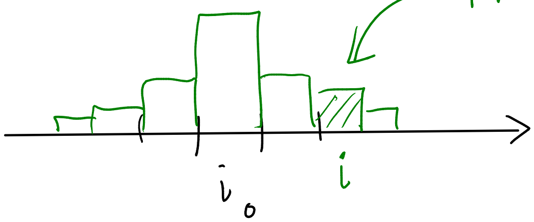


$p_i(t)$ = prob. to be in box i at time t

build an eqn for $p_i(t)$ as a func. of time:

$$p_i(t+\delta t) = p_i(t) - \left[\begin{array}{l}\text{loss in prob. due to} \\ \text{particles in } i \text{ moving} \\ \text{left / right}\end{array}\right]$$

$$+ \left[\begin{array}{l}\text{gain in prob. from} \\ \text{neighbors entering } i\end{array}\right]$$

$$= p_i(t) \underbrace{- \underbrace{2w\,\delta t}_{\substack{\text{prob.} \\ \text{you} \\ \text{leave } i}} \underbrace{p_i(t)}_{\substack{\text{prob to} \\ \text{be in } i \\ \text{at time } t}}}_{\text{loss}} \underbrace{+ w\,\delta t\, p_{i+1}(t) + w\,\delta t\, p_{i-1}(t)}_{\text{gain}}$$

$$\frac{p_i(t+\delta t) - p_i(t)}{\delta t} = -2w\,p_i(t) + w\left(p_{i-1}(t) + p_{i+1}(t)\right)$$

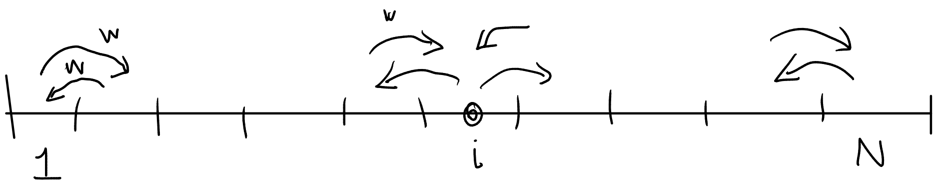
at timescales $t \gg \delta t$ we approx LHS as a continuous time quantity (continuum limit)

$$\Rightarrow \quad \frac{dp_i(t)}{dt} = -2w\,p_i(t) + w\left(p_{i-1}(t) + p_{i+1}(t)\right)$$

$1 < i < N$

treat time as a continuous variable

example of master equation: how prob. changes in time



$$i = 1: \quad \frac{dp_1}{dt} = -w\, p_1(t) + w\, p_2(t)$$

$$i = N: \quad \frac{dp_N}{dt} = -w\, p_N(t) + w\, p_{N-1}(t)$$

N equations for N unknowns $p_i(t)$ $i = 1, \ldots, N$

$$\vec{p}(t) = \begin{pmatrix} p_1(t) \\ \vdots \\ p_N(t) \end{pmatrix}$$

ith comp of $\vec{p}(t) = p_i(t)$

set of equ's:

$$\frac{d\vec{p}}{dt} = \Omega\, \vec{p}(t) \quad \Rightarrow \quad \frac{dp_i}{dt} = \sum_j \Omega_{ij}\, p_j(t)$$

Ω: N×N matrix

ith row of matrix-vector prod.

$$\frac{d}{dt}\begin{pmatrix} p_1(t) \\ p_2(t) \\ \vdots \\ p_N(t) \end{pmatrix} = \begin{array}{c c} & \begin{array}{cccccc} & & \text{start } 3 & & & \end{array} \\ \begin{array}{c} \\ \text{end } 2 \\ \\ \\ \\ \\ \end{array} & \begin{pmatrix} -w & +w & 0 & 0 & 0 & 0 \\ w & -2w & w & 0 & 0 & 0 \\ 0 & w & -2w & w & 0 & 0 \\ 0 & 0 & w & -2w & w & 0 \\ 0 & 0 & 0 & w & -2w & w \\ 0 & 0 & 0 & 0 & +w & -w \end{pmatrix} \end{array} \begin{pmatrix} p_1(t) \\ p_2(t) \\ \vdots \\ p_N(t) \end{pmatrix}$$

more generally: model consists a set of states $i = 1, \ldots, N$

+ set of transition rates

$i \neq j$: Ω_{ij} = prob. rate for transition $j \to i$

i: row, j: column

(could be zero if no trans. is allowed)

universal property of Ω matrix:
every column must sum to zero

proof: $\sum_{i=1}^{N} p_i(t) = 1$ at every time t

$$\frac{d}{dt} \sum_i p_i(t) = 0$$

$$\sum_i \frac{dp_i}{dt} = 0$$

$$\sum_i \sum_j \Omega_{ij} p_j = 0$$

$$\sum_j \left[\sum_i \Omega_{ij} \right] \underbrace{p_j}_{1 \geq p_j \geq 0} = 0$$

must be true for all t

true for all p_j

only possible if $\boxed{\sum_i \Omega_{ij} = 0}$ for any column j

master equ: $\frac{dp_i}{dt} = \sum_j \Omega_{ij} p_j$ (eq. *)

$\Downarrow$

can derive equ's for moments

nth moment: $\langle i^n \rangle_t = \sum_{i=1}^{N} i^n p_i(t)$

$$\frac{d}{dt}\langle i^n \rangle_t = \sum_{i=1}^{N} i^n \frac{d}{dt} p_i(t) \leftarrow \text{plug in eq. } *$$

$$= \sum_i \sum_j i^n \Omega_{ij} p_j$$

$$= \sum_j \sum_{i \neq j} i^n \Omega_{ij} p_j + \sum_j j^n \Omega_{jj} p_j$$

$$\sum_{i,j} = \underbrace{\sum_j \sum_{i \neq j}}_{\substack{\text{off-diag} \\ \text{elements} \\ (i,j)}} + \underbrace{\sum_j}_{\substack{\text{diag.} \\ \text{elements} \\ (i=j)}} \qquad \Omega_{jj} = -\sum_{i \neq j} \Omega_{ij}$$

$$\frac{d\langle i^n \rangle_t}{dt} = \sum_j \sum_{i \neq j} \left[i^n \Omega_{ij} p_j - j^n \Omega_{ij} p_j \right]$$

$$= \sum_j \sum_{i \neq j} (i^n - j^n) \Omega_{ij} p_j$$

recall: $\text{MSD} = \langle \Delta_i^2 \rangle_t = a^2\left(\langle i^2 \rangle_t - 2 i_0 \langle i \rangle_t + i_0^2\right)$

$n = 1$: $\frac{d\langle i \rangle_t}{dt} = w\, p_1(t) - w\, p_N(t) \leftarrow$ plug in Ω

$n = 2$: $\frac{d\langle i^2 \rangle_t}{dt} = 2w \sum_{j=2}^{N-1} p_j(t) + 3w\, p_1(t) + (1-2N)\, w\, p_N(t)$

assume N is large + i_0 is $1 \ll i_0 \ll N$

$p_1(t) \approx 0 \qquad p_N(t) \approx 0$

$$\langle i \rangle_0 = i_0 \qquad \frac{d\langle i\rangle_t}{dt} = 0$$

$$\sum_{j=2}^{N-1} p_j \approx \sum_{j=1}^{N} p_j = 1$$

$$\langle i^2 \rangle_0 = i_0^2 \qquad \frac{d\langle i^2\rangle_t}{dt} = 2w$$

initial conditions
all particles at $i = i_0$
at $t = 0$

$$\langle i \rangle_t = i_0$$

$$\langle i^2 \rangle_t = 2wt + i_0^2$$

$\Longrightarrow$ plug into MSD

$$\langle \Delta_i^2 \rangle_t = 2\underbrace{wa^2}_{D}\, t = 2Dt$$

D = diffusion const.