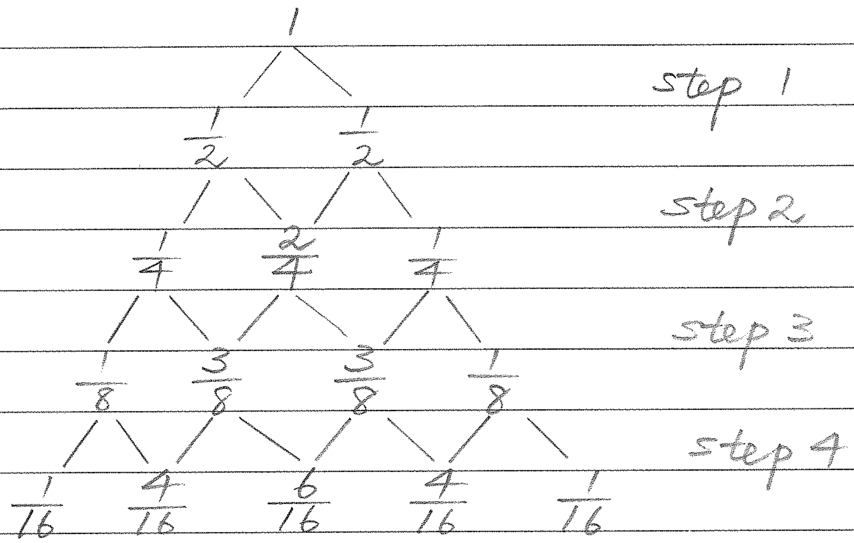
Probability Distribution.

Random walk, distribution of a stochastic variable — position



After N steps, we have a distribution between $-N$ and N:

$-N,\ -N+2,\ \cdots,\ N-2,\ N$ for possible positions

$$\frac{N-(-N)}{2}+1 = N+1 \quad \text{possibilities}$$

n forward steps and $N-n$ backward steps

net move $= n-(N-n) = -N+2n$,

$n = 0, 1, \cdots, N-1, N$

net move between $-N$ and N.

Number for differend ways to reach $-N+2n$

$$C_n^N = \frac{N!}{n!(N-n)!}$$

The probability to reach $-N+2n$. —

$$P_n = C_n^N \left(\frac{1}{2}\right)^N = \frac{N!}{n!(N-n)!}\left(\frac{1}{2}\right)^n\left(\frac{1}{2}\right)^{N-n}.$$

probability.

P_n : probability distribution.

Taylor Expansion.

Taylor expansion

$$\sum_{n=0}^{N} P_n = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \left(\frac{1}{2}\right)^n \left(\frac{1}{2}\right)^{N-n}$$

$$= \left(\frac{1}{2} + \frac{1}{2}\right)^N = 1$$

Sum of all probabilities $= 1$

Change of variable. $n = \frac{N+m}{2}$

$N - n = \frac{N-m}{2}$

net move $= \frac{N+m}{2} - \frac{N-m}{2} = m$

$$\ln \frac{N!}{n!(N-n)!} = N \ln N - N - n \ln n + n - (N-n)\ln(N-n) + N - n$$

$$= N \ln N - n \ln n - (N-n) \ln (N-n)$$

$$= N \ln N - \frac{N+m}{2} \ln \frac{N+m}{2} - \frac{N-m}{2} \ln \frac{N-m}{2}$$

$$= g(m)$$

$$\frac{d}{dm} g(m) = -\frac{1}{2} \ln \frac{N+m}{2} - \frac{N+m}{2} \frac{1}{2} \frac{1}{\frac{N+m}{2}}$$

$$- \left(-\frac{1}{2}\right) \ln \frac{N-m}{2} - \frac{N-m}{2} \left(-\frac{1}{2}\right) \frac{1}{\frac{N-m}{2}}$$

$$= -\frac{1}{2} \ln \frac{N+m}{2} + \frac{1}{2} \ln \frac{N-m}{2} = \frac{1}{2} \ln \frac{N-m}{N+m}$$

$$\left.\frac{d}{dm} g(m)\right|_{m=0} = 0 \quad , \quad \text{Maximum at } m = 0$$

$$\frac{d^2}{dm^2} g(m) = -\frac{1}{2} \frac{1}{N+m} + \frac{1}{2} \frac{(-1)}{N-m} = -\frac{1}{2}\left(\frac{1}{N+m} + \frac{1}{N-m}\right)$$

$m = 0$, $g''(m) = -\frac{1}{N} < 0$, for maximum.

$$g(m) \simeq -\frac{1}{2N} m^2 + g(0) = -\frac{1}{2N} m^2 + N \ln N - N \ln \frac{N}{2}$$

$$= N \ln 2 - \frac{m^2}{2N}$$

MSD.

$MSD = N$

$$P_m = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!}\left(\frac{1}{2}\right)^N$$

$$= e^{g(m)}\left(\frac{1}{2}\right)^N = e^{N\ln 2 - \frac{m^2}{2N}}\left(\frac{1}{2}\right)^N$$

$$= e^{-\frac{m^2}{2N}}$$

Higher-order terms neglected, not normalized.

$$p(m) = \frac{1}{\sqrt{2\pi N}}\, e^{-\frac{m^2}{2N}}, \quad \int_{-\infty}^{\infty} dm\; p(m) = 1$$

$\langle m^2 \rangle_p = N$. mean square displacement

$$\left\langle \left(\sum_{j=1}^{N} x_j\right)^2 \right\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle x_i x_j\rangle$$

$$= \sum_{i=1}^{N}\langle x_i^2\rangle + \sum_{i=1}\sum_{j\neq i}\langle x_i x_j\rangle$$

$$= N$$

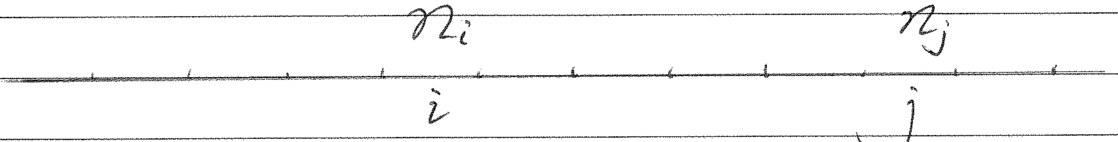
$\langle x_i^2 \rangle = 1$ & $\langle x_i x_j \rangle = 0$ if $i \neq j$

$x_i = +1$ or -1

Here $\sum_{j=1}^{N} x_j = m$, net displacement after N steps.

$MSD = \langle m^2 \rangle = N$, number of steps

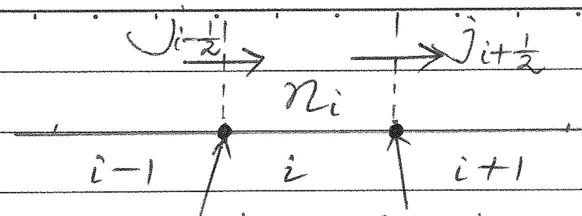
Now consider many non-interacting particles in 1D space, each under a random walk.



i : used to label a short interval in space

n_i : number of particles in that interval

Diffusion Equation.



$$\frac{d}{dt} n_i = -j_{i+\frac{1}{2}} + j_{i-\frac{1}{2}}$$

$-$ outgoing flux $+$ incoming flux

$(i-\frac{1}{2})$, $(i+\frac{1}{2})$, ✓✓

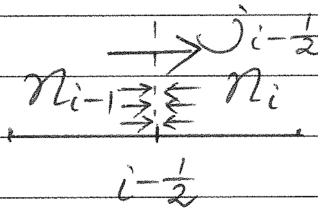
$j_{i-\frac{1}{2}}$, $j_{i+\frac{1}{2}}$, ✓✓

incoming outgoing. ✓✓

$$\frac{d}{dt}\frac{n_i(t)}{\Delta} = -\frac{j_{i+\frac{1}{2}} - j_{i-\frac{1}{2}}}{\Delta}$$

$$\frac{n_i(t)}{\Delta} \to c(x_i,t) \qquad \frac{j_{i+\frac{1}{2}} - j_{i-\frac{1}{2}}}{\Delta} \to \partial_x j(x_i,t)$$

$$\frac{\partial}{\partial t} c(x,t) = -\partial_x j(x,t)$$



$$j_{i-\frac{1}{2}} \propto n_{i-1} - n_i = -(n_i - n_{i-1})$$

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$$j \propto -\partial_x c, \qquad j = -D\partial_x c$$

$$\frac{\partial}{\partial t} c = -\partial_x(-D\partial_x c) = D\partial_x^2 c$$

$$c(x,0) = \delta(x)$$

$$c(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

$$\int c\,dx = 1 \qquad \text{normalized density}$$

$$\int x^2 c\,dx = \langle x^2 \rangle = 2Dt \propto t$$

MSD of particles $\propto t$

Consistent with MSD $= N$, obtained before.

$\hookrightarrow \langle m^2 \rangle = N$

Entropy Increase via Diffusion

A system partitioned into L boxes.

$L \times \Delta$

$L \times \Delta$

$n_1 \; n_2 \; n_3 \quad \rightarrow \Delta \leftarrow \quad n_L$

$1 \;\; 2 \;\; 3 \;\; \cdots\cdots \;\; L-1 \;\; L$

$$\sum_{j=1}^{L} n_j = N, \quad \text{total number of particles}$$

$$S = \ln \frac{N!}{n_1!\, n_2! \cdots n_L!}$$

$$= (N \ln N - N) - \sum_{j=1}^{L} (n_j \log n_j - n_j)$$

$$= \text{Const} - \sum_{j=1}^{L} \underbrace{\Delta}_{\text{box size}} \left(\frac{n_j}{\Delta} \ln \frac{n_j}{\Delta} - \frac{n_j}{\Delta} \right)$$

$\frac{n_j}{\Delta} \rightarrow$ density at jth box

$$= -\int dx \, (c \ln c - c)$$

c is density

$c = c(x)$

$$\frac{d}{dt} S = -\int dx \, \ln c \, \frac{\partial c}{\partial t}$$

continuity equation $\frac{\partial c}{\partial t} = -\partial_x j$

$$= -\int dx \, \ln c \, (-\partial_x j)$$

$$= -\int dx \, \partial_x (\ln c) \cdot j$$

$$= -\int dx \, \frac{1}{c} \partial_x c \cdot j$$

$$j = -D \partial_x c$$

$$\frac{dS}{dt} = \int dx \, \frac{1}{c} D (\partial_x c)^2 > 0$$

Diffusion is to increase entropy until its maximum is reached at a homogeneous distribution. $c = \frac{N}{L\Delta}$.