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 treatment
- 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, but 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
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
Observations of "active molecules" by scientist Robert Brown in 1827
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
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 existed.

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

\[
\frac{N_r(v)}{N} = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{kT}{kT}}
\]

Fraction of Molecules moving at speed \(v\)

\[
v_p = \sqrt{2 \frac{kT}{m}} \quad v_{av} = \sqrt{\frac{8 kT}{\pi m}} \quad v_{rms} = \sqrt{\frac{3 kT}{m}}
\]
Kinetic theory of gases

- Under discussion in ~1900: \( \frac{1}{2}mv^2 = \frac{3}{2}k_BT \)

- 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 μm) 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

... 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 $<\Delta r^2>$ of suspended particles undergoing brownian motion rather then their velocities are suitable observable and measurable quantities, and directly related to their diffusion coefficient $D$:

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

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

$<\Delta r^2>$ (and therefore $D$), $\eta, T$ measurable $\Rightarrow$ obtain $P$!
Einstein suggests that mean square displacements $<\Delta r^2>$ of suspended particles undergoing brownian motion rather than their velocities are suitable observable and measurable quantities, and directly related to their diffusion coefficient $D$:

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

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

$<\Delta r^2>$ (and therefore $D$), $\eta, T$ measurable $\Rightarrow$ obtain $P$!
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.

<table>
<thead>
<tr>
<th>From Mass Transfer Theory:</th>
<th>From Thermodynamics:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{flux} = \frac{\mu Wc}{\text{migration in gravity}}$</td>
<td>$\frac{d\phi}{dx} + RT \frac{d\ln c}{dx} = 0$</td>
</tr>
<tr>
<td>$-D \frac{dc}{dx} = 0$</td>
<td>gravitational potential</td>
</tr>
<tr>
<td>$W = \text{net weight of one particle}$</td>
<td>$\phi = WNx = \text{PE per mole}$</td>
</tr>
<tr>
<td>$c = \text{concentration of particles}$</td>
<td>$N = \text{Avogadro's number}$</td>
</tr>
<tr>
<td>$\mu = \text{mobility} = \frac{\text{velocity}}{\text{force}} = \frac{1}{6\pi \eta P}$</td>
<td>$R = \text{universal gas constant}$</td>
</tr>
<tr>
<td>$\eta = \text{viscosity of fluid}$</td>
<td>$T = \text{absolute temperature}$</td>
</tr>
<tr>
<td>$P = \text{particle radius}$</td>
<td>$RT[=\text{energy/mole}]$</td>
</tr>
</tbody>
</table>

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

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

Compare: exponentials must be equal! $\Rightarrow$ Obtain $\mu$; from $\mu$ (and $\eta$, known) we get particle size $P$.

$N, R, T \text{ known; } D \text{ measurable, according to Einstein}$

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

Fick's 2nd law:
\[
\frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial x^2}
\]
Initial Condition:
\[p(x, 0) = \delta(x)\]
B.C.'s:
\[p(\pm \infty, t) = 0\]

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

remember the gaussian:
\[p(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-x^2/(2\sigma^2)}\]

with \(\sigma^2 = 2Dt\)

The **mean square displacements** \(<\Delta r^2>\) 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 $\rightarrow$ brownian motion
- modified (interacting) RW $\rightarrow$ 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
A walker can walk either left or right:

\( N \) : number of steps
\( \ell \) : length of the random displacement (random direction)
\( s_i = \pm \ell \) : relative displacement of the \( i \) step
\( x_N \) : displacement from the starting point after \( N \) steps
\( \langle x_N \rangle = \sum_{i=1}^{N} s_i, \quad x_N \in [-N\ell, +N\ell] \)
\( p\rightarrow, p\leftarrow \) : probability of left or right displacement

What can we calculate?

\( \langle x_N \rangle \) : average net displacement after \( N \) steps
\( \langle x^2_N \rangle \) : 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
Exact analytic expressions can be easily derived for \( p_{\leftarrow} = p_{\rightarrow} \):

\[
\langle x_N \rangle = \langle \sum_{i=1}^{N} s_i \rangle = \ldots (\text{if } p_{\leftarrow} = p_{\rightarrow}) \ldots = 0
\]

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

More general:

\[ x_N = n_{\leftarrow}(-\ell) + n_{\rightarrow}(+\ell) \] (with \( N = n_{\leftarrow} + n_{\rightarrow} \))

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

Therefore:

\[
\langle \Delta x^2 \rangle = N \ell^2
\]
In general, average quantities can be calculated from $P_N(x)$:

$$\langle x_N \rangle = \sum_{x=\pm N\ell} x P_N(x)$$

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

... (how many different walks of length N?)
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!)

... 

(There are $2^N$ different possible walks of $N$ steps...)
RW 1D

Generalizing the expression for $P_N(x)$:

From:

$$
P_1(1) = p\to; \quad P_1(-1) = p\leftarrow
\]

$$
P_{N+1}(x) = P_N(x - 1)p\to + 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)!} \left(\frac{N}{2} + \frac{x}{2}\right) p\to + \frac{N}{2} - \frac{x}{2} p\leftarrow
\]

<table>
<thead>
<tr>
<th>$n \setminus x$</th>
<th>-5</th>
<th>-4</th>
<th>-3</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1/4</td>
<td></td>
<td>0</td>
<td>1/4</td>
<td>0</td>
<td>1/4</td>
<td>0</td>
<td>1/4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1/8</td>
<td>0</td>
<td>3/8</td>
<td>0</td>
<td>3/8</td>
<td>0</td>
<td>1/8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>1/16</td>
<td>0</td>
<td>4/16</td>
<td>0</td>
<td>6/16</td>
<td>0</td>
<td>4/16</td>
<td>0</td>
<td>1/16</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1/32</td>
<td>0</td>
<td>5/32</td>
<td>0</td>
<td>10/32</td>
<td>0</td>
<td>10/32</td>
<td>0</td>
<td>5/32</td>
<td>0</td>
</tr>
</tbody>
</table>

$P_N(x)$ for $p\leftarrow = p\to$ (Pascal triangle)
\[
P_N(x) = \frac{N!}{\left(\frac{N}{2} + \frac{x}{2}\right)! \left(\frac{N}{2} - \frac{x}{2}\right)!} p_{\rightarrow}^{N/2} + \frac{x}{2} p_{\leftarrow}^{N/2} - \frac{x}{2}
\]

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

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

which looks like a Gaussian.

Why?
Let’s describe the RW problem with a space/time differential equation...
**RW ID: Diffusion - continuum limit**

\[
\text{(case } p_- = p_+) \]

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

**Defining:** \( t = N\tau, \quad x = il \) \quad \text{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 \( \tau \to 0, \ l \to 0 \) but where the ratio \( l^2/\tau \) is finite, this becomes an exact relation.
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.
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
- **x_N, x2_N** = cumulative quantities
- **rnd(N)** = sequence of N random numbers

```fortran
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)
This slide summarizes some Brownian dynamics simulations for 1-D. At each time step, the particle (red circle in top graph) must move either left or right exactly one spatial increment, depending on the flip of a coin. The results for the net displacement from the origin \(x\) or \(x^2\) is shown in the lower two graphs. Averaging over as few as 10 such simulations yields results in reasonable agreement with the expectations from the previous slide. By making such observations (in 2-D), Jean Baptiste Perrin was able to deduce the diffusion coefficient for single colloidal particles.
RW 1D: simulation

P_N(x)

'prob_N64_ntrial0100'
RW 1D: simulation
RW 1D: simulation

\[ P_N(x) \]

Graph showing the probability distribution of \( x_N \) with histograms labeled as follows:

- "prob_N64_ntrial1000" (green line)
- "prob_N64_ntrial9999" (blue line)
RW 1D: simulation

![Graph showing probability distribution](image-url)
Random Walk Simulation

Many physical processes such as Brownian motion, electron transport through metals, and round off errors on computers are modeled as a random walk. In this model, many steps are taken with the direction of each step independent of the direction of the previous one. For our model, we start at the origin and take steps of lengths (not coordinates) in the x and y directions, where there are a total of N steps.

The distance from the starting point \( R \) is related to these steps by:

\[
\text{Now while } (2) \text{ is quite general for any walk you may take, if it is a random walk then you are equally likely to move forwards as backwards in each step - as well as to the right or left. So on the average, for a large number of steps, all the cross terms in (2) will vanish and we are left with:}
\]

\[
\text{where } \frac{1}{N} \text{ is the square root of the average squared step size or root mean squared step size. Note, the same result obtains for a three dimensional walk. According to (3), even though the total distance walked is, on the average, the distance from the starting point is only:}
\]
Random Walks 2D

\[ \langle R_N^2 \rangle = \langle (\Delta x_1 + \ldots + \Delta x_N)^2 + (\Delta y_1 + \ldots + \Delta y_N)^2 \rangle = \ldots = N \langle \Delta x_i^2 + \Delta y_i^2 \rangle = N \ell^2 \]

\[ \langle R^2 \rangle \propto N \]

also in 2D! (and in general in each dimension)
Although the theory of RW predicts that $\langle R^2 \rangle \propto N$ for large $N$, this holds only on the average after many trials, and even then only if particular care is used in generating the random walk.
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 \([-\sqrt{2}, \sqrt{2}]\). Although the step size is generally not 1, it becomes 1 on the average.

Although all these methods seem to be reasonable, only the last one gives us good results when we are dealing with a large number of steps.
Although the theory of RW predicts that $\langle R^2 \rangle \propto N$ for large $N$, this holds only on the average after many trials, and even then only if particular care is used in generating the random walk.
### Random Walks 2D

<table>
<thead>
<tr>
<th>i</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0000000</td>
<td>0.0000000</td>
</tr>
<tr>
<td>10</td>
<td>0.2242774</td>
<td>3.7794106</td>
</tr>
<tr>
<td>20</td>
<td>-1.7333623</td>
<td>1.3218992</td>
</tr>
<tr>
<td>30</td>
<td>-1.4481916</td>
<td>-3.1119978</td>
</tr>
<tr>
<td>40</td>
<td>-2.2553353</td>
<td>-3.5246484</td>
</tr>
<tr>
<td>50</td>
<td>-3.8911035</td>
<td>-6.665235</td>
</tr>
<tr>
<td>60</td>
<td>-3.6508965</td>
<td>-8.0110636</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>i</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6946244</td>
<td>0.7193726</td>
</tr>
<tr>
<td>2</td>
<td>0.9359566</td>
<td>1.6898152</td>
</tr>
<tr>
<td>3</td>
<td>1.8891419</td>
<td>1.9922019</td>
</tr>
<tr>
<td>4</td>
<td>0.9642899</td>
<td>2.3725290</td>
</tr>
<tr>
<td>5</td>
<td>0.1308700</td>
<td>2.9251692</td>
</tr>
<tr>
<td>6</td>
<td>0.2071800</td>
<td>3.922534</td>
</tr>
<tr>
<td>7</td>
<td>0.9160752</td>
<td>4.6275673</td>
</tr>
<tr>
<td>8</td>
<td>0.2856980</td>
<td>3.8512783</td>
</tr>
<tr>
<td>9</td>
<td>1.0143363</td>
<td>3.1663797</td>
</tr>
<tr>
<td>10</td>
<td>0.2242774</td>
<td>3.7794106</td>
</tr>
<tr>
<td>11</td>
<td>-0.7752404</td>
<td>3.8104627</td>
</tr>
<tr>
<td>12</td>
<td>-1.7280728</td>
<td>3.5069659</td>
</tr>
<tr>
<td>13</td>
<td>-2.0930278</td>
<td>4.4379911</td>
</tr>
<tr>
<td>14</td>
<td>-3.0587580</td>
<td>4.1784425</td>
</tr>
<tr>
<td>15</td>
<td>-2.0729706</td>
<td>4.0104446</td>
</tr>
<tr>
<td>16</td>
<td>-1.8304152</td>
<td>3.0403070</td>
</tr>
<tr>
<td>17</td>
<td>-2.2890768</td>
<td>2.1516960</td>
</tr>
<tr>
<td>18</td>
<td>-1.7717266</td>
<td>1.2959222</td>
</tr>
<tr>
<td>19</td>
<td>-1.1920205</td>
<td>0.4810965</td>
</tr>
<tr>
<td>20</td>
<td>-1.7333623</td>
<td>1.3218992</td>
</tr>
<tr>
<td>21</td>
<td>-1.5798329</td>
<td>0.3337551</td>
</tr>
</tbody>
</table>

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

```plaintext
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
Examples of the random path of a raindrop to the ground

The probability of a step down is larger than the probability of a step up; furthermore, this is a restricted RW, i.e. limited by boundaries.
Self-avoiding Random Walks

(a) Schematic illustration of a linear polymer in a good solvent: head-tail mean square distance is (in 3D):
\[ \langle \Delta R_N^2 \rangle \sim N^{2\nu} \]
\[ \nu = 0.592 \]

(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 (superdiffusive behaviour)
- ....
Some programs:

on
/home/peressi/comp-phys/IV-random-walk/f90
[do: cp /home/peressi/.../f90/* .]
or 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 '1.ps'
p [-20:5][-10:15] '1.dat' u 2:3 w l
set out '10.ps'
p [-40:20][-10:50] '10.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)
Other program:

on
${/home/peressi/comp-phys/IV-random-walk/f90
[do: $cp /home/peressi/.../f90/* .]}

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

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..., \(m\ll M..., \ldots\)) \(\Rightarrow\)

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:

\[
M \Delta V/\Delta t = \Delta V_s /\Delta t - \gamma V(t)
\]

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

with:

\[
\Delta V_s = 2mv/M = (...) = 1/M \frac{v}{|v|} \sqrt(2\gamma k_B T/n);
\]

At each collision \(v/|v|\) is -1 or +1 ⇒ after \(N\) collisions ???

the result is a **gaussian random variable**

\(w_q\) centered in 0, s.d.=\(\sqrt(N/2)\) ⇒ (see also next lectures)
The numerical approach: discretized equations for positions and velocities

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

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

- 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

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

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

Input parameters – II

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

- time step \(\Delta t\): cannot be fixed a priori!

Some suggestions from physical and rough numerical considerations

\((\frac{\gamma}{M})\Delta t < 1\) 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...

\[ k_B T = 4 \cdot 10^{-21} \text{J}, \ M = 1.4 \cdot 10^{-10} \text{kg}, \]
\[ \gamma \approx 8 \cdot 10^{-7} \text{Ns/m} \]

Snapshot of a numerical simulation of the Brownian motion in 2D of many large particles. The trajectories of four of them are shown.
We can prove by numerical experiments:

(i) the linear behavior of the mean square displacement $<R^2>$ with time:

$$<R^2> = 2dD \, t$$

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

$$<R^2> = \left(2d \, \frac{k_B T}{\gamma}\right) \, t$$
IV part:
Brownian motion in finance
- mathematical formulation
Brownian motion in finance

Simulated Returns (Geometric Brownian Motion)

Real Returns (Financial Time-Series)

Random Walk in Finance

• **Geometric Brownian motion**: \( \mu \): drift; \( \sigma \): volatility; \( \epsilon \): random variable following **normal distribution** with unit variance

\[
dS = \mu S dt + \sigma S \epsilon \sqrt{dt}
\]

• Let the 2nd term be 0,

\[
S(t) = S_0 \exp(\mu t)
\]

• Let the 1st term be 0, then for \( U = \ln S \) (\( dU = dS/S \))

\[
dU = \sigma \epsilon \sqrt{dt}
\]

\[
U(t) - U(0) = \sigma \sqrt{\Delta t} \sum_{i=1}^{N} \epsilon_i
\]

• Central-limit theorem states that \( \Sigma_i \epsilon_i \) is normal distribution with variance \( N \); let \( t = N \Delta t \)

\[
U(t) - U(0) = \sigma \sqrt{t} \epsilon
\]

• Log-normal distribution

![Log-normal distribution graph](image)

credits: Nakano
MC Simulation of Stock Price

\[
\frac{dS}{S} = \mu dt + \sigma \sqrt{dt} \xi
\]

\( \mu = 0.14 \)
Stochastic Model of Stock Prices

Basis of Black-Scholes analysis of option prices

\[ dS = \mu S dt + \sigma S \epsilon \sqrt{dt} \]

Computational stock portfolio trading

The Bank of Sweden Prize in Economic Sciences in Memory of Alfred Nobel 1997

"for a new method to determine the value of derivatives"

Robert C. Merton

1/2 of the prize

USA

Myron S. Scholes

1/2 of the prize

USA

Technology Stock Basket Performance
Basis of Black-Scholes analysis of option prices

\[ dS = \mu S dt + \sigma S \varepsilon \sqrt{dt} \]

The Bank of Sweden Prize in Economic Sciences in Memory of Alfred Nobel 1997

"for a new method to determine the value of derivatives"

Robert C. Merton

Myron S. Scholes