MATH3104 Lecture 1 (Bracken)

•**Diffusion:** random movement of molecules or small particles in a gas or liquid, due to thermal energy of surrounding molecules.

•Recall: **Absolute** (or **Kelvin**) temperature scale.

$$27^oC \approx 300^oK$$

• Particle in fluid that is in thermal equilibrium at T^oK, has **average** K.E. associated with motion along each coord. axis equal to $\frac{1}{2}kT$

— so $\frac{3}{2}kT$ in total.

• Here k is Boltzmann's constant

$$k \approx 1.38 \times 10^{-16} \quad gm(cm/sec)^2/^oK$$

• When $T = 300^o K$, $kT \approx 4.14 \times 10^{-14} gm (cm/sec)^2$ ($ergs$).

— a very small energy on human scales: a $70kg$ human walking at $5kph$ has a K.E.

$$\frac{1}{2} mv^2 \approx 7 \times 10^8 ergs$$

•However, consider a molecule of the enzyme/protein **lysozyme**, in water at $300^o K$. (Lysozyme is found in egg-white, tears, . . .)

•**Mass?** Molecular weight $\approx 14,000 gm$

$=$ mass of N_A molecules, where $N_A =$ **Avogadro Number** $\approx 6 \times 10^{23}$

So now

$$m \approx \frac{14000}{6 \times 10^{23}} \approx 2.3 \times 10^{-20} gm$$

•**Speed?** $\frac{1}{2} m v_x^2 \approx \frac{1}{2} kT$

$$\Rightarrow v_x \approx \sqrt{\frac{kT}{m}} \approx \sqrt{\frac{4.14 \times 10^{-14}}{2.3 \times 10^{-20}}} \approx 1.3 \times 10^3 cm/sec \quad (\approx 45 kph)$$

— would cross swimming pool in about $1 sec$.

•Each water molecule has a similar **average** K.E. along each coordinate axis. But now

$MW = 18gm$, so $m \approx (18)/(6 \times 10^{23}) \approx 3 \times 10^{-23}gm$

$\Rightarrow v_x$ about $\sqrt{\frac{14000}{18}} \approx 30$ times greater.

— would cross pool in about $1/30sec$.

•Of course, this is not what happens. Molecules collide repeatedly and get redirected. The lysozyme molecule in water is forced to conduct a **random walk**.

•A small cloud of such particles will wander about and spread — this is **diffusion**.

• Let's consider a simple model of this process:

The one-dimensional random walk

A particle ('the walker') starts at $x = 0$ at time $t = 0$. After each interval of time τ, it receives a kick and moves one step of length δ to L or R along the X-axis, each with probability $1/2$.

(Toss a coin at each stage!)

e.g. after 3 steps (at $t = 3\tau$),
particle could be at

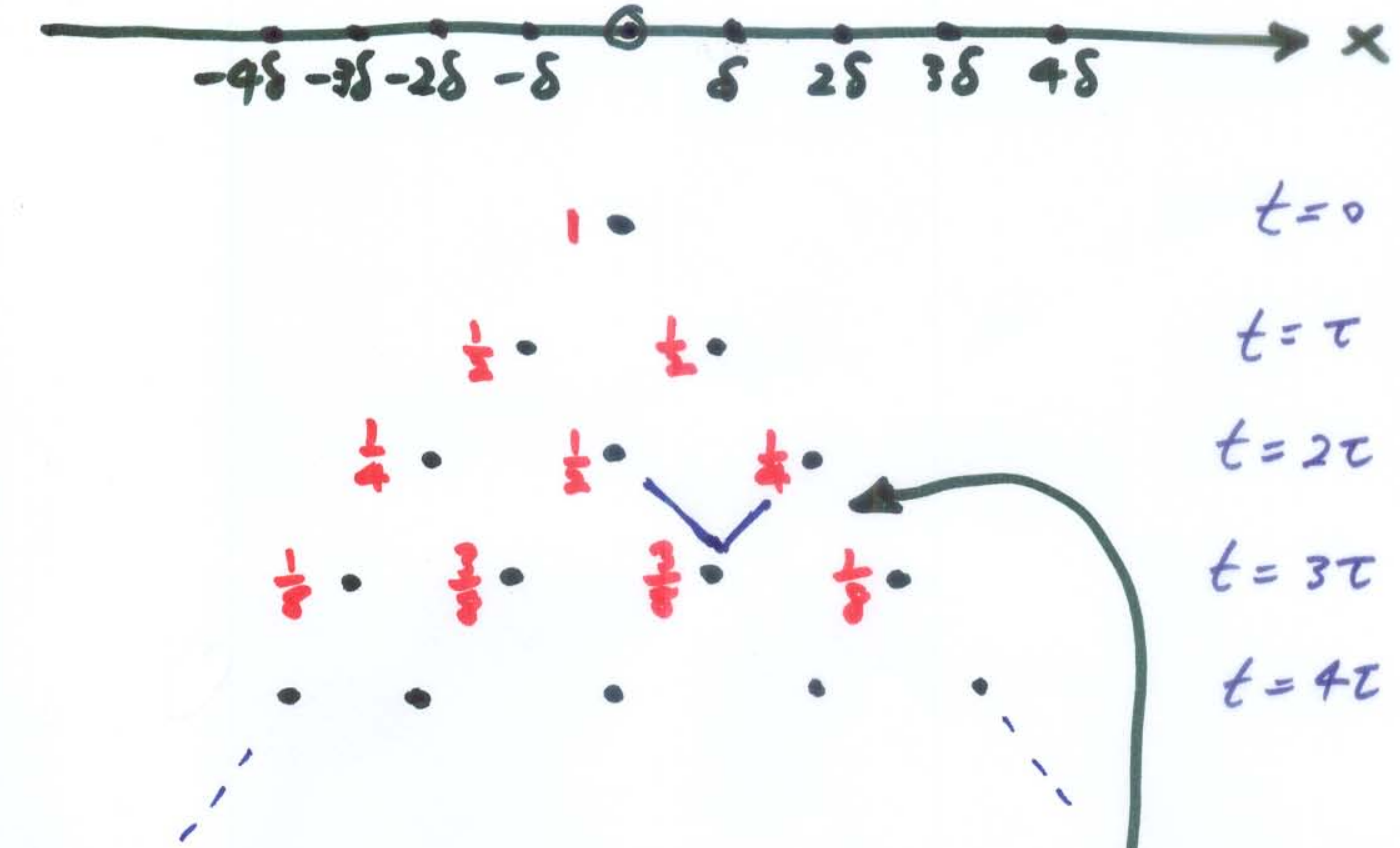
	Steps	Probability
$x = 3\delta$	RRR	$\left(\frac{1}{2}\right)^3 = \frac{1}{8}$
$x = \delta$	RRL, RLR, LRR	$\left(\frac{1}{2}\right)^3 3 = \frac{3}{8}$
$x = -\delta$	LLR, LRL, RLL	$\left(\frac{1}{2}\right)^3 3 = \frac{3}{8}$
$x = -3\delta$	LLL	$\left(\frac{1}{2}\right)^3 = \frac{1}{8}$

sum =

$$\frac{1}{8} + \frac{3}{8} + \frac{3}{8} + \frac{1}{8} = 1$$

– particle must be somewhere!

• See the pattern:—



Pascal Triangle

$\frac{3}{8} = \frac{1}{2}\left(\frac{1}{2}+\frac{1}{4}\right)$ etc.

After N steps ($t = N\tau$), particle could be at any of

$$x = N\delta\,, \quad x = (N-2)\delta\,, \quad \ldots \quad x = -(N-2)\delta\,, \quad x = -N\delta$$

$i.e.$ particle is at

$$x = m\delta\,, \quad m \in \{N,\, N-2,\, \cdots - (N-2),\, -N\}$$

For a given m, this requires a sequence of steps of which r are to the RIGHT and l are to the LEFT, with

$$r - l = m\,.$$

Since

$$r + l = N\,,$$

it follows that

$$r = \frac{N+m}{2}\,, \qquad l = \frac{N-m}{2}\,.$$

• The probability of any one sequence of N steps is $(1/2)^N$.

So, probability that $x = m\delta$ after N steps is

$$P(m, N) = \left(\tfrac{1}{2}\right)^N [\text{ No. of sequences of length } N \text{ with } r = (N+m)/2]$$

$$= \left(\tfrac{1}{2}\right)^N [\text{ No. of ways of getting } r \text{ Heads in } N \text{ coin tosses}]$$

$$= \left(\tfrac{1}{2}\right)^N C_r^N,$$

where $C_r^N = \frac{N!}{r!(N-r)!}$ $\quad (= N \quad \text{choose} \quad r)$.

So we have

$$P(m, N) = \left(\tfrac{1}{2}\right)^N \frac{N!}{r!(N-r)!} = \left(\tfrac{1}{2}\right)^N \frac{N!}{(\frac{N+m}{2})!(\frac{N-m}{2})!}.$$

EX: $N = 3\,, \quad m = -1 \qquad (\Rightarrow r = 1\,, \quad l = 2)$

$$P(-1,3) = \left(\tfrac{1}{2}\right)^3 \frac{3!}{1!\,2!} = \left(\tfrac{1}{2}\right)^3 3 = \tfrac{3}{8}$$

— as on page 1.6

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Note that we must have

$$\sum_{m=-N}^{N}{}' \, P(m,N) = \sum_{m=-N}^{N}{}' \left(\tfrac{1}{2}\right)^N \frac{N!}{(\frac{N+m}{2})!(\frac{N-m}{2})!} = 1\,,$$

as in the example on p. 1.6. Can you see how to prove it in the general case? (Binomial Theorem!)

(Here $\sum{}'$ means sum over $m = -N, \, -(N-2), \, \ldots, \, N-2, \, N$.)

•Where is the particle **on average** after N steps?

$$\langle x \rangle = \sum_{m=-N}^{N}{}' P(m,N)\, m\delta = 0$$

because $P(-m,N) = P(m,N)$

— particle is just as likely to go L or R at each step — **on average** it gets nowhere!

More interesting is the **mean-square displacement** of the particle from its mean position:–

$\langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2\langle x \rangle x + \langle x \rangle^2 \rangle$

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

$= \langle x^2 \rangle - \langle x \rangle^2$. This reduces to $\langle x^2 \rangle$ here, because $\langle x \rangle = 0$.

We have

$\langle x^2 \rangle$	No. of steps
$(1)(0)^2 = 0$	0
$(\frac{1}{2})(-\delta)^2 + (\frac{1}{2})(\delta)^2 = \delta^2$	1
$(\frac{1}{4})(-2\delta)^2 + (\frac{1}{2})(0)^2 + \frac{1}{4}(2\delta)^2 = 2\delta^2$	2
$(\frac{1}{8})(-3\delta)^2 + (\frac{3}{8})(-\delta)^2 + (\frac{3}{8})(\delta)^2 + (\frac{1}{8})(3\delta)^2 = 3\delta^2$	3

The pattern is clear: after N steps,

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

i.e. $$\sum_{m=-N}^{N}{}' \, P(m,N)(m\delta)^2 = N\delta^2$$

— but can you prove it?

•The **root-mean-square displacement** $\sqrt{\langle (x - \langle x \rangle)^2 \rangle}$ is a convenient measure of **how far** we expect the particle to be **from its mean position**.

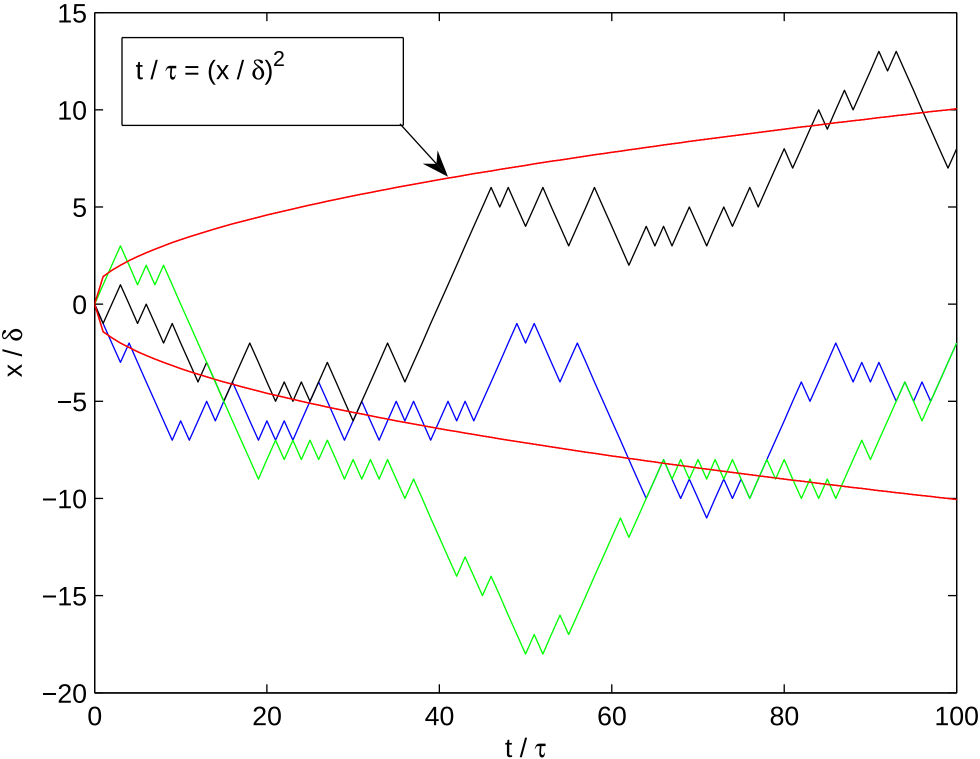
We have $\sqrt{\langle (x - \langle x \rangle)^2 \rangle} = \sqrt{\langle x^2 \rangle} = \sqrt{N}\,\delta$ after N steps.

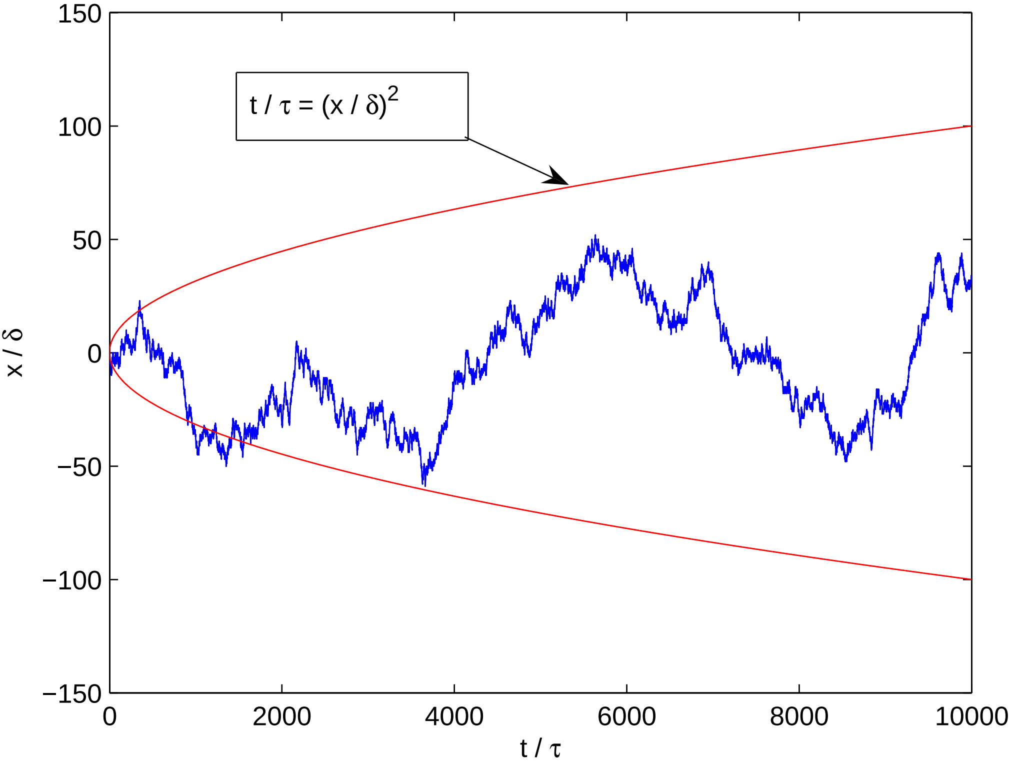
This is an **important** and **characteristic** feature of the random walk!

After 100 steps, each of length δ, we expect the particle to be **about** 10δ from its starting point.

After $10,000$ steps, we expect it to be **about** 100δ away, and so on.

Note that we are talking about **average behaviour**. No two **realisations** of a random walk will look the same in general: see the following figures:–


t / τ = (x / δ)²
15
10
5
0
−5
−10
−15
−20
x / δ
0
20
40
60
80
100
t / τ



t / τ = (x / δ)^2
150
100
50
0
−50
−100
−150
0
2000
4000
6000
8000
10000
x / δ
t / τ

•Consider again

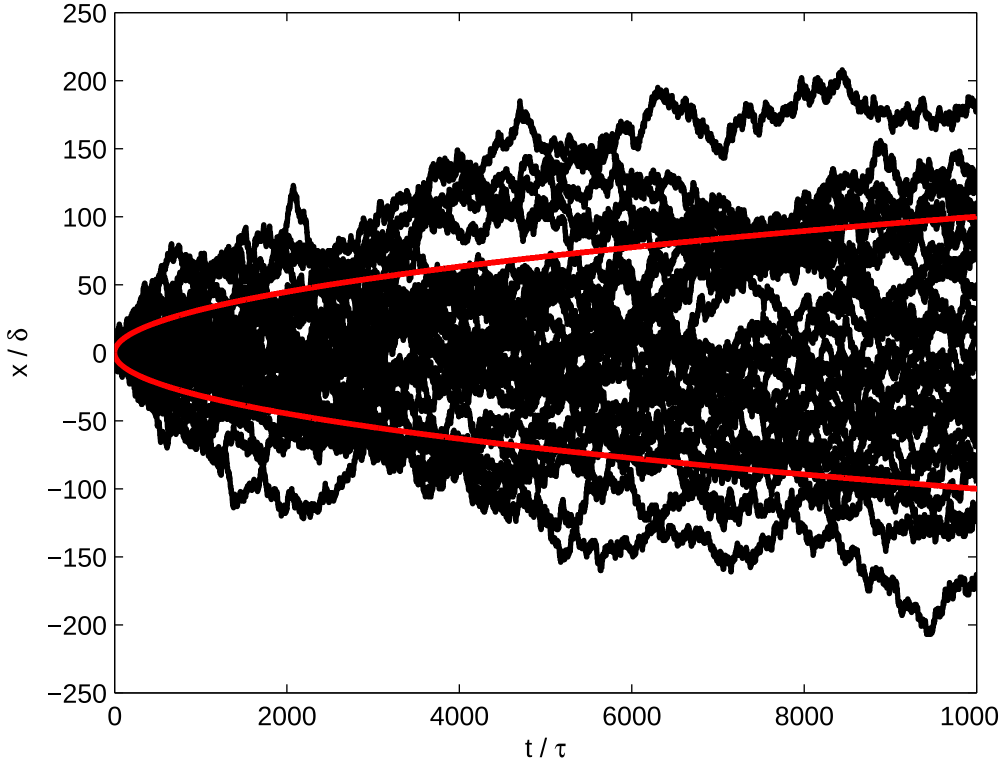
$$P(m,N) = \left(\tfrac{1}{2}\right)^N \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} \, .$$

Using **Stirling's approximation** for $K!$ when K is large, we can show that when N and $|m|$ are large, with m^2/N not too large, then

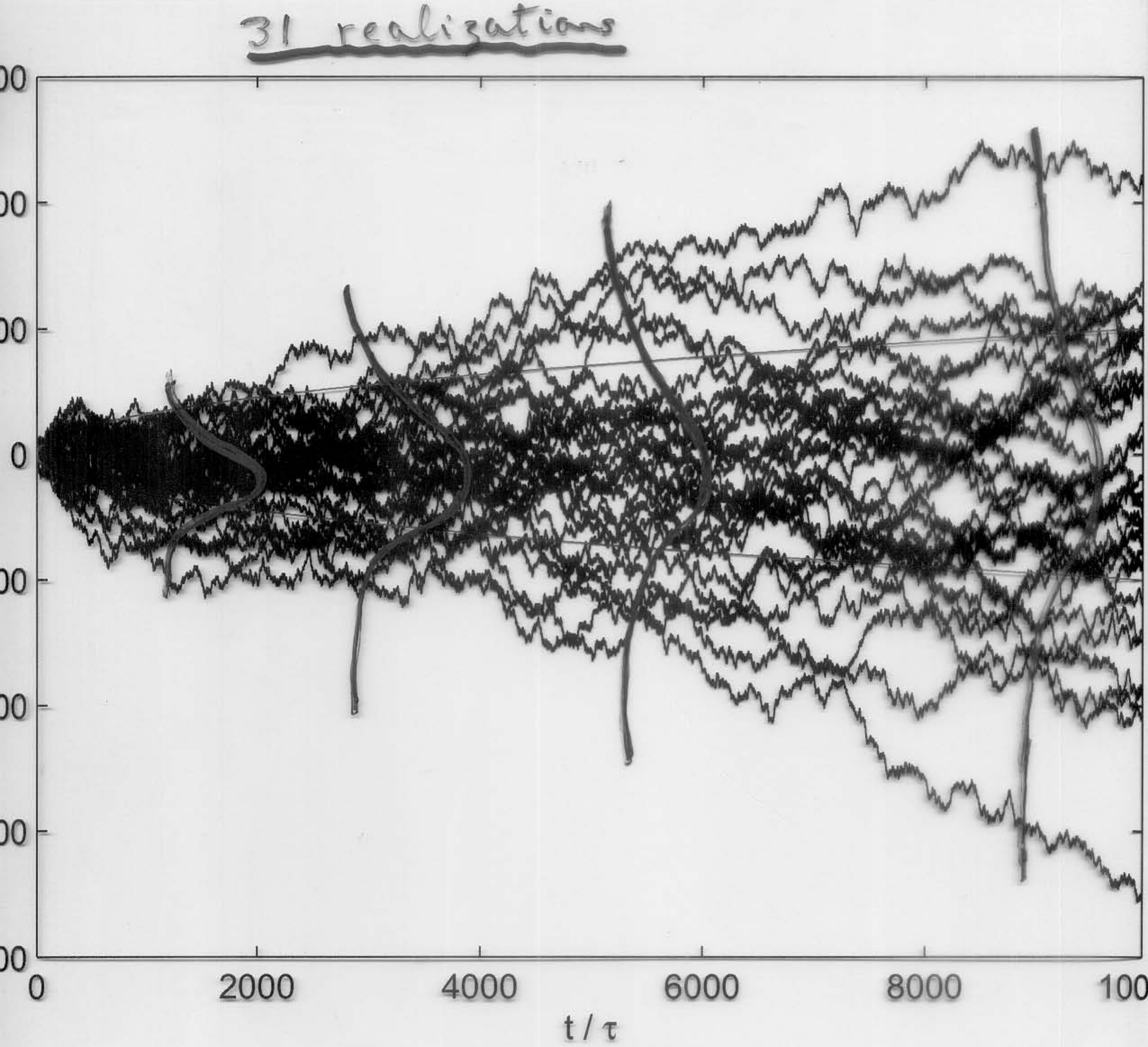
$$P(m,N) \approx \sqrt{\frac{2}{\pi N}}\, e^{-m^2/2N} \, .$$

This is a good approximation even for quite small values of $|m|$ and N:–

(m, N)	$P(m, N)$	$\sqrt{\frac{2}{\pi N}}\, e^{-m^2/2N}$	Relative Error
$(\pm 2, 10)$	0.2051	0.2066	0.73%
$(\pm 5, 27)$	0.09714	0.09668	0.5%
$(\pm 200, 10000)$	0.0010799	0.0010798	0.01%



250
200
150
100
50
0
−50
−100
−150
−200
−250
x / δ
0
2000
4000
6000
8000
10000
t / τ

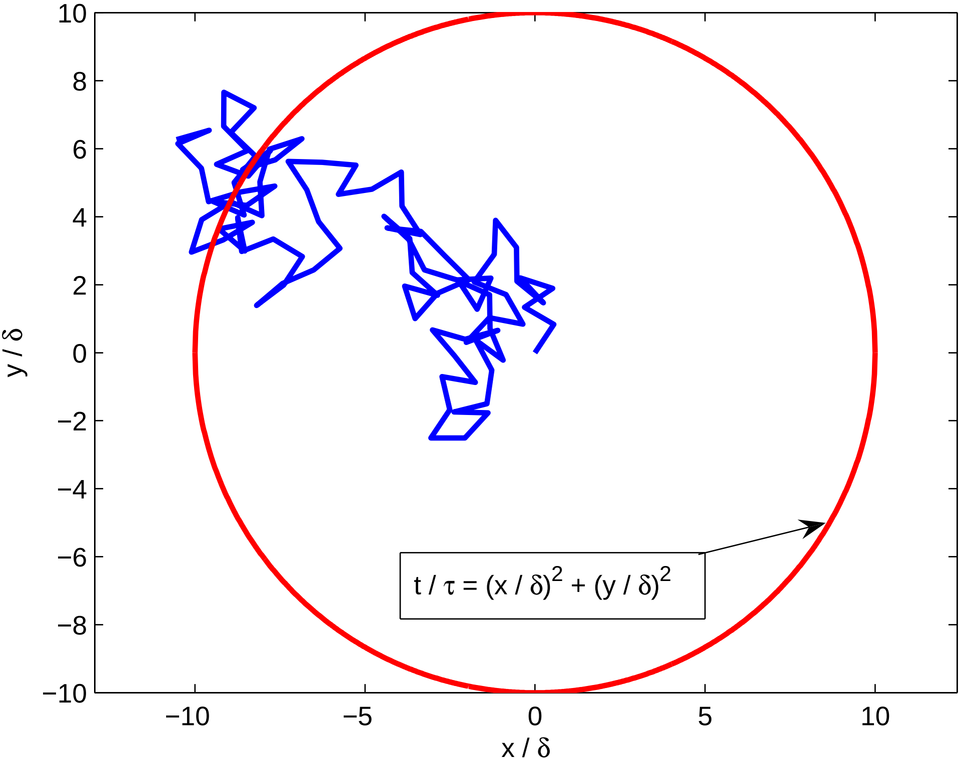

31 realizations
0
2000
4000
6000
8000
t / τ

•What about random walks in two and three dimensions?

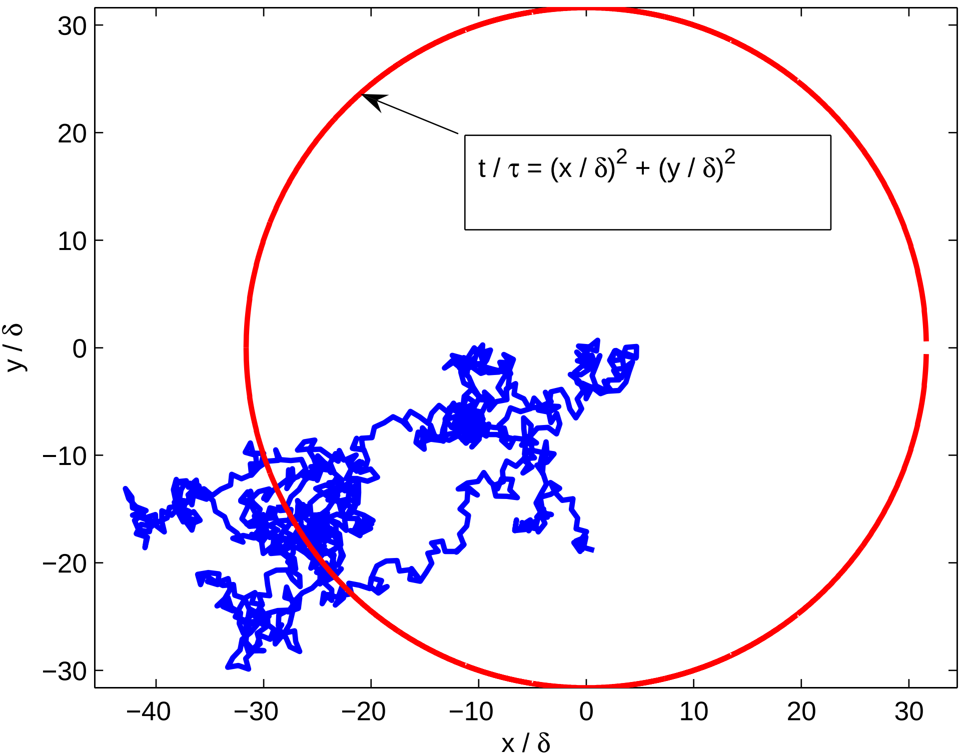
Again we find that the mean displacement after N steps is zero, and the rooot-mean-square displacement is proportional to N.

See the next two figures, showing realisations of a 2-D random walk with $N = 100$ and $N = 1000$, respectively.

[We have assumed that after each time interval of length τ, the particle steps a distance δ in an arbitrary direction, making an angle with the X-axis that is uniformly distributed over $[0,\, 2\pi)$.]



10
8
6
4
2
0
−2
−4
−6
−8
−10
−10
−5
0
5
10
x / δ
y / δ
t / τ = (x / δ)^2 + (y / δ)^2



t / τ = (x / δ)^2 + (y / δ)^2
y / δ
x / δ
30
20
10
0
−10
−20
−30
−40
−30
−20
−10
0
10
20
30

Reading: H.C. Berg, *Random Walks in Biology*, Chapter 1.