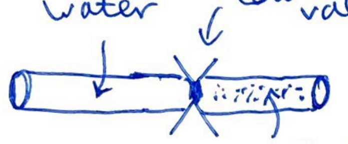
Applications

① Diffusion in few-particle systems

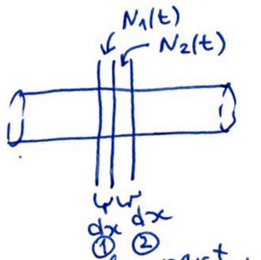
Rob Phillips & Co:



valve opens → diffusion of fluorescent beads

Can track $\langle J\rangle = -D\frac{\partial c}{\partial x}$, but also

$$\langle J^2\rangle_c = \langle J^2\rangle - \langle J\rangle^2 .$$



Initial state: $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$

$\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ or $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

on the left   on the right

Then single-part. part'n f'n: $Q = a^{+}G^{T}\cdot v$

[consider pairwise constraints only] $\Rightarrow G = \begin{pmatrix} e^{-\lambda_{11}} & e^{-\lambda_{12}} \\ e^{-\lambda_{21}} & e^{-\lambda_{22}} \end{pmatrix}$

Single time step: $\quad v_i = e^{-\frac{d_i}{2}} = 1$ since $d_i = 0$

$$\begin{cases} q_1 = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} e^{-\lambda_{11}} & e^{-\lambda_{12}} \\ e^{-\lambda_{21}} & e^{-\lambda_{22}} \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} e^{-\lambda_{11}} + e^{-\lambda_{12}} \\ e^{-\lambda_{21}} + e^{-\lambda_{22}} \end{pmatrix} = e^{-\lambda_{11}} + e^{-\lambda_{12}}, \\ q_2 = \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} \;\ldots\; \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = e^{-\lambda_{21}} + e^{-\lambda_{22}}. \end{cases}$$

For N_1 indep. particles on the left & N_2 indep. part. on the right,

$$Q = q_1^{N_1} q_2^{N_2}$$

We're interested in flux J between states 1 & 2:

$$P(J) = \frac{Q'}{Q}$$

Q' ← sum over microstates w/flux J

Q ↑ sum over all microstates

Note that

integer (# jumps)

$$Q' = \int \frac{dz}{2\pi i}\, z^{-J-1}\, \hat{q}_1^{\,N_1}\, \hat{q}_2^{\,N_2} \quad (*)$$ Why?

Indeed,

$$Q' = \left(\sum_{l,p=0}^{N_1,N_2} \delta_{l-p,J}\right) \binom{N_1}{l}\binom{N_2}{p} \left(e^{-\lambda_{12}}\right)^{l}\left(e^{-\lambda_{11}}\right)^{N_1-l} \times \left(e^{-\lambda_{21}}\right)^{p}\left(e^{-\lambda_{22}}\right)^{N_2-p}$$

↗

$$\left(e^{-\lambda_{12}} + e^{-\lambda_{11}}\right)^{N_1}\left(e^{-\lambda_{21}} + e^{-\lambda_{22}}\right)^{N_2}$$

Now, $\delta_{l-p,J} = \oint \frac{dz}{2\pi i}\, z^{l-p-J-1}$.

Then

$$Q' = \sum_{l,p=0}^{N_1,N_2} \oint \frac{dz}{2\pi i}\, z^{l-p-J-1} \binom{N_1}{l}\binom{N_2}{p} \times \left(e^{-\lambda_{12}}\right)^{l}\left(e^{-\lambda_{11}}\right)^{N_1-l} \times \left(e^{-\lambda_{21}}\right)^{p}\left(e^{-\lambda_{22}}\right)^{N_2-p} =$$

=

$-J = J - 2J = J - 2(l-p) =$

$= J - 2$

$$\left(\frac{e^{-\lambda_{12}}}{z}\right)^{l}\left(e^{-\lambda_{11}} z\right)^{N_1-l}\left(\frac{e^{-\lambda_{21}}}{z}\right)^{p}\left(e^{-\lambda_{22}} z\right)^{N_2-p} =$$

$$= z^{-l} z^{N_1-l} z^{-p} z^{N_2-p} \Rightarrow$$

old $\Rightarrow z^{N_1-2l+N_2-2p}$

$$z^{2l-N_1+2p-N_2}\, z^{l-p+2J}$$

$$\stackrel{=}{} \oint \frac{dz}{2\pi i} z^{-J-1} \overbrace{(e^{-\lambda_{12}} z)^{\ell} (e^{-\lambda_{11}})^{N_1-\ell}}^{\sum_{\ell,p=0}^{N_1,N_2} \binom{N_1}{\ell}\binom{N_2}{p}} \times$$

$$\times (e^{-\lambda_{21}}/z)^{p} (e^{-\lambda_{22}})^{N_2-p} =$$

$$= \oint \frac{dz}{2\pi i} z^{-J-1} \underbrace{(e^{-\lambda_{12}} z + e^{-\lambda_{11}})^{N_1} \left(\frac{e^{-\lambda_{21}}}{z} + e^{-\lambda_{22}}\right)^{N_2}}_{m(z) \equiv e^{C(z)}}$$

$$z = e^{i\varphi}$$

$$\text{So,} \quad P(J) = \frac{1}{q_{\theta 1}^{N_1} q_{\theta 2}^{N_2}} \int_{-\pi}^{\pi} \frac{d\varphi}{2\pi} e^{-i\varphi(J+1)} e^{\underbrace{C(e^{i\varphi})}_{\text{expand to 2nd order}}}$$

$$\text{Now}, \quad C(e^{i\varphi}) = \log m(e^{i\varphi}) =$$

$$= \log\left[(e^{-\lambda_{12}} e^{i\varphi} + e^{-\lambda_{11}})^{N_1} (e^{-\lambda_{21}} e^{-i\varphi} + e^{-\lambda_{22}})^{N_2}\right] =$$

$$= N_1 \log\left[\underbrace{e^{-\lambda_{12}}}_{\alpha_1} e^{i\varphi} + \underbrace{e^{-\lambda_{11}}}_{\beta_1}\right] + N_2 \log\left[\underbrace{e^{-\lambda_{21}}}_{\alpha_2} e^{-i\varphi} + \underbrace{e^{-\lambda_{22}}}_{\beta_2}\right] \simeq$$

$$\simeq \underbrace{N_1 \log(e^{-\lambda_{12}} + e^{-\lambda_{11}}) + N_2 \log(e^{-\lambda_{21}} + e^{-\lambda_{22}})}_{\log(q_{\theta 1}^{N_1} q_{\theta 2}^{N_2})} \oplus$$

$$\log(\alpha e^{i\varphi} + \beta) \simeq \frac{1}{\alpha+\beta} \alpha i \times \varphi - \frac{1}{2} \frac{\alpha\beta}{(\alpha+\beta)^2} \varphi^2 + \ldots$$

1st deriv.: $\frac{1}{\alpha e^{i\varphi} + \beta} \alpha i e^{i\varphi}$; $\varphi = 0$: $\frac{\alpha i}{\alpha+\beta}$

2nd deriv.: $\frac{-\alpha e^{i\varphi}}{\alpha e^{i\varphi} + \beta} + \alpha i e^{i\varphi} \left(-\frac{1}{(\alpha e^{i\varphi} + \beta)^2}\right) \alpha i e^{i\varphi} \Rightarrow$

$$\Rightarrow \varphi = 0: \quad -\frac{\alpha}{\alpha+\beta} + \frac{\alpha^2}{(\alpha+\beta)^2} = \frac{\alpha^2 - \alpha(\alpha+\beta)}{(\alpha+\beta)^2} =$$

$$= -\frac{\alpha\beta}{(\alpha+\beta)^2}$$

$$\oplus \; N_1 \frac{e^{-\lambda_{12}} i\varphi}{e^{-\lambda_{12}} + e^{-\lambda_{11}}} - N_2 \frac{e^{-\lambda_{21}} i\varphi}{e^{-\lambda_{21}} + e^{-\lambda_{22}}} \ominus$$

$$\ominus\ \frac{1}{2} N_1 \frac{e^{-\lambda_{12}} e^{-\lambda_{11}}}{(e^{-\lambda_{12}}+e^{-\lambda_{11}})^2}\varphi^2 - \frac{1}{2} N_2 \frac{e^{-\lambda_{21}} e^{-\lambda_{22}}}{(e^{-\lambda_{21}}+e^{-\lambda_{22}})^2}\varphi^2 + \dots =$$

$$= \log(q_1^{N_1} q_2^{N_2}) + \underbrace{\langle J_{12}\rangle i\varphi - \langle J_{21}\rangle i\varphi}_{i\varphi\langle J\rangle} - \frac{1}{2}\underbrace{\left[\langle J_{12}^2\rangle_c + \langle J_{21}^2\rangle_c\right]}_{\langle J^2\rangle_c}\varphi^2 .$$

So, $\cancel{\langle J\rangle = \frac{N_1 e^{-\lambda_{12}} - N_2 e^{-\lambda_{21}}}{e^{-}}}$

[cf. opposite page]
$$\begin{cases} \langle J_{12}\rangle = \dfrac{N_1 e^{-\lambda_{12}}}{e^{-\lambda_{11}}+e^{-\lambda_{12}}} \\[2ex] \langle J_{21}\rangle = \dfrac{N_2 e^{-\lambda_{21}}}{e^{-\lambda_{22}}+e^{-\lambda_{21}}} \end{cases}$$

$$\langle J\rangle = \langle J_{12}\rangle - \langle J_{21}\rangle$$

$$\langle J_{12}^2\rangle_c = \frac{\partial^2 \log Q}{\partial \lambda_{12}^2} = -\frac{\partial}{\partial\lambda_{12}}\langle J_{12}\rangle =$$

$$\underset{(-)}{=} \frac{-N_1 e^{-\lambda_{12}}}{(e^{-\lambda_{11}}+e^{-\lambda_{12}})} - \frac{N_1 e^{-\lambda_{12}}}{(e^{-\lambda_{11}}+e^{-\lambda_{12}})^2}(-e^{-\lambda_{12}}) =$$

$$= N_1\left[\frac{e^{-2\lambda_{12}} - e^{-\lambda_{12}}(e^{-\lambda_{11}}+e^{-\lambda_{12}})}{(e^{-\lambda_{11}}+e^{-\lambda_{12}})^2}\right] =$$

$$= N_1\left[\frac{-e^{-\lambda_{12}}e^{-\lambda_{11}}}{(e^{-\lambda_{11}}+e^{-\lambda_{12}})^2}\right].$$

Likewise, $\langle J_{21}^2\rangle_c = N_2 \dfrac{+e^{-\lambda_{21}}e^{-\lambda_{22}}}{(e^{-\lambda_{22}}+e^{-\lambda_{21}})^2}$

$$\langle J^2\rangle_c = \langle J_{12}^2\rangle_c + \langle J_{21}^2\rangle_c$$

$$Q = q_1^{N_1} q_2^{N_2} = \left(e^{-\lambda_{11}} + e^{-\lambda_{12}}\right)^{N_1} \left(e^{-\lambda_{21}} + e^{-\lambda_{22}}\right)^{N_2}$$

$$\log Q = N_1 \log\left(e^{-\lambda_{11}} + e^{-\lambda_{12}}\right) + N_2 \log\left(e^{-\lambda_{21}} + e^{-\lambda_{22}}\right)$$

$$\langle J_{12} \rangle = -\frac{\partial \log Q}{\partial \lambda_{12}} = \frac{N_1 e^{-\lambda_{12}}}{e^{-\lambda_{11}} + e^{-\lambda_{12}}}$$

Likewise, $\langle J_{21} \rangle = -\dfrac{\partial \log Q}{\partial \lambda_{21}} = \dfrac{N_2 e^{-\lambda_{21}}}{e^{-\lambda_{21}} + e^{-\lambda_{22}}}$

Note that $\langle J \rangle = \underset{= N_{12}}{\langle J_{12} \rangle} - \underset{= N_{21}}{\langle J_{21} \rangle}$

Further,

$$\langle J^2 \rangle_c = \langle (N_{12} - N_{21})^2 \rangle - \langle (N_{12} - N_{21}) \rangle^2 =$$

$$= \langle N_{12}^2 \rangle + \langle N_{21}^2 \rangle - 2 \langle N_{12} N_{21} \rangle - \left[\langle N_{12} \rangle - \langle N_{21} \rangle \right]^2 =$$

$$= \langle N_{12}^2 \rangle + \langle N_{21}^2 \rangle - \underbrace{\cancel{2 \langle N_{12} \rangle \langle N_{21} \rangle}}_{\text{indep.}} - \langle N_{12} \rangle^2 - \langle N_{21} \rangle^2 +$$

$$+ \cancel{2 \langle N_{12} \rangle \langle N_{21} \rangle} = \langle N_{12}^2 \rangle_c + \langle N_{21}^2 \rangle_c .$$

$$\text{o,} \quad P(J) \simeq \int_{-\infty}^{\overset{\text{extend..}}{\infty}} \frac{d\varphi}{2\pi} e^{-i\varphi(J \cancel{+1})} e^{i\varphi \langle J \rangle} e^{-\frac{1}{2} \underbrace{\langle J^2 \rangle_c \varphi^2}_{<0 \text{ here, so OK}}} \; =$$

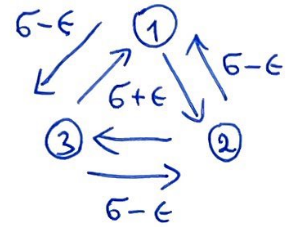
$$\oint \frac{dz}{2\pi i} \Rightarrow \int_{-\pi}^{\pi} \frac{d(e^{i\varphi})}{2\pi i} = \int_{-\pi}^{\pi} \frac{d\varphi}{2\pi} e^{i\varphi}$$

$$= \frac{1}{\sqrt{2\pi \langle J^2 \rangle_c}} e^{-\frac{(J - \langle J \rangle)^2}{2 \langle J^2 \rangle_c}}.$$

Then $$\frac{P(J)}{P(-J)} = e^{-\frac{(J-\langle J \rangle)^2}{2\langle J^2 \rangle_c}} e^{\frac{(-J-\langle J \rangle)^2}{2\langle J^2 \rangle_c}} =$$

$$= \underbrace{e^{\frac{2\langle J \rangle J}{\langle J^2 \rangle_c}}}_{\text{fluct'n theorem for flux}}.$$

Consider a 3-state system:



Consider flux between states 1 & 2

Define
$$\begin{cases} p_{12} = \dfrac{e^{-\lambda_{12}}}{e^{-\lambda_{11}}+e^{-\lambda_{12}}+e^{-\lambda_{13}}} \equiv \sigma+\epsilon & \text{forward jump prob.} \\ p_{21} = \dfrac{e^{-\lambda_{21}}}{e^{-\lambda_{21}}+e^{-\lambda_{22}}+e^{-\lambda_{23}}} \equiv \sigma-\epsilon & \text{backward jump prob.} \end{cases}$$

& similarly for p_{13}/p_{31} ; p_{23}/p_{32}

SS:
$$\begin{cases} \dfrac{dN_1}{dt} = p_{31}N_3 + p_{21}N_2 - (p_{12}+p_{13})N_1 = 0, \\ \quad\quad = N_3(\sigma+\epsilon) + N_2(\sigma-\epsilon) - 2\sigma N_1 = 0 \\ \dfrac{dN_2}{dt} = N_1(\sigma+\epsilon) + N_3(\sigma-\epsilon) - 2\sigma N_2 = 0, \\ \dfrac{dN_3}{dt} = N_2(\sigma+\epsilon) + N_1(\sigma-\epsilon) - 2\sigma N_3 = 0. \end{cases}$$

Solved by $N_1 = N_2 = N_3 = \dfrac{N}{3}$ ← total # part.

For ex. $(\sigma+\epsilon)\underbrace{\dfrac{N}{3}}_{N_3} + \underbrace{\dfrac{N}{3}}_{N_2}(\sigma-\epsilon) - 2\sigma\underbrace{\dfrac{N}{3}}_{N_1} = 0$

So, equal occupancy; ~~bee~~ detailed balance broken

Now, consider $\langle J\rangle = \langle J_{12}\rangle - \langle J_{21}\rangle =$

$$= N_1 p_{12} - N_2 p_{21} = \frac{N}{3}(\sigma+\epsilon) - \frac{N}{3}(\sigma-\epsilon) =$$

$$= \frac{2N}{3}\epsilon. \qquad \epsilon\to 0: \langle J\rangle \to 0 \text{ as expected}$$

Now, $\langle J^2\rangle_c = \langle N_{12}^2\rangle_c + \langle N_{21}^2\rangle_c =$

$$= N_1 p_{12} \overbrace{}^{(1-p_{12})} + N_2 p_{21} (1-p_{21}) =$$

$$= \frac{N}{3}(1-\sigma-\epsilon)(\sigma+\epsilon) + \frac{N}{3}(\sigma-\epsilon)(1-\sigma+\epsilon) =$$

$$= \frac{N}{3}\left[\sigma+\cancel{\epsilon} - (\sigma+\epsilon)^2 + \sigma - \cancel{\epsilon} - (\sigma-\epsilon)^2\right] =$$

$$= \frac{N}{3}\left[2\sigma - 2\sigma^2 - 2\epsilon^2\right] = \frac{2N}{3}\left[\underbrace{\sigma(1-\sigma)}_{\text{like } pq \text{ in binomial var.}} - \epsilon^2\right].$$

$$Q = (e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}})^{N_1}(e^{-\lambda_{21}} + e^{-\lambda_{22}} + e^{-\lambda_{23}})^{N_2} \times$$
$$\times (e^{-\lambda_{31}} + e^{-\lambda_{32}} + e^{-\lambda_{33}})^{N_3}$$

Then

$$\begin{cases} \langle J_{12}\rangle = \dfrac{N_1 e^{-\lambda_{12}}}{e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}}} = N_1 p_{12}, \\[2ex] \langle J_{21}\rangle = \dfrac{N_2 e^{-\lambda_{21}}}{e^{-\lambda_{21}} + e^{-\lambda_{22}} + e^{-\lambda_{23}}} = N_2 p_{21} \end{cases}$$

$$\langle J_{12}^2\rangle_c \underset{-\frac{\partial}{\partial\lambda_{12}}\langle J_{12}\rangle}{=} -\left[\frac{-N_1 e^{-\lambda_{12}}}{e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}}} + \frac{N_1 e^{-\lambda_{12}}(-1)(-e^{-\lambda_{12}})}{(e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}})^2}\right] =$$

$$= \frac{N_1\left[e^{-2\lambda_{12}} - e^{-\lambda_{12}}(e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}})\right]}{(\ldots)^2} =$$

$$= \frac{N_1\left[e^{-\lambda_{12}}e^{-\lambda_{11}} + e^{-\lambda_{12}}e^{-\lambda_{13}}\right]}{(e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}})^2} =$$

$= N_1[p_{12}p_{11} + p_{12}p_{13}] = N_1 p_{12}[1-p_{12}]$.

$p_{11}+p_{12}+p_{13}=1$

Likewise, $\langle J_{21}^2\rangle_c = N_2 p_{21}[1-p_{21}]$.

So,

$$\langle J^2\rangle_c \underset{=}{\overset{\langle N_{12}^2\rangle_c + \langle N_{21}^2\rangle_c}{=}} \frac{N}{3}(\sigma+\epsilon)(1-(\sigma+\epsilon)) + \frac{N}{3}(\sigma-\epsilon)(1-(\sigma-\epsilon)) =$$

$$= \frac{N}{3}[2\sigma - (\sigma+\epsilon)^2 - (\sigma-\epsilon)^2] =$$

$$= \frac{N}{3}[\underbrace{2\sigma - 2\sigma^2}_{2\sigma(1-\sigma)} - 2\epsilon^2] =$$

$$q_1 = \underbrace{1\ 0\ 0}\begin{pmatrix} e^{-\lambda_{11}} & e^{-\lambda_{12}} & e^{-\lambda_{13}} \\ e^{-\lambda_{21}} & e^{-\lambda_{22}} & e^{-\lambda_{23}} \\ e^{-\lambda_{31}} & e^{-\lambda_{32}} & e^{-\lambda_{33}} \end{pmatrix}\begin{pmatrix}1\\1\\1\end{pmatrix} =$$

$$= e^{-\lambda_{11}} + e^{-\lambda_{12}} + e^{-\lambda_{13}}$$

Likewise,

$$q_2 = e^{-\lambda_{21}} + e^{-\lambda_{22}} + e^{-\lambda_{23}}$$

$$q_3 = e^{-\lambda_{31}} + e^{-\lambda_{32}} + e^{-\lambda_{33}}$$

$$Q = q_1^{N_1} q_2^{N_2} q_3^{N_3}$$