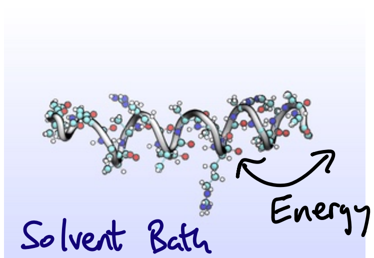
Statistical Mechanics "@" Telluride

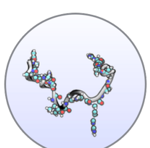
- Todd Gingrich (todd.gingrich@northwestern.edu)

- A Stochastic Thermodynamics Primer (Monday)
- Statistical Mechanics and Phase Transitions from a Large Deviation Theory perspective (Tuesday)
- Nonequilibrium Fluctuations (Wednesday)
- The Doi-Peliti Framework (Friday)

- A Stochastic Thermodynamics Primer



$$\beta = \frac{1}{k_B}\left(\frac{\partial S_B}{\partial E}\right)$$

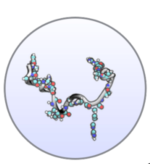


ν

$$P(\nu) \propto e^{-\beta E(\nu)}$$

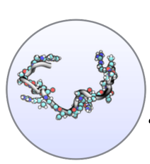
Configurations visited in proportion to the Boltzmann distribution.

Suppose $\exists$ only two microstates:



ν_1

$E(1)$



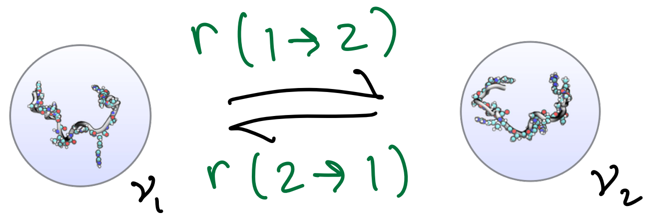
ν_2

$E(2)$

$$\frac{P(1)}{P(2)} = e^{-\beta(E(1)-E(2))} = e^{\beta \Delta E}$$

$\Delta E \equiv E(2) - E(1)$

What can we say about transitions between the microstates @ equilibrium?



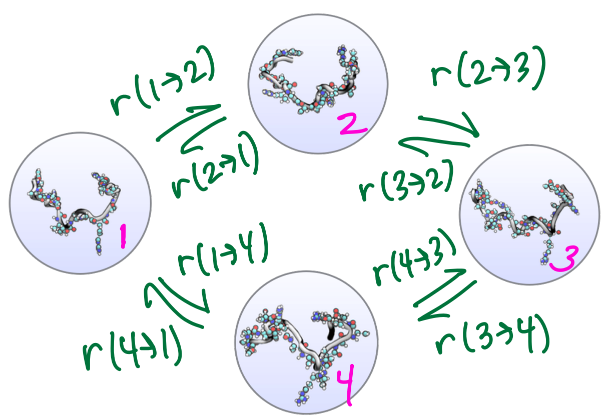
Detailed Balance:

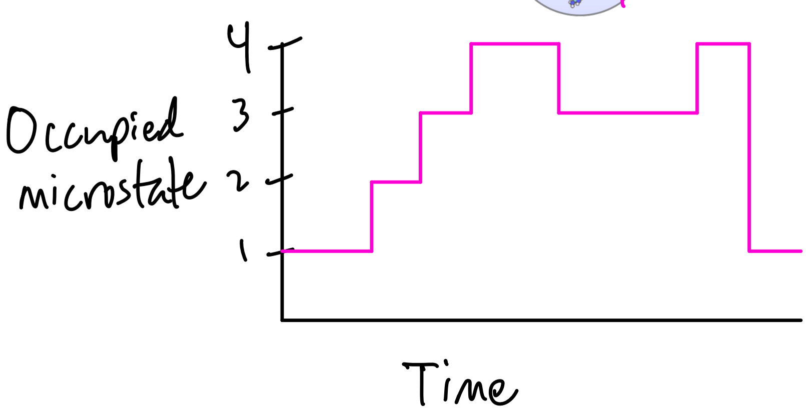
$$P(1)\,r(1\to2) = P(2)\,r(2\to1)$$

$$P(1)\propto e^{-\beta E(1)} \;\&\; P(2)\propto e^{-\beta E(2)} \Rightarrow \Delta E = k_BT\ln\frac{P(1)}{P(2)}$$

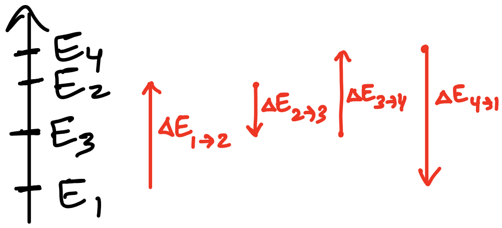
$$= k_BT\ln\frac{r(2\to1)}{r(1\to2)}$$

Reservoir's contributed energy is encoded in the rates

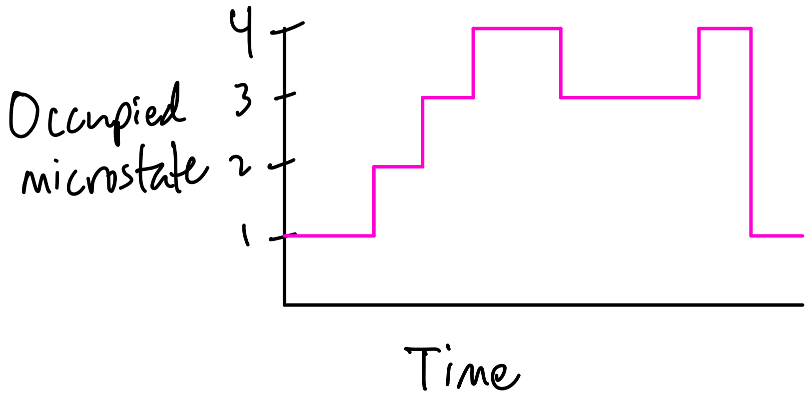


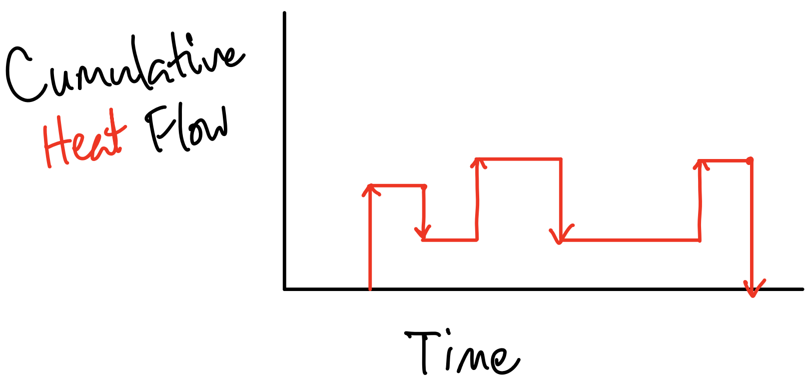


A realization of a jump process



Are these energies or free energies?





$Q = \frac{\Delta S}{T}$ ← change in entropy of ideal thermal reservoir @ temperature T

> Stochastic Thermodynamics relates the entropy production of one (or more) reservoirs to the stochastic dynamics (master eqn or Langevin) assuming "local detailed balance".

Stochasic Trajectory ⇒ Heat flow ⇒ Entropy gain of the reservoir

Complete a full cycle...

$$1 \xrightarrow[\Delta E_{1\to2}]{} 2 \xrightarrow[\Delta E_{2\to3}]{} 3 \xrightarrow[\Delta E_{3\to4}]{} 4 \xrightarrow[\Delta E_{4\to1}]{} 1$$

$$(E_2 - E_1) + (E_3 - E_2) + (E_4 - E_3) + (E_1 - E_4) = 0$$

$$k_B T \left[\ln \frac{P(1)\, P(2)\, P(3)\, P(4)}{P(2)\, P(3)\, P(4)\, P(1)} \right] = 0$$

$$k_B T \left[\ln \frac{r(2\to1)\, r(3\to2)\, r(4\to3)\, r(1\to4)}{r(1\to2)\, r(2\to3)\, r(3\to4)\, r(4\to1)} \right] = 0$$

Komolgorov's Criterion

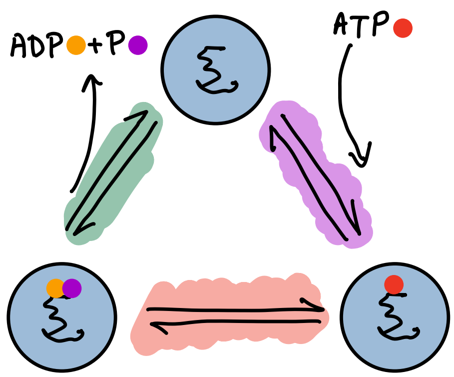
$$\frac{r(2\to1)\, r(3\to2)\, r(4\to3)\, r(1\to4)}{r(1\to2)\, r(2\to3)\, r(3\to4)\, r(4\to1)} = 1$$

When the system equilibrates with a single reservoir, trajectories have a time reversal symmetry and the reservoir entropy does not grow with time.

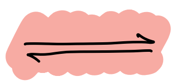
$\Rightarrow$ Equilibrium + no cycles

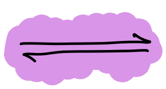
What if each "edge" tries to equilibrate with a different reservoir?

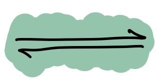
[Seifert Eur. Phys. J. E (2011)]



Separation of time scales justifies a Markovian description for the slow protein configurational changes

 : As before, heat flows between a thermal (solvent) reservoir and the enzyme.

 : An ideal particle reservoir with temperature T and chemical potential μ_{ATP}

 : An ideal particle reservoir with temperature T and chemical potentials μ_{ADP} + μ_P.

When $\mu_{ATP} - \mu_{ADP} - \mu_P \neq 0$, $\quad p(1)\, r(1\to 2) \neq p(2)\, r(2\to 1)$

(Detailed balance is broken due to flows out of some reservoirs and into some other.)

Even though DB is broken by having multiple reservoirs, the entropy production of any one reservoir is still described using flows into and out of that equilibrium reservoir.

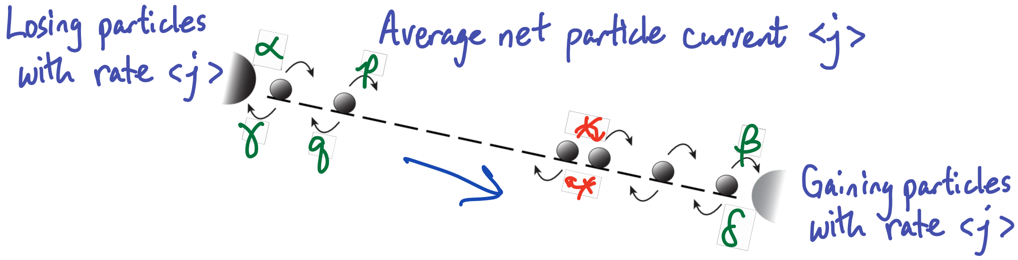
There is a local equilibrium — local detailed balance.

Let's spell things out more explicitly with an example.

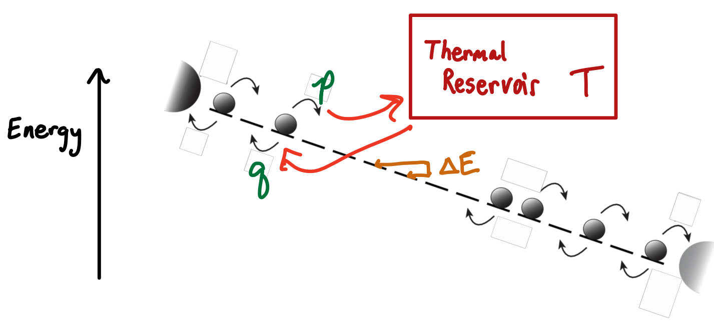
Imagine charged colloidal particles moving in 1D between two particle reservoirs...

ASEP

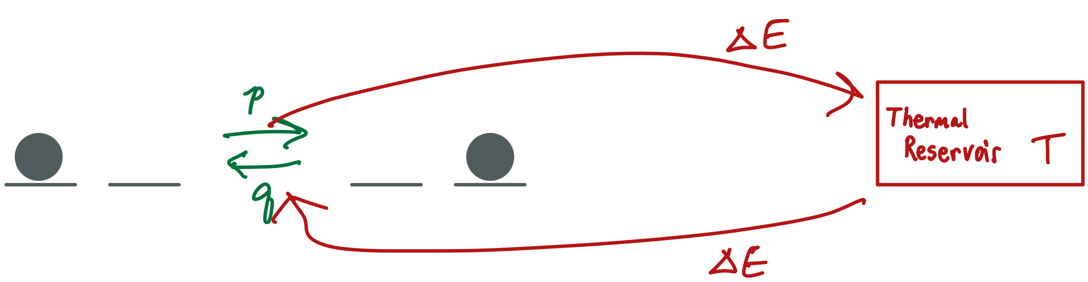
(with a field)

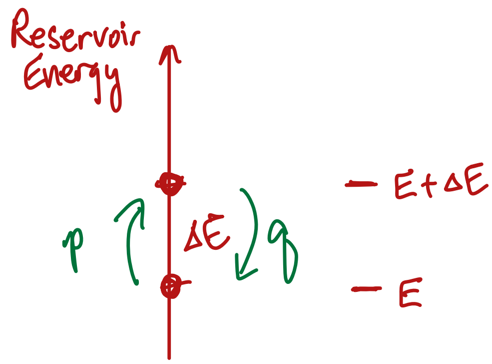


The system is not gaining or losing particles on average.
Its configurations are being sampled from a nonequilibrium steady state (NESS)



Probability that the reservoir has an extra ΔE of energy : $\dfrac{P(E+\Delta E)}{P(E)} = e^{\beta\Delta E}$

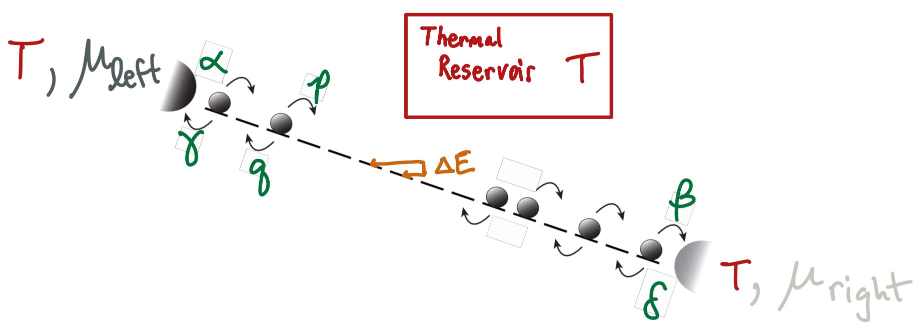




$$\underbrace{p(E+\Delta E)\, q = p(E)\, p}_{\text{Reservoir dynamics obeys DB.}}$$

Why?

$$\Rightarrow \frac{q}{p} = e^{\beta \Delta E} \quad \Rightarrow \quad k_B T \ln \frac{q}{p} = \Delta E$$



$$\frac{\gamma}{\alpha} = e^{-(\mu_{left} - E_{left})/k_B T} \qquad \frac{\delta}{\beta} = e^{(\mu_{right} - E_{right})/k_B T}$$

$$\ln \frac{\gamma}{\alpha} = -\frac{(\mu_{left} - E_{left})}{k_B T}$$

What does it cost to move a particle from left to right?

$$\frac{\mu_{left} - \mu_{right}}{k_B T} = \ln\frac{\alpha}{\gamma} + \ln\frac{\beta}{\delta} + \frac{E_{left} - E_{right}}{k_B T}$$

$$= \ln\frac{\alpha}{\gamma} + \ln\frac{\beta}{\delta} + \frac{(\Delta E)N-1}{k_B T}$$

$$= \ln\frac{\alpha}{\gamma} + \ln\frac{\beta}{\delta} + \ln\left(\frac{p}{q}\right)^{N-1}$$

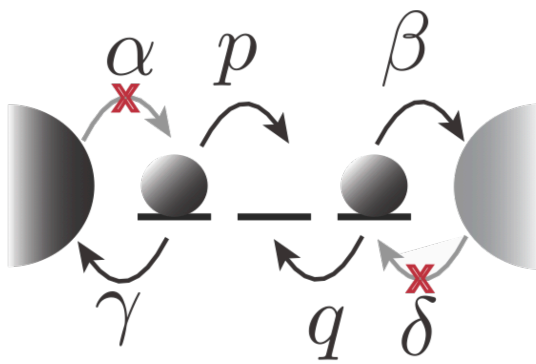
$$= \ln\frac{\alpha p^{N-1}\beta}{\gamma q^{N-1}\delta}$$

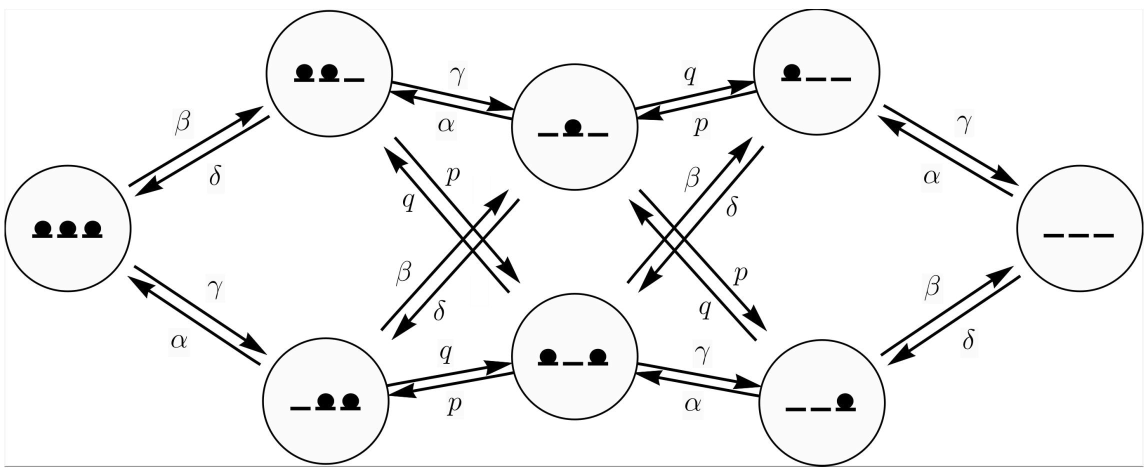
$$= \ln\frac{P_{left \to right}}{P_{right \to left}}$$

$$\underbrace{\frac{\mu_{left} - \mu_{right}}{k_B T}}_{\text{Thermodynamic cost for one particle}} = \underbrace{\ln\frac{P_{left \to right}}{P_{right \to left}}}_{\text{Ratio of forward and reversed trajectories.}}$$

I usually find it useful to think of a graphical picture...

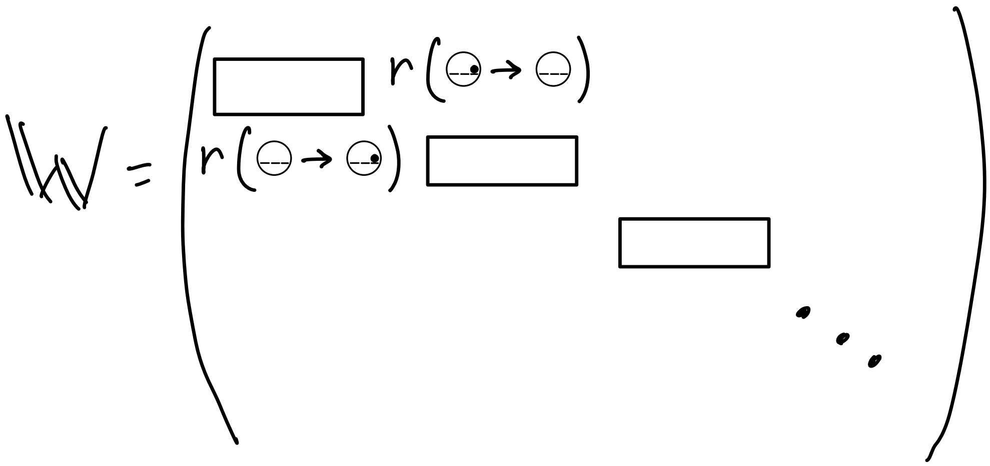
ASEP w/ 3 sites





$$\vec{p}(t) = \begin{pmatrix} p(\_\,\_\,\_) \\ p(\_\,\_\,\bullet) \\ p(\_\,\bullet\,\_) \\ p(\_\,\bullet\,\bullet) \\ p(\bullet\,\_\,\_) \\ p(\bullet\,\_\,\bullet) \\ p(\bullet\,\bullet\,\_) \\ p(\bullet\,\bullet\,\bullet) \end{pmatrix}$$

Master Equation $\quad \frac{\partial \vec{p}}{\partial t} = \mathbb{W}\vec{p} \quad \Rightarrow \quad \vec{p}(t) = e^{\mathbb{W}t}\,\vec{p}(0)$



Off-diagonal elements are simply the rates:

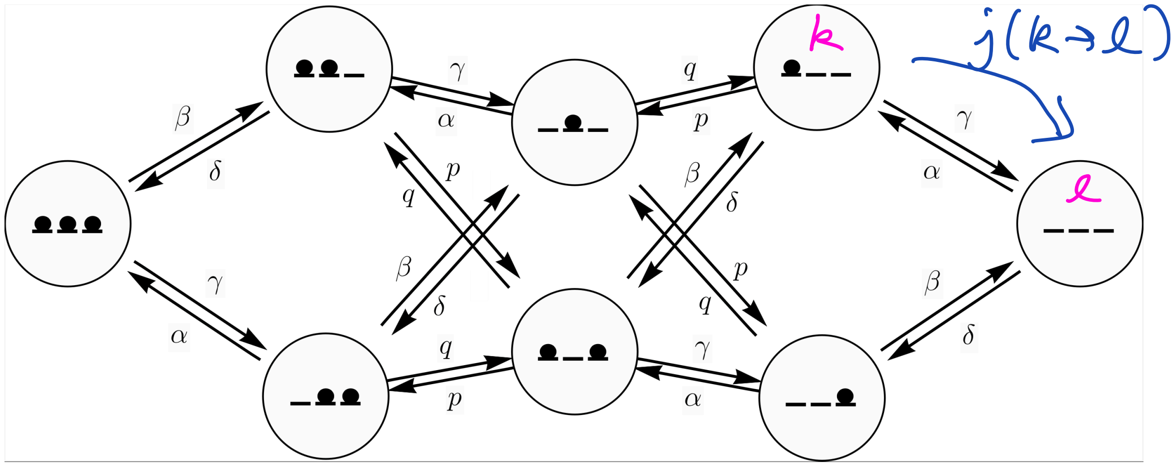
$$r(\ominus \to \ominus) = r(2\to 1) = \mathbb{W}_{12}$$

row 1
column 2

Diagonal elements enforce conservation of probability:

$$\mathbb{W}_{ii} = -\sum_{j\neq i} \mathbb{W}_{ji}$$

HW: Show that these diagonal matrix elements are required in order that a normalized $\vec{p}(0)$ would evolve into a normalized $\vec{p}(t)$ a time t later.



Current from $k \to \ell$: $j(k \to \ell)$ or $j_{\ell k}$

$$j(k \to \ell) = p(k)\, r(k \to \ell) - p(\ell)\, r(\ell \to k)$$

Entropy production associated with the reservoir upon when the $k \to \ell$ transition occurs:

$$k_B \ln \frac{r(k \to \ell)}{r(\ell \to k)}$$

Rate of entropy production associated with an "edge" of the graph

$$\sigma_{\ell k} = k_B\, j(k \to \ell) \ln \frac{r(k \to \ell)}{r(\ell \to k)}$$

Total entropy production for the stochastic dynamics

$$\Sigma = \sum_{\substack{\text{edges} \\ \ell k}} \sigma_{\ell k}$$

(Like a spatial average)

Equivalently we could write a temporal average:

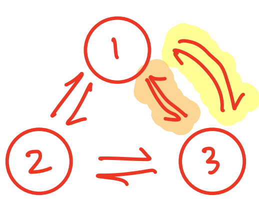
$$\Sigma_i / k_B = \sum_{\substack{\text{trajectories} \\ i\to k\to l\to\cdots\to z}} p(i\to k\to l\to\cdots)\ln\frac{p(i\to k\to l\to\cdots\to z)}{p(z\to\cdots\to l\to k\to i)}$$

$$= \underline{\left\langle \ln \frac{P_{forward}}{P_{reverse}} \right\rangle}$$

We can interpret the calculation as having ascribed an "entropy production" to a trajectory, meaning the total entropy production including the reservoirs.

What makes things "Stochastic thermodynamics" is the relationship between thermodynamics and forward/backward rates which all traces back to local detailed balance

WARNING: When transitions can be mediated by multiple pathways, the pathways must be handled separately!

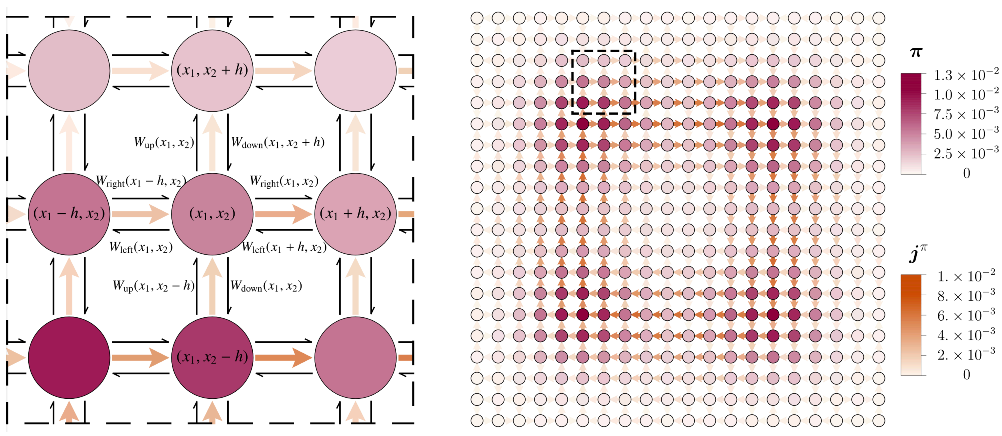


$$\underline{r(1\to 3)} = r_{ATP}(1\to 3) + r_{\Delta E}(1\to 3)$$

$$\ln \frac{r(1\to 3)}{r(3\to 1)}$$

History: Ken Sekimoto Stochastic Energetics
Udo Seifert Stochastic Thermodynamics (Langevin first)
PRL 95 040602
(2005)

I prefer playing with master equations because I happen to enjoy linear algebra. The Langevin picture can follow



Gingrich, Rotskoff, Horowitz, J. Phys. A 2017

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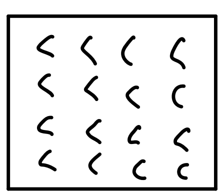
- Statistical Mechanics and Phase Transitions from a Large Deviation Theory perspective
  [H. Touchette, Physics Reports, 2009]

Let's start with a cartoon of phase transitions

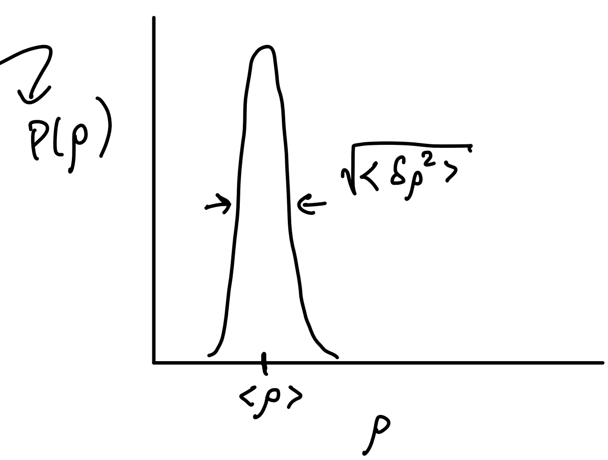


N, T, p

What is the density of H_2O in the box?

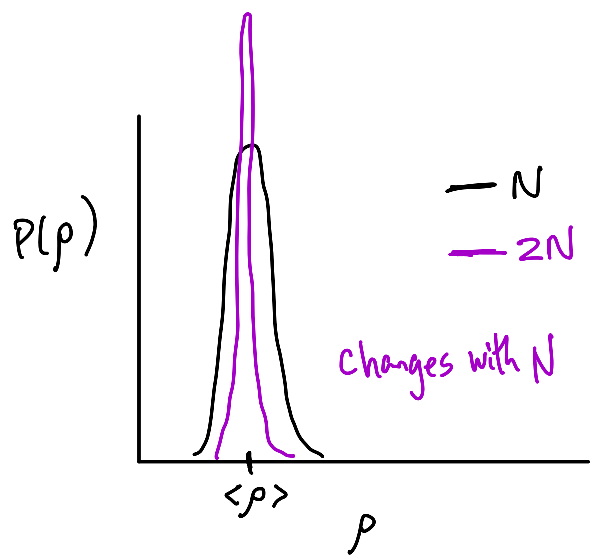
($p = 1\,\text{atm}$, $T = 200\,\text{K}$)

A distribution



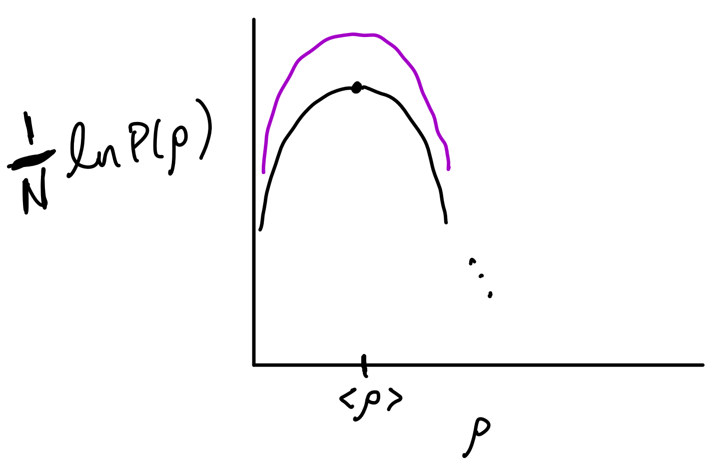
What changes when the system (N) grows?

system size	N	$2N$
mean	$\langle \rho \rangle \rightarrow$	$\langle \rho \rangle$
variance	$\langle \delta\rho^2 \rangle_N \rightarrow$	$\langle \delta\rho^2 \rangle_N / N$



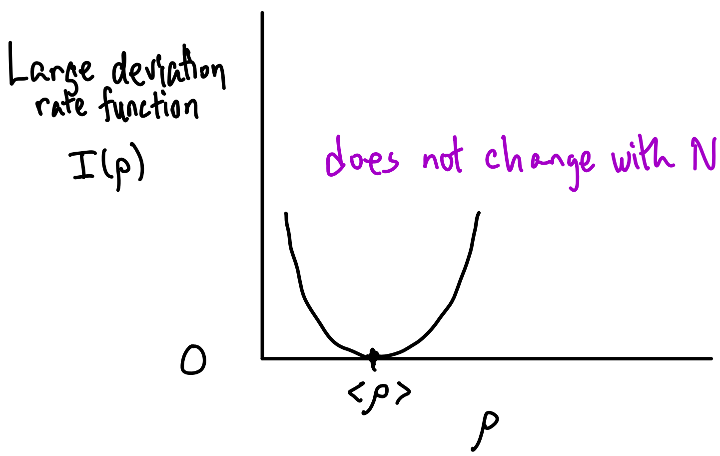
In the thermodynamic limit ($N \to \infty$), we stop thinking of $P(\rho)$ as a distribution and accept that

$$\rho = \langle \rho \rangle$$



$$I(\rho) = -\frac{1}{N}\ln P(\rho) + \frac{1}{N}\ln P(\langle\rho\rangle)$$

shifts up and down so I's min is at 0.

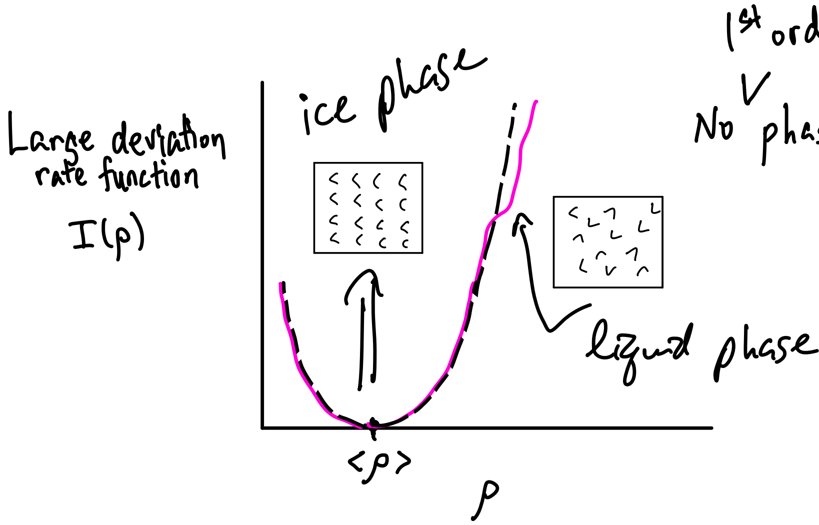


Large deviation form

$\Rightarrow P(\rho) \sim e^{-N I(\rho)}$

Gaussian $P(\rho) \Rightarrow$ Quadratic $I(\rho)$

Because of the ln, $I(\rho)$ can reveal the impact of large deviations away from $\langle\rho\rangle$.



No 1st order phase transition

Why would anyone care about a blip in the tail?

- It makes a big difference when you change the pressure.

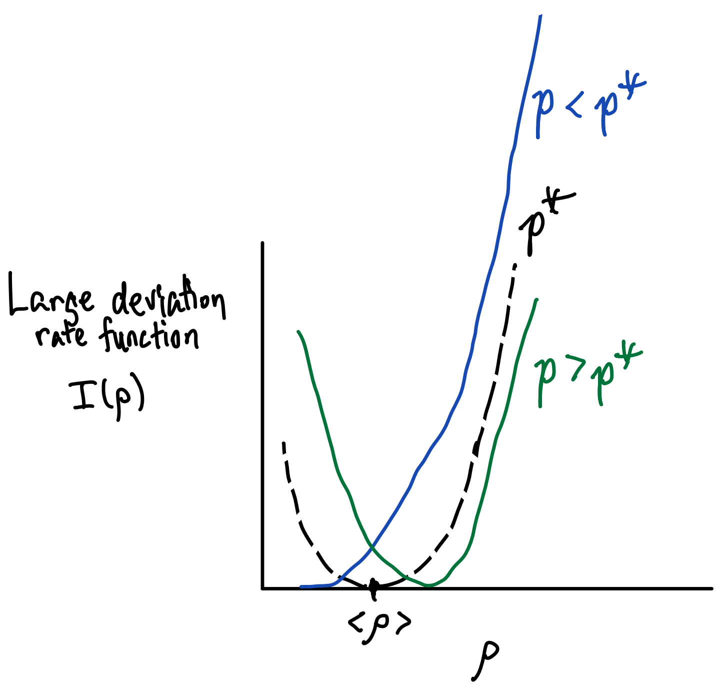
In the N, p, T ensemble, a microstate ν is observed w/ prob.

$$P_p(\nu) \propto e^{-\beta(E+pV)} = e^{-\beta(E+p^*V)}\, e^{-\beta V(p-p^*)}$$

$$= P_{p^*}(\nu)\, e^{-\beta V(p-p^*)}$$

$$\Rightarrow P_p(\rho) = P_{p^*}(\rho)\, \exp\left[\frac{-\beta(p-p^*)}{\rho}\right]$$

$$\Rightarrow I_p(\rho) = I_{p^*}(\rho) + \frac{\beta(p-p^*)}{\rho}$$

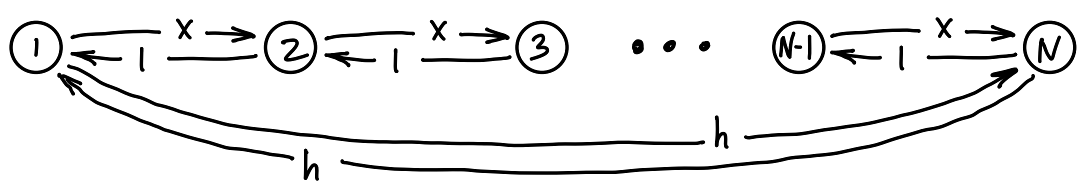


Changing the pressure tilts the rate function.

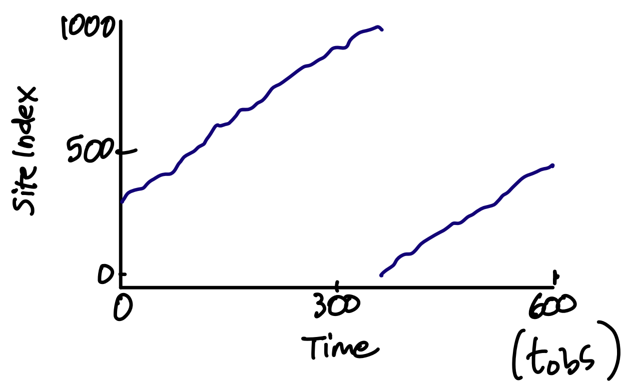
The large deviation rate function is a free energy per particle, so why the use the LD name?

One reason is that it highlights the scaling of distributions in an asymptotic limit, and that can extend beyond large N.

Rather than sampling H_2O configurations from N, p, T and measuring ρ, lets sample trajectories from a Markov jump process and measure Σ.



Typical trajectories are fairly obvious



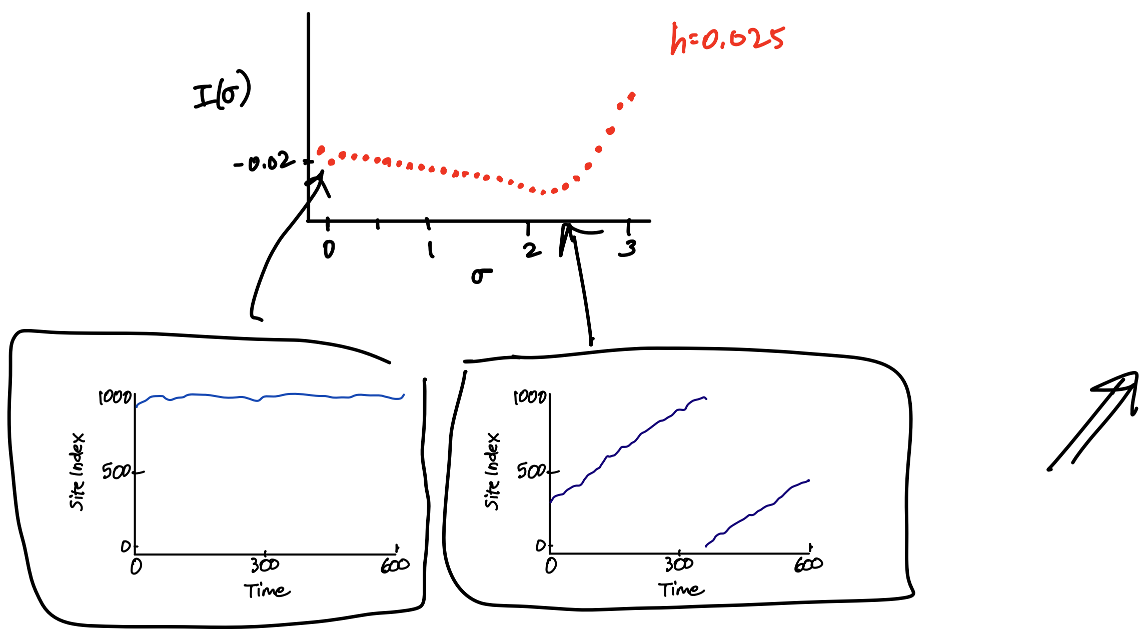
Just run KMC (Gillespie)

$\left(x=3,\ h=0.05,\ N=1000 \right)$

$$\Sigma_i = \sum_{\text{jumps}} \ln \frac{k_f}{k_r} \qquad \sigma = \frac{\Sigma_i}{t_{obs}}$$

In the limit of large t_{obs}, what can be said about $P(\Sigma)$?

Distribution of entropy production collected from repeated simulations



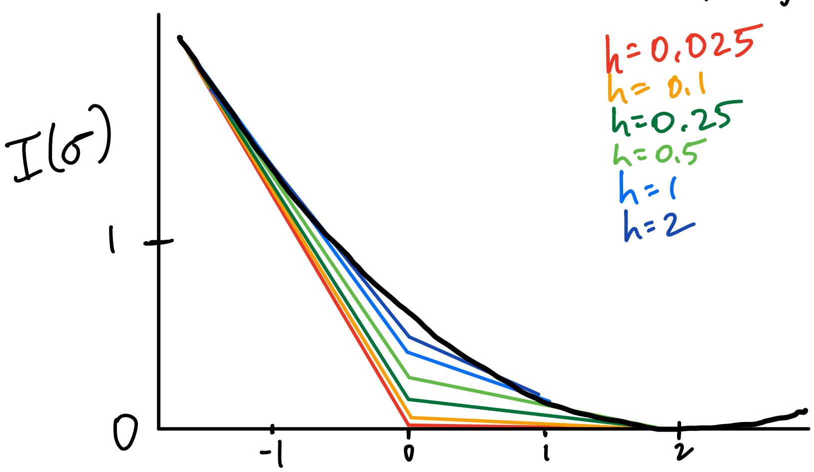
Conditioned upon a value of σ, what does the likely trajectory look like?

It's possible for the answer to undergo a <u>qualitative</u> change from one type of trajectory (delocalized) to another (localized) as you change the constraint (σ).

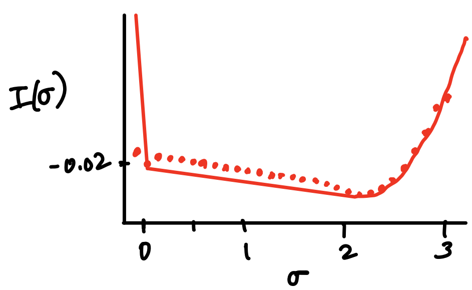
A discontinuous phase transition between two classes of trajectories — a dynamic phase transition.

This (embarrassingly) simple model has helped me understand a little more about phase transitions because it is possible to perform some analytical calculations*...

*[Vaikuntanathan, Gingrich, Geissler, PRE 2014]



Entropy Production Rate
$\sigma \equiv \Sigma / t_{obs}$



Rather than immediately going for $I(\sigma)$, let's define a scaled cumulant generating function

$$\psi(\lambda) \equiv \lim_{t\to\infty} \frac{1}{t} \ln \underline{\langle e^{-\lambda \Sigma} \rangle}$$

An average over trajectories of length t

Taking one derivative gives the 1^{st} cumulant (mean)

$$-\frac{\partial \psi}{\partial \lambda}\bigg|_{\lambda=0} = \lim_{t\to\infty} \frac{1}{t} \frac{\langle \Sigma e^{-\lambda\Sigma} \rangle}{\langle e^{-\lambda \Sigma}\rangle}\bigg|_{\lambda=0} = \lim_{t\to\infty} \frac{1}{t} \langle \Sigma \rangle = \langle \sigma \rangle$$

Taking a second derivative gives the 2^{nd} cumulant (variance)

$$\frac{\partial^2 \psi}{\partial \lambda^2}\bigg|_{\lambda=0} = \lim_{t\to\infty} \frac{1}{t} \frac{\langle \Sigma^2 e^{-\lambda\Sigma}\rangle \langle e^{-\lambda\Sigma}\rangle - \langle \Sigma e^{-\lambda \Sigma}\rangle^2}{\langle e^{-\lambda\Sigma}\rangle^2}\bigg|_{\lambda=0}$$

$$= \lim_{t\to\infty} \frac{\langle \Sigma^2 \rangle - \langle \Sigma \rangle^2}{t} = \lim_{t\to\infty} \frac{\mathrm{Var}(\Sigma)}{t}$$

But what does this have to do with $I(\sigma)$?!

$$\psi(\lambda) = \lim_{t\to\infty} \frac{1}{t} \ln \langle e^{-\lambda \Sigma} \rangle = \lim_{t\to\infty} \frac{1}{t} \ln \int d\Sigma \, e^{-\lambda t \sigma} P(\Sigma)$$

$$= \lim_{t\to\infty} \frac{1}{t} \ln \int d\Sigma \, e^{-\lambda t\sigma} e^{-t I(\sigma)}$$

$$= \lim_{t\to\infty} \frac{1}{t} \ln \int d\Sigma \, e^{-t(\lambda\sigma + I(\sigma))}$$

saddle point / Laplace's method

$$\approx \lim_{t\to\infty} \frac{1}{t} \ln e^{-t \min_{\sigma}(\lambda\sigma + I(\sigma))}$$

$$= -\min_{\sigma}\left(\lambda\sigma + I(\sigma)\right)$$

$$\therefore \quad \Psi(\lambda) \xLeftrightarrow{\text{Legendre-Fenchel}} I(\sigma)$$

Gärtner-Ellis Thm.

Remarkably, $\Psi(\lambda)$ can be computed from an eigenvalue calculation

$$\Psi(\lambda) \equiv \lim_{t\to\infty} \frac{1}{t} \ln \langle e^{-\lambda\Sigma_t} \rangle$$

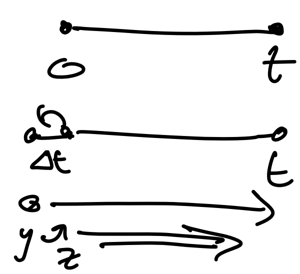
Notice that $\langle e^{-\lambda\Sigma_t} \rangle$ is a weighted average over trajectories from time 0 to time t. How does this weighted average change if the time interval grows by an infinitesimal amount?

[Lebowitz + Spohn 1999]

Let's define $\quad g(y,0,t) \equiv \langle e^{-\lambda\Sigma} \mid y \text{ at time } 0 \rangle_{[0,t]}$

Interval I'm averaging over

$$\frac{\partial g(y,0,t)}{\partial t} = \lim_{\Delta t\to 0} \frac{g(y,0,t) - g(y,-\Delta t,t)}{-\Delta t}$$



$$g(y,-\Delta t,t) = \langle e^{-\lambda\Sigma} \mid y @ -\Delta t \rangle_{[-\Delta t,t]}$$

$$= \sum_{z \neq y} \left(\frac{r(y \to z)}{r(z \to y)} \right)^{-\lambda} \Delta t \, r(y \to z) \, \langle e^{-\lambda \Sigma} | z @ 0 \rangle_{[0,t]} + 1 \left(1 - \sum_{z \neq y} r(y \to z) \Delta t \right) \langle e^{-\lambda \Sigma} | y @ 0 \rangle_{[0,t]}$$

Contribution to the weighted average

Probability of $y \to z$ in time Δt

Probability of staying in y for time Δt

$$= \sum_{z \neq y} \left(\frac{r(y \to z)}{r(z \to y)} \right)^{-\lambda} \Delta t \, r(y \to z) \, g(z,0,t) + \left(1 - \sum_{z \neq y} r(y \to z) \Delta t \right) g(y,0,t)$$

canceled

$$\Rightarrow \quad \frac{\partial g(y,0,t)}{\partial t} = \sum_{z \neq y} \left(\frac{r(y \to z)}{r(z \to y)} \right)^{-\lambda} \Delta t \, r(y \to z) \, g(z,0,t) - \sum_{z \neq y} r(y \to z) \Delta t \, g(y,0,t)$$

Let

$$\vec{g} = \begin{pmatrix} g(1,0,t) \\ g(2,0,t) \\ \vdots \end{pmatrix}$$

$$\Rightarrow \quad \frac{\partial \vec{g}}{\partial t} = \begin{pmatrix} -\sum_{z \neq 1} r(1 \to z) & r(1 \to 2)^{1-\lambda} r(2 \to 1)^{\lambda} & \cdots \\ r(2 \to 1)^{1-\lambda} r(1 \to 2)^{\lambda} & -\sum_{z \neq 2} r(2 \to z) & \\ \vdots & & \ddots \end{pmatrix} \vec{g}$$

$$= \mathbb{W}(\lambda) \, \vec{g}$$

Tilted/Twisted/Deformed generator

Same diagonal matrix elements as $\mathbb{W}$ but new off-diagonal

$$\vec{p}(t) = e^{\mathbb{W}t}\,\vec{p}(0) \xrightarrow[\text{time}]{\text{Long}} e^{\nu t}\,|\nu\rangle$$

where ν is the maximum eigenvalue of $\mathbb{W}$ (Perron-Frobenius) and $|\nu\rangle$ is the associated (right) eigenvector. $\nu = 0$, $|\nu\rangle$ = steady state density

$$\vec{g}(t) = e^{\mathbb{W}(\lambda)t}\,\vec{g}(0) \xrightarrow[\text{time}]{\text{Long}} e^{\nu(\lambda)}\,|\nu(\lambda)\rangle$$

$$\psi(\lambda) \equiv \lim_{t\to\infty} \frac{1}{t} \ln \langle e^{-\lambda \Sigma_t} \rangle$$

$$= \lim_{t\to\infty} \frac{1}{t} \ln \sum_y p_0(y)\, g(y,0,t)$$

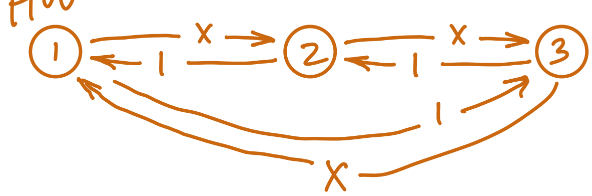
$$= \lim_{t\to\infty} \frac{1}{t} \ln \langle p_0 | e^{\nu(\lambda)t} | \nu(\lambda)\rangle$$

$$= \lim_{t\to\infty} \frac{1}{t}\nu(\lambda)t + \frac{1}{t}\langle p_0 | \nu(\lambda)\rangle$$

$$= \nu(\lambda)$$

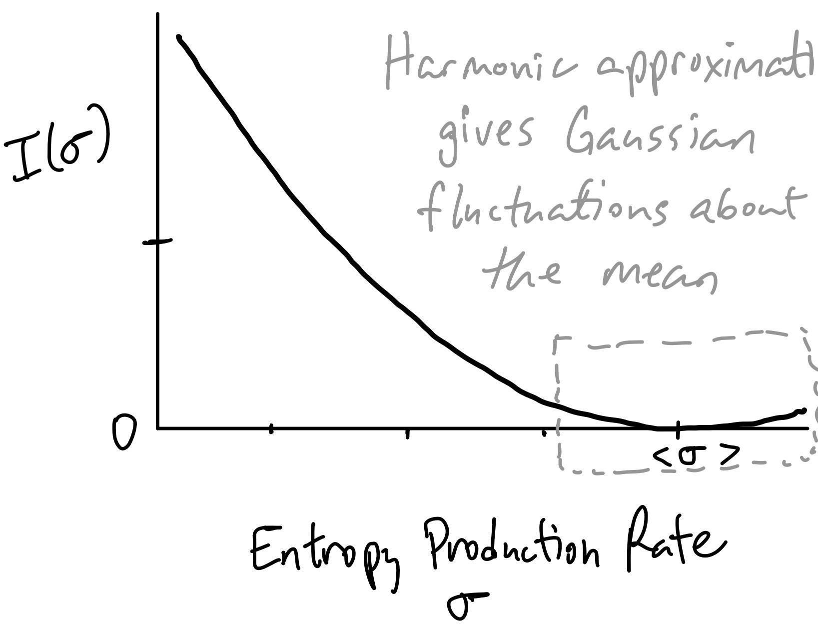
$\therefore$ $\psi(\lambda)$ <u>is</u> the maximal real eigenvalue of $\mathbb{W}(\lambda)$!

HW:

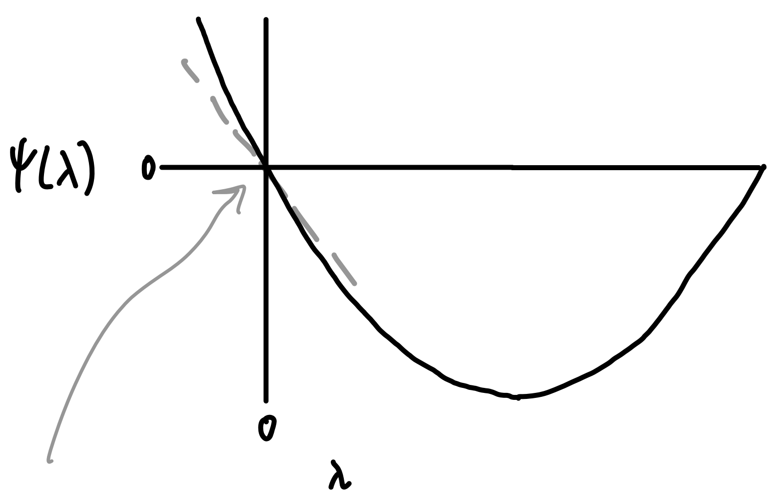


3-state w/ translational symmetry.

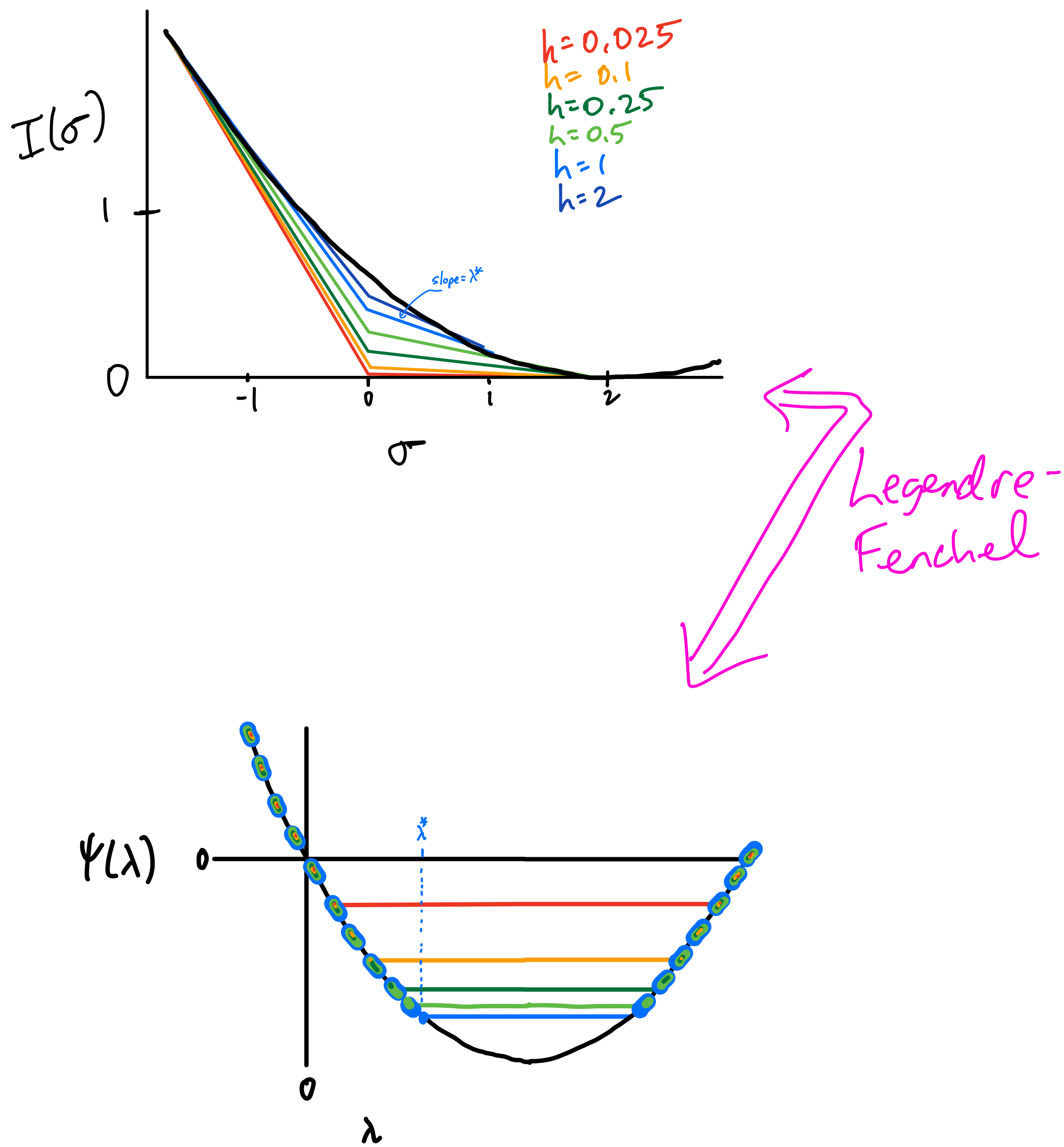
Construct $\mathbb{W}(\lambda)$ to compute $\psi(\lambda)$ and $I(\sigma)$.



Legendre-Fenchel



$\psi'(\lambda)\big|_{\lambda=0} = -\langle \sigma \rangle$



∃ a singularity in the scaled cumulant generating function!

Singularity in a free energy $\Longleftrightarrow$ phase transition

[Vaikuntanathan, Gingrich, Geissler, PRE 2014]

Statistical Mechanics "@" Telluride

- Todd Gingrich (todd.gingrich@northwestern.edu)

- A Stochastic Thermodynamics Primer (Monday)
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- Nonequilibrium Fluctuations

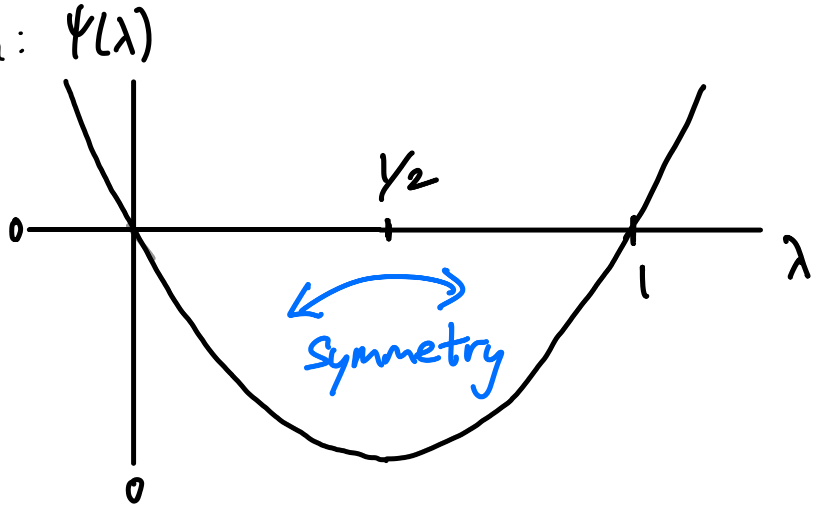
Remember that yesterday we showed

$$\underbrace{\psi(\lambda)}_{\text{scaled cumulant generating function}} = \nu(\lambda)$$

largest (real) eigenvalue of a "tilted" rate matrix $\mathbb{W}(\lambda)$

$$\mathbb{W}(\lambda) = \begin{pmatrix} -\sum_{z\neq 1} r(1\to z) & r(1\to 2)^{\lambda}\, r(2\to 1)^{1-\lambda} & \cdots \\ r(2\to 1)^{\lambda}\, r(1\to 2)^{1-\lambda} & -\sum_{z\neq 2} r(2\to z) & \cdots \\ \vdots & & \ddots \end{pmatrix}$$

Claim:



$$\psi(\lambda) = \psi(1-\lambda)$$

[Lebowitz + Spohn 1999]

So what?

Remember the Legendre relationship between $\psi(\lambda)$ + $I(\sigma)$
The $\psi(\lambda) = \psi(1-\lambda)$ symmetry can be translated...

$$\psi(\lambda) = -\min_{\sigma} \left(\lambda\sigma + I(\sigma) \right)$$

Why? Legendre transform is its own inverse.

$$I(\sigma) = -\min_{\lambda} \left[\lambda\sigma + \psi(\lambda) \right]$$

$$= -\min_{\lambda} \left[\lambda\sigma + \psi(1-\lambda) \right]$$

$$= -\sigma - \min_{\lambda} \left[(\lambda-1)\sigma + \psi(1-\lambda) \right]$$

$$= -\sigma - \min_{1-\lambda}\left[-(1-\lambda)\sigma + \Psi(1-\lambda)\right]$$

$$= -\sigma - \min_{\delta}\left[-\delta\sigma + \Psi(\delta)\right]$$

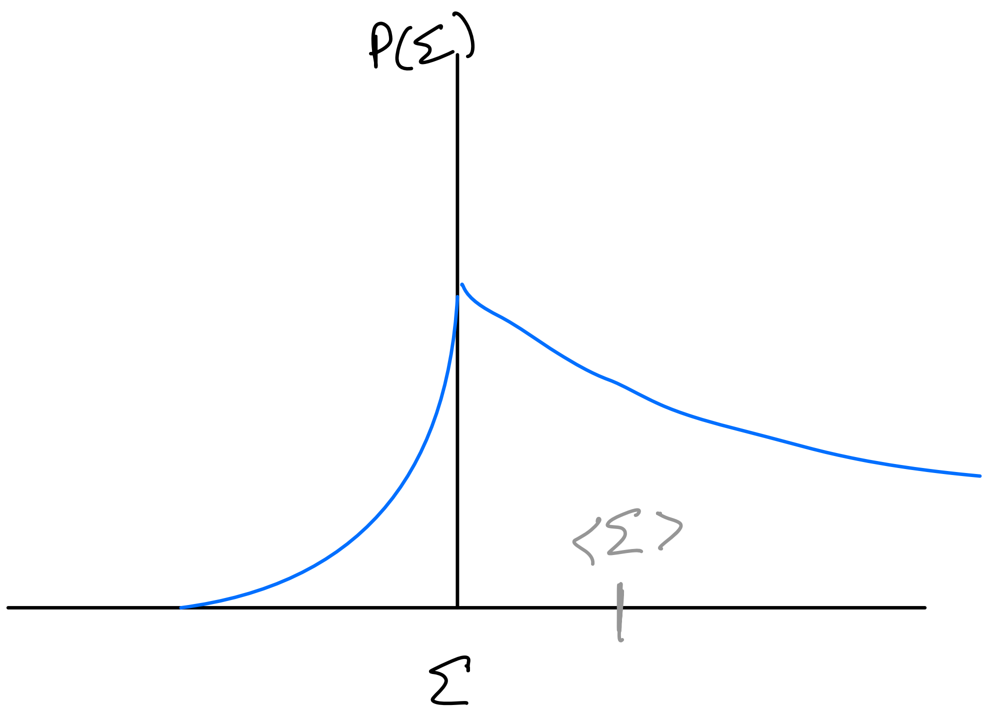
δ: dummy variable

$$= -\sigma + I(-\sigma)$$

$$\boxed{I(\sigma) - I(-\sigma) = -\sigma}$$

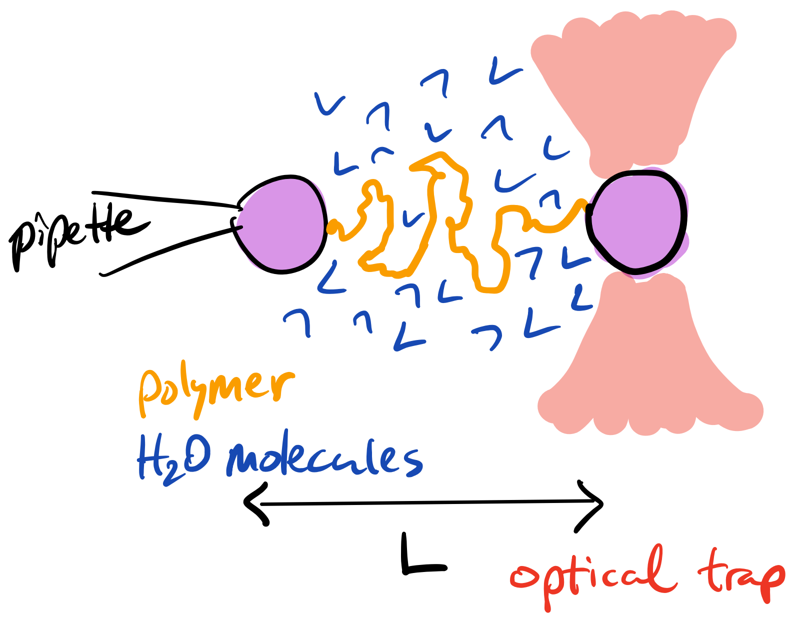
$$\frac{P(\sigma)}{P(-\sigma)} \sim e^{-t_{obs}[I(\sigma) - I(-\sigma)]} = e^{t_{obs}\sigma}$$

In English, the probability of producing entropy $\sigma t_{obs} = \Sigma_i$ is $\exp(\Sigma_i)$ times greater than the probability of entropy going down by Σ_i.



This "entropy production fluctuation theorem" is a more refined view of the second law. Entropy increases on average because $+\Sigma$ is always more likely than $-\Sigma$, but it is possible to observe trajectories which appear to violate the second law ($-\Sigma$).

These ideas have had the biggest impact on biophysical pulling experiments



My microstates ν are given by the polymer configurations

$$\nu = (L, \{i\})$$

end-to-end distance   everything else

$$P(\nu) = \frac{e^{-\beta E(\nu)}}{Q}$$

(β from H_2O molecules)

What is $P(L)$? (Free polymer at this point — free to fluctuate that is)

$$P(L) \propto \sum_{\{i\}} e^{-\beta E(L,\{i\})}$$

Marginalize (average) over degrees of freedom I'm not measuring

$$\Rightarrow \ln P(L) = \ln(\text{const.}) + \ln\left(\sum_{\{i\}} e^{-\beta E(L,\{i\})}\right)$$

$$\Rightarrow \frac{\partial \ln P(L)}{\partial L} = \frac{\beta \sum_{\{i\}} \left(-\frac{dE(L,\{i\})}{dL}\right) e^{-\beta E(L,\{i\})}}{\sum_{\{i\}} e^{-\beta E(L,\{i\})}}$$

The statistical weight for microstate $\{i\}$ when L is fixed

Therefore

$$\frac{d\ln P(L)}{dL} = \beta \left\langle \frac{-dE(L,\{i\})}{dL} \right\rangle_{\{i\}}$$

Averaging over all possible polymers with length L

$$= \beta \left(\begin{array}{c} \text{mean force } \underline{\text{by polymer}} \\ \text{on coordinate } L \end{array} \right)$$

$$= -\beta \left(\begin{array}{c} \text{mean force applied to} \\ \text{the polymer to fix } L \end{array} \right)$$

$$\int_{L_i}^{L_f} dL \, \frac{d\ln P(L)}{dL} = -\beta \int_{L_i}^{L_f} dL \left(\begin{array}{c} \text{mean force applied to} \\ \text{the polymer to fix } L \end{array} \right)$$

$$\ln P(L_f) - \ln P(L_i) = \beta \int_{L_i}^{L_f} \underbrace{dL}_{\text{distance}} \left\langle \underbrace{- \frac{dE(L,\{i\})}{dL}}_{\text{mean force}} \right\rangle_{\{i\}}$$

$$= -\beta W_{rev}(L_i \to L_f)$$

Reversible Work Theorem:

$$\frac{P(L_f)}{P(L_i)} = e^{-\beta W_{rev}(L_i \to L_f)}$$

$$= e^{-\beta [A(L_f) - A(L_i)]}$$

If I pull quickly, how much work do I do?

Usually $W > W_{rev}$, but not *always* true. It depends on the trajectory's particular fluctuations.

on average

If I pull quickly, how much work do I do?

$\langle W \rangle > W_{rev}$

That extra work is dissipation — the thermal bath increases in entropy by $W_{diss} = W - W_{rev}$

Suppose I want to measure a free energy difference. How do I do that?

- Perform a reversible process by perturbing S L O W L Y.
  Measure the work to execute that reversible process.

- $$\frac{P_F(W_{diss})}{P_R(-W_{diss})} = e^{\beta W_{diss}}$$ Crooks Fluctuation Relation

$$\Rightarrow \int dW_{diss}\, P_F(W_{diss})\, e^{-\beta(\underline{W}-\Delta A)} = \int dW_{diss}\, P_R(-W_{diss})$$

$$\langle e^{-\beta(W-\Delta A)} \rangle_F = 1$$

Jarzynski Equality

Average over trajectories being stretched from 0 to L

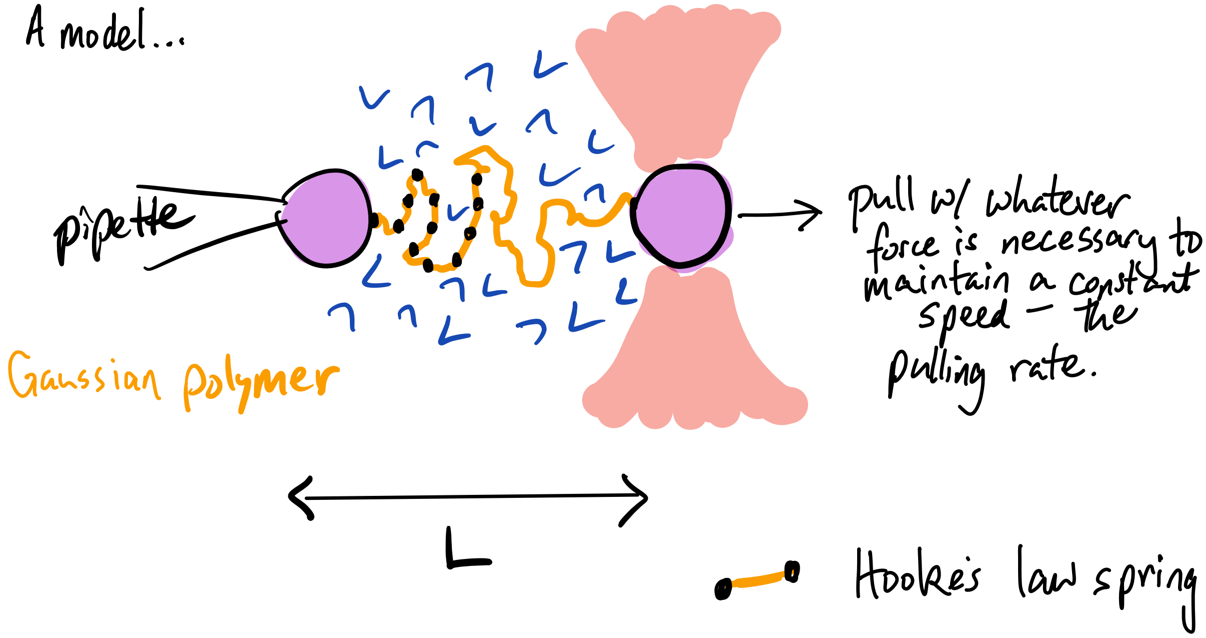
Will depend on the trajectory

$$\Rightarrow \quad e^{\beta\Delta A} \langle e^{-\beta W} \rangle_F = 1$$

$$\Rightarrow \quad \langle e^{-\beta W} \rangle_F = e^{-\beta\Delta A}$$

$$W_{rev} = \Delta A = -k_B T \ln \langle e^{-\beta W} \rangle_F$$

A model...



$$\text{Work} = \int dt\, F(t) \left(\frac{dL}{dt}\right)$$

pulling rate

What is $W_{rev}(0 \to L)$?

Prob. dist. for free polymer

$$\text{Rev. Work Thm.}: \quad W_{rev}(L_i \to L_f) = k_B T \ln \frac{P(L_i)}{P(L_f)}$$

When the springs are linear (Hookean), the energy is quadratic, so the Boltzmann probability of a polymer configuration is a (high-dimensional) Gaussian

$$P(\underline{\vec{R}_0}, \underline{\vec{R}_1, \vec{R}_2, \ldots}, \underline{\vec{R}_N}) \propto \exp\left[-\frac{\beta k}{2} \sum_{i=1}^{N} |\vec{R}_i - \vec{R}_{i-1}|^2\right]$$

Integrate out coordinates we won't measure

$$P(\underline{\vec{R}_N} - \underline{\vec{R}_0}) \Rightarrow \text{a Gaussian } P(L)$$

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- The Doi-Peliti Framework

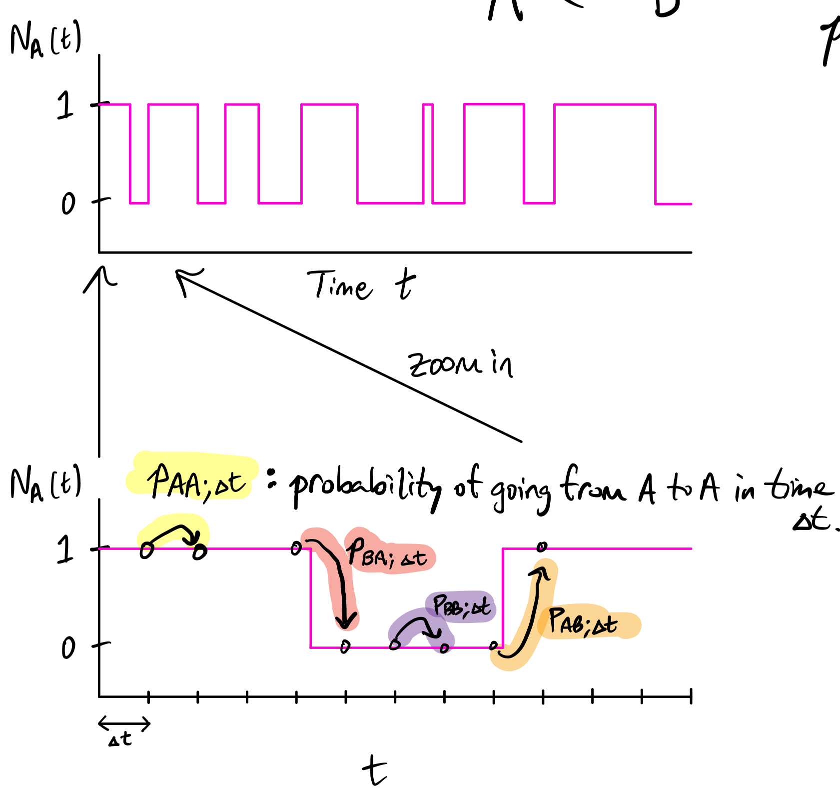
  How to make classical stochastic kinetics look a lot like an electronic structure problem.

Stochastic kinetics?

$$A \rightleftharpoons B$$

p_A: probability of A

p_B: probability of B



Markov approximation:

Only my current state impacts the probability of my next event. The history doesn't matter.

Start in A.

Probability of being in A at Δt? $p_{AA;\Delta t}$

Probability of being in B at Δt? $p_{BA;\Delta t}$

Probability of being in some state, A or B, at Δt? $p_{AA;\Delta t} + p_{BA;\Delta t} = 1$

Start in B.

Probability of being in A at Δt? $p_{AB;\Delta t}$

Probability of being in B at Δt? $p_{BB;\Delta t}$

Probability of being in some state, A or B, at Δt? $p_{AB;\Delta t} + p_{BB;\Delta t} = 1$

Start in a mixed state

Initial probability p_A of starting in A and p_B of starting in B.

$$p_A(\Delta t) = \left(\begin{matrix}\text{start in A \&} \\ \text{stay there}\end{matrix}\right) + \left(\begin{matrix}\text{start in B \&} \\ \text{move to A}\end{matrix}\right) = p_A(0)\, p_{AA;\Delta t} + p_B(0)\, p_{AB;\Delta t}$$

$$\begin{pmatrix} p_A(\Delta t) \\ p_B(\Delta t) \end{pmatrix} = \begin{pmatrix} p_{AA;\Delta t} & p_{AB;\Delta t} \\ p_{BA;\Delta t} & p_{BB;\Delta t} \end{pmatrix} \begin{pmatrix} p_A(0) \\ p_B(0) \end{pmatrix}$$

What is the right Δt?

Δt may be more of an artifact & you want to imagine being able to measure the state infinitely quickly, in which case $\Delta t \to 0$.

$$\frac{d}{dt}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix} = \lim_{\Delta t \to 0} \frac{1}{\Delta t}\left[\begin{pmatrix} p_A(t+\Delta t) \\ p_B(t+\Delta t) \end{pmatrix} - \begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}\right]$$

$$= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\left[\begin{pmatrix} p_{AA;\Delta t} & p_{AB;\Delta t} \\ p_{BA;\Delta t} & p_{BB;\Delta t} \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right]\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

$$= \lim_{\Delta t \to 0} \begin{pmatrix} \frac{p_{AA;\Delta t} - 1}{\Delta t} & \frac{p_{AB;\Delta t}}{\Delta t} \\ \frac{p_{BA;\Delta t}}{\Delta t} & \frac{p_{BB;\Delta t} - 1}{\Delta t} \end{pmatrix}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

Rate constant

$$\lim_{\Delta t \to 0} \frac{p_{AB;\Delta t}}{\Delta t} = k_{AB}$$

$$\lim_{\Delta t \to 0} \frac{p_{BA;\Delta t}}{\Delta t} = k_{BA}$$

Probability per unit time of transitioning from B to A in an infinitesimal moment of time.

Diagonal Matrix Element?

Remember

$1 = p_{AA;\Delta t} + p_{BA;\Delta t}$

$$\lim_{\Delta t \to 0} \frac{p_{AA;\Delta t} - 1}{\Delta t} = \lim_{\Delta t \to 0} \frac{(1 - p_{BA;\Delta t}) - 1}{\Delta t} = -k_{BA}$$

$$\frac{d}{dt}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix} = \underbrace{\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB} \end{pmatrix}}_{\mathbb{W}}\begin{pmatrix} p_A(t) \\ p_B(t) \end{pmatrix}$$

$$\vec{p}(t) = e^{\mathbb{W} t}\vec{p}(0)$$

$\mathbb{W}$ has eigenvalues ν_0 and ν_1 with associated left and right eigenvectors

$$\langle 0|\mathbb{W} = \langle 0|\nu_0 \qquad \mathbb{W}|0\rangle = \nu_0|0\rangle$$

$$\langle 1|\mathbb{W} = \langle 1|\nu_1 \qquad \mathbb{W}|1\rangle = \nu_1|1\rangle$$

$$\exp\left[\begin{pmatrix} -k_{BA} & k_{AB} \\ k_{BA} & -k_{AB}\end{pmatrix} t\right]$$

$$= |0\rangle\langle 0| e^{\nu_0 t} + |1\rangle\langle 1| e^{\nu_1 t}$$

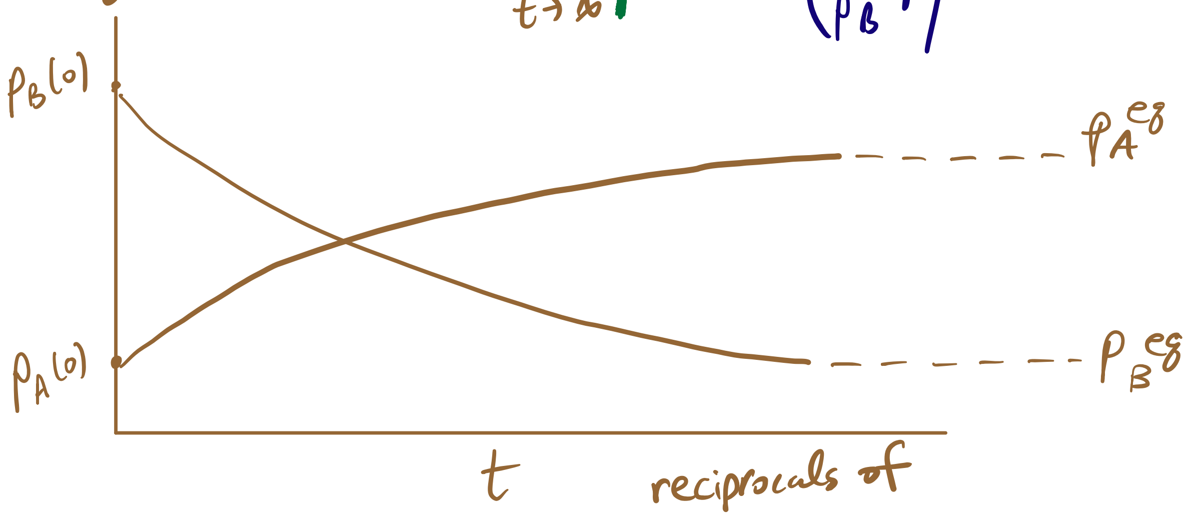
$$\mathbf{p}(t) = \left(|0\rangle\langle 0| e^{\nu_0 t} + |1\rangle\langle 1| e^{\nu_1 t}\right)\mathbf{p}(0)$$

$$= \left[\begin{pmatrix} p_A^{eq} \\ p_B^{eq}\end{pmatrix}(1 \ \ 1)e^{0t} + \begin{pmatrix} 1 \\ -1\end{pmatrix}(1 \ -1)e^{-(k_{AB}+k_{BA})t}\right]\mathbf{p}(0)$$

$$= \left[\begin{pmatrix} p_A^{eq} \\ p_B^{eq}\end{pmatrix}\left(p_A(0)+p_B(0)\right) + \begin{pmatrix} 1 \\ -1\end{pmatrix}e^{-(k_{AB}+k_{BA})t}\left(p_A(0)-p_B(0)\right)\right]$$

$$\mathbf{P}(t) = \left[\begin{pmatrix} c_A^{eq} \\ c_B^{eq} \end{pmatrix} + \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_{AB}+k_{BA})t} \left(p_A(0) - p_B(0) \right) \right]$$

Long time... ? $\lim_{t\to\infty} \mathbf{P}(t) = \begin{pmatrix} p_A^{eq} \\ p_B^{eq} \end{pmatrix}$



Relaxation timescales are reciprocals of eigenvalues of $\mathbb{W}$ and steady-state probabilities (concentrations) are an eigenvector.

Perhaps that looks like QM, but not exactly electronic structure. Where's the connection?

- The many-body problem strikes again.

Let there be n_A A molecules and n_B B molecules with a total of $N = n_A + n_B$ molecules.

The possible microstates are

$$\begin{pmatrix} n_A \\ n_B \end{pmatrix} = \underbrace{\begin{pmatrix} 0 \\ N \end{pmatrix}, \begin{pmatrix} 1 \\ N-1 \end{pmatrix}, \ldots, \begin{pmatrix} N-1 \\ 0 \end{pmatrix}, \begin{pmatrix} N \\ 0 \end{pmatrix}}_{N+1 \text{ options}}$$

$$\frac{d}{dt}\begin{pmatrix} p\begin{pmatrix} 0 \\ N \end{pmatrix} \\ p\begin{pmatrix} 1 \\ N-1 \end{pmatrix} \\ \vdots \end{pmatrix} = \begin{pmatrix} -\sum\ldots & r\left[\begin{pmatrix} 1 \\ N-1 \end{pmatrix} \to \begin{pmatrix} 0 \\ N \end{pmatrix}\right] & \cdots \\ r\left[\begin{pmatrix} 0 \\ N \end{pmatrix} \to \begin{pmatrix} 1 \\ N-1 \end{pmatrix}\right] & -\sum\ldots & \\ \vdots & & \end{pmatrix} \begin{pmatrix} p\begin{pmatrix} 0 \\ N \end{pmatrix} \\ p\begin{pmatrix} 1 \\ N-1 \end{pmatrix} \\ \vdots \end{pmatrix}$$

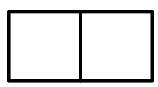
$$r\left[\begin{pmatrix} 1 \\ N-1 \end{pmatrix} \to \begin{pmatrix} 0 \\ N \end{pmatrix}\right] = k_{BA} \qquad r\left[\begin{pmatrix} 0 \\ N \end{pmatrix} \to \begin{pmatrix} 1 \\ N-1 \end{pmatrix}\right] = N k_{AB}$$

$$r\left[\begin{pmatrix} 2 \\ N-2 \end{pmatrix} \to \begin{pmatrix} 1 \\ N-1 \end{pmatrix}\right] = 2 k_{BA} \qquad r\left[\begin{pmatrix} 1 \\ N-1 \end{pmatrix} \to \begin{pmatrix} 2 \\ N-2 \end{pmatrix}\right] = (N-1) k_{AB}$$

$$r\left[\begin{pmatrix} n_A \\ n_B \end{pmatrix} \to \begin{pmatrix} n_A - 1 \\ n_B + 1 \end{pmatrix}\right] = n_A k_{BA}$$

$$r\left[\begin{pmatrix} n_A \\ n_B \end{pmatrix} \to \begin{pmatrix} n_A + 1 \\ n_B - 1 \end{pmatrix}\right] = n_B k_{AB}$$

For simplicity, let's work things out for $k_{AB} = k_{BA} = D$



Diffusion

Left side is A   Right side is B

$$\Rightarrow \mathbb{W} = \begin{pmatrix} -ND & D & & 0 \\ ND & -ND & 2D & \\ & (N-1)D & -ND & \\ 0 & & & \ddots \end{pmatrix}$$

An $(N+1) \times (N+1)$ matrix!

But there is also a "second quantized" way to view the problem, which becomes necessary for the same reasons as in QM:

- There are lots of particles
- The # of particles might not be conserved (fixed chemical potential or $A+B \rightleftarrows C$)

We work in a Fock space that keeps track of the occupation # of A & of B.

$$|n_A\rangle = (0, 0, \ldots, 1, 0, \ldots 0)^T$$

n_A^{th} entry is 1; all others are 0

A (classical) creation operator acting on A is

$$a^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \\ 1 & 0 & 0 & 0 & \\ 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 1 & 0 & \ddots \\ & \vdots & & & \end{pmatrix}$$

Why?

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \\ 1 & 0 & 0 & 0 & \\ 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 1 & 0 & \ddots \\ & \vdots & & & \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$$

2A particles

3A particles

Shorthand: $a^{+}|n_A\rangle = |n_A+1\rangle$

A (classical) annihilation operator acting on A is

$$a = \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 2 & 0 & \cdots \\ 0 & 0 & 0 & 3 & \cdots \\ & & \vdots & & \end{pmatrix}$$

Why?

$$\begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 2 & 0 & \cdots \\ 0 & 0 & 0 & 3 & \cdots \\ & & \vdots & & \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} = \underline{\underline{2}} * \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

There were two choices of which particle to annihilate.

These a^{+} + a are not adjoints but they do satisfy $[a, a^{+}] = \delta_{ij}$ and

$$a^{+}a = \begin{pmatrix} 0 & 0 & 0 & 0 & \\ 1 & 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 1 & 0 & \cdots \\ & \vdots & & & \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 2 & 0 & \cdots \\ 0 & 0 & 0 & 3 & \cdots \\ & & \vdots & & \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & 2 & 0 & \cdots \\ & \vdots & & & \ddots \end{pmatrix}$$

$= n_A$ (the number operator)

We can define similar b^{+} + b then write our

$$\begin{pmatrix} n_A \\ n_B \end{pmatrix} = |n_A\rangle \otimes |n_B\rangle = |n_A, n_B\rangle = (a^{+})^{n_A} (b^{+})^{n_B} |0\rangle$$

a vacuum state

Any configuration of a many particle system is a (classical) superposition:

$$|\psi(t)\rangle = \sum_{n_A, n_B} p(n_A, n_B) |n_A, n_B\rangle$$

$$\langle n_A \rangle = \langle \underline{\mathbb{1}} | n_A | \psi(t) \rangle$$

Expectation values work a little differently

Old:

$$\frac{\partial \vec{p}(n_A, n_B, t)}{\partial t} = \mathbb{W}(n_A, n_B, n_A', n_B')\ \vec{p}(n_A, n_B, t)$$

2nd Quantized:

$$\hat{W} = \sum_{\substack{n_A, n_B \\ n_A', n_B'}} |n_A, n_B\rangle\, \mathbb{W}(n_A, n_B, n_A', n_B') \langle n_A', n_B'|$$

and $\dfrac{\partial |\psi(t)\rangle}{\partial t} = \hat{W} |\psi(t)\rangle$

$$\frac{\partial |\psi(t)\rangle}{\partial t} = D \sum_{n_A, n_B} \Big[a\, b^{\dagger} p(n_A+1, n_B-1)(a^{\dagger})^{n_A+1}(b^{\dagger})^{n_B-1}|0\rangle$$
$$+ a^{\dagger} b\, p(n_A-1, n_B+1)(a^{\dagger})^{n_A-1}(b^{\dagger})^{n_B-1}|0\rangle$$
$$- (a^{\dagger}a + b^{\dagger}b)\, p(n_A, n_B)(a^{\dagger})^{n_A}(b^{\dagger})^{n_B}|0\rangle \Big]$$

$A \to B$ term

$B \to A$ term

"Diagonal term" (no reaction)

$$= D\left[b^{\dagger}a + a^{\dagger}b - a^{\dagger}a - b^{\dagger}b\right]|\psi(t)\rangle$$

$$\Rightarrow \hat{W} = (b^{\dagger} - a^{\dagger})(a - b)$$

We've only waved hands at the <u>simplest</u> of all possible problems, but my goal was only to introduce the existence of this "Doi-Peliti formalism"

For more...

John Cardy Reaction-Diffusion Processes

Täuber, Howard, Vollmayr-Lee, J. Phys. A (2005)