Random walks

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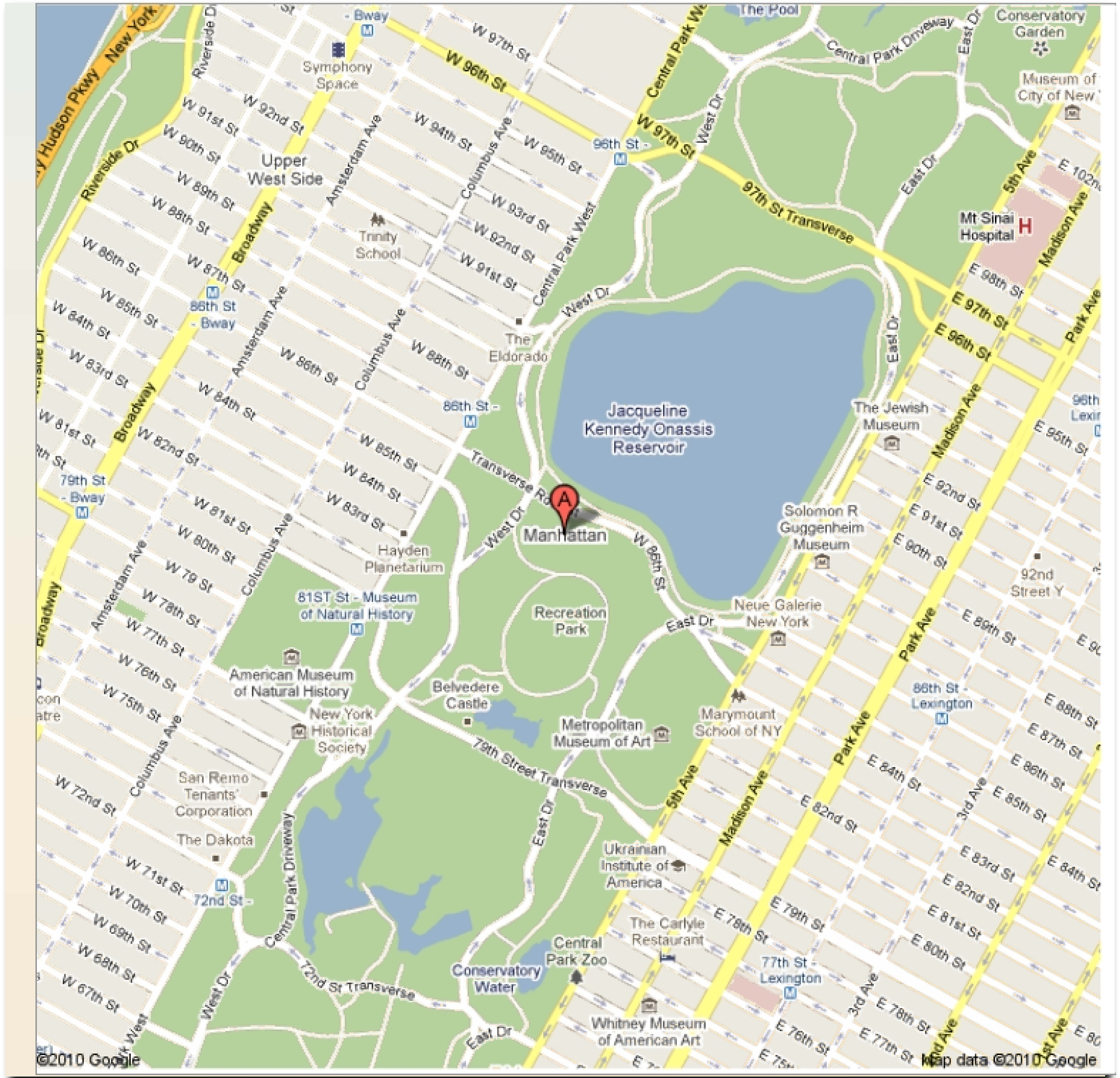
What is a random walk?



Questions

~~Having started at t=0 in x=0, what will his position at t=T be?~~

What is the probability that at t=T he will be at distance X from the origin?

Random walk -1d

- N = number of total steps
- p = probability to go right
- q = probability to go left

- n_1 = number of steps to the right
- n_2 = number of steps to the left
- $N = n_1 + n_2$
- $m = n_1 - n_2$ distance?

What is the probability of having done n_1 steps to the right for such a walker ?

$$P_N(n_1) = \binom{N}{n_1} p^{n_1} q^{N-n_1}$$

What is the average distance made by our walker of N steps?

$$\langle m \rangle = \langle n_1 \rangle - \langle n_2 \rangle$$

$$\langle n_1 \rangle = \sum_{n_1} n_1 \binom{N}{n_1} p^{n_1} q^{N-n_1}$$

Calculating averages

$$F(x,y) = (x+y)^N = \sum_{n_1} \binom{N}{n_1} x^{n_1} y^{n_2}$$

$$\langle n_1 \rangle = \left(x \frac{\partial F}{\partial x} \right)_{p,q} \longrightarrow \langle m \rangle = (p-q)N$$

- if p=q=1/2 <m> = 0

$$\langle \Delta m^2 \rangle = \langle (m - \langle m \rangle)^2 \rangle = \langle m^2 \rangle - \langle m \rangle^2 = 4Npq$$

- if we assume that N is a measure of time elapsed

$\sqrt{\langle \Delta m^2 \rangle} = \sqrt{N}$ huge difference for long times!

Continuum limit

- Let's express evtg in m and N

$$P_N(m) = \frac{N!}{(\frac{N+m}{2})!(\frac{N-m}{2})!} p^{\frac{N+m}{2}} q^{\frac{N-m}{2}}$$

- x = ml, l unit step << smallest measurable distance
- m increases of ±2 (it can be only always odd or even)
- x ~ continuum variable if $|P(m+2) - P(m)| << P(m)$

$$\frac{P(m+2)}{P(m)} = \frac{1}{\frac{N+m}{2}+1}\frac{N-m}{2}p/q = \frac{N-m}{N+m+2}p/q$$

$$\frac{P(m+2)}{P(m)} - 1 << 1$$

$$\frac{N(1-m/N)}{N(1+m/n+2/N})\simeq 1$$

if m/N << 1

- P(x)/2l dx probability of finding the walker at a distance $\in$ (x, x+dx)

$N \longrightarrow \infty$

$$|P(m+2) - P(m)| << P(m)$$

- P(m) slowly varying in this limit
- Expansion around its maximum? $\quad (1+x)^N \simeq 1 + Nx + \binom{N}{2} x^2 + \ldots$
- Expansion of the logarithm

$$\ln P_N(n_1) \simeq \ln P_N(\tilde{n}_1) - \frac{1}{2} B (n_1 - \tilde{n}_1)^2$$

- $\tilde{n}_1$ maximum, B >0 $\quad B = -\left(\frac{\partial^2 P_N(n_1)}{\partial n_1^2} \right)_{\tilde{n}_1}$

$$\ln P_N(n_1) = \ln N! - \ln (N - n_1)! - \ln n_1! + n_1 \ln p + (N - n_1) \ln q$$

- Using Stirling formula $\quad \tilde{n}_1 = Np = \langle n_1 \rangle$

$$\ln P_N(n_1) \simeq \ln P_N(\tilde{n}_1) - \frac{1}{2} \frac{(n_1 - Np)^2}{Np(1-p)}$$

Can we neglect terms of order > 2?

- Check that

$$\left|\frac{O(3)}{O(2)}\right| \le \frac{1}{3}\frac{1}{\sqrt{Npq}}$$

Negligible for large N!

and finally ...

- from $\ln P_N(n_1) \simeq \ln P_N(\tilde{n}_1) - \frac{1}{2}\frac{(n_1 - Np)^2}{Np(1-p)}$

$$P_N(n_1) \simeq P_N(\langle n_1 \rangle) e^{-\frac{1}{2}\frac{(n_1 - \langle n_1 \rangle)^2}{\sigma^2}}$$

- a Gaussian distribution with central value and variance coinciding with the first 2 moments of the binomial distribution.

- in terms of m, <m>=N(p-q)

$$P_N(m) \simeq \frac{1}{\sqrt{(2\pi Npq)}} e^{-\frac{(m - \langle m \rangle)^2}{8Npq}}$$

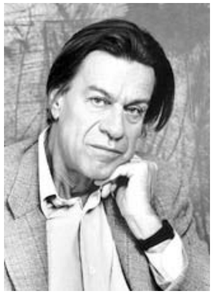
- if p=q, Gaussian centered in 0, otherwise the max is moving with N

RW all around...

Used as a first statistical model in the most diverse fields:

- Economics, random walk hypothesis to model share prices, fluctuations...
- Population genetics , to study statistics of genetic evolution
- Brain research, to model cascade of firing neurons
- Mathematics: as the starting point in various combinatorics analysis, to solve differential equations, calculate integrals...
- Vision science, to describe fixational eye movements
- Psychology, to model the relation between the time needed to make a decision and the probability that a certain decision will be made...

RW for polymers



- Many properties of long flexible macromolecules, on length-scales >> chemical unit, do not depend on actual chemistry.
- A polymer as a RW in d-dimensions, N steps, constant step length b_0
- b_0 length-scale over which correlations between segments are lost.

$$\langle \mathbf{R}^2 \rangle = N b_0^2$$

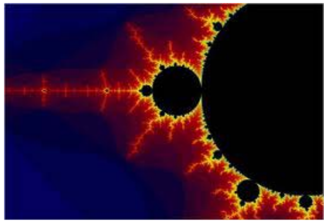
- End-to-end distance $\mathbf{R} \equiv \mathbf{x_N} - \mathbf{x_0}$

$$f(\mathbf{R}) = \left(\frac{3}{2\pi N b_0^2} \right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2 N b_0^2} \right)$$

Fractal object

$d_f = 2$

$$f(\mathbf{R}) d\mathbf{R} = 4\pi f(R) R^2 dR$$



Radius of gyration

- Gyration tensor $\mathbf{R}_g \equiv \frac{1}{N}\sum_{i=1}^{N}(\mathbf{x}_i - \mathbf{x}_{cm})(\mathbf{x}_i - \mathbf{x}_{cm})$

$$\mathbf{x}_{cm} = \frac{1}{N}\sum_{i}^{N}\mathbf{x}_i$$

$$R_g^2 \equiv Tr\mathbf{R}_g = \frac{1}{N}\sum_{i=1}^{N}(\mathbf{x}_i^2 - 2\mathbf{x}_i \cdot \mathbf{x}_{cm} + \mathbf{x}_{cm}^2) = \ldots$$

$$= \frac{1}{N}\sum_{i}^{N^2}\sum_{j=i}^{N}(\mathbf{x}_i - \mathbf{x}_j)^2$$

the gyration radius can be measured in scattering experiments: interference effects from the relative distance between scatterers.

- $\langle \mathbf{R}^2 \rangle / R_g^2 = 1/6$

Entropy and elasticity

- Macromolecule described as RW, number N_c of possible RW with origin in 0, N steps and end-to-end distance R

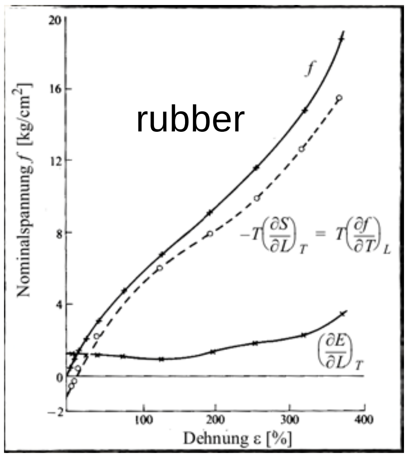
$$f(\mathbf{R}) = N_c(\mathbf{R}) / \sum_R N_c(\mathbf{R})$$

- Entropy associated to a certain R, $S(\mathbf{R}) = k_B \ln N_c(\mathbf{R})$

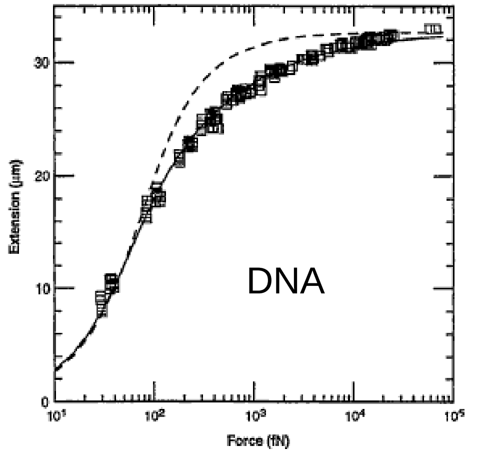
- Stretching causes S(R) to decrease, restoring force

$$\Delta F = \Delta U + k_B T \frac{3\Delta R^2}{2Nb_0^2}$$

Entropic source of elastic behavior



R.L. Anthony, R.H. Caston and E. Guth, J. Phys. Chem. 1942



Bustamante, Marko, Siggia & Smith, Science 1994

Other ideal chains

- Freely rotating chain: segment-segment correlations, rapid decay

$$\mathbf{Q}_i \equiv \mathbf{x}_{i+1} - \mathbf{x}_i$$

$$\langle \mathbf{Q}_i \cdot \mathbf{Q}_j \rangle = \delta_{ij} b_0^2$$

RW

$$\langle \mathbf{Q}_i \cdot \mathbf{Q}_j \rangle = b_0^2 (\cos\theta)^{|i-j|}$$

$$\cos^k\theta = e^{k \ln\cos\theta} \equiv e^{-k/s_p} \qquad s_p \equiv -\frac{1}{\ln\cos\theta}$$

Persistence length

$$\langle R^2 \rangle = N b_0^2 C_\infty \qquad C_\infty \simeq \frac{1+\cos\theta}{1-\cos\theta}$$

- Worm-like chain (Kratky-Porod): small angles, $\cos\theta \simeq 1 - \theta^2/2$

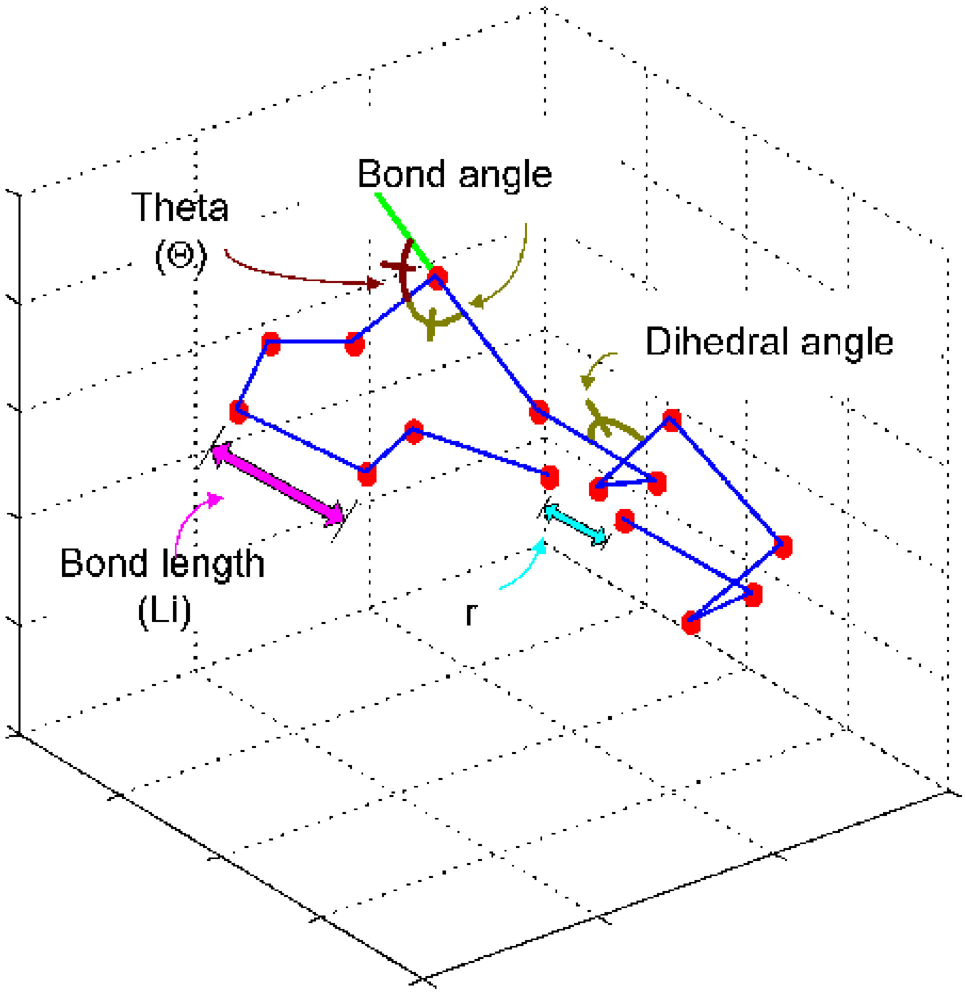
$$s_p \simeq 2/\theta^2$$

b Kuhn length of the equivalent RW

$$b \equiv \frac{\langle R^2 \rangle}{N b_0}$$

$$b = \frac{b_0 C_\infty}{\cos\theta/2} \simeq b_0 \frac{4/\theta^2}{1-\theta^2/4} \simeq 2 b_0 s_p$$

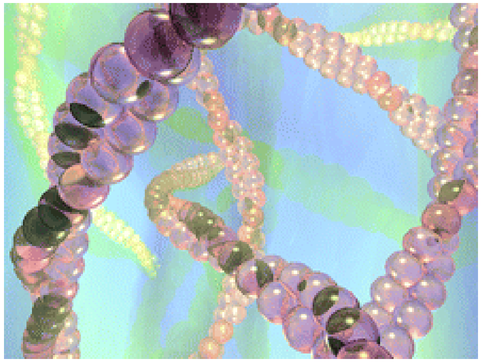
Freely rotating chain



J. E, Bemis, PhD Thesis,
University of Pittsburgh, 1998

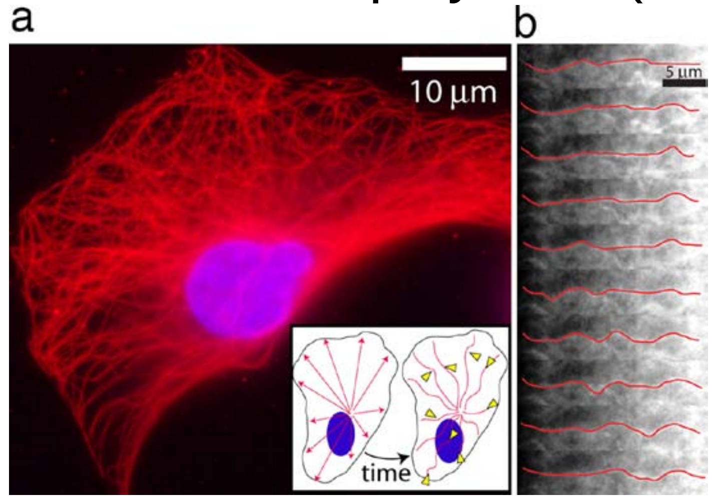
Worm like chains around

- Bio-polymers



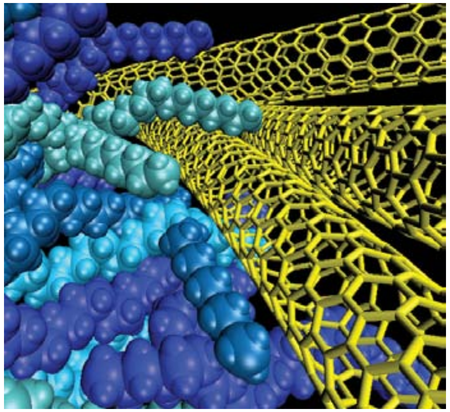
K. Kroy, Soft Matter 2008

- Semi-flexible polymers (microtubules...)

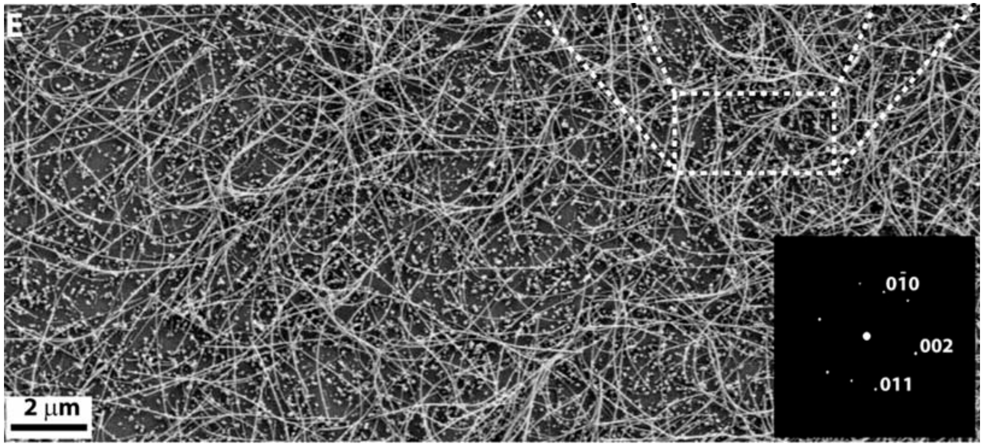


C. P. Brangwynne, F.C. Mackintosh and D.A. Weitz, PNAS 2007

- Single wall nano-tubes



P.M. Ajayan & J.M. Tour, Nature 2007

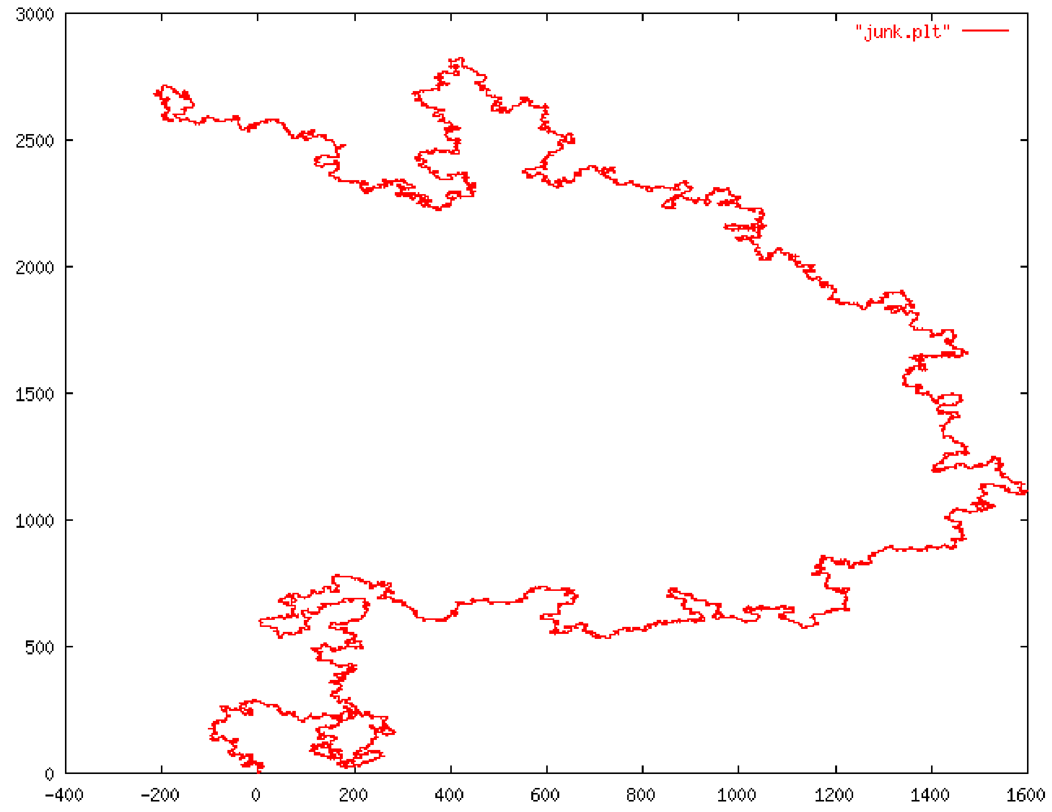


S. Morin et al., Science 2010

From random to self-avoiding

- RW with no possibility of self-crossing: much more complicated statistics, not analytically solvable

$$\langle R^2 \rangle = N^{2\nu} b_0$$



Flory's estimate

- Flory's estimate of ν: typical size must arise from balance between entropic contribution and intra-segment repulsion (excluded volume)
- mean-field approximation for repulsion: disregard chain connectivity and consider interaction energy of a "segment gas" confined in a volume R^3

$\tilde{c} \simeq N/R^3$ av. segment density

$v k_B T \tilde{c}^2 R^3$

av. interaction energy due to excluded volume v

$$F(\mathbf{R}) \simeq k_B T \left(\frac{3R^2}{2Nb_0^2} + v \frac{N^2}{R^3} \right)$$

$$d_f = 1/\nu \simeq 1.67$$

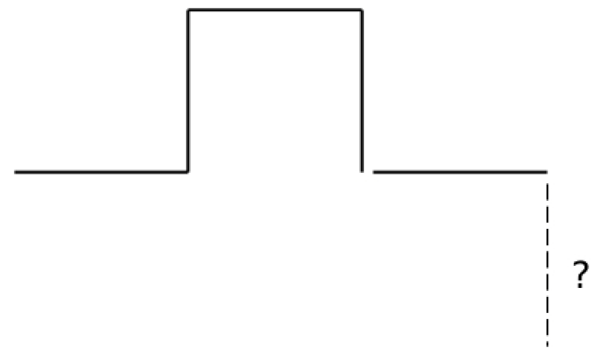
- upon minimizing,

$$\tilde{R} \simeq \sqrt{(N)} b_0 \left(\frac{\sqrt{N} v}{b_0^3} \right)^{1/5} \propto N^{3/5}$$

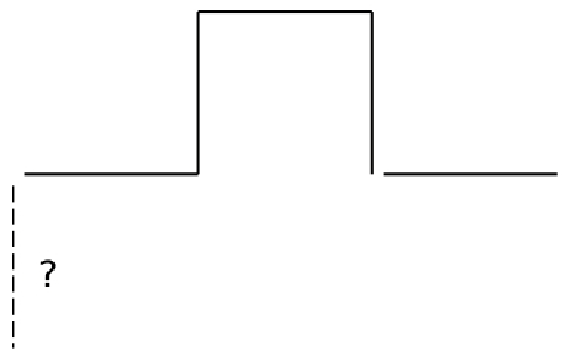
- agreement with calculations, simulations and experiments!!

Algorithms for SAW

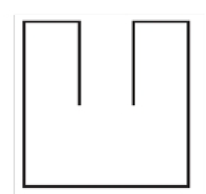
- Slithering snake



No?

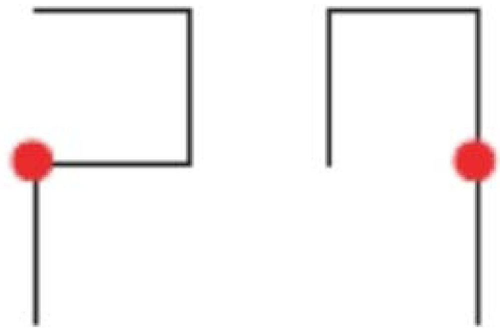


But:

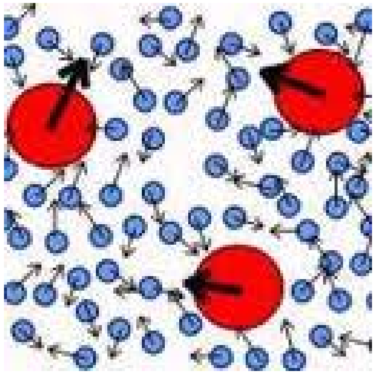


Algorithms for SAW

- Pivot



Diffusion, RW and Brownian motion



- number density of the particles $n(\mathbf{r},t)$
- current density $\mathbf{j}(\mathbf{r},t) = n(\mathbf{r},t)\mathbf{v}(\mathbf{r},\mathbf{t})$
- Fick's law $\mathbf{j}(\mathbf{r},t) = -D\nabla n(\mathbf{r},t)$

  D diffusion coefficient

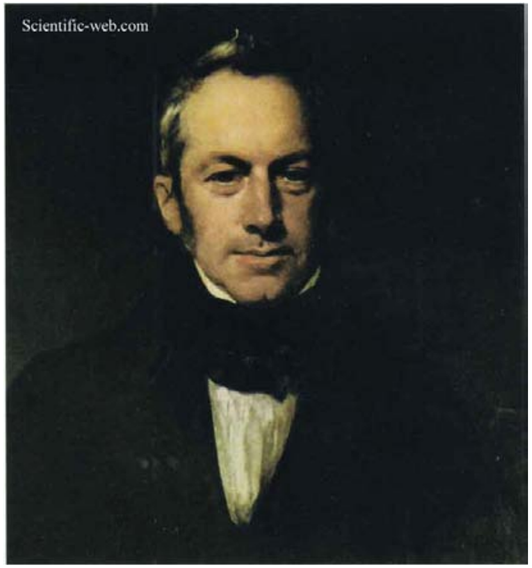
- + continuity, diffusion equation $\nabla^2 n(\mathbf{r},t) - \frac{1}{D}\frac{\partial n(\mathbf{r},t)}{\partial t} = 0$
- spherically symmetric normalized solution

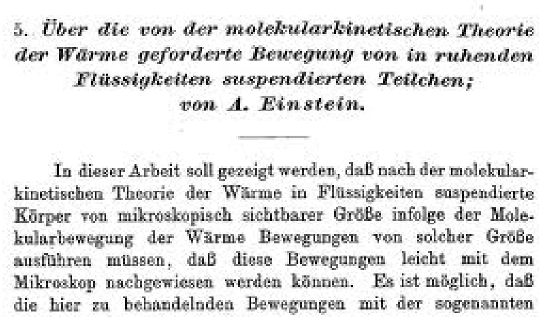
$$n(\mathbf{r},t) = \frac{N}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

$$\langle r(t)\rangle = 0$$

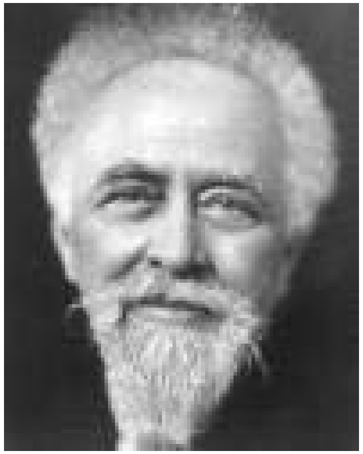
$$\langle r^2(t)\rangle = 6Dt$$

Brownian motion




5. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen; von A. Einstein.

In dieser Arbeit soll gezeigt werden, daß nach der molekularkinetischen Theorie der Wärme in Flüssigkeiten suspendierte Körper von mikroskopisch sichtbarer Größe infolge der Molekularbewegung der Wärme Bewegungen von solcher Größe ausführen müssen, daß diese Bewegungen leicht mit dem Mikroskop nachgewiesen werden können. Es ist möglich, daß die hier zu behandelnden Bewegungen mit der sogenannten



http://www.aip.org/history/einstein/brownian.htm

$$m\frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v}}{B} + \mathbf{F}(\mathbf{t}) \qquad \overline{\mathbf{F}(t)} = 0$$

B mobility, i.e. drift velocity per unit external force

- Ensemble average

$$\langle \mathbf{v}(t) \rangle = \mathbf{v}(0)e^{-t/\tau} \qquad \langle \mathbf{F}(t) \rangle = 0 \qquad \tau = mB$$

Relaxation time, dissipation due to viscosity

Averages and fluctuations

- For instantaneous acceleration:

$$\overline{\mathbf{A}(t)} = 0 \qquad \frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v}}{\tau} + \mathbf{A}(t) \qquad \cdot\mathbf{r}$$

- Using that: $$\frac{d}{dt}(\mathbf{r}\cdot\mathbf{r}) = 2\mathbf{r}\cdot\mathbf{v}$$

- For fluctuations: $$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2\langle v^2\rangle$$

- Equipartition $$\langle v^2\rangle = \frac{3k_BT}{m} \qquad \langle r^2\rangle = \frac{6k_BT}{m}\left[\frac{t}{\tau} - (1 - e^{-t/\tau})\right]$$

$$t << \tau \qquad \langle r^2\rangle \simeq \frac{3k_BT}{m}t^2$$

Consistent with reversible equations of motion $\mathbf{r} = \mathbf{v}t$

Einstein relation

$$\langle r^2 \rangle = \frac{6k_BT}{m}\left[\frac{t}{\tau} - (1 - e^{-t/\tau})\right]$$

$$t >> \tau \qquad \langle r^2 \rangle \simeq 6\underbrace{k_BTB}_{D}t$$

- Direct relation between diffusion (fluctuations) and viscosity (dissipation)

- Microscopic origin of diffusion

Velocity

- From $\dfrac{d\mathbf{v}}{dt} = -\dfrac{\mathbf{v}}{\tau} + \mathbf{A}(t)$ $\qquad \overline{\mathbf{A}(t)} = 0$

$$\int_0^t \frac{d\mathbf{v}}{du} e^{u/\tau} = -\int_0^t \frac{\mathbf{v}(u)}{\tau} e^{u/\tau} + \int_0^t \mathbf{A}(u) e^{u/\tau}$$

using $\dfrac{d}{du}\left(\mathbf{v}(u)e^{u/\tau}\right) = e^{u/\tau}\dfrac{d\mathbf{v}}{du} + \dfrac{1}{\tau}e^{u/\tau}\mathbf{v}(u)$

$$\int_0^t \left(e^{u/\tau}\frac{d\mathbf{v}}{du} + \frac{\mathbf{v}(u)}{\tau}e^{u/\tau}\right) du = \left(\mathbf{v}(u)e^{u/\tau}\right)_0^t = \mathbf{v}(t)e^{t/\tau} - \mathbf{v}(0)$$

$$\mathbf{v}(t) = \mathbf{v}(0)e^{-t/\tau} + e^{-t/\tau}\int_0^t \mathbf{A}(u)e^{u/\tau} du$$

$$\langle \mathbf{v}(t) \rangle = 0 \qquad \langle \mathbf{A}(u) \rangle = 0 \qquad \langle \mathbf{v}(t) \rangle = \mathbf{v}(0)e^{-t/\tau}$$

Velocity fluctuations and autocorrelation

$$\mathbf{v}(t)\cdot\mathbf{v}(t) = v^2(0)e^{-2t/\tau} + 2\left(\mathbf{v}(0)\cdot\int_0^t \mathbf{A}(u)e^{u/\tau}du\right)e^{-2t/\tau}$$

$$+2e^{-2t/\tau}\int_0^t\int_0^t e^{(u_1+u_2)/\tau}\mathbf{A}(u_1)\cdot\mathbf{A}(u_2)du_1du_2$$

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + e^{-2t/\tau}\int_0^t\int_0^t e^{(u_1+u_2)/\tau}\langle\mathbf{A}(u_1)\cdot\mathbf{A}(u_2)\rangle du_1du_2$$

- Properties of K(s):

$$K(0) > 0$$

$$|K(s)| \leq K(0)$$

$$s >> \tau$$

$$K(s) \rightarrow 0$$

Autocorrelation function $K(u_1 - u_2)$

Velocity fluctuations

- Then we can consider: $C = \int_{-\infty}^{\infty} K(s)ds$

$$\langle v^2 \rangle = v^2(0)e^{-2t/\tau} + C\frac{\tau}{2}\left(1 - e^{-2t/\tau}\right)$$

$t << \tau$ $\quad v^2(0) = \frac{3k_BT}{M} \Rightarrow \langle v^2 \rangle = v^2(0)$

$t >> \tau$ $\quad \langle v^2 \rangle \simeq C\frac{\tau}{2}$ $\quad C = \frac{6k_BT}{m^2B}$

- The origin of the viscous force is in the fluctuations of the stochastic forces due to incessant collisions of the fluid particles.

- From the fluctuations of the system at rest one obtains information on its response when perturbed.