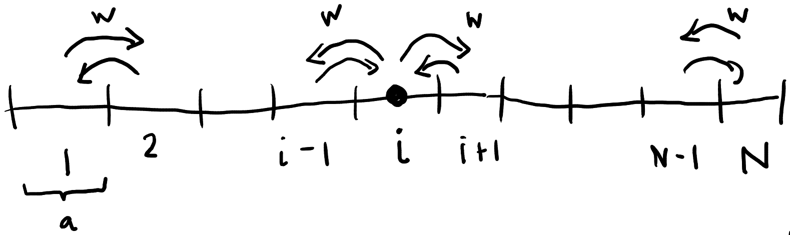

prob. of jumping $= w\,\delta t$

equ. for $p_i(t) =$ prob. to be at i at time t

$$1 < i < N \qquad \frac{dp_i}{dt} = \underbrace{-2w\,p_i(t)}_{\text{net loss out of } i} + \underbrace{w\left(p_{i+1}(t) + p_{i-1}(t)\right)}_{\text{net gain into } i}$$

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

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

complete sys. of equations for $p_i(t)$ $i=1,\dots,N$

$$\vec{p}(t) = \begin{pmatrix} p_1(t) \\ p_2(t) \\ \vdots \\ p_N(t) \end{pmatrix}$$

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

ith row of matrix-vector mult.

$$\frac{d\vec{p}}{dt} = \underbrace{\Omega}_{\substack{N\times N\\ \text{matrix}}}\,\vec{p}(t) \Rightarrow \frac{dp_i}{dt} = \sum_{j=1}^{N} \Omega_{ij}\,p_j(t)$$

N equ. for $i=1,\dots,N$

$$\frac{d}{dt}\begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_N \end{pmatrix} = \begin{pmatrix} -w & +w & 0 & 0 & 0 & 0 & \cdots \\ w & -2w & w & 0 & 0 & 0 \\ 0 & w & -2w & w & 0 & 0 \\ & & & \ddots & & \\ 0 & 0 & 0 & 0 & w & -w \end{pmatrix}\begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_N \end{pmatrix}$$

more generally: a set of states $j = 1, \ldots, N$

+ a set of transition rates:

$i \neq j$: $\Omega_{ij} \equiv$ prob. rate for transitions from $j \to i$

row column

(= 0 if no transitions can occur)

universal prop. of Ω matrix:

every column must sum to zero

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

$$\frac{d}{dt} \sum_i p_i = 0$$

$$|\vec{p}| = \sqrt{p_1^2 + p_2^2 + \cdots p_N^2}$$

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

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

$$\Rightarrow \sum_j \Big[\sum_i \Omega_{ij} \Big] \underbrace{p_j(t)}_{1 \geq p_j(t) \geq 0} = 0$$

must be true at all t

could be anything

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

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

can derive a series of useful equations for other properties, like moments

average of i^n $\Rightarrow$ nth moment

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

$$\frac{d\langle i^n \rangle_t}{dt} = \sum_i i^n \frac{dp_i}{dt} \swarrow \text{ plug in Eq. *}$$

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

$$\sum_{i,j} = \underbrace{\sum_{j=1}^{N} \sum_{i \neq j}}_{\text{off-diag. elements}} + \underbrace{\sum_{j=1}^{N}}_{\text{diag. elements}}$$

know:

$$\Omega_{jj} = -\sum_{i \neq j} \Omega_{ij}$$

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

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

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

$n=1$: $$\frac{d\langle i\rangle_t}{dt} = w\,p_1(t) - w\,p_N(t)$$ (plugging 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 (a small) + molecule is far from walls

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

$$\frac{d\langle i\rangle_t}{dt} = 0 \qquad \sum_{j=2}^{N-1} p_j \approx \sum_{j=1}^{N} p_j = 1$$

$$\Rightarrow \frac{d\langle i^2\rangle_t}{dt} = 2w$$

initial cond: all particles start at $i=i_0$ at $t=0$

$$\langle i\rangle_0 = i_0 \qquad \langle i^2\rangle_0 = i_0^2$$

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

MSD $\Rightarrow$ $$\langle \Delta_i^2\rangle_t = 2wa^2 t$$
$$\equiv 2Dt$$

$D = wa^2$ diffusion const.

units: $\frac{\text{length}^2}{\text{time}}$

by symmetry, same answer for other axes (y or z axes)

3D box location: $\vec{r} = a\,(i, j, k)$

initial location: $\vec{r}_0 = a\,(i_0, j_0, k_0)$

1D displacements:

$$\Delta_i = a\,(i - i_0)$$
$$\Delta_j = a\,(j - j_0)$$
$$\Delta_k = a\,(k - k_0)$$

3D MSD: $\langle (\vec{r} - \vec{r}_0)^2 \rangle_t$

$$= \langle a^2 (i - i_0)^2 + a^2 (j - j_0)^2 + a^2 (k - k_0)^2 \rangle_t$$

$$= \underbrace{\langle \Delta_i^2 \rangle_t}_{2Dt} + \underbrace{\langle \Delta_j^2 \rangle_t}_{2Dt} + \underbrace{\langle \Delta_k^2 \rangle_t}_{2Dt}$$

$$= 6Dt$$

rough timescale for covering a distance L by diffusion in 3D:

$$MSD \sim L^2 = 6Dt \Rightarrow t = \frac{L^2}{6D}$$

compare to:

Classical "ballistic" motion: constant vel. v

$$L = vt \Rightarrow t = \frac{L}{v}$$