium steady states.**
*EPL (Europhysics Letters)*, 82(3):30003, 2008.

P. Pietzonka, A. C. Barato, and U. Seifert.
**Affinity-and topology-dependent bound on current fluctuations.**
*Journal of Physics A: Mathematical and Theoretical*, 49(34):34LT01, 2016.

P. Pietzonka, A. C. Barato, and U. Seifert.
**Universal bounds on current fluctuations.**
*Physical Review E*, 93(5):052145, 2016.

P. Pietzonka, F. Ritort, and U. Seifert.
**Finite-time generalization of the thermodynamic uncertainty relation.**
*Physical Review E*, 96(1):012101, 2017.

K. Proesmans, L. Peliti, and D. Lacoste.
**A case study of thermodynamic bounds for chemical kinetics.**
*arXiv:1804.00859*, 2018.

U. Seifert.
**Stochastic thermodynamics: From principles to the cost of precision.**
*Physica A*, 2017.
https://doi.org/10.1016/j.phys.2017.10.024.

H. Touchette.
**The large deviation approach to statistical mechanics.**
*Physics Reports*, 478(1-3):1–69, 2009.

K. Visscher, M. J. Schnitzer, and S. M. Block.
**Single kinesin molecules studied with a molecular force clamp.**
*Nature*, 400(6740):184, 1999.