3. Root Mean Square Displacement X_{rms}

$|\vec{x}_i| = a$ Fixed step length

$\langle \vec{x}_i \rangle = 0$ no bias

$\langle \vec{x}_i \cdot \vec{x}_j \rangle = 0$ no correlations
$i \neq j$

$$\langle \vec{X}_N \rangle = \left\langle \sum_{i=1}^{N} \vec{x}_i \right\rangle$$

$$= 0$$

$$\langle (\vec{X}_N)^2 \rangle = \left\langle \left(\sum_{i=1}^{N} \vec{x}_i \right)^2 \right\rangle$$

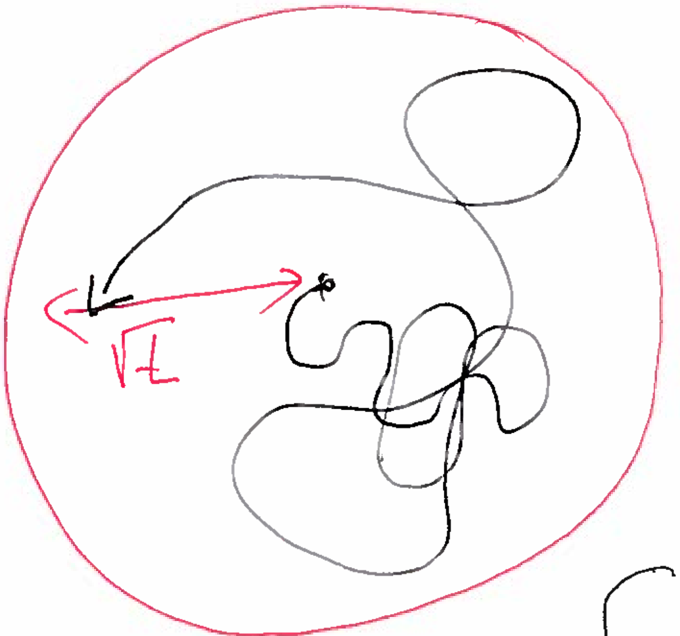
$$= \left\langle \sum_{i=1}^{N} \vec{x}_i^{\,2} + \cancel{\sum_{i \neq j} \vec{x}_i \cdot \vec{x}_j} \right\rangle$$

$$= N a^2$$

$$X_{rms} \equiv \sqrt{\langle \vec{X}_N^{\,2} \rangle}$$

$$= \sqrt{N}\, a$$

4. Role of the Spatial Dimension d



density of visited sites

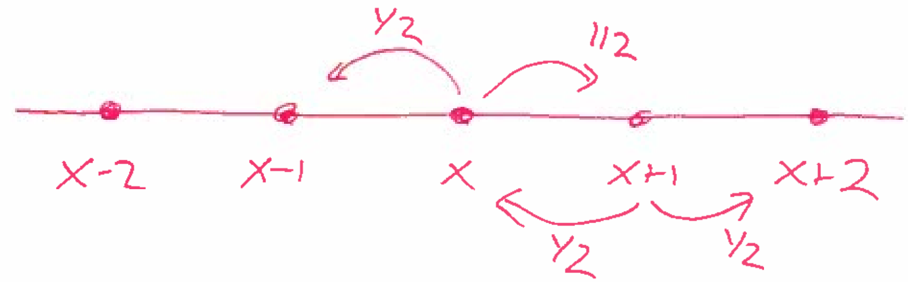
$$\rho \sim \frac{t}{(\sqrt{t})^d} \sim t^{1-d/2}$$

$$\rho \to \begin{cases} 0 & d>2 \\ \cancel{\text{const.}}\ \ln t & d=2 \\ \infty & d<2 \end{cases}$$

$d>2$: transient, return uncertain

$d \le 2$: recurrent, return certain

5. Probability Distribution



$P(x,t)$ = probability that a random walk is at x at time t

$$= \frac{1}{2}P(x-1,t-1) + \frac{1}{2}P(x+1,t-1)$$

r = # steps right
l = # steps left

$r + l = t$
$r - l = x$

$r = \frac{t+x}{2}$ $\quad l = \frac{t-x}{2}$

$$P(r,t) = \frac{t!}{r!\,l!}\left(\frac{1}{2}\right)^t$$

$$P(x,t) = \frac{t!}{\left(\frac{t+x}{2}\right)!\left(\frac{t-x}{2}\right)!}\left(\frac{1}{2}\right)^t$$

$$\xrightarrow[t\to\infty]{} \sqrt{\frac{2}{\pi t}}\, e^{-\cancel{2}x^2/2t}$$

Gaussian

Stirling's approx

5 (cont) Diffusion Equation

$$P(x, t+dt) = \frac{1}{2} P(x-dx, t) + \frac{1}{2} P(x+dx, t)$$

$$\cancel{P(x,t)} + dt \frac{\partial P}{\partial t} + \cdots\cdots = \frac{1}{2}\left[\cancel{P(x,t)} - \cancel{dx \frac{\partial P}{\partial x}} + \frac{1}{2} dx^2 \frac{\partial^2 P}{\partial x^2} + \cdots\right]$$

$$\frac{1}{2}\left[\cancel{P(x,t)} + \cancel{dx \frac{\partial P}{\partial x}} + \frac{1}{2} dx^2 \frac{\partial^2 P}{\partial x^2} + \cdots\right]$$

$$\boxed{\frac{\partial P}{\partial t} = \underbrace{\frac{(dx)^2}{2dt}}_{= D} \frac{\partial^2 P}{\partial x^2}}$$

diffusion eqn

$\lim dx, dt$

such that $\frac{dx^2}{2dt} = \text{const} \equiv D$ diffusion coefficient

general dimension $\boxed{\frac{\partial P}{\partial t} = D \nabla^2 P}$

$$[D] = \frac{l^2}{t} \quad ; \quad [x^2] = [Dt]$$

5 (cont.) Solution to the Diffusion Equation

$$\int_{-\infty}^{\infty}\left[\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}\right]e^{ikx}dx \qquad P(x,t=0)=\delta(x)$$

$$\int_{0}^{\infty}\left[\frac{\partial P(k,t)}{\partial t} = -Dk^2P(k,t)\right]e^{-st}dt$$

$$s\,P(k,s) - \underbrace{P(k,t=0)}_{1} = -Dk^2P(k,s)$$

$$\boxed{P(k,s) = \frac{1}{s+Dk^2}}$$

$$P(k,t) = \frac{1}{2\pi i}\int_C \frac{1}{s+Dk^2}e^{st}ds$$

$$= e^{-Dk^2t}$$

$$P(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-Dk^2t}e^{-ikx}dk$$

Fourier transform

$$f(k,t) = \int_{-\infty}^{\infty} f(x,t)e^{ikx}dx$$

$$f(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(k,t)e^{-ikx}dk$$

Laplace transform

$$f(x,s) = \int_0^{\infty} f(x,t)\,e^{-st}dt$$

$$f(x,t) = \frac{1}{2\pi i}\int_C f(x,s)e^{st}ds$$

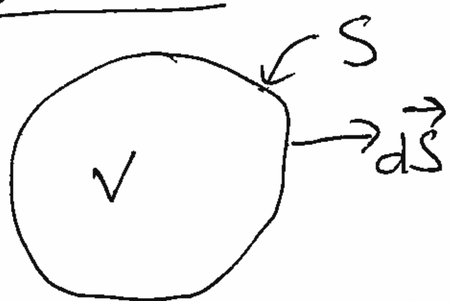
$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\,e^{-x^2/4Dt} \qquad d=1$$

$$P(\vec{r},t) = \frac{1}{(4\pi Dt)^{d/2}}\,e^{-r^2/4Dt} \qquad d \text{ arbitrary}$$

Gaussian

5. (cont) Connection with Kinetic Theory and Particle Conservation

Conservation

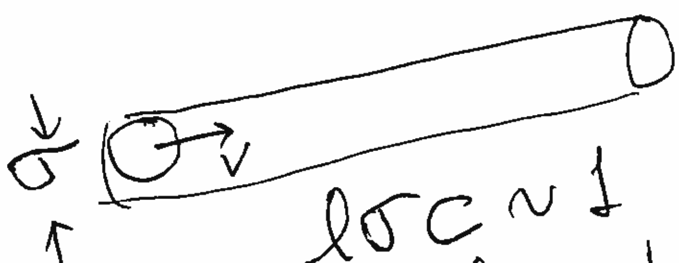


$$\frac{\partial N}{\partial t} = -\int \vec{j} \cdot d\vec{S}$$

$$\int \frac{\partial}{\partial t} c(r,t)\, dV = -\int \vec{\nabla} \cdot \vec{j}\, dV$$

$$\boxed{\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{j}}$$

mean-free path

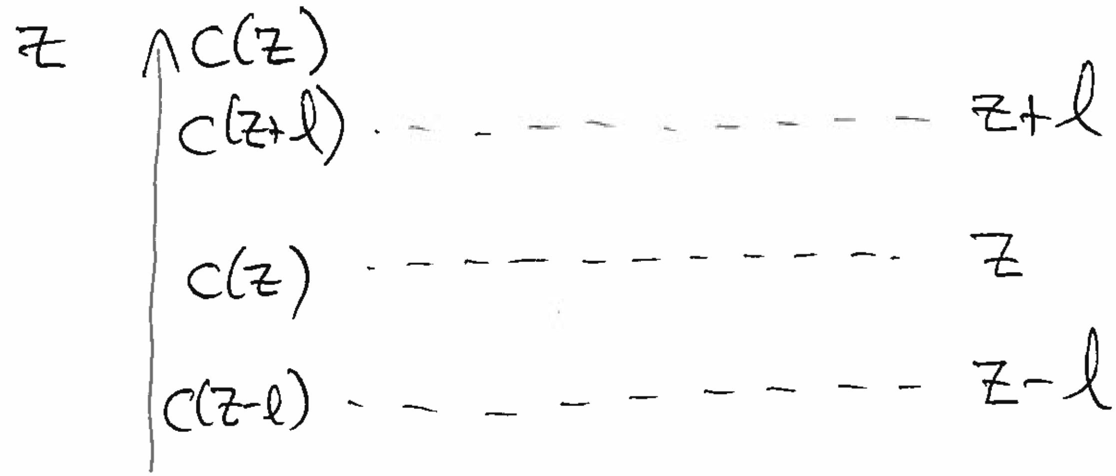


collision

$$l \sigma c \sim 1$$

$$\Rightarrow l \sim \frac{1}{c\sigma}$$

determine j by kinetic



$$j_{up} \approx c(z-l)\frac{v}{6} \; ; \; j_{down} = c(z+l)\frac{v}{6}$$

$$j_{net} = \frac{v}{6}\left[c(z-l) - c(z+l)\right] \approx -\frac{vl}{3}\frac{\partial c}{\partial z}$$

$$\boxed{j \equiv -D\frac{\partial c}{\partial z}} \rightarrow \boxed{D \propto vl}$$

$$\boxed{\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{j} = D\nabla^2 c}$$

$$J = -\frac{v\ell}{3}\frac{\partial c}{\partial x} \equiv -D\frac{\partial c}{\partial x}$$

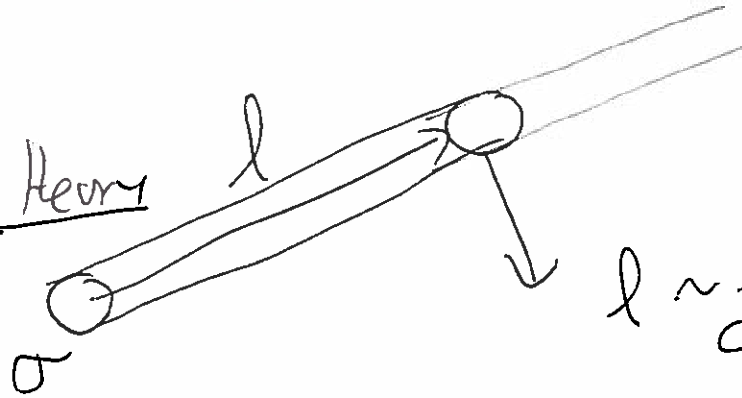
dissipation

equal. — are these equal?

$$\frac{\partial c}{\partial t} = \frac{(dx)^2}{2dt}\frac{\partial^2 c}{\partial x^2} \equiv D\frac{\partial^2 c}{\partial x^2}$$

Fluctuation yes: fluctuation dissipation relation

from kinetic theory



$c\ell\sigma \sim 1$ defines collision

$$\ell \sim \frac{1}{c\sigma} \sim \frac{1}{10^{20}/\text{cm}\ \ 10^{-15}\text{cm}} \sim 10^{-5}\text{cm}$$

$\sim 100-1000$ molecular diameters

$$\tau \sim \frac{\ell}{v} \sim \frac{10^{-5}\text{cm}}{30000\text{cm/sec}}$$

$\sim 10^{-9} - 10^{-10}$ sec

RW picture

$$\langle x^2 \rangle = N\ell^2$$

$$= \frac{t}{\tau}\ell^2 = \frac{t}{\ell/v}\ell^2 = \underbrace{(v\ell)}_{\equiv D}\, t$$

6. Central Limit Theorem

x, $p(x)$

Assume are i.i.d variables
(independent identically distributed)

Assume $\langle x \rangle < \infty$
$\langle x^2 \rangle < \infty$

Then $$P_N(X) = \frac{1}{\sqrt{2\pi N\sigma^2}} e^{-(X - N\langle x \rangle)^2 / 2N\sigma^2}$$ Central Limit Theorem

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$\langle X \rangle = \int X P_N(X)\, dX = N\langle x \rangle$$

$$\langle X^2 \rangle - \langle X \rangle^2 = \int X^2 P_N(X)\, dX - \langle X \rangle^2$$
$$= N\sigma^2$$

6. Proof of Central Limit Theorem

$$P_N(X) = \int P_{N-1}(x')\, p(x' \to x)\, dx'$$

Fourier transform $P_N(k) = P_{N-1}(k)\, p(k) = P_{N-2}(k)\, (p(k))^2$

$$= P_0(k)\, [p(k)]^N = [p(k)]^N$$

$$P_N(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} [p(k)]^N e^{ikx}\, dk$$

$$p(k) = \int p(x)\, e^{ikx} dx = \int p(x) \left[1 + ikx - k^2 \frac{x^2}{2} + \cdots \right] dx$$

$$= 1 + \cancel{ik\langle x\rangle} - \frac{k^2}{2} \langle x^2 \rangle + \cdots$$

$$P_N(x) = \frac{1}{2\pi} \int \left[1 - \frac{k^2 \langle x^2 \rangle}{2}\right]^N e^{-ikx} dk \simeq \frac{1}{2\pi} \int e^{-Nk^2\langle x^2\rangle/2 - ikx} dx$$

$$= \frac{1}{\sqrt{2\pi N \langle x^2 \rangle}}\, e^{-X^2/2N\langle x^2\rangle}$$

- Gaussian
- independent of almost all details of the individual steps

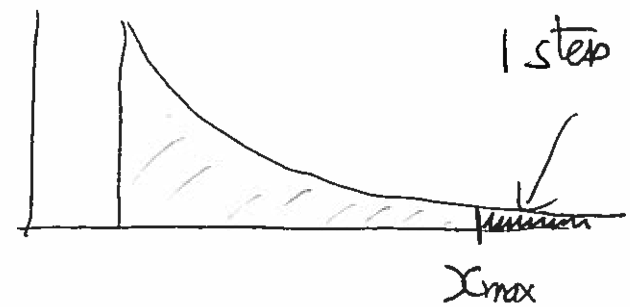
6 (cont) Failure of the Central Limit Theorem

$$p(x) = \begin{cases} 0 & x<1 \\ \mu x^{-(1+\mu)} & x>1 \end{cases} \qquad \langle x \rangle = \infty$$

$\mu < 1$

Consider N steps

x_{max} determined by $\boxed{\int_{x_{max}}^{\infty} p(x)\,dx = \frac{1}{N}}$



$x_{max} \sim N^{1/\mu}$

$$p_{eff} = \begin{cases} 0 & x<1 \\ \dfrac{\mu x^{-(1+\mu)}}{1-x_{max}^{-\mu}} & 1<x<x_{max} \\ 0 & x>x_{max} \end{cases}$$

$$\langle x \rangle_{eff} = \frac{\mu}{1-x_{max}^{-\mu}} \int_1^{x_{max}} x \, x^{-(1+\mu)}\,dx = \begin{cases} \text{finite} & \mu>1 \\ \ln x_{max} \sim \ln N & \mu=1 \\ x_{max}^{1-\mu} \sim N^{\frac{1}{\mu}-1} & \mu<1 \end{cases}$$

$$\langle X \rangle_N = N \langle x \rangle_{\text{eff}}$$

$$= \begin{cases} N & \mu > 1 \\ N \ln N & \mu = 1 \\ N \cdot N^{\frac{1}{\mu}-1} \sim N^{1/\mu} & \mu < 1 \end{cases}$$

$$x_{max} \sim N^{1/\mu}$$

7. First Passage Phenomena

Questions: 1. What is the prob of eventually hitting 0 when starting from x?

2. What is the time to hit the origin?

Solve
$$\begin{cases} \dfrac{\partial c}{\partial t} = D\dfrac{\partial^2 c}{\partial x^2} \\ c(x, t=0) = \delta(x-x_0) \\ c(x=0,t) = 0 \quad \text{absorbing} \end{cases}$$

$$c(x,t) = \frac{1}{\sqrt{4\pi Dt}}\left[e^{-(x-x_0)^2/4Dt} - e^{-(x+x_0)^2/4Dt}\right]$$

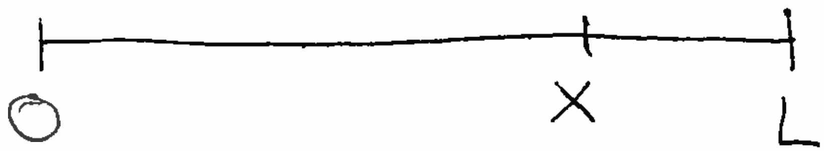
$$j = -D\frac{\partial c}{\partial x}\bigg|_{x=0} = \frac{D}{\sqrt{4\pi Dt}}\left[\frac{x-x_0}{2Dt} - \frac{(x+x_0)}{2Dt}\right]e^{-x_0^2/4Dt}$$

$$j = -\frac{x_0}{\sqrt{4\pi Dt^3}}\, e^{-x_0^2/4Dt} \equiv \text{first passage prob to the } 0$$

$$\boxed{\begin{aligned} J &= \int_0^\infty j\,dt = 1 \quad \text{return is certain} \\ \langle t\rangle &= \int_0^\infty t\, j(t)\,dt \Big/ \int_0^\infty j(t)\,dt = \infty \end{aligned}}$$

return time $= \infty$

7. Application: First Passage in an Interval



$E(x)$ = prob that I win starting with x

$t(x)$ = time of the game starting with x

$$E(x) = \sum_{\text{paths}} P_{x\to L} = \frac{1}{2}\sum_{\text{paths}'} P_{x+dx\to L} + \frac{1}{2}\sum_{\text{paths}''} P_{x-dx\to L}$$

$$= \frac{1}{2}E(x+dx) + \frac{1}{2}E(x-dx)$$

$E(0) = 0$

$E(L) = 1$

$$E''(\cancel{x}) = 0 \longrightarrow \boxed{E(x) = x/L}$$

even simpler $\langle x\rangle \equiv$ invariant

$t=0 \quad \langle x\rangle = x$

$t=\infty \quad \langle x\rangle = (1-E)\cdot 0 + E\cdot L$

$E(x) = x/L$

$$t(x) = \sum_{\text{paths}} t_{x\to 0,L} = \frac{1}{2}\Big(dt + \sum_{\text{paths}'} t_{x+dx\to 0,L}\Big) + \frac{1}{2}\Big(dt + \sum_{\text{paths}''} t_{x-dx\to 0,L}\Big)$$

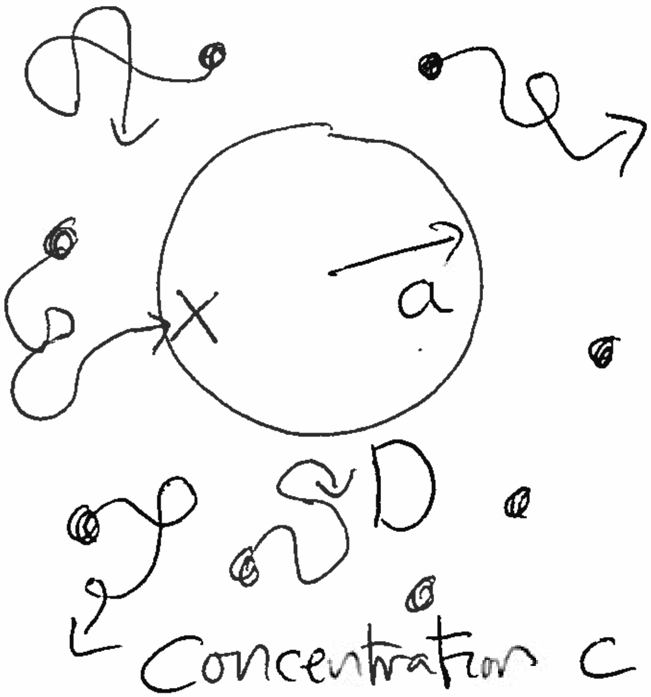
$$t(x) = dt + \frac{1}{2}t(x+dx) + \frac{1}{2}t(x-dx)$$

$$0 = dt + \frac{1}{2}(dx)^2\, t''(x) \Rightarrow t''(x) = -\frac{2dt}{(dx)^2} = -\frac{1}{D}$$

$Dt'' = -1 \qquad t(0) = t(L) = 0$

$$\boxed{t(x) = \frac{\cancel{X}}{2D}(L-x)}$$

7. Application: Reaction Rate Theory



$k \equiv$ reaction rate

$= \dfrac{\#\text{particles absorbed / time}}{c}$

$[D] = l^2/t$

$[k] = \dfrac{l^d}{t}$; $k = k(D, a)$

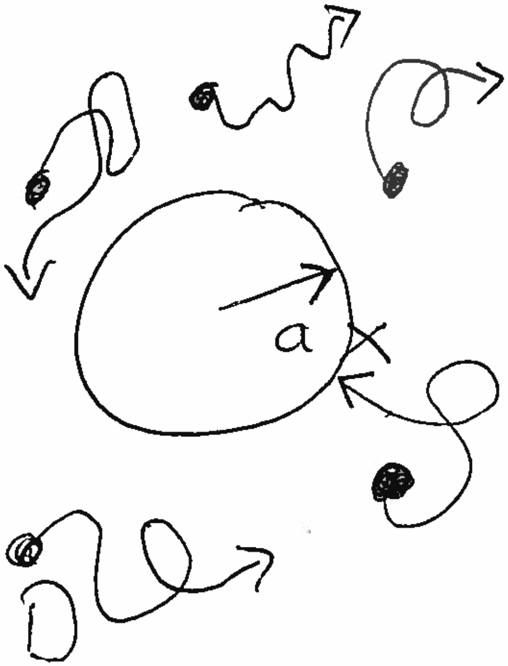
$\Rightarrow \boxed{k \propto D a^{d-2}}$

$d=3$: $k \propto a$!!

$d<2$: $\cancel{k \uparrow \text{ as } a \downarrow}$!

$\Rightarrow$ now dependence on system parameters

7. Application: Reaction Rate Theory in 3 Dimensions



Solve

$$\begin{cases} \dfrac{\partial c}{\partial t} = D\nabla^2 c \\ c(r>a, t=0) = 1 \\ c(r=a, t>0) = 0 \end{cases}$$

Instead

$$\begin{cases} D\nabla^2 c = 0 \\ c(r=a) = 0 \\ c(r\to\infty) = 1 \end{cases}$$

$$c(r) = 1 - \frac{a}{r} \quad \equiv \text{escape probability}$$

$$K = \int (-D\vec{\nabla} c)\cdot(-d\vec{S})$$

$$= Da \int \frac{1}{a^2} dS = \boxed{4\pi Da\left(1 + \frac{a}{\sqrt{\pi D t}}\right)}$$