



# 993SM - Laboratory of Computational Physics lecture 4 March 31, 2021

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# Random Walks and Diffusion

- random motion and diffusion - analytic treatment
- a simplified model: random walks
- Brownian motion: implementation of an algorithm based on the Langevin equation
- Brownian motion: mathematical eqs. & miscellanea

M. Peressi - UniTS - Laurea Magistrale in Physics  
Laboratory of Computational Physics - Unit IV

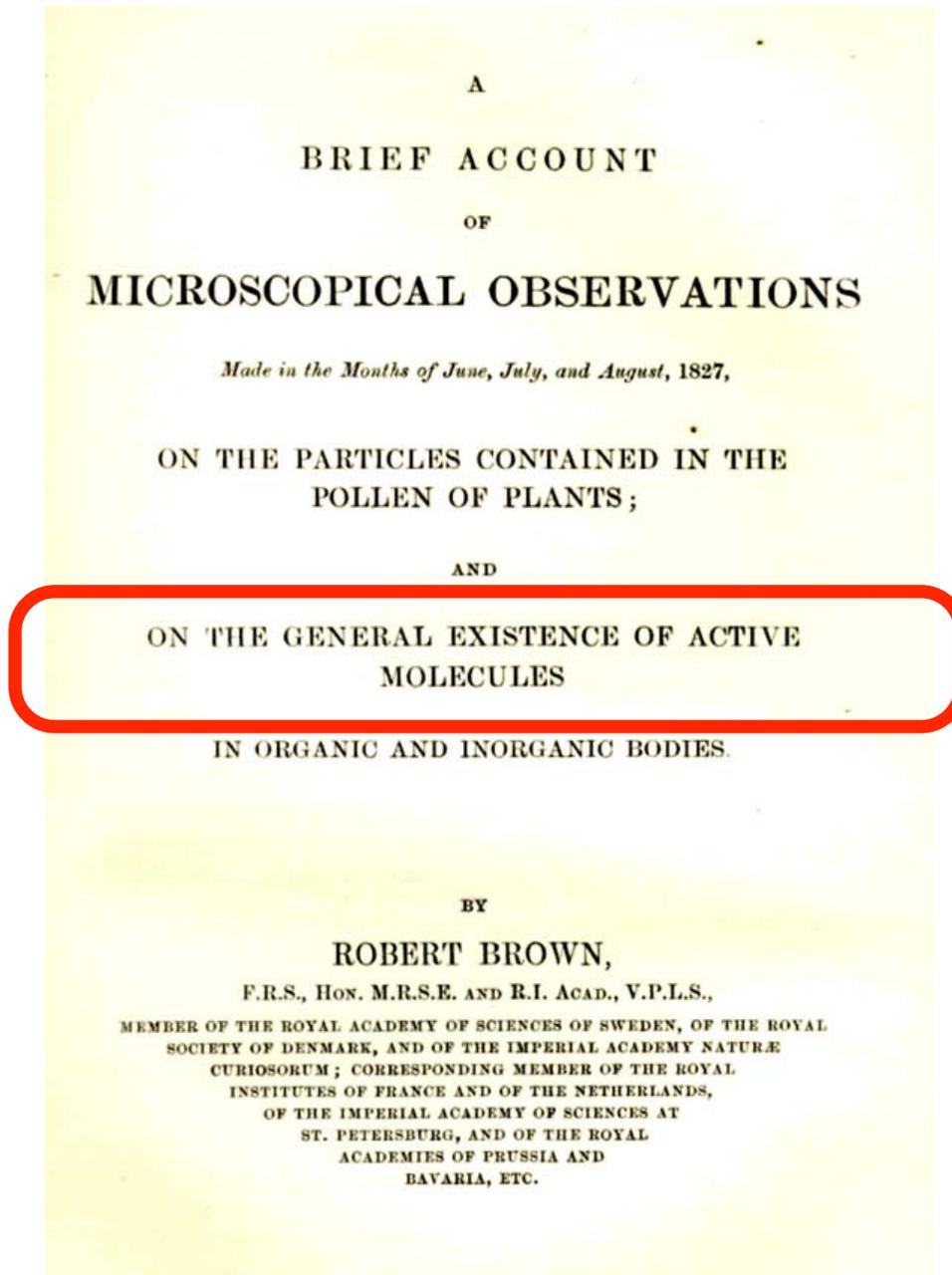
I part:  
Random motion and  
diffusion  
-history and analytic treatment-

# Random motion

Brownian motion is by now a well-understood problem, and the concepts, techniques and models have proven fruitful in many different fields, from **statistical mechanics** to **econophysics**. A brief history:

- Robert Brown 1828
- J.C. Maxwell 1867
- Albert Einstein 1905
- Maryan Smoluchowski 1906
- Jean Perrin 1912
- J. Bardeen , C. Herring 1950

# Observations of "active molecules" by scientist Robert Brown in 1827



# Random motion

- random motion of tiny particles had been reported early in scientific literature
- before 1827, random motion was attributed to living particles.
- random motion = “brownian motion”, after 1827, when the British botanist **Robert Brown** claimed that even dead particles could exhibit a random motion

# ~~Random motion~~ “Brownian”

- random motion of tiny particles had been reported early in scientific literature
- before 1827, random motion was attributed to living particles.
- random motion = “brownian motion”, after 1827, when the British botanist **Robert Brown** claimed that even dead particles could exhibit a random motion
- **What is the origin of the brownian motion?**  
In 1870, Loschmidt suggested that it is caused by thermal agitation <sub>7</sub>

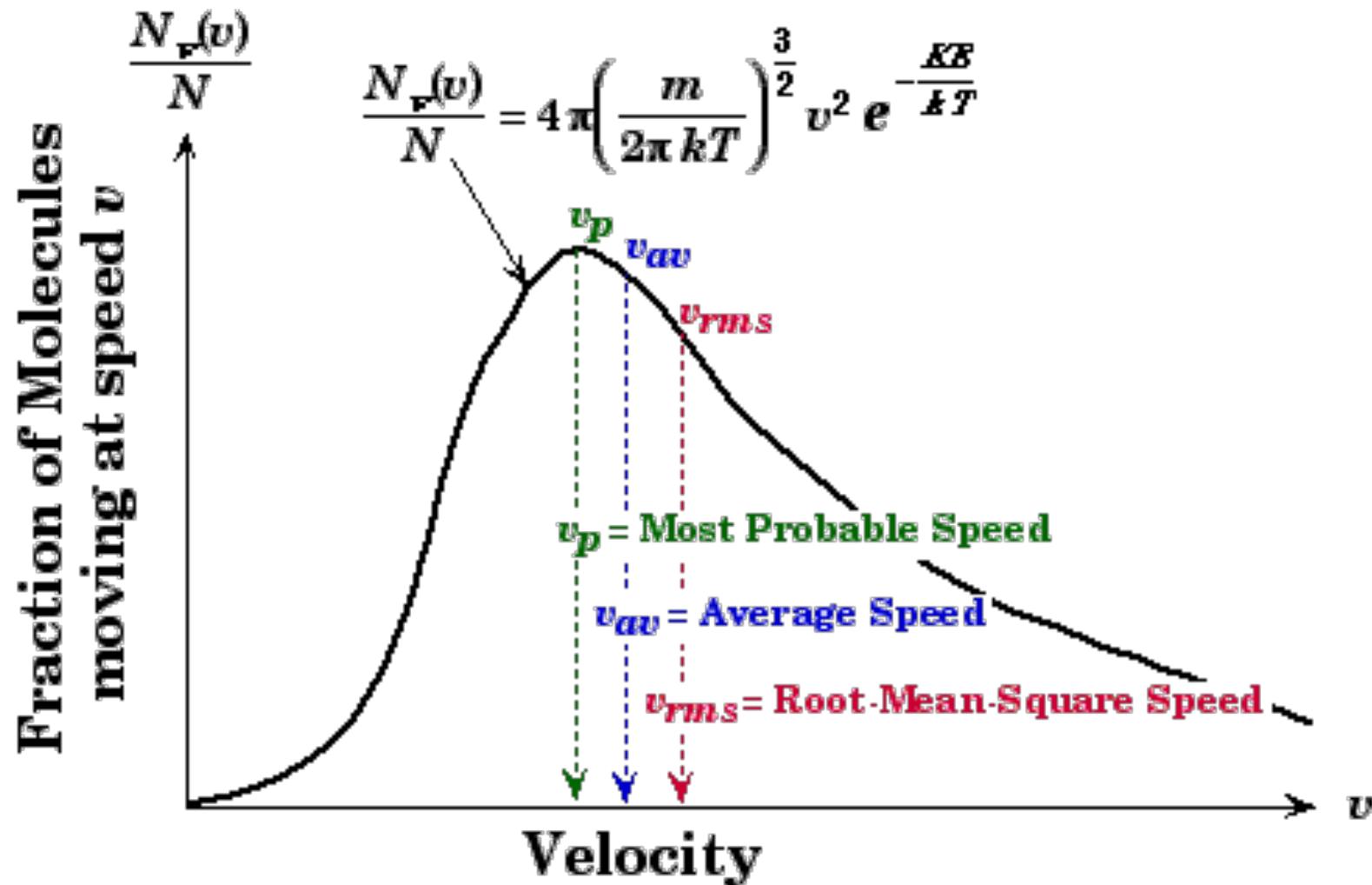
# Brownian motion -open questions-

Observations of "active molecules" made by Brown in 1827 led the physics community to **search for the proof that molecules indeed exist.**

At the turn of 20th century, the **atomic nature of matter** was fairly widely accepted among scientists, but not universally (there was **NO direct evidence!**)

Another argument under discussion: **the kinetic theory of gases**

# Maxwell-Boltzmann distribution of velocity



$$v_p = \sqrt{2 \frac{kT}{m}}$$

$$v_{av} = \sqrt{\frac{8 kT}{\pi m}}$$

$$v_{rms} = \sqrt{3 \frac{kT}{m}}$$

# Kinetic theory of gases

- Under discussion in ~1900:  $\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$  ???
- Can we prove its validity from the observation of the Brownian motion?
- Could  $m$  be obtained from that relationship? In principle yes, provided one can measure  $v$ . But  $v$  cannot be measured from the erratic trajectory of particles observed at the microscope!
- so... **What can we really measure?**

# Brownian motion

## -Einstein's 1905 paper-

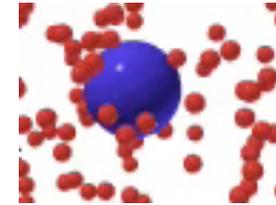
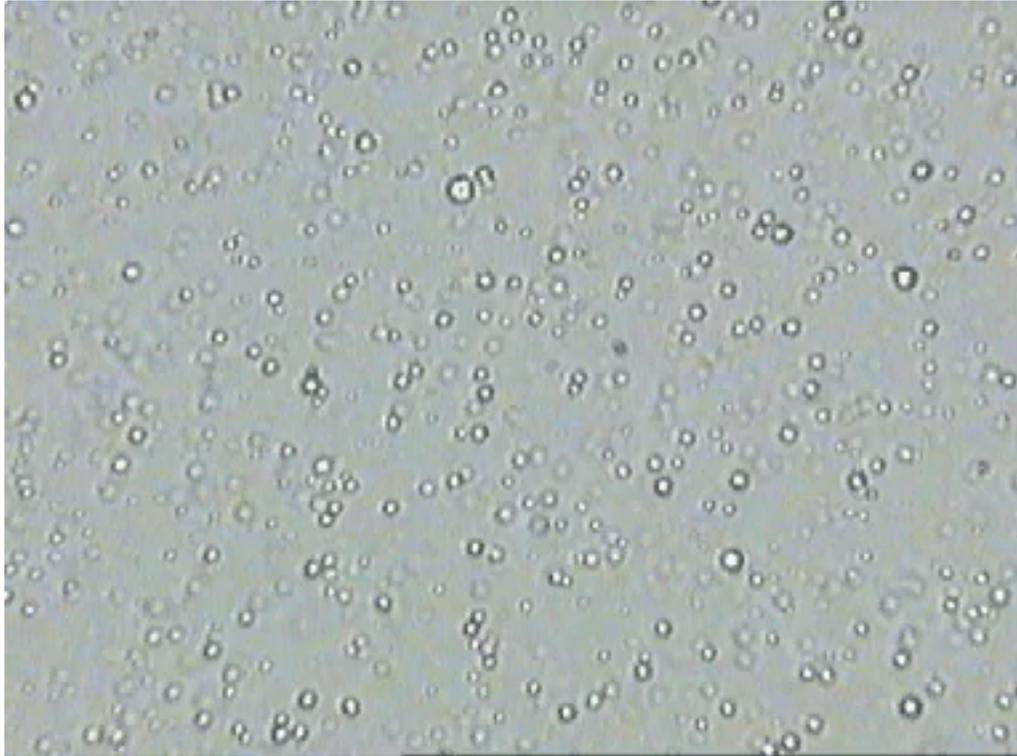
In essence, the Einstein's paper provides:

- evidence for existence of atoms/molecules
- estimation of the size of atoms/molecules
- estimation of the Avogadro's number

Einstein predicted that **microscopic particles** dispersed in water **undergo random motion as a result of collisions** (stochastic forces) **with water molecules much smaller and light** (not visible on the chosen observation scale).

diameter of Brownian particles:  $\sim 1 \mu$ , water:  $\sim 10^{-4} \mu$

# Brownian motion



fat droplets (0.5-3  $\mu\text{m}$ ) in milk

<http://www.microscopy-uk.org.uk/dww/home/hombrown.htm>

*credit to David Walker, Micscape*

**larger** particles (**blue** = fat droplets) jiggle more slowly than **smaller** (**red** = water) particles;  
**only the larger particles are visible**

## A. Einstein:

"On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular-Kinetic Theory of Heat"  
Annalen der Physik 19, p. 549 (1905)

...  
In this paper it will be shown that, according to the molecular-kinetic theory of heat, **bodies of a microscopically visible size** suspended in liquids must, as a result of thermal molecular motions, **perform motions** of such magnitude that they can be **easily observed with a microscope**. It is possible that the motions to be discussed here are identical with so-called Brownian molecular motion; however, the data available to me on the latter are so imprecise that I could not form a judgment on the question.

**If the motion to be discussed here can actually be observed, together with the laws it is expected to obey, then [...] an exact **determination of actual atomic sizes becomes possible****. On the other hand, if the prediction of the motion were to be proved wrong, this fact would provide a far-reaching argument against the molecular-kinetic conception of heat....

*Later Einstein wrote: "My major aim in this was to find facts which would guarantee as much as possible the existence of **atoms** of definite finite size."*

# Brownian motion

## -Einstein's 1905 paper-

Einstein suggests that **mean square displacements**  $\langle \Delta r^2 \rangle$  of suspended particles undergoing brownian motion rather than their velocities are suitable **observable and measurable quantities, and directly related to their diffusion coefficient D:**

$$\langle \Delta r^2 \rangle = 2dDt \quad \text{with} \quad D = \mu k_B T = k_B T / (6\pi\eta P)$$

(t time, d dimensionality of the system,  $\mu$  mobility,  
P radius of brownian particles (???);  $\eta$  solvent viscosity;  $k_B = R/N$ )

$\langle \Delta r^2 \rangle$  (and therefore D),  $\eta, T$  measurable  $\Rightarrow$  obtain **P** !

# Brownian motion

## -Einstein's 1905 paper-

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(t time, d dimensionality of the system,  $\mu$  mobility,  
**P radius of brownian particles (???)**;  $\eta$  solvent viscosity;  $k_B = R/N$ )

$\langle \Delta r^2 \rangle$  measurable  $\Rightarrow$  from (\*\*) we get D;  
 $\eta, T$  measurable  $\Rightarrow$  from (\*) we obtain P

# Diffusion

## Part I – Sedimentation Equilibrium Compare Two Independent Analyses of Final State

First Fick's law  
(particle  
diffusion eq.)

states that the flux ( $\mu Wc$ ) goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient

From Mass Transfer Theory:

$$\text{flux} = \underbrace{\mu Wc}_{\text{migration in gravity}} - \underbrace{D \frac{dc}{dx}}_{\text{diffusion}} = 0$$

$W$  = net weight of one particle

$c$  = concentration of particles

$$\mu = \text{mobility} = \frac{\text{velocity}}{\text{force}} = \frac{1}{6\pi\eta P}$$

$\eta$  = viscosity of fluid

$P$  = particle radius

$$c(x) = c_0 \exp\left(-\frac{\mu Wx}{D}\right)$$

From Thermodynamics:

$$\underbrace{\frac{d\phi}{dx}}_{\text{gravitational potential}} + RT \underbrace{\frac{d \ln c}{dx}}_{\text{chemical potential}} = 0$$

$\phi = WNx = \text{PE per mole}$

$N$  = Avogadro's number

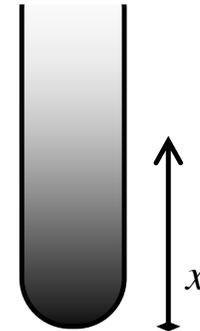
$R$  = universal gas constant

$T$  = absolute temperature

$RT$  [=] energy/mole

$$c(x) = c_0 \exp\left(-\frac{N}{RT} Wx\right)$$

If there is a variation in the **potential energy** of a system, an **energy** flow will occur.



Compare: exponentials must be equal!  $\Rightarrow$   $N = RT \frac{\mu}{D}$  (\*)

$N, R, T$  known; if  $D$  is measurable (according to Einstein)

$\Rightarrow$  Obtain  $\mu$ ; from  $\mu$  (and  $\eta$ , known) **we get particle size  $P$**

# Brownian motion and diffusion

## Fick's law of diffusion (1855): a continuum model

### Part II – Statistical Analysis of B.M.

one dimension:  $d=1$

Here:  $p=c$  (concentration)

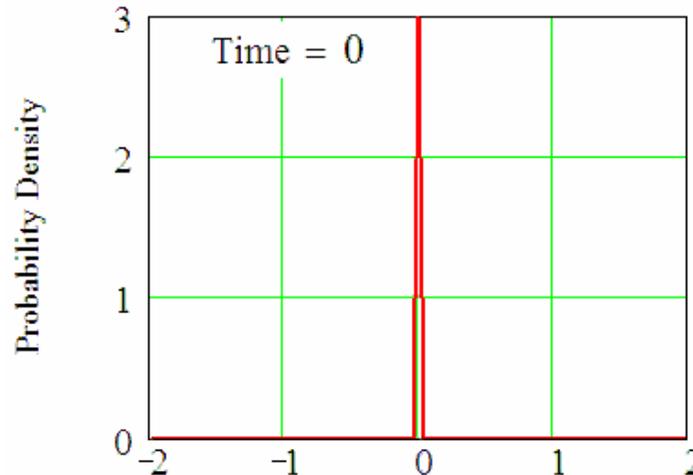
$$\left. \begin{array}{l} \text{Fick's 2nd law: } \frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2} \\ \text{Initial Condition: } p(x,0) = \delta(x) \\ \text{B.C.'s: } p(\pm\infty, t) = 0 \end{array} \right\}$$

$$p(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

remember the gaussian:

$$p(x) = \frac{1}{\sigma} \frac{1}{\sqrt{2\pi}} e^{-x^2/(2\sigma^2)}$$

with  $\sigma^2 = 2Dt$



$$1 = \int_{-\infty}^{\infty} p(x,t) dx \quad \text{for all } t$$

$$\bar{x}(t) = \int_{-\infty}^{\infty} xp(x,t) dx = 0$$

$$\overline{x^2}(t) = \int_{-\infty}^{\infty} x^2 p(x,t) dx = 2Dt$$

(\*\*)

The **mean square displacements**  $\langle \Delta r^2 \rangle$  of suspended particles are suitable observable quantities and give **D**

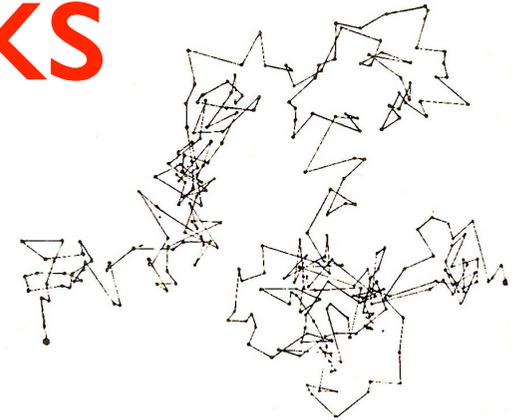
# Random motion in nature

- **in gases or diluted matter: random motion** (after how many collisions on average a particle covers a distance  $\Delta r$ ? or which is the distance from the starting point covered on average by a particle after N collisions?)
- **in solids: diffusion** of impurities (molten metals) or vacancies..., electronic **transport** in metals...

# II part: Random walks

A very simplified **model**  
for many phenomena,  
including brownian motion

# Random Walks



- **traditional RW** ➔ brownian motion
- **modified (interacting) RW** ➔ the motion of the walker depends on his previous trajectory

# Scaling properties of RW

Dependence of  $\langle R^2(t) \rangle$  on  $t$  :

- **normal behavior:**  $\langle R^2(t) \rangle \sim t$   
for the brownian motion
- **superdiffusive behavior:**  $\langle R^2(t) \rangle \sim t^{2\nu}$  with  $\nu > 1/2$   
in models where autointersections are unfavoured
- **subdiffusive behavior**  $\langle R^2(t) \rangle \sim t^{2\nu}$  with  $\nu < 1/2$   
in models where autointersections are favoured

# One-dimensional RW



A walker at each step can go either left or right:

$N$  : number of steps

$l$  : length of the random displacement (random direction)

(  $s_i = \pm l$  relative displacement of the  $i$  step )

$x_N$  : displacement from the starting point after  $N$  steps

(  $x_N = \sum_{i=1}^N s_i$ ,  $x_N \in [-Nl, +Nl]$  )

$p_{\rightarrow}$ ,  $p_{\leftarrow}$  : probability of left or right displacement

**What can we calculate? Averaging over walkers:**

$\langle x_N \rangle$  : average net displacement after  $N$  steps

$\langle x_N^2 \rangle$  : average square displacement after  $N$  steps

$P_N(x)$  : probability for  $x$  to be the final net displacement from the starting point after  $N$  steps

# RW 1D

Exact analytic expressions can be easily derived for  $p_{\leftarrow} = p_{\rightarrow}$

$$\langle x_N \rangle = \left\langle \sum_{i=1}^N s_i \right\rangle = \dots \text{ (if } p_{\leftarrow} = p_{\rightarrow} \text{)} \dots = 0$$

$$\langle x_N^2 \rangle = \left\langle \left( \sum_{i=1}^N s_i \right)^2 \right\rangle = \left\langle \sum_{i=1}^N s_i^2 \right\rangle + \left\langle \sum_{i \neq j} s_i s_j \right\rangle = \dots \text{ (if } p_{\leftarrow} = p_{\rightarrow} \text{)} \dots = N\ell^2$$

More general, if  $p_{\leftarrow} \neq p_{\rightarrow}$  :

$$\langle x_N \rangle = n_{\leftarrow}(-\ell) + n_{\rightarrow}(+\ell) \quad \text{with } n_{\leftarrow} = Np_{\leftarrow} \text{ and } n_{\rightarrow} = Np_{\rightarrow}$$

$$\langle x_N \rangle = N(p_{\rightarrow} - p_{\leftarrow})\ell \quad \langle x_N^2 \rangle = [N(p_{\rightarrow} - p_{\leftarrow})\ell]^2 + 4p_{\rightarrow}p_{\leftarrow}N\ell^2$$

therefore:

$$\langle \Delta x_N^2 \rangle = \langle x_N^2 \rangle - \langle x_N \rangle^2 = 4p_{\rightarrow}p_{\leftarrow}N\ell^2$$

We expect this behavior for averages over many walkers

# RW 1D

In general, average quantities can be calculated from  $P_N(x)$ :

$$\langle x_N \rangle = \sum_{x=-N\ell}^{x=+N\ell} x P_N(x)$$

Let's make an example  
of analytical calculation of  $P_N(x)$   
( $N=3$  is enough!)

...

(how many  
different walks of length  $N$ ?)

# RW ID

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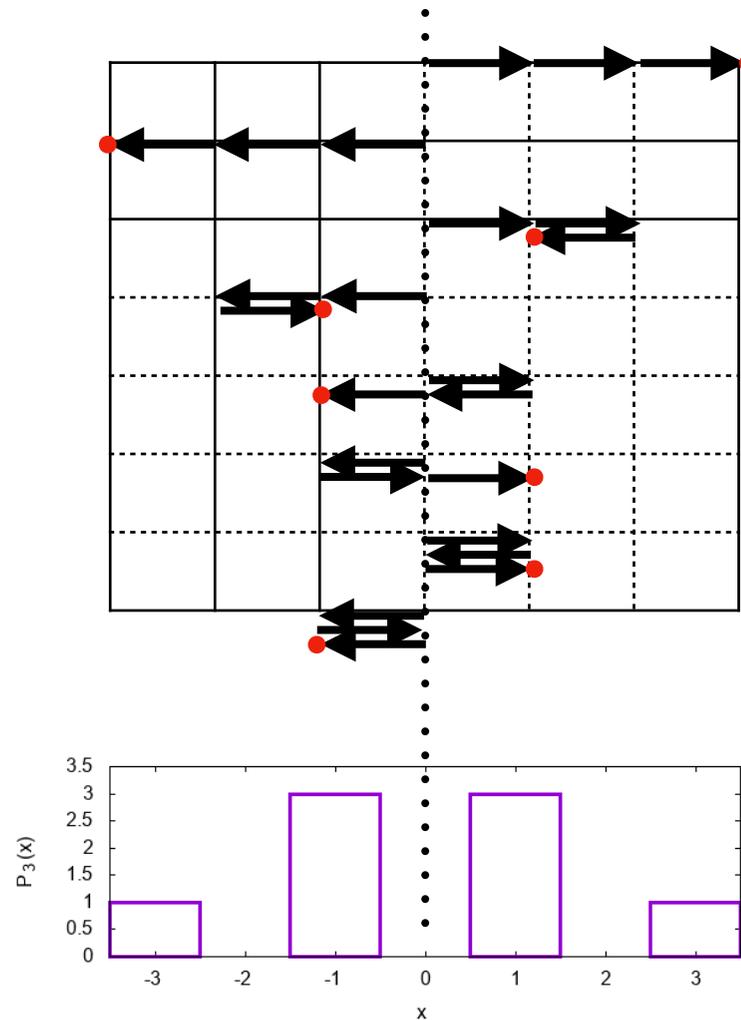
Let's make an example  
of analytical calculation of  $P_N(x)$   
( $N=3$  is enough!)

...

(There are  $2^N$  different possible walks  
of  $N$  steps...)

# RW 1D

$N = 3 \Rightarrow 8$  possible different walks



$$\Rightarrow P_3(0) = P_3(\pm 2) = 0; \quad P_3(\pm 1) = 3, \quad P_3(\pm 3) = 1$$

# RW ID

Generalizing the expression for  $P_N(x)$ :

From:  $P_1(1) = p_{\rightarrow}; P_1(-1) = p_{\leftarrow}$   
 $P_{N+1}(x) = P_N(x-1)p_{\rightarrow} + P_N(x+1)p_{\leftarrow}$

we have:

$$P_N(x) = \frac{N!}{\left(\frac{N}{2} + \frac{x}{2}\right)! \left(\frac{N}{2} - \frac{x}{2}\right)!} p_{\rightarrow}^{\frac{N}{2} + \frac{x}{2}} p_{\leftarrow}^{\frac{N}{2} - \frac{x}{2}}$$

number of steps

$n \setminus x$	-5	-4	-3	-2	-1	0	1	2	3	4	5
0						1					
1					$\frac{1}{2}$	0	$\frac{1}{2}$				
2				$\frac{1}{4}$	0	$\frac{2}{4}$	0	$\frac{1}{4}$			
3			$\frac{1}{8}$	0	$\frac{3}{8}$	0	$\frac{3}{8}$	0	$\frac{1}{8}$		
4		$\frac{1}{16}$	0	$\frac{4}{16}$	0	$\frac{6}{16}$	0	$\frac{4}{16}$	0	$\frac{1}{16}$	
5	$\frac{1}{32}$	0	$\frac{5}{32}$	0	$\frac{10}{32}$	0	$\frac{10}{32}$	0	$\frac{5}{32}$	0	$\frac{1}{32}$

$P_N(x)$   
for  
 $p_{\leftarrow} = p_{\rightarrow}$

(Pascal  
triangle)

# RW ID

$$P_N(x) = \frac{N!}{\left(\frac{N}{2} + \frac{x}{2}\right)! \left(\frac{N}{2} - \frac{x}{2}\right)!} p_{\rightarrow}^{\frac{N}{2} + \frac{x}{2}} p_{\leftarrow}^{\frac{N}{2} - \frac{x}{2}}$$

Can be generalized to large N (put  $N = t/\Delta t$ , then  $\Delta t \rightarrow 0$ , continuum limit):

$$P(x, N\Delta t) = \sqrt{\frac{2}{\pi N}} e^{-x^2/(2N)} \quad (*)$$

which looks like a Gaussian (a part from the normalization).  
Why?

Let's describe the RW problem with a space/time differential equation...

# RW 1D: Diffusion - continuum limit

(case  $p_{\leftarrow} = p_{\rightarrow}$ )

$$P(i, N) = \frac{1}{2}P(i+1, N-1) + \frac{1}{2}P(i-1, N-1)$$

Defining:  $t = N\tau$ ,  $x = i\ell$  we have:

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

We rewrite this by subtracting  $P(x, t-\tau)$  and dividing by  $\tau$

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

we get

$$\frac{\partial P(x, t)}{\partial t} \approx \frac{l^2}{2\tau} \frac{\partial^2 P(x, t)}{\partial x^2}$$

In the limit  $\tau \rightarrow 0$ ,  $l \rightarrow 0$  but where the ratio  $l^2/\tau$  is finite, this becomes an exact relation.

# RW | D: Diffusion - continuum limit

The fundamental solution of the continuum diffusion equation of the previous slide, defining  $D = \frac{\ell^2}{2\tau}$  is:

$$P(x, t) = \sqrt{\frac{1}{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right).$$

The discretized solution of the RW problem:

$$P_N(x) = \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{x^2}{2N}\right)$$

considering  $t = N\tau$  and the definition of  $D$ , can be rewritten as:

$$P(x, t) = \sqrt{\frac{1}{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

a part from the normalization which is a factor of 2 larger in this form because of the spatial discretization that excludes alternatively odd or even values of  $x$ .

The solution is therefore a Gaussian distribution with  $\sigma^2 = 2Dt$  which describes a pulse gradually decreasing in height and broadening in width in such a manner that its area is conserved.

# RW ID: Diffusion - continuum limit

physical meaning!  
(hint: try to simulate a number of particles  
initially concentrated at 0 and  
evolving according to the RW model:  
... the 'cloud' is progressively expanding)

# RW 1D: simulation

The basic algorithm:

`ix` = position of the walker

(1 run = 1 particle = 1 walker)

`x_N, x2_N` = cumulative quantities

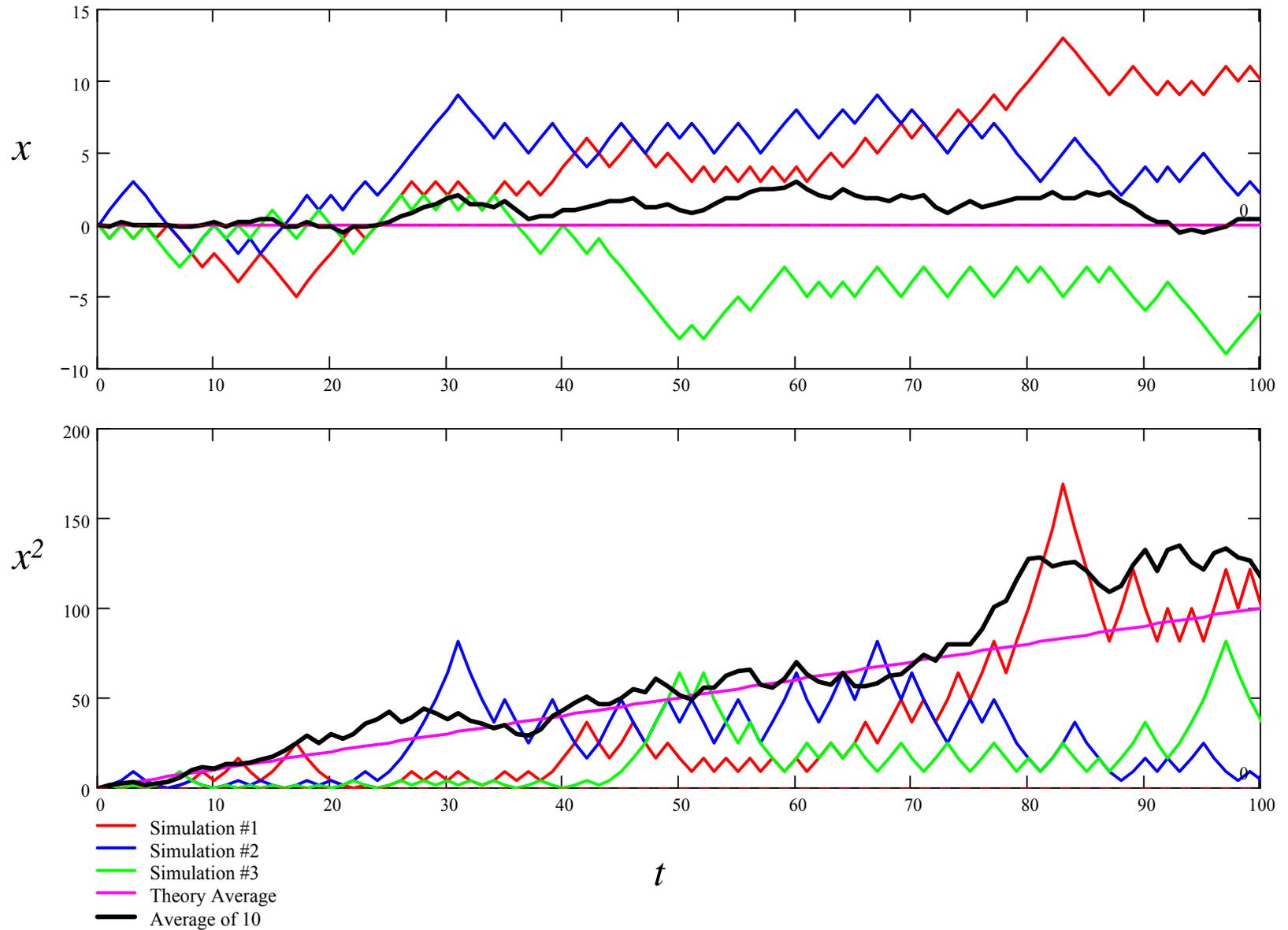
`rnd(N)` = sequence of `N` random numbers

```
do irun = 1, nruns
  ix = 0 ! initial position of each run
  call random_number(rnd) ! get a sequence of random numbers
  do istep = 1, N
    if (rnd(istep) < 0.5) then ! random move
      ix = ix - 1 ! left
    else
      ix = ix + 1 ! right
    end if
    x_N (istep) = x_N (istep) + ix
    x2_N(istep) = x2_N(istep) + ix**2
  end do
  P_N(ix) = P_N(ix) + 1 ! accumulate (only for istep = N)
end do
```

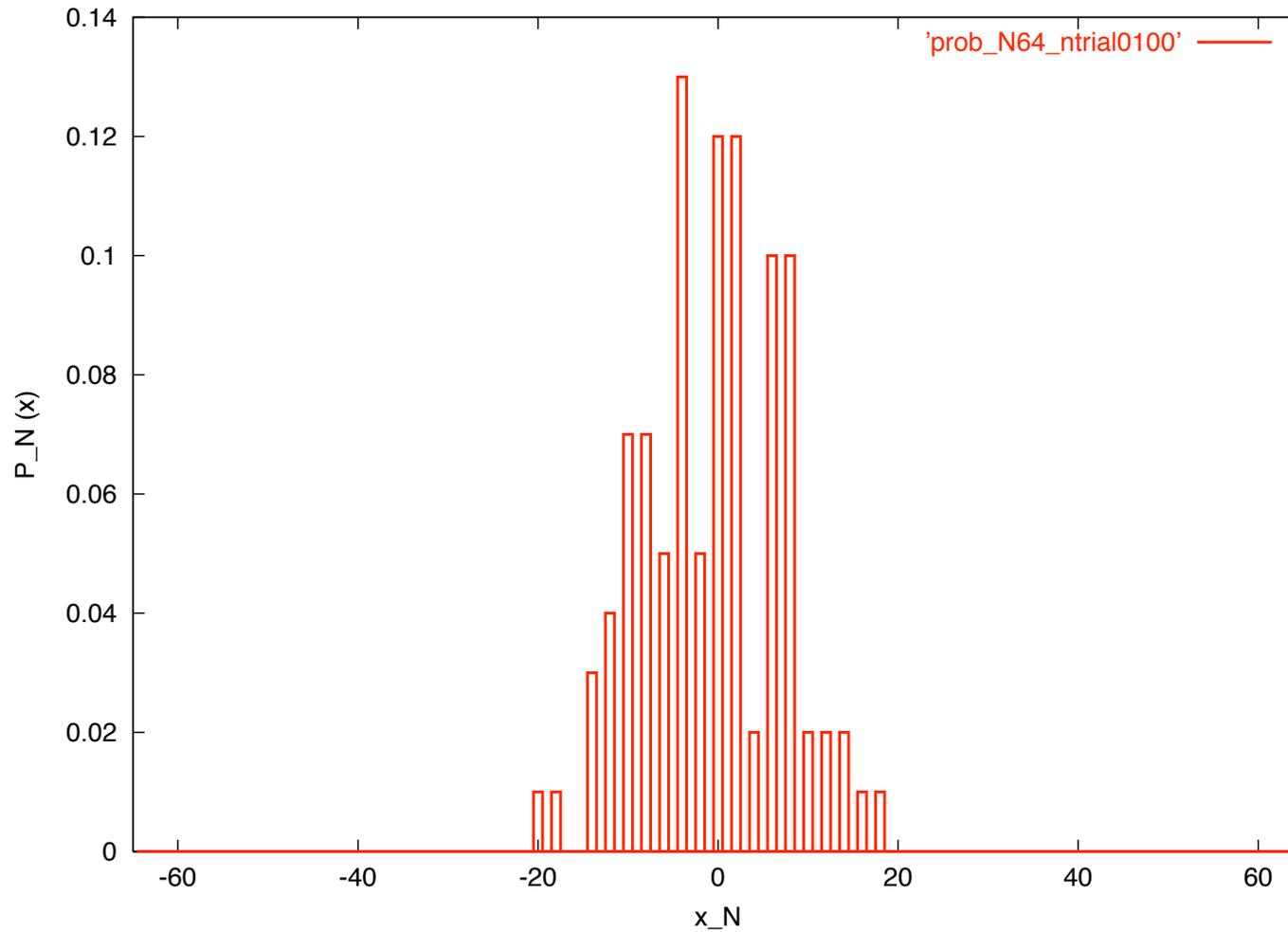
Note:

`x_N` and `x2_N` are NOT reset to zero, but summed over the runs (walkers)

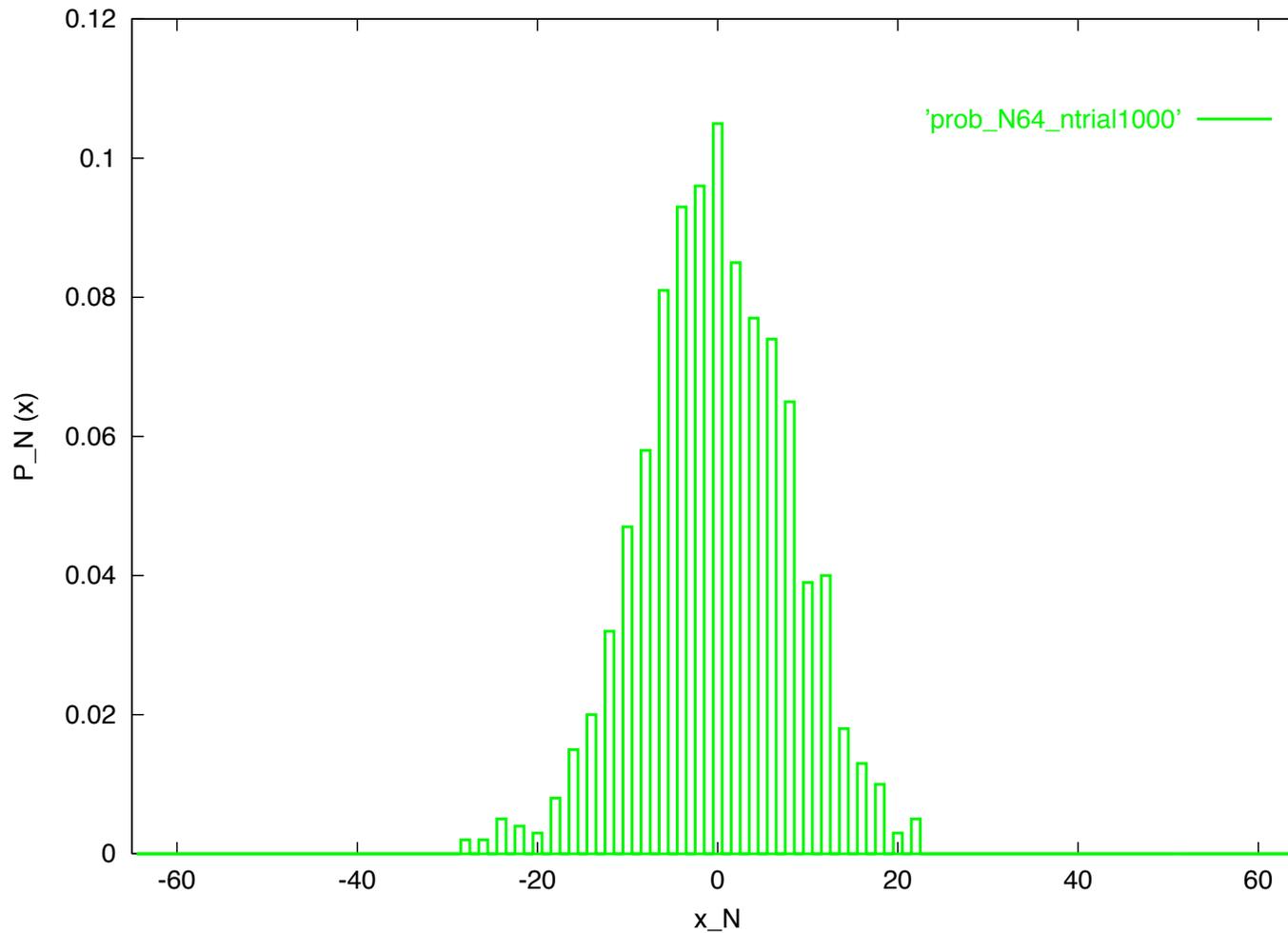
# RW 1D: simulation



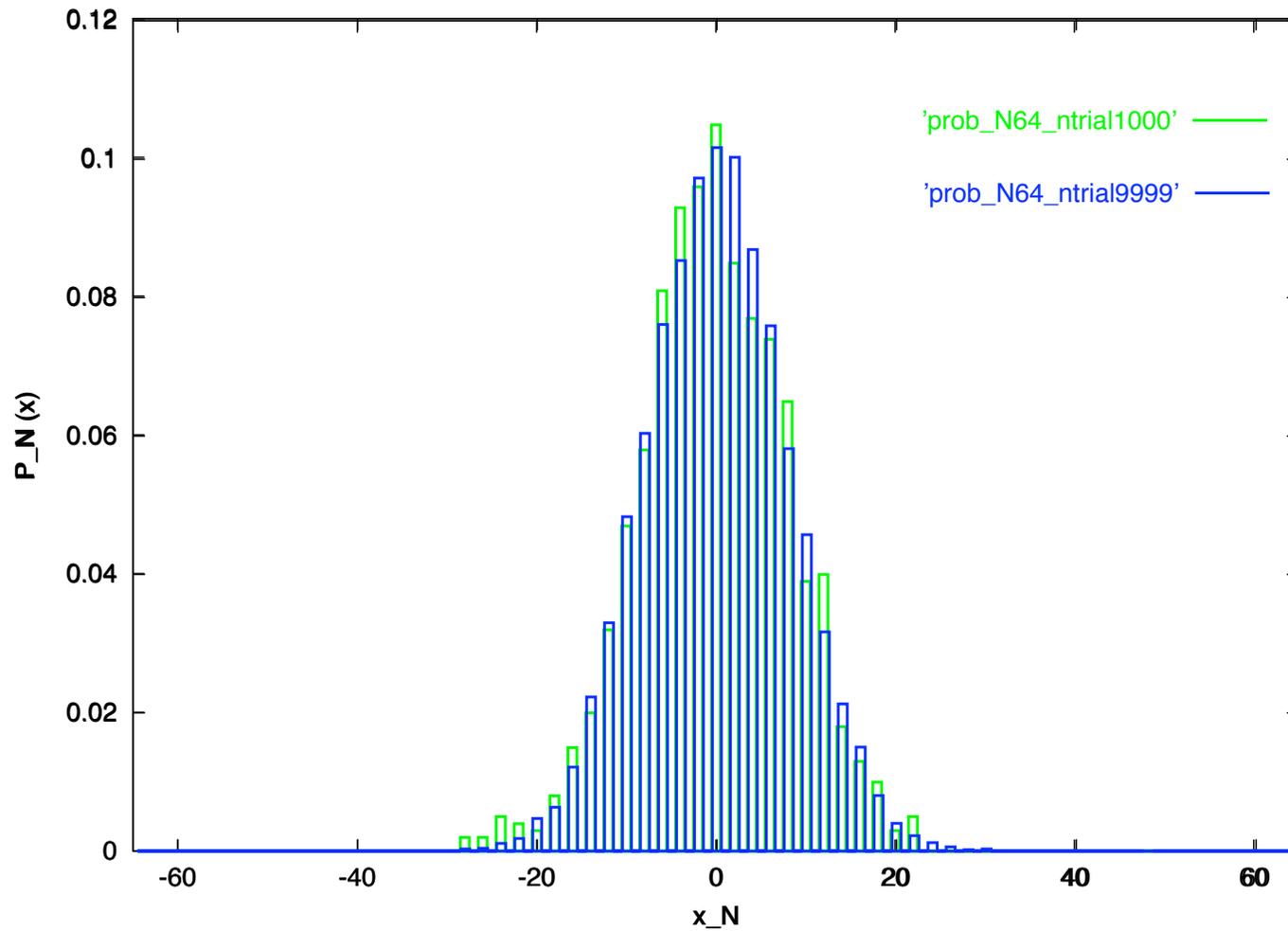
# RW ID: simulation



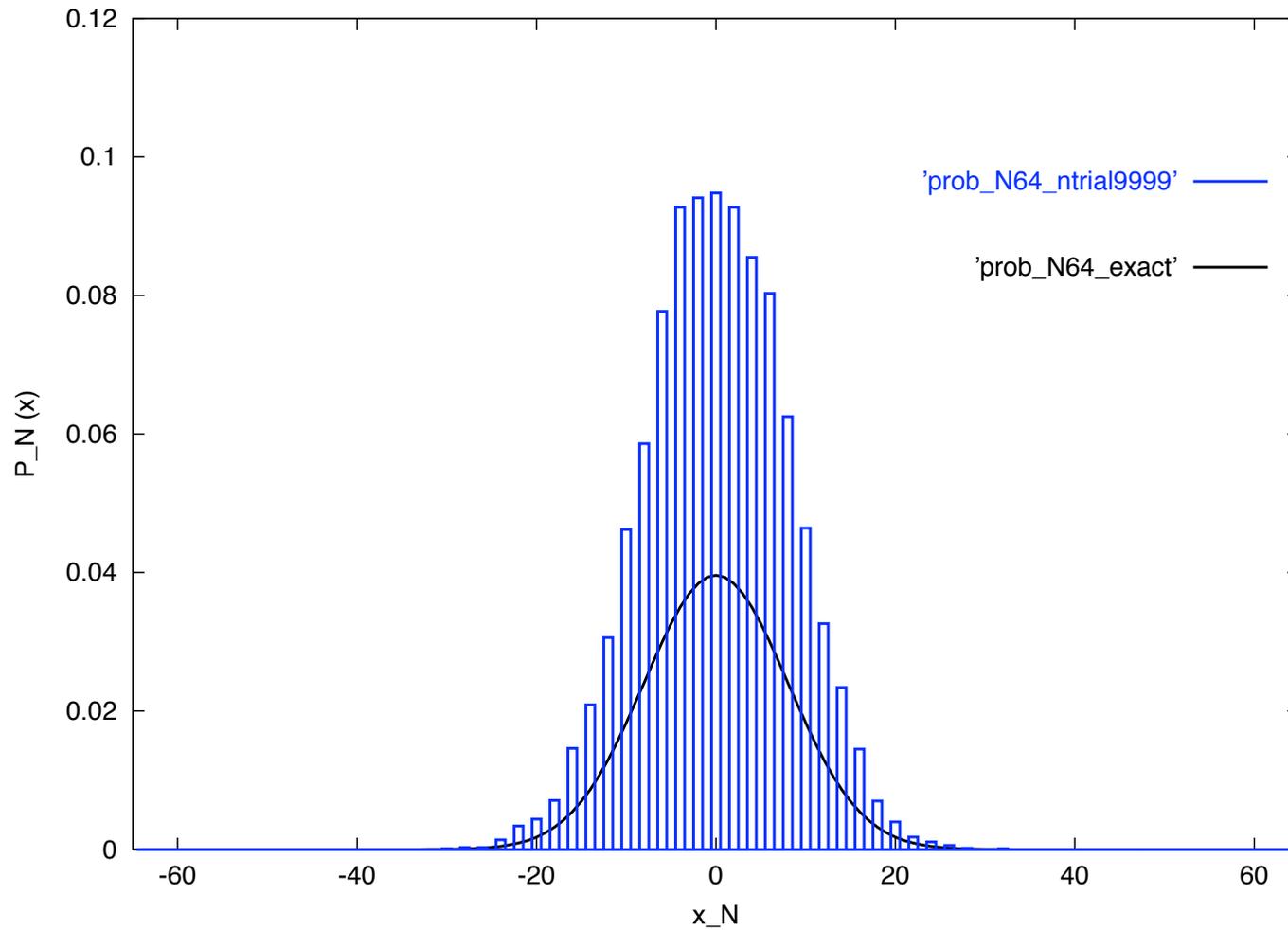
# RW ID: simulation



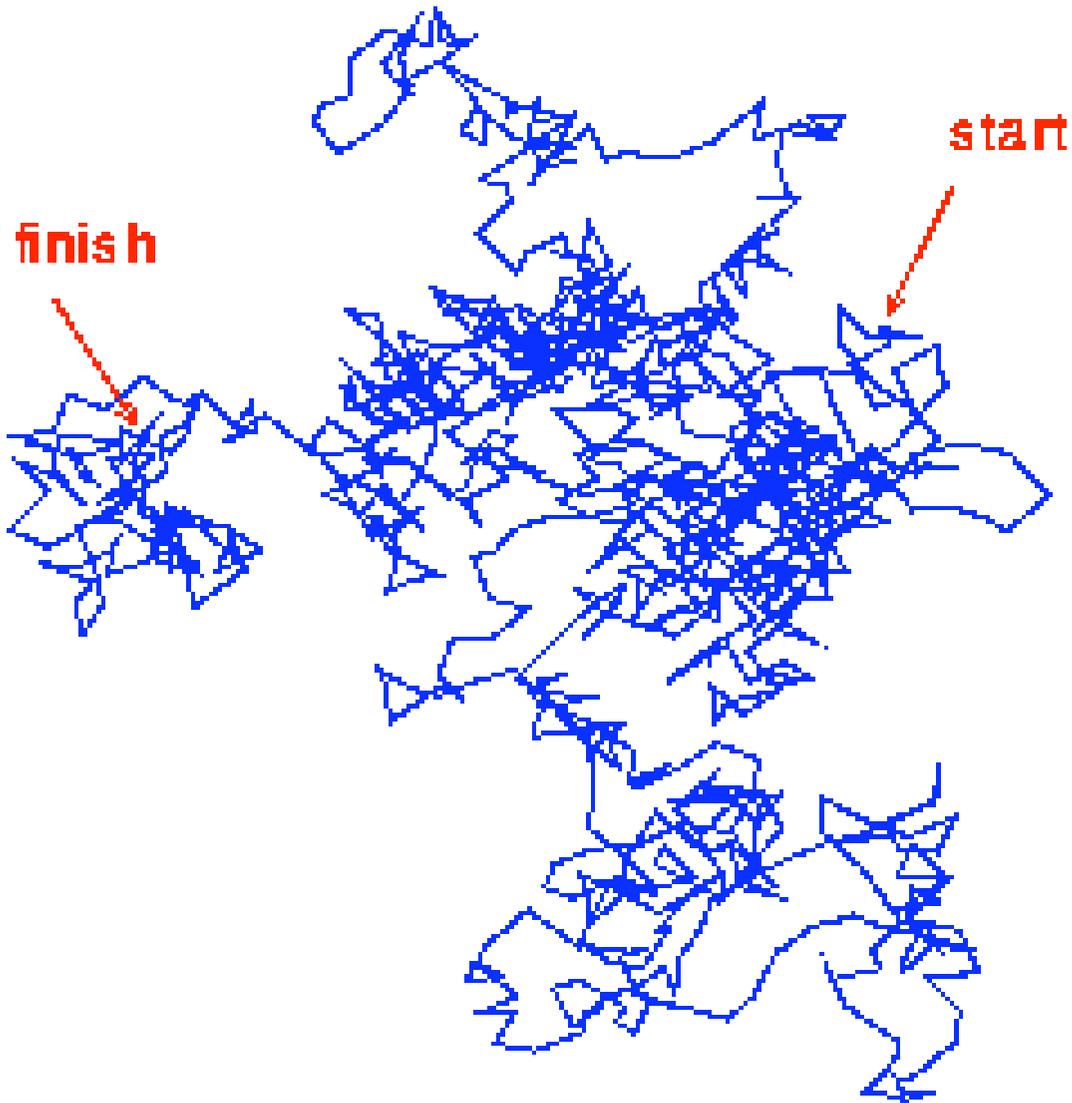
# RW ID: simulation



# RW 1D: simulation

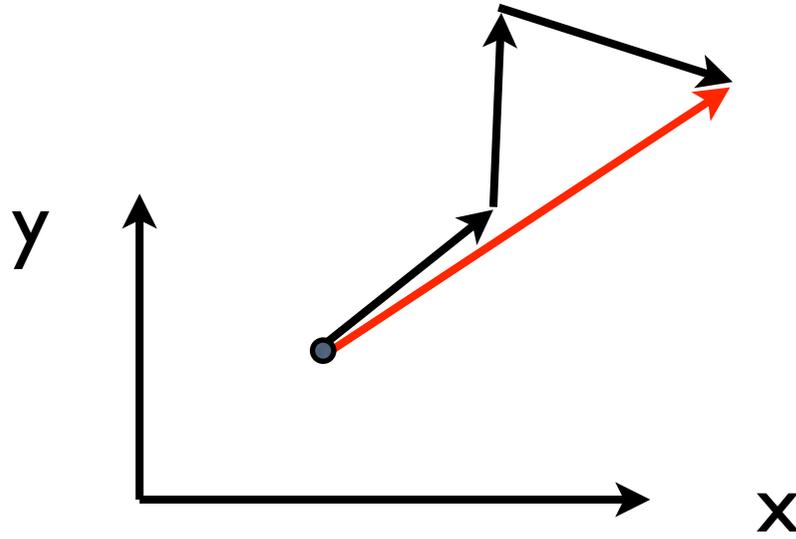


# Random Walks



In the continuum space, or discretised on a lattice...

# Random Walks 2D

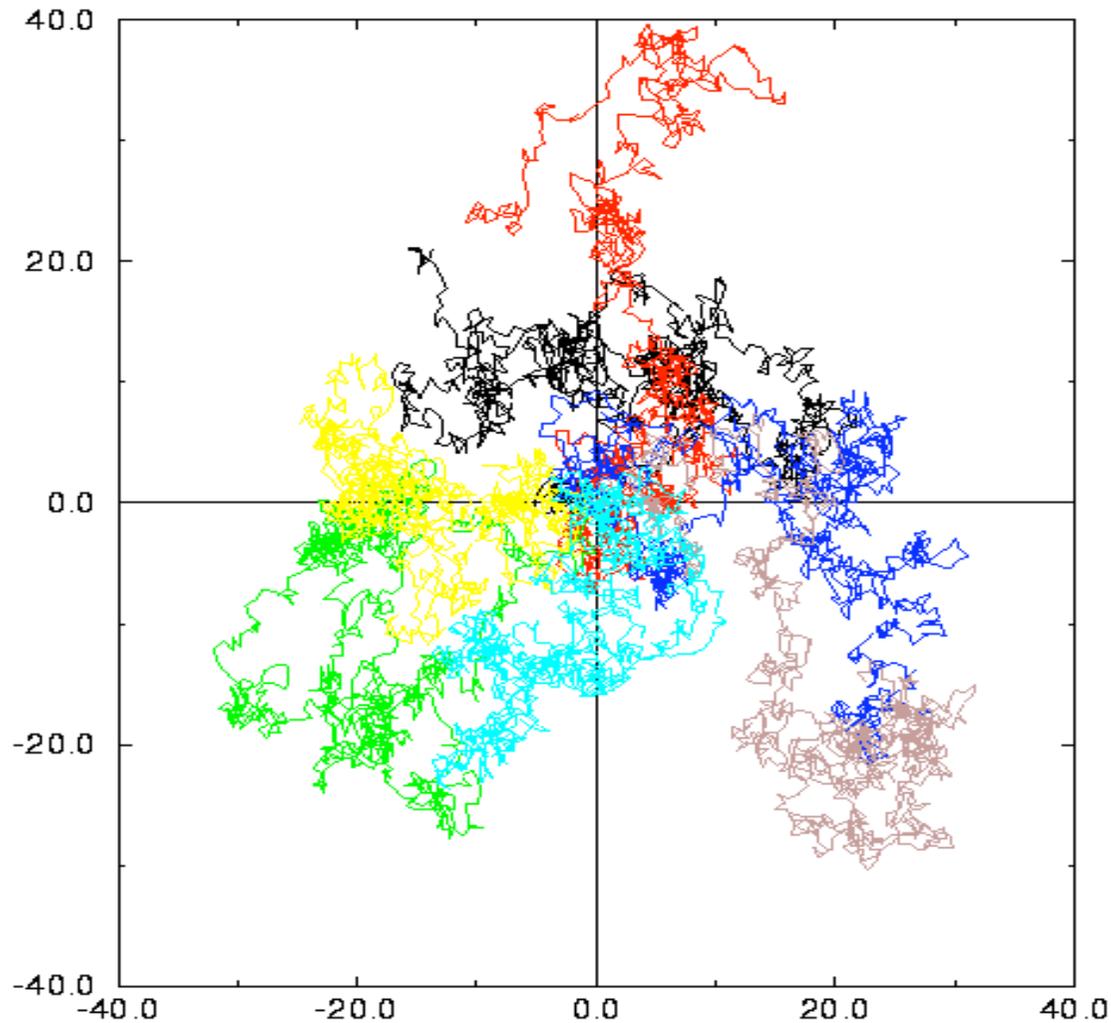


$$\langle \Delta R_N^2 \rangle = \langle (\Delta x_1 + \dots + \Delta x_N)^2 + (\Delta y_1 + \dots + \Delta y_N)^2 \rangle = \dots = N \langle \Delta x_i^2 + \Delta y_i^2 \rangle = N \ell^2$$

$$\langle \Delta R_N^2 \rangle \propto N$$

also in 2D! (and in general in each dimension)

# Random Walks 2D



Theory predicts that  $\langle \Delta R_N^2 \rangle \propto N$ , but this holds only for averages on many walkers!

# Random Walks 2D

## Generating 2-D random unit steps

1. Choose  $\theta$  a random number in the range  $[0, 2\pi]$  and then set  $x = \cos \theta, y = \sin \theta$ .
2. Choose a random value for  $\Delta x$  in the range  $[-1, 1]$  and  $\Delta y = \pm\sqrt{1 - \Delta x^2}$  (choose the sign randomly too).
3. Choose separate random values for  $\Delta x, \Delta y$  in the range  $[-1, 1]$  (but not  $\Delta x = 0, \Delta y = 0$ ).  
Normalize  $\Delta x, \Delta y$  so that the step size is 1.
4. Choose a direction (N, E, S, W) randomly as the step direction (no trigonometric functions are then needed). Note, choosing one of four directions is equivalent to choosing a random *integer* on  $[0,3]$ .
5. Choose separate random values  $\Delta x, \Delta y$  in the range  $[-\sqrt{3/2}, \sqrt{3/2}]$

**TEST DIFFERENT ALGORITHMS!**

WHAT IS THE BEST? THE ONE WHICH GIVES THE BEST BEHAVIOR?

WHAT IS THE MOST EFFICIENT?

## Generating 2D random unit steps Comment on the algorithm n. 5

Indicating with  $x$  and  $y$  the individual displacements,

$$p(x) = \frac{1}{2\sqrt{3/2}} \quad \text{for } |x| < \sqrt{3/2} \text{ or } 0 \text{ otherwise; the same for } p(y)$$

the average step size is:

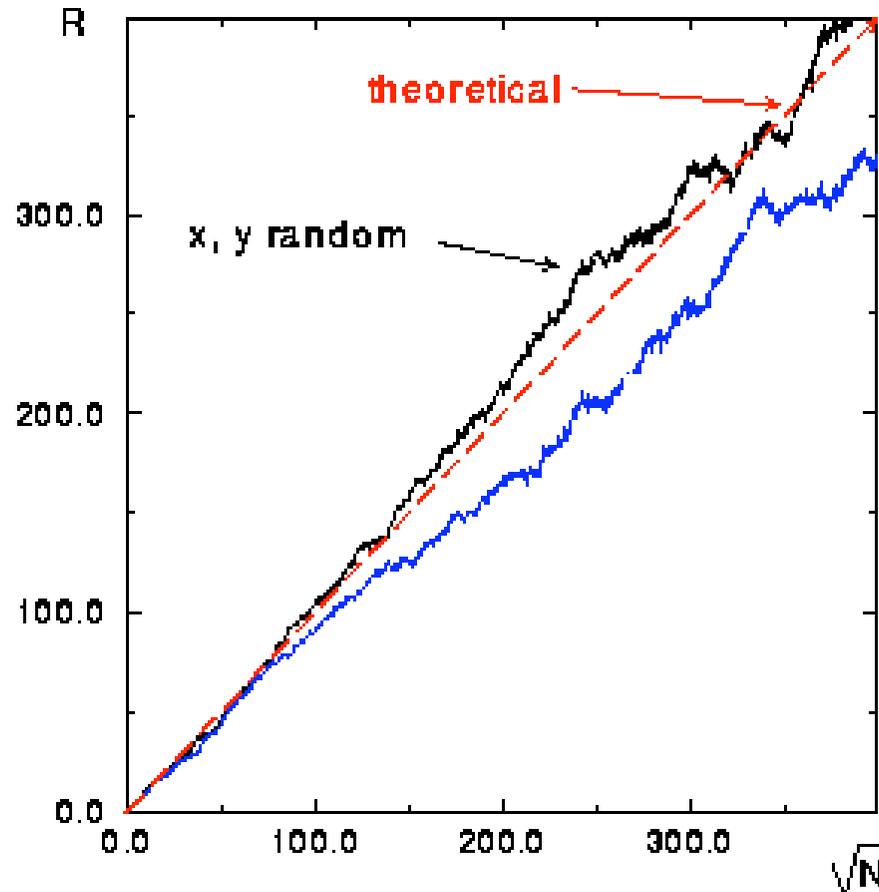
$$\langle x^2 + y^2 \rangle = \int_{-\sqrt{3/2}}^{\sqrt{3/2}} \int_{-\sqrt{3/2}}^{\sqrt{3/2}} (x^2 + y^2) p(x)p(y) dx dy = \dots = 1$$

Therefore, with  $x$  and  $y$  generated in this way, the behaviour of the simulated  $\langle \Delta R_N^2 \rangle$  should be  $N$  (since  $\langle \Delta R_N^2 \rangle = N\ell^2$ ).

(the code `rw2d-with-averages-3methods.f90` checks this)

# Random Walks 2D

TEST DIFFERENT ALGORITHMS!



Theory predicts that  $\langle \Delta R_N^2 \rangle \propto N$ , but this holds only for averages on many walkers! Consider this before extracting your conclusions...

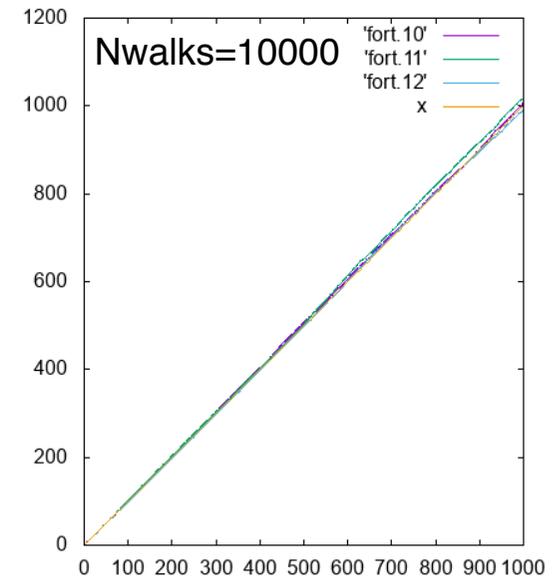
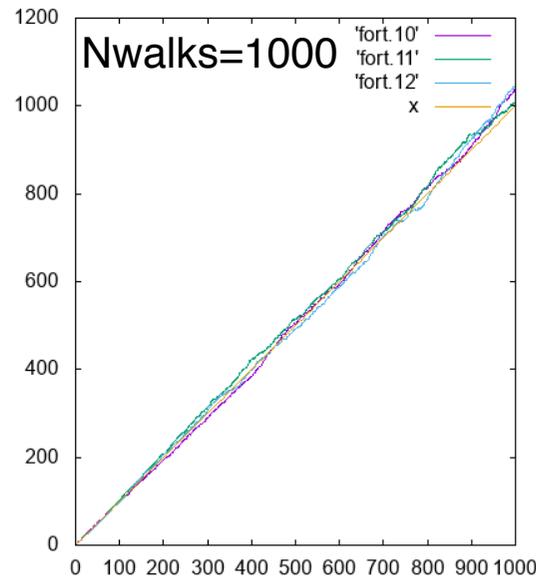
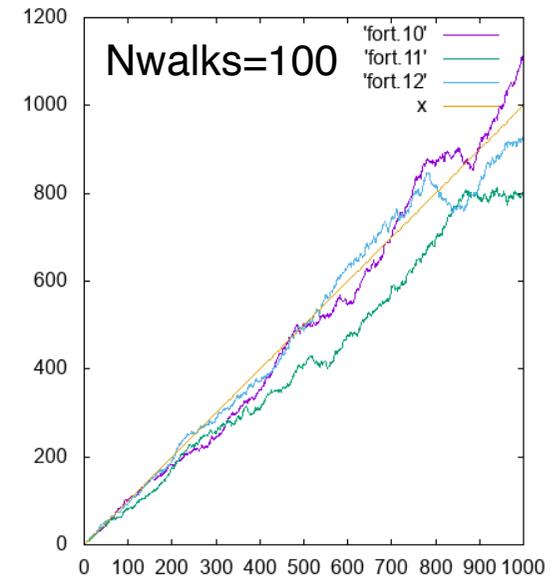
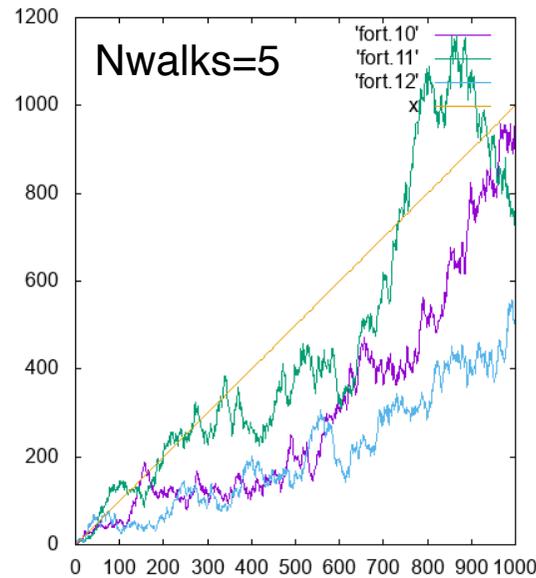
# Random Walks 2D

$\langle \Delta R^2 \rangle$  vs  
Nsteps

Test algorithm  
n. 1 (fort.10)  
n. 3 (fort.11)  
n. 5 (fort.12)

with  
Nsteps = 1000

averaged over  
A different  
number of  
Nwalks



# Random Walks 2D

0	0.0000000	0.0000000
10	0.2242774	3.7794106
20	-1.7333623	1.3218992
30	-1.4481916	-3.1119978
40	-2.2553353	-3.5246484
50	-3.8911035	-6.6665235
60	-3.6508965	-8.0110636

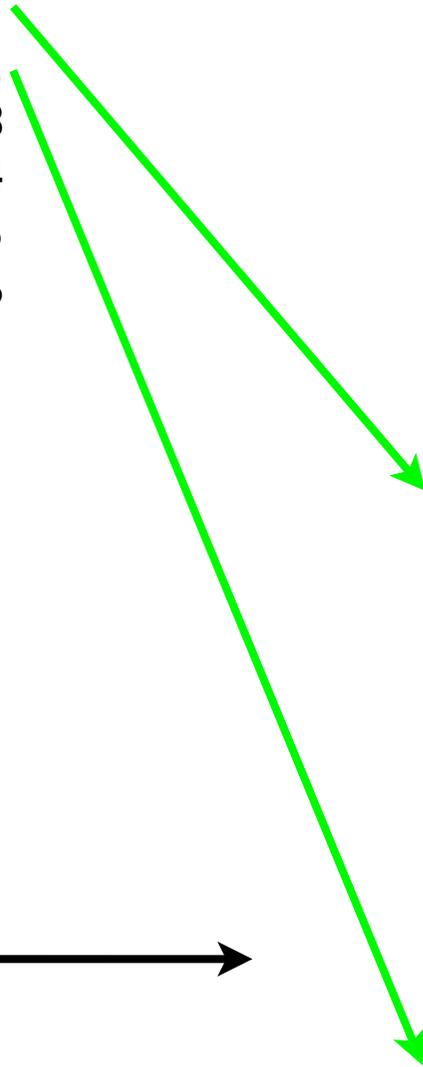
0	0.0000000	0.0000000
1	0.6946244	0.7193726
2	0.9359566	1.6898152
3	1.8891419	1.9922019
4	0.9642899	2.3725290
5	0.1308700	2.9251692
6	0.2071800	3.9222534
7	0.9160752	4.6275673
8	0.2856980	3.8512783
9	1.0143363	3.1663797
10	0.2242774	3.7794106
11	-0.7752404	3.8104627
12	-1.7280728	3.5069659
13	-2.0930278	4.4379911
14	-3.0587580	4.1784425
15	-2.0729706	4.0104446
16	-1.8304152	3.0403070
17	-2.2890768	2.1516960
18	-1.7717266	1.2959222
19	-1.1920205	0.4810965
20	-1.7333623	1.3218992
21	-1.5798329	0.3337551

.....



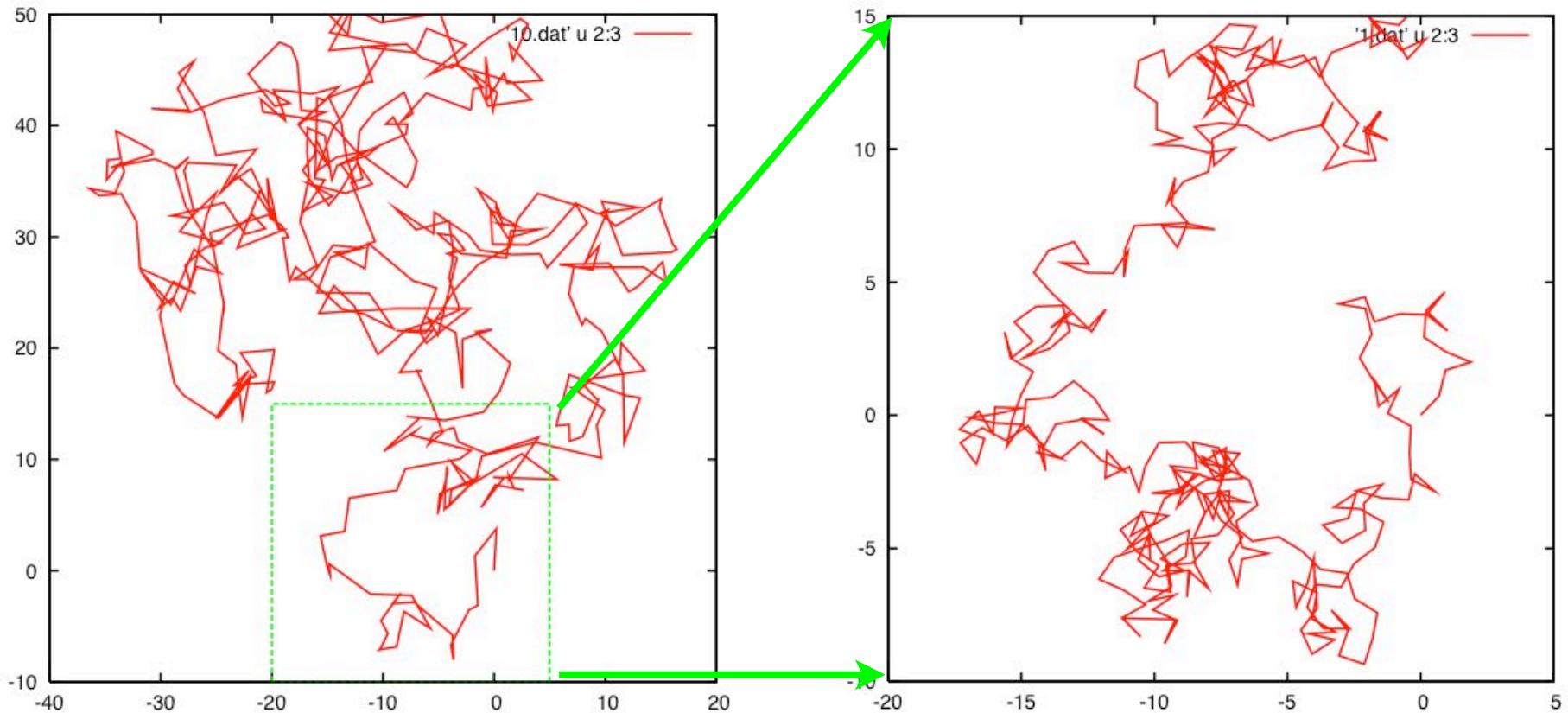
```
if (mod(i,10)==0) then  
  WRITE (...) i,x,y  
end if
```

```
WRITE (...) i,x,y
```



# Random Walks 2D

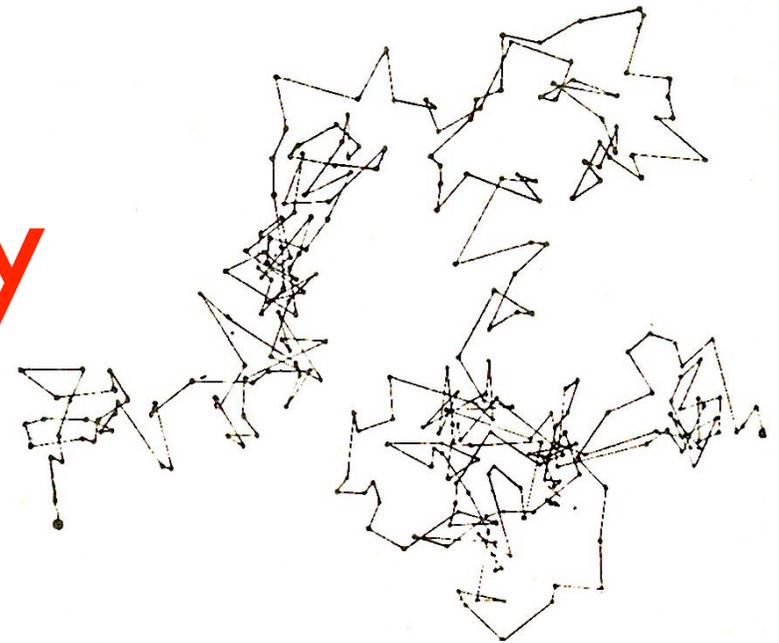
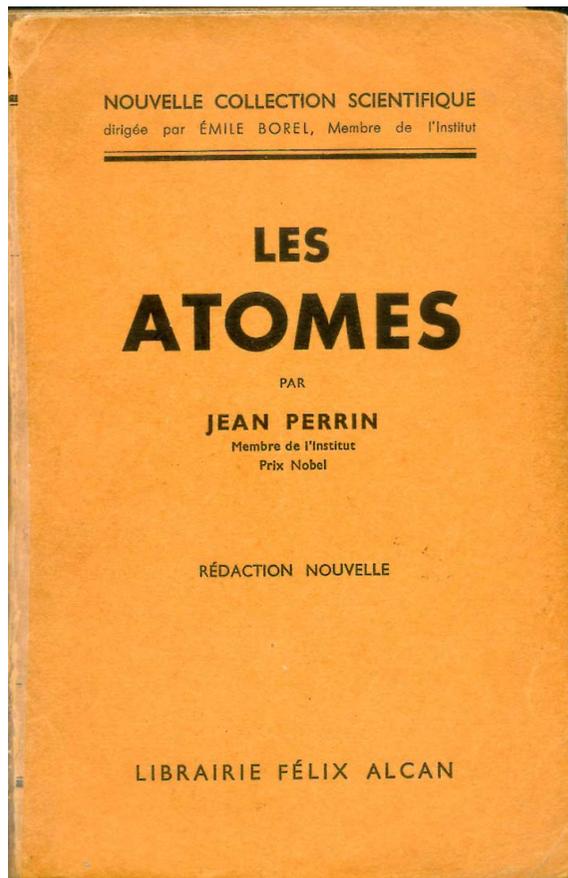
self-similarity!



plot every 10 steps

plot every step

# Brownian motion and fractal trajectory

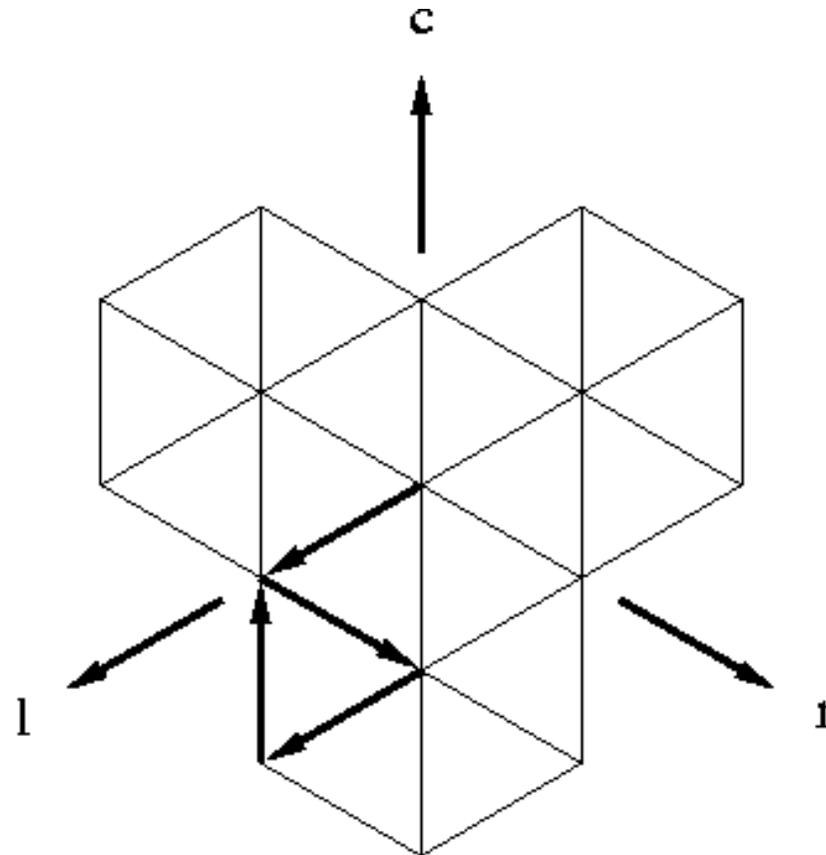


Si on faisait des pointés à des intervalles de temps 100 fois plus rapprochés, chaque segment serait remplacé par un contour polygonal relativement aussi compliqué que le dessin entier, et ainsi de suite. *On voit comment s'évanouit ... la notion de trajectoire.*

Jean Perrin

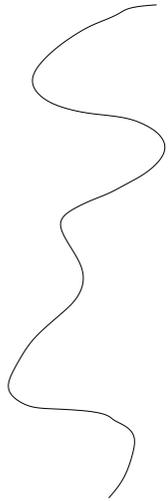
(1912)

# Random Walks 2D on a triangular lattice

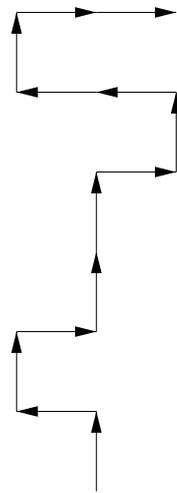




# Self-avoiding Random Walks



(a)



(b)

a) Schematic illustration of a linear polymer in a good solvent :

head-tail mean square distance is (in 3D):

$$\langle \Delta R_N^2 \rangle \sim N^{2\nu} \quad \nu = 0.592$$

b) Simulation with a SAW on a square lattice:  
2D model gives  $\nu = 3/4$

(independent on details such as monomers and solvent structures)

# Other Random Walks

- RW with traps
- persistent RW (a *correlated random walk* in which the walker has probability  $\alpha$  of continuing in the same direction as the previous step)  $\Rightarrow$  superdiffusive behaviour
- ....

## Some programs:

on <https://moodle2.units.it>

rw1d.f90

rw2d.f90

rw2zoom.f90

contour, pl => see following slide

**‘pl’**: macro for gnuplot for plotting trajectories  
(suppose column 1 is ‘time’, 2 is x, 3 is y)  
and check self-similarity:

```
set term postscript color
set size square
set out 'l.ps'
p [-20:5][-10:15] 'l.dat' u 2:3 w l
set out 'l0.ps'
p [-40:20][-10:50] 'l0.dat' u 2:3 w l, 'contour' u 1:2 w l
```

**Use:**

```
gnuplot$ load 'pl'
```

III part:  
algorithm for the  
Brownian motion  
(Langevin treatment)

(see code: brown.f90)

# The numerical approach: the ingredients

Here: NOT Einstein's, but Langevin's (1906) approach arriving at a Newtonian equation of motion including a *random force due to the solvent*

See: De Groot BG, Am. J. Phy. 67, 1248 (1999)

Ingredients:

\* large Brownian particles - solvent interactions described by: **elastic collisions** between large particle (mass  $M$ , velocity  $V$ ) and small (solvent) particles ( $m$ ,  $v$ );

\* **momentum and energy conservation** at each collision

$$MV + mv = MV' + mv'$$

$$MV^2/2 + mv^2/2 = MV'^2/2 + mv'^2/2$$

# The numerical approach: the equation of motion

After **reasonable assumptions** (*many collisions (i) in a time interval  $\Delta t$ , where  $V_i$  are the same...,  $m \ll M$ ..., ...*)  $\Rightarrow$

arrive at a simple expression for  $M\Delta V/\Delta t = M(V' - V)/\Delta t$  :

$$Ma = F_s - \gamma V(t)$$

$F_s$  : **stochastic force**, i.e. the cumulative effect, in the time interval, of many collisions with smaller particles

$-\gamma V(t)$  : **drag force**, opposite to  $V(t)$  ( $\gamma > 0$ );  $\gamma$  can be expressed (using Stokes' formula for a sphere of radius  $P$ ) as:

$$\gamma = 6\pi\eta P$$

(both forces have the same origin, in the collisions with the smaller particles)

# The numerical approach: discretization of the equation of motion

$$Ma = F_s - \gamma V(t)$$

Rewritten as:  $M\Delta V/\Delta t = \Delta V_s / \Delta t - \gamma V(t)$

$$\Rightarrow V_{q+1} = V_q + \Delta V_s - \gamma(\Delta t/M)V_q$$

with:

$$\Delta V_s = 2mv/M = (\dots) = 1/M v/|v| \sqrt{(2\gamma k_B T/n)};$$

At each collision  $v/|v|$  is  $-1$  or  $+1$   $\Rightarrow$  after  $N$  collisions ???

the result is a **gaussian random variable**

$w_q$  centered in 0, s.d.= $\sqrt{(N/2)}$   $\Rightarrow$  (see also next lectures)

# The numerical approach: discretized equations for positions and velocities

$$V_{q+1} = V_q - (\gamma/M)V_q\Delta t + w_q(\sqrt{2\gamma k_B T \Delta t})/M$$

$$X_{q+1} = X_q + V_{q+1}\Delta t$$

- the hearth of our numerical approach
- can be easily implemented for iterative execution

NOTE : we are NOT imposing any specific time dependence behavior: it will come out as an “**experimental**” result of the simulation

# The numerical approach:

## Input parameters - I

$$V_{q+1} = V_q [1 - (\gamma/M)\Delta t] + w_q(\sqrt{(2\gamma k_B T \Delta t)})/M$$

- physical parameters of the system:  $T$  and  $\gamma$   
(through  $\eta$  and  $P$ :  $\gamma=6\pi\eta P$ )

# The numerical approach:

## Input parameters - II

$$V_{q+1} = V_q [1 - (\gamma/M)\Delta t] + w_q(\sqrt{2\gamma k_B T \Delta t})/M$$

- **time step  $\Delta t$**  : cannot be fixed a priori!

Some suggestions from physical and rough numerical considerations  
[[ $(\gamma/M)\Delta t < 1$  to reproduce the situation of  $T \approx 0$  (damped motion)

$\Delta t$  too small: too long numerical simulations necessary...

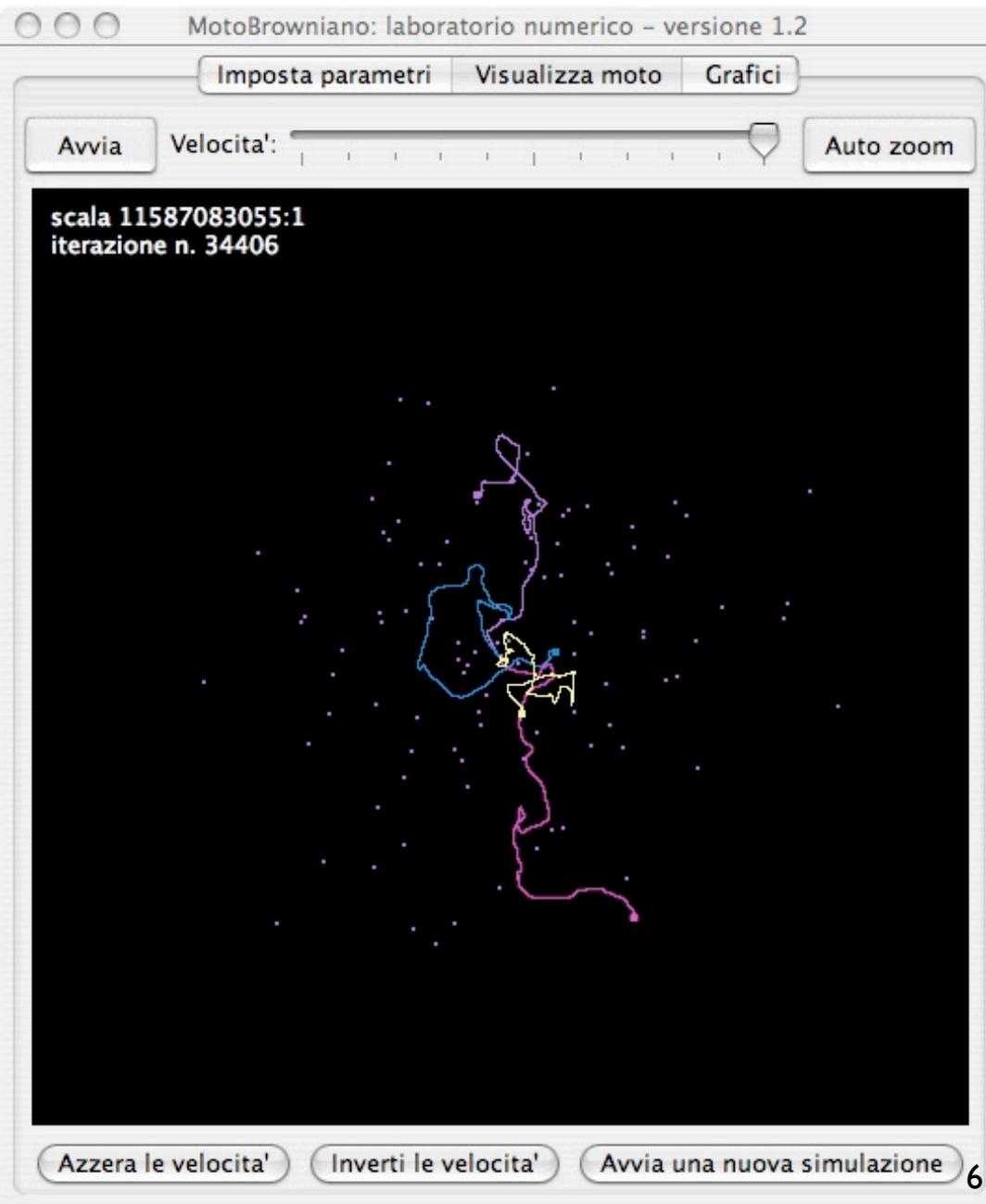
$\Delta t$  too large: serious numerical uncertainties...]

**Our numerical work:**

**choice of  $\Delta t$  is analogous of an instrument calibration !!!**

suggestion: start from small  $\Delta t$  s.t.  $\gamma\Delta t/M \ll 1$ , increase  $\Delta t$  until important changes in the diffusion coefficient are observed.

# Running the code...



$$k_B T = 4 \cdot 10^{-21} \text{ J}, \quad M = 1.4 \cdot 10^{-10} \text{ kg},$$

$$\gamma \approx 8 \cdot 10^{-7} \text{ N s/m}$$

*Snapshot of a numerical simulation of the Brownian motion in 2D of many large particles.*

*The trajectories of four of them are shown*

# Discovering the results

We can prove by numerical experiments:

- (i) the linear behavior of the mean square displacement  $\langle R^2 \rangle$  with time:

$$\langle R^2 \rangle = 2dD t$$

- (i) the validity of the Einstein relation between the slope of this line and the solvent parameters (temperature and drag coefficient):

$$\langle R^2 \rangle = (2d k_B T / \gamma) t$$