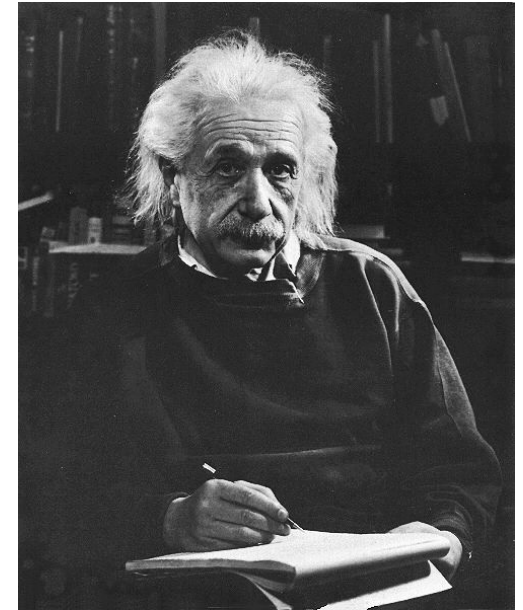
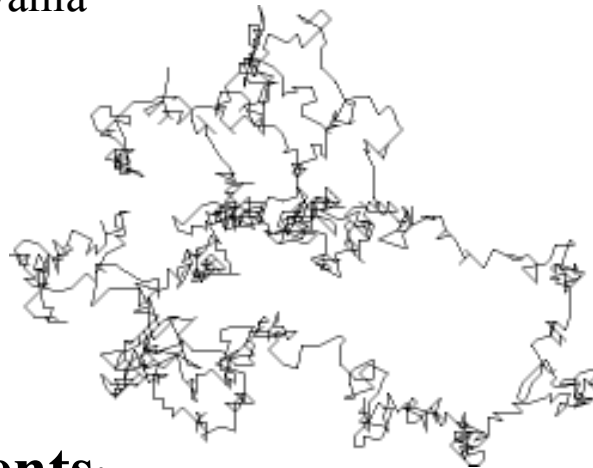


Random Walks, Diffusion, & Einstein

Arjun G. Yodh

Department of Physics & Astronomy
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University of Pennsylvania
Philadelphia, PA

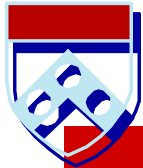


Acknowledgements:

Peter Yunker, Piotr Haldas (Saint Joseph's University)

National Science Foundation (MRSEC)

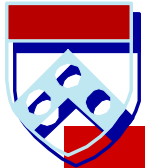
Random Walks in Biology (Berg), *Noise & Fluctuations* (McDonald), *Selected Papers on Noise & Stochastic Processes* (Editor, Wax)





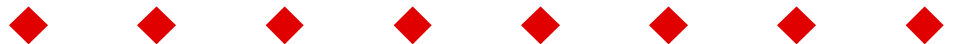
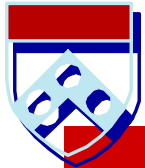
Outline

- **Examples of Random Walks**
- **Random Walks (quantitative)**
- **Connection to Diffusion**
 - Brownian Motion
 - Diffusion Equation
- **Other Examples**
 - Polymers
 - Light Diffusion



◆◆◆ Physics Problems Worth Knowing...

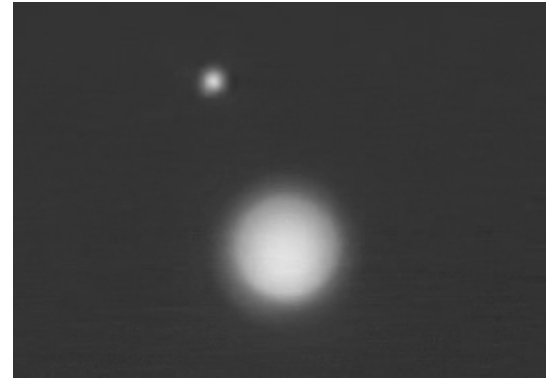
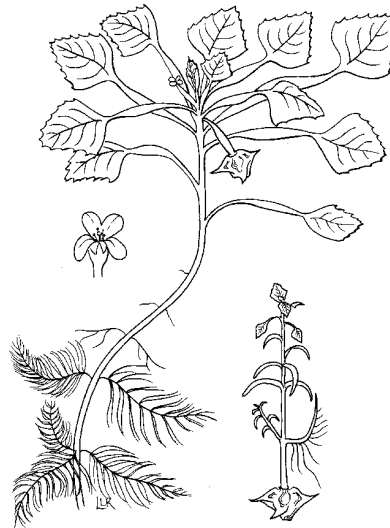
- Harmonic Oscillator
- Hydrogen Atom / Particle in Box
- Ideal Gas
- Random Walk
- ...



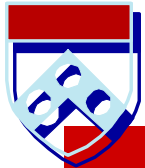
Random Walk Physics underlies a diversity of phenomena

[Click Image to Play Movie](#)

- **Brownian Motion**



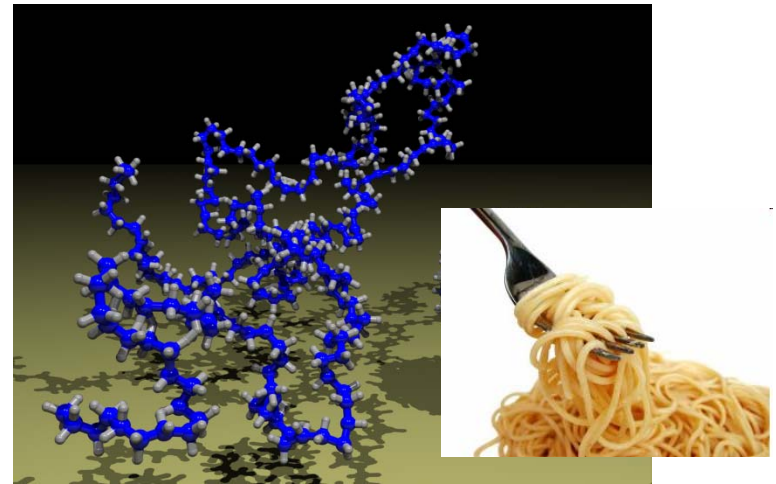
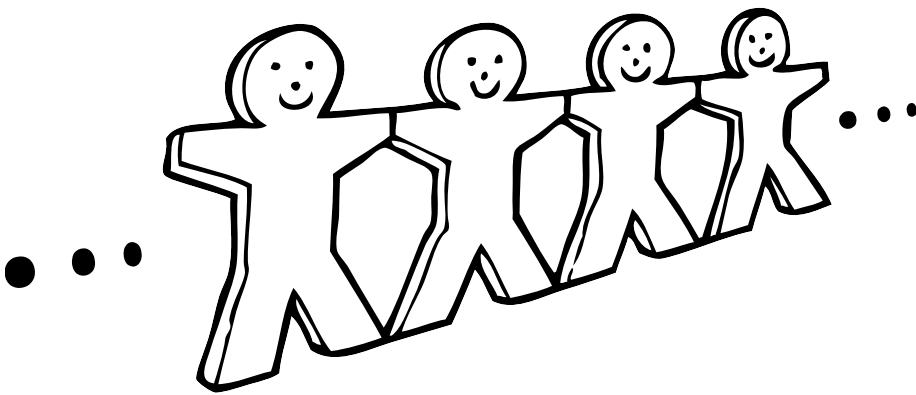
Brown (1827), Einstein (1905), von Smoluchowski (1906), Perrin (1909)



Random Walk Physics underlies a diversity of phenomena

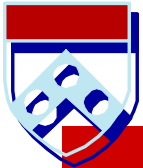
- **Polymers (size, shape, ...)**

http://polymer.physik.uni-ulm.de/mol_graphics/



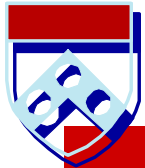
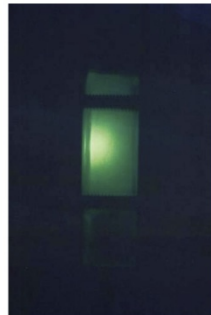
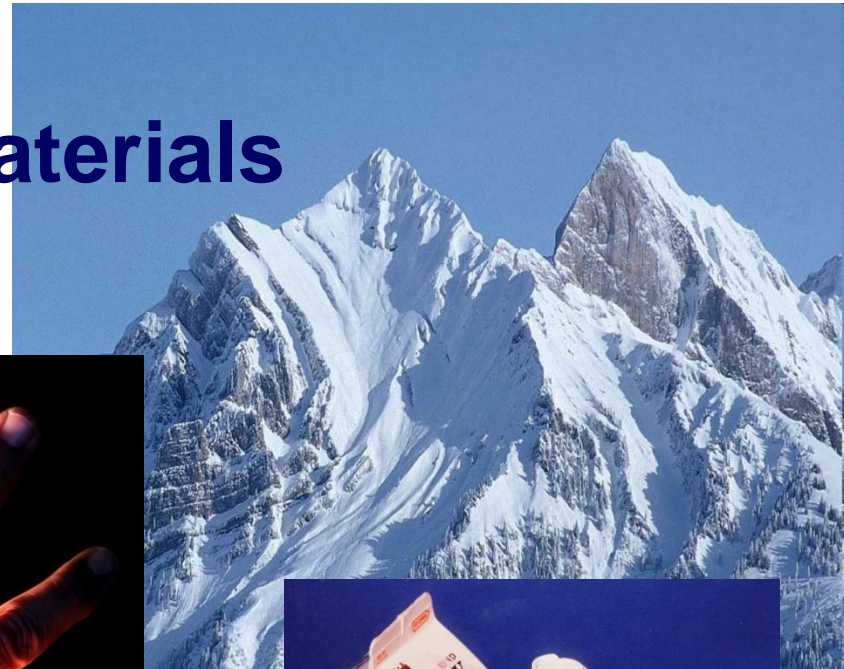
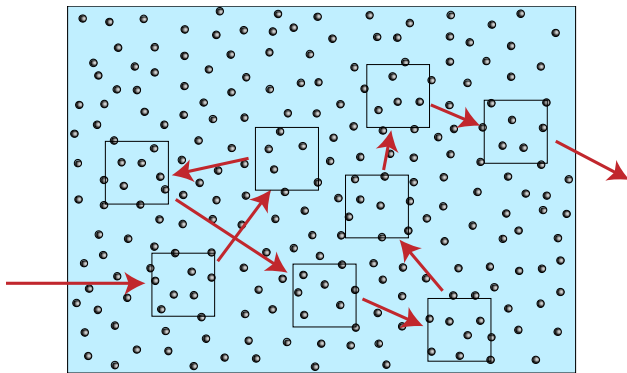
Very, very long chain molecules

Polyethylene: $\cdots - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \cdots$ or $[\text{CH}_2]_N$



Random Walk Physics underlies a diversity of phenomena

- **Light Transport in Highly Scattering Materials**



Even More Phenomena

- **Random Flights in Nature**



Food foraging

5×10^{-3} cm

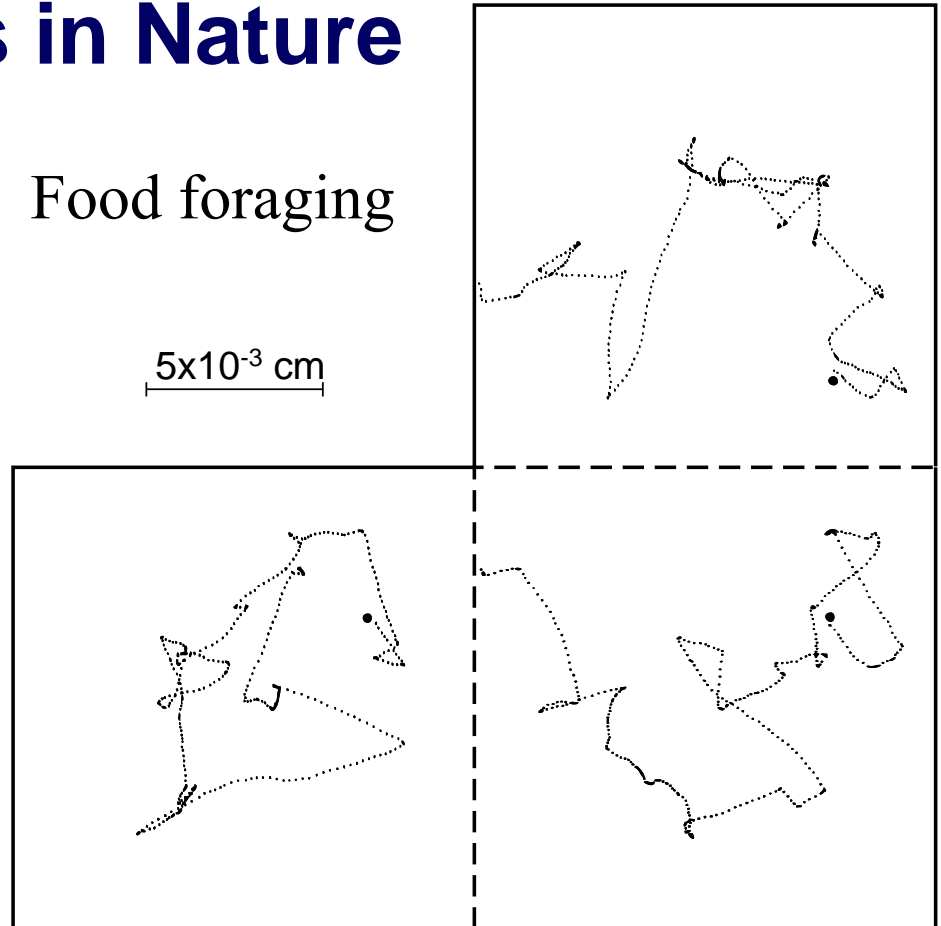
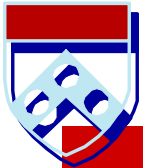
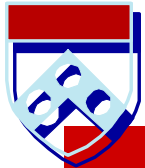


Figure from: *Random Walks in Biology*, by Howard C. Berg

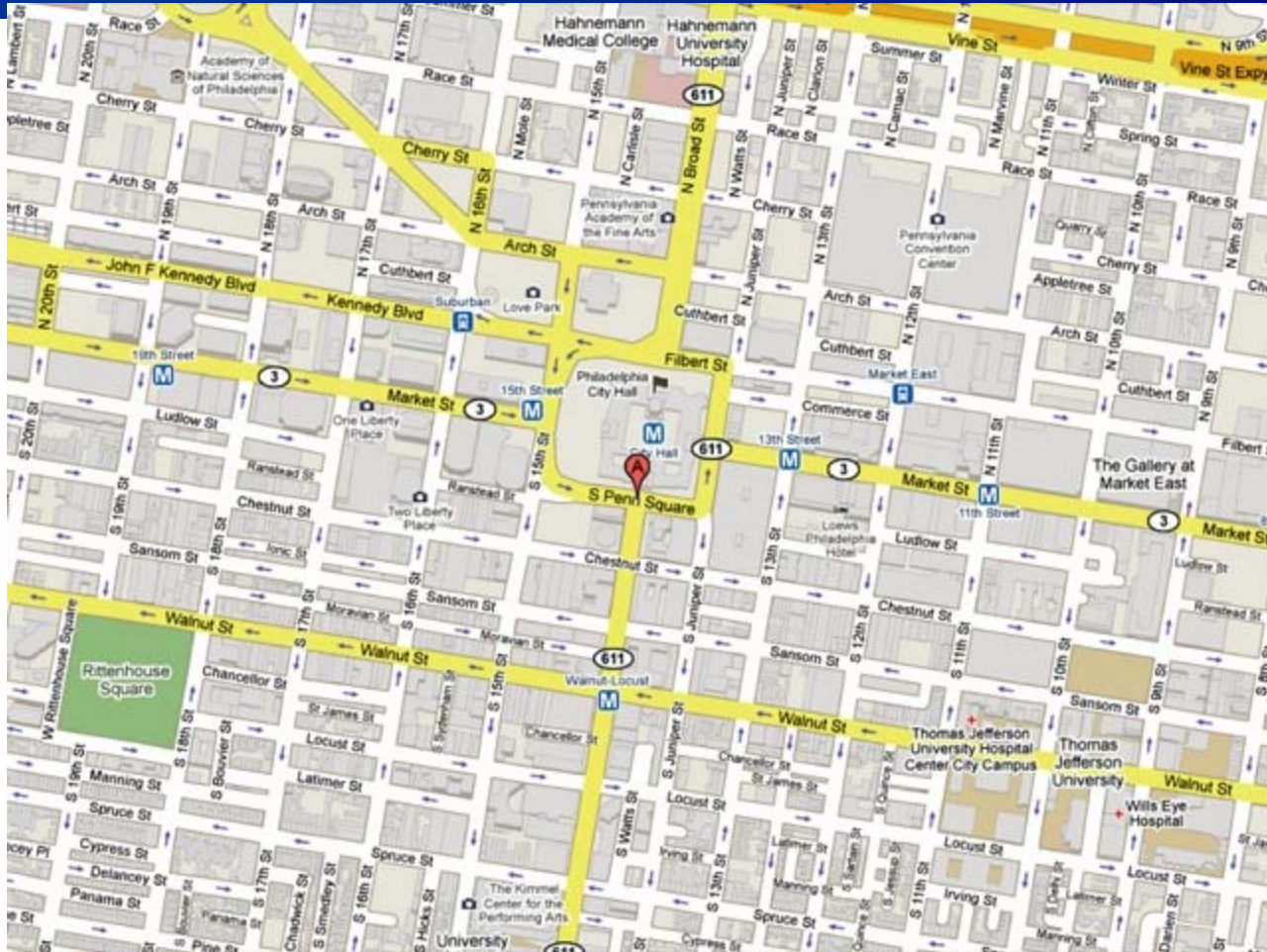


What is a Random Walk?

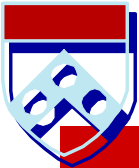
- **Definition**
- **Quantitative Features**



Example: Random Walks from Philadelphia's City Hall

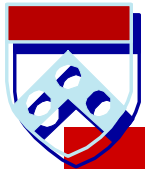
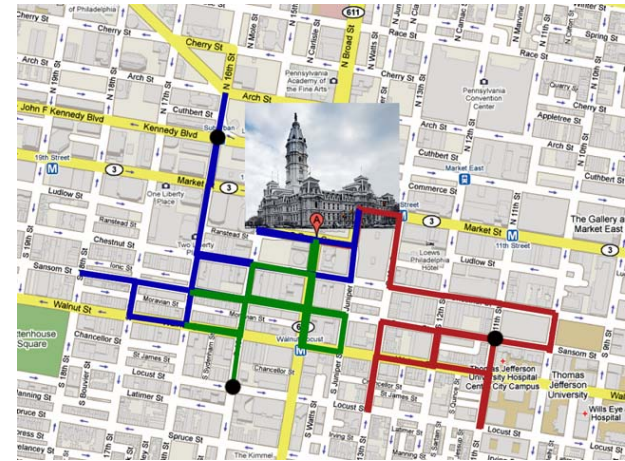


[Click Image to Play Movie](#)



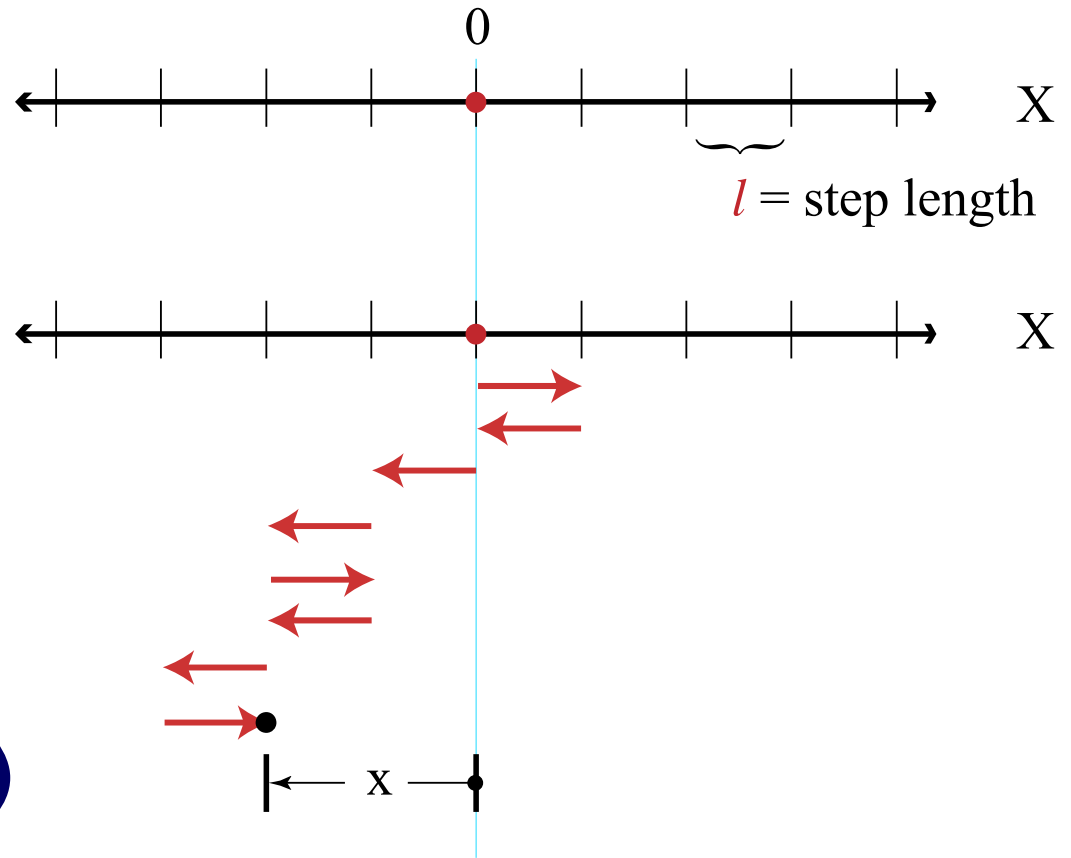
Example: Random Walks from Philadelphia's City Hall

- How far is **typical walker** from starting point after encountering N intersections?
- How much time will it take **typical walker** to travel distance D from starting point?
- What does typical path look like?
- How to get quantitative about problem?

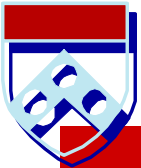


Random Walk in One Dimension

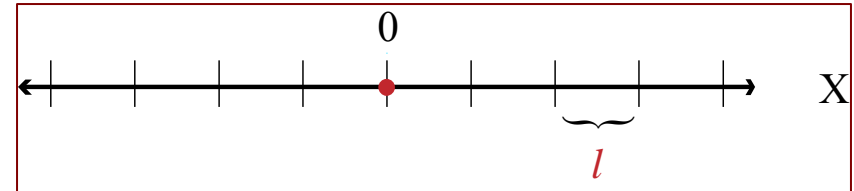
- Start at Origin
- Flip Coin:
 - heads \Rightarrow go right
 - tails \Rightarrow go left
- Flip Coin again & again (N times)



$$x = -2l \text{ after } 8 \text{ random steps}$$



Mean Displacement from Starting Point



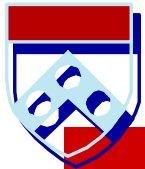
l_i = displacement of i^{th} step = $\pm l$

x = distance traveled by Random Walker after N steps

$$x = l_1 + l_2 + l_3 + \dots + l_N = \sum_{i=1}^N l_i$$

$\langle x \rangle$ = Average value of x for many independent walkers
 $= \langle l_1 + l_2 + \dots + l_N \rangle = \langle l_1 \rangle + \langle l_2 \rangle + \dots + \langle l_N \rangle = 0$

Equally probable to land Right/Left.



Mean-Square (Root-Mean-Square) Displacement from Starting Point

$$\mathbf{x}^2 = (l_1 + l_2 + \dots + l_N) (l_1 + l_2 + \dots + l_N) = \sum_{i=1}^N l_i^2 + \sum_{i \neq j} l_i l_j$$

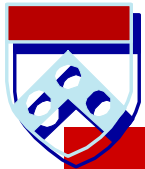
$$\langle \mathbf{x}^2 \rangle = \sum_{i=1}^N \langle l_i^2 \rangle + \sum_{i \neq j} \langle l_i l_j \rangle$$

$$\langle l_i^2 \rangle = \frac{1}{2} [(+l \cdot +l) + (-l \cdot -l)] = l^2$$

$$\langle l_i l_j \rangle = \frac{1}{4} [(+l \cdot +l) + (+l \cdot -l) + (-l \cdot +l) + (-l \cdot -l)] = 0$$

$$\langle \mathbf{x}^2 \rangle = Nl^2$$

$$\begin{aligned} \sqrt{\langle \mathbf{x}^2 \rangle} &= \text{Root mean-square displacement} \\ &= \sqrt{N} l \end{aligned}$$

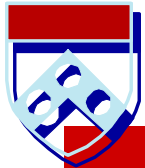


Random Walk in One Dimension

After N steps, typical walker will be $\sqrt{N}l$ from starting point!

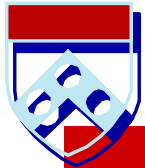
\sqrt{N} factor is THE fundamental feature of Random Walks

To travel distance $10l$ from starting point, require ~ 100 random steps of length l !



Random Walk in One Dimension

- **What about time dependence?**
- **How does typical displacement distance from starting point depend on time?**



Random Walks: Time Dependence

$\langle x^2(t) \rangle$ = Typical mean-square displacement after time, t .

Assume: v = walker speed during step

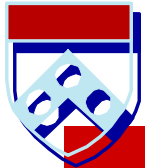
t_0 = time for step

$$\Rightarrow l = v t_0 \Rightarrow N = \frac{t}{t_0} = \# \text{ steps in time, "t"}$$

$$\langle x^2(t) \rangle = N l^2 = \left(\frac{t}{t_0}\right) (v t_0)^2 = (v^2 t_0) t = (v l) t$$

$$\sqrt{\langle x^2(t) \rangle} \sim \sqrt{t}$$

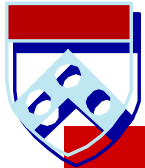
Walker Displacement Distance Scales with \sqrt{t} !



Random Walks: Time Dependence

$\sqrt{\text{time}}$ Behavior is a Fundamental Feature of Random Walks

If it takes 1 minute to travel 1 meter, then it will take 100 minutes to travel 10 meters from starting point.



Random Walks: Diffusion Coefficient

1-Dimension



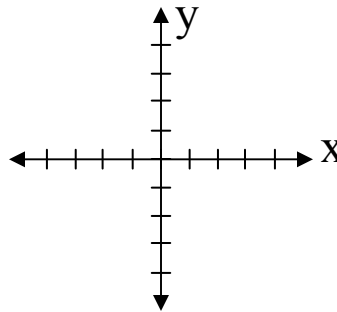
$$\langle x^2 \rangle = 2Dt$$

↑ Diffusion Coefficient

$$D = \frac{1}{2} (v^2 t_0) = \frac{1}{2} (vl)$$

Similarly

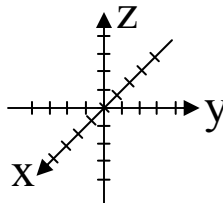
2-Dimensions



$$r^2 = x^2 + y^2$$

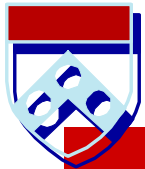
$$\langle r^2 \rangle = 4Dt$$

3-Dimensions



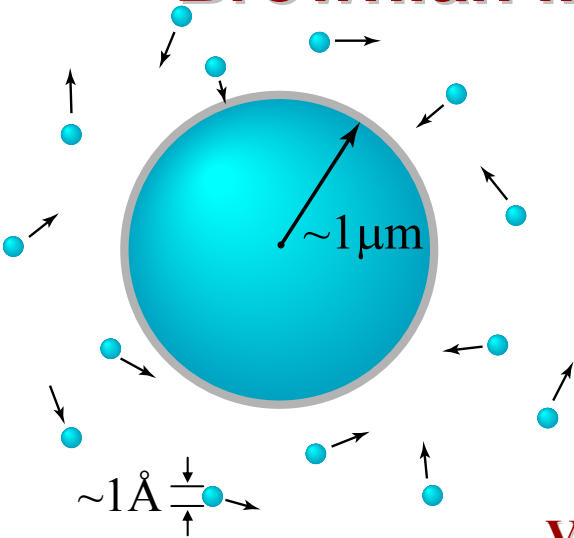
$$r^2 = x^2 + y^2 + z^2$$

$$\langle r^2 \rangle = 6Dt$$



Random Walks: Connection to Diffusion

Brownian Motion

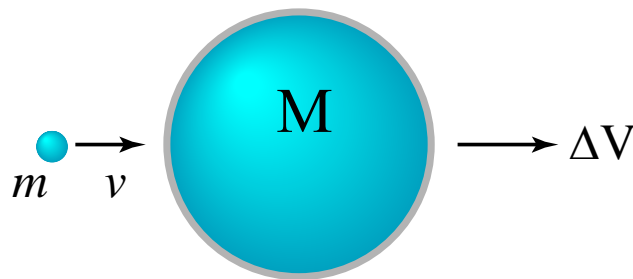


Perpetual Motion of Small Particles in Water?
Is it alive?
Why do particles move?



Robert Brown, Botanist

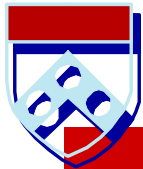
Von Nageli (1879): Suggested molecular bombardment causes movement.



$$\Delta V \sim \frac{m}{M} v$$

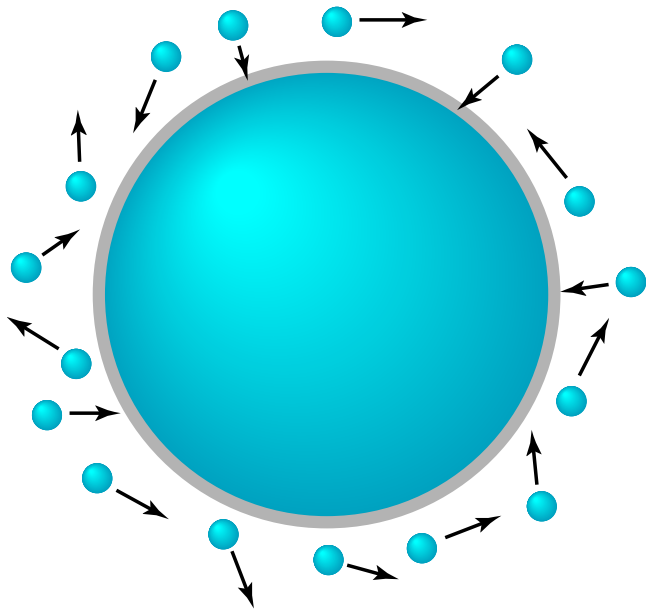
Single molecule at room temperature: $\Delta V \sim 2 \times 10^{-6}$ cm/sec.

But concluded effect, WAY TOO SMALL!



Random Walks: Connection to Diffusion

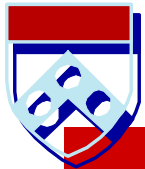
Deeper Idea (underlying Einstein's thinking)



Many (N) molecules collide **randomly** with large particle.

If ΔV is velocity change due to one collision, then $\sim\sqrt{N} \Delta V$ is velocity change induced by N random collisions.

Perpetual Movement is due to Random Fluctuations of the Collision Impulses of many (N) molecules.



Brownian Motion: What is the Diffusion Coefficient?

Random “Impulses” Cause the Particle to Travel the Path of a Random Walker.

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

$$D \sim v^2 t_0 \sim vl$$

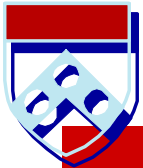
velocity
during step

step
time
duration

step
length

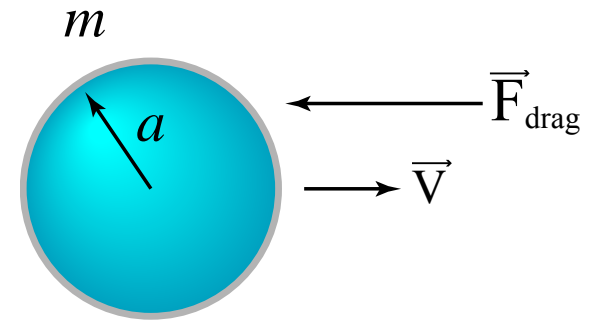
What is step duration, t_0 ?

What is mean-square velocity during step, $\langle v^2 \rangle$?



What is Step Duration t_0 ?

How long for particle to slow down?



Friction, Stokes Drag

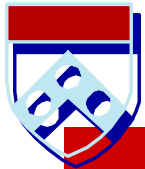
Stoke's Law: $F_{\text{drag}} = -6\pi\eta a\vec{V} = -f\vec{V}$

↑ opposes motion ↑ viscosity of solvent ↑ friction drag coefficient

Newton's Law: $m\vec{a} = \Sigma\vec{F}_{\text{on sphere}}$

$$m \frac{d\vec{V}}{dt} = -f\vec{V}$$

$$\Rightarrow V(t) = V(0)e^{-t/t_0}, \quad t_0 = \frac{m}{f} = \frac{m}{6\pi\eta a} = \text{step duration}$$



What is $\langle v^2 \rangle$?

Equipartition:

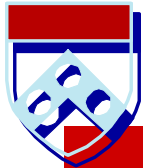
$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

Particle mass

Boltzmann's constant
($N_{\text{Avogadro}} \cdot k = R$)

Temperature

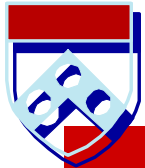
$$\langle v^2 \rangle = \frac{3 kT}{m}$$



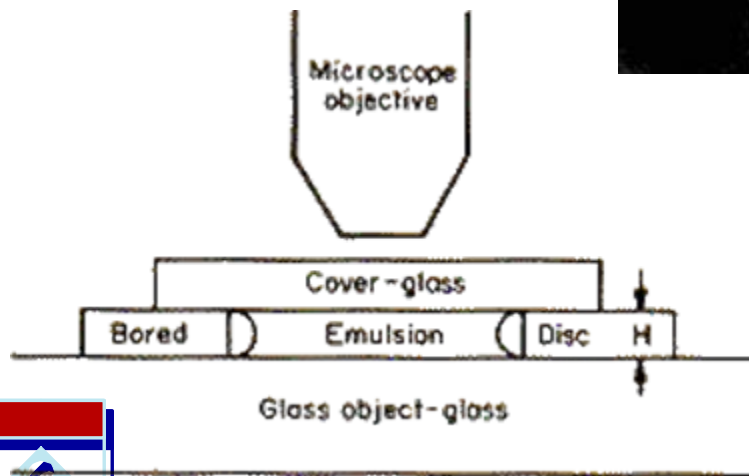
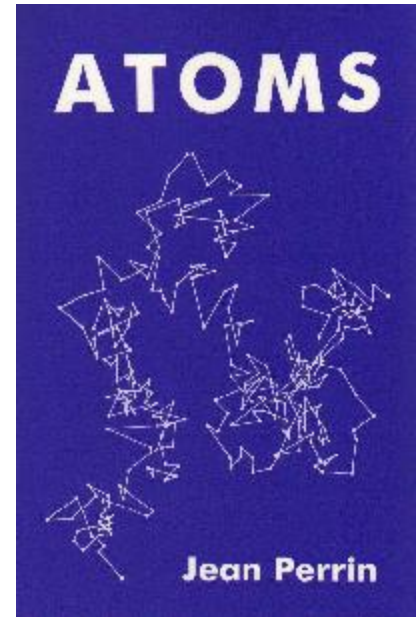
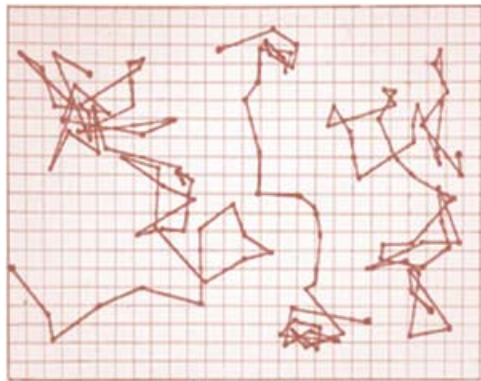
Putting it all together: Brownian Diffusion Coefficient

$$\mathbf{D} \sim \langle v^2 \rangle t_0 \sim \frac{kT}{6 \pi \eta a} \quad \text{Einstein 1905}$$

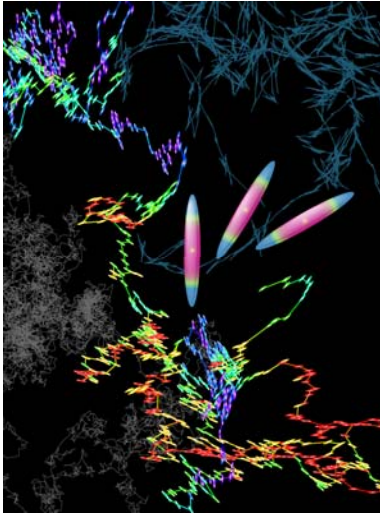
- Brownian Motion is from random fluctuations due to collisions with solvent molecules.
- Simple (relatively) diffusion measurement checks theories.
- Sizes of particles, macromolecules, molecules.
- Friction in fluids.
- New connections between friction, fluctuations, random walks, diffusion.
- Avogadro's Number.



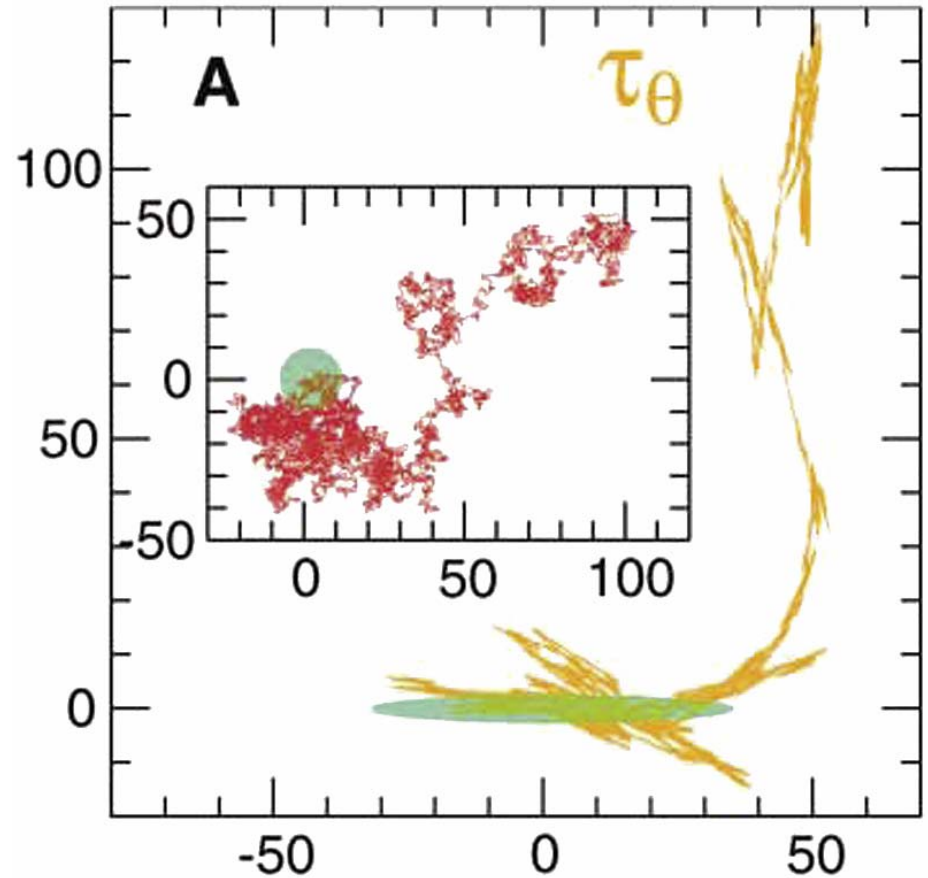
Experiment: Jean Perrin



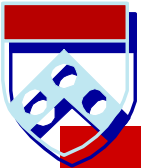
Continued Interest



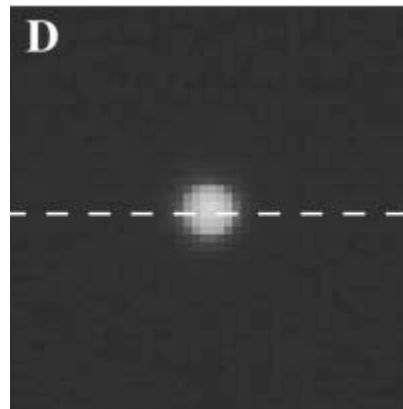
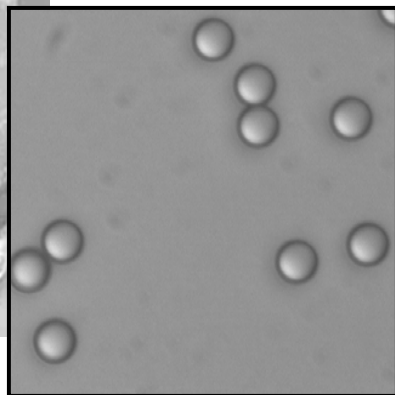
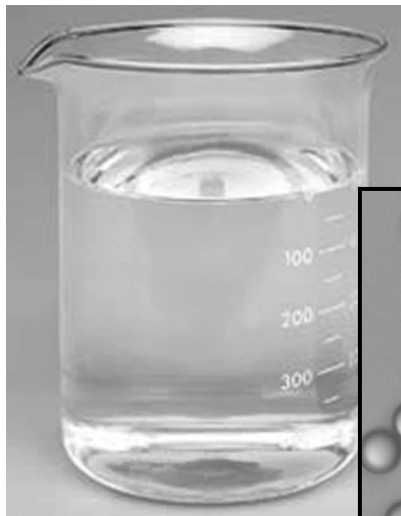
- Translation–Rotation Coupling
- Complex hydrodynamics (shape, dimension, concentration,...), microrheology, starting point for more...



Brownian Motion of an Ellipsoid, Y. Han, A.M. Alsayed, M. Nobili, J. Zhang, T.C. Lubensky, A.G. Yodh, *Science*, 2006

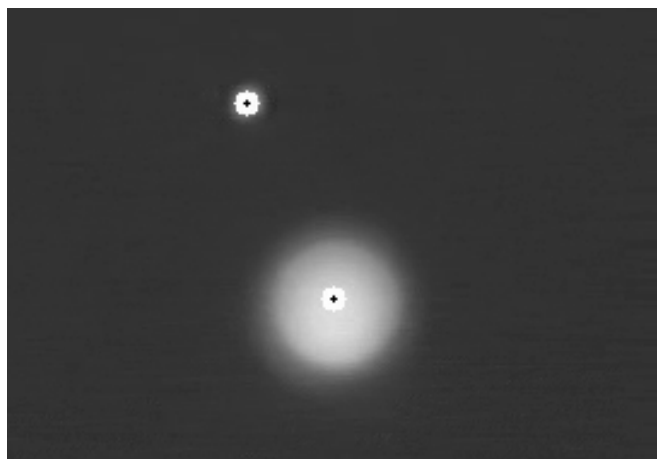
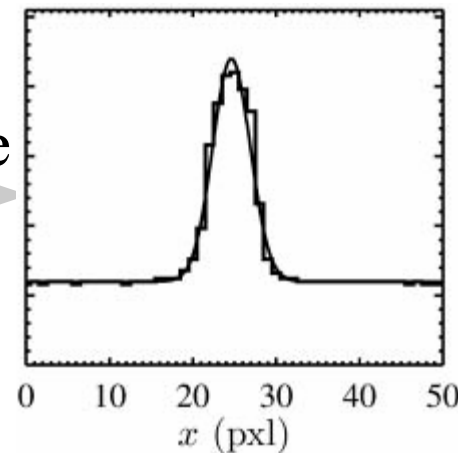


Hands-On Workshop

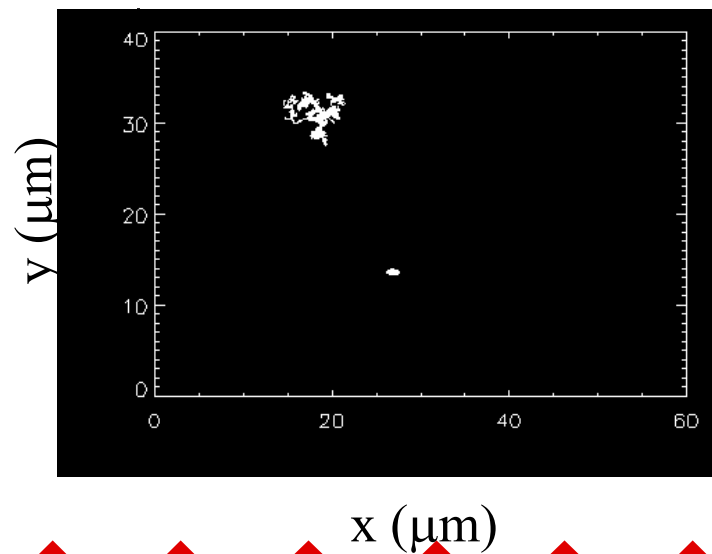


profile

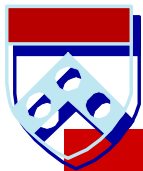
centroid



trajectory



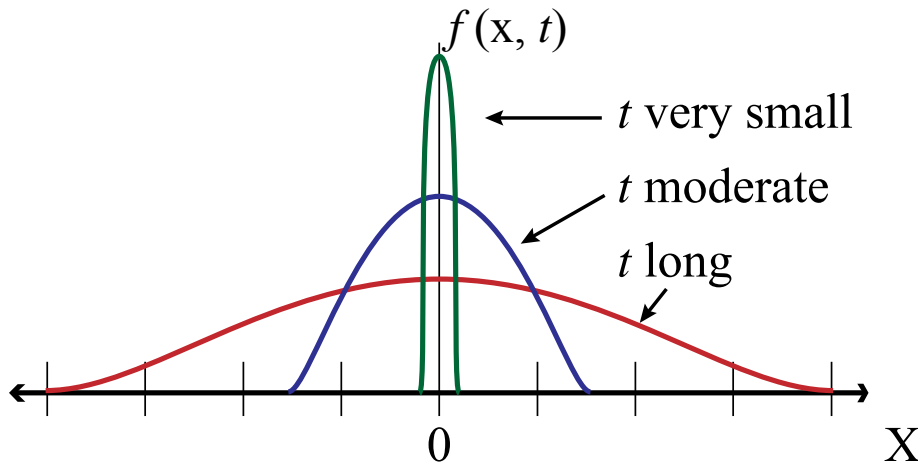
[Click Image to Play Movie](#)



Diffusion Equation

$f(x, t)$ = probability particle at position x at time t , for the $x=0, t=0$ initial condition.

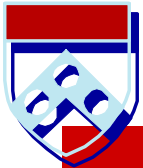
$$f(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$



$$\langle x^2(t) \rangle = 2Dt$$

$$\int_{-\infty}^{+\infty} f(x, t) dx = 1$$

$$\langle x^n \rangle = \int_{-\infty}^{+\infty} x^n f(x, t) dx$$



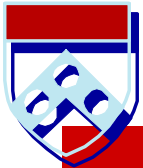
Diffusion Equation

$f(x,t)$ is “Impulse” solution (Green’s Function) of a partial differential equation.

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

What is that Differential Equation?

Suppose many particles are in the system, and each particle moves like a random walker.



Diffusion Equation

Let $n(x,t)$ = Particle concentration x, t .

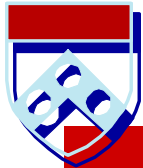
$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \quad (1\text{-dimension})$$

$$\frac{\partial n(\vec{r},t)}{\partial t} = D \nabla^2 n(\vec{r},t) \quad (3\text{-dimension})$$

Boundary + Initial Conditions \rightarrow Solutions for $n(\vec{r},t)$

* If all particles initially at $x=0$
 $n(x,t) \propto f(x,t) !$

Random Walk Physics \leftrightarrow Diffusion Physics



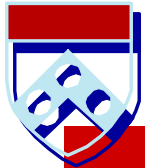
Diffusion Equation

Random walks provide microscopic pictures for diffusive process.

- **Mixing**
- **Heat transport**
- **Irreversible Phenomena**

▪
▪
▪

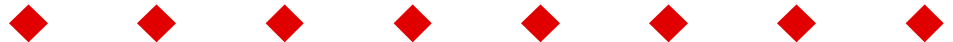
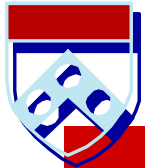
Diffusion Equation provides simple means to compute macroscopic effects, i.e. the effects due to many random walkers.



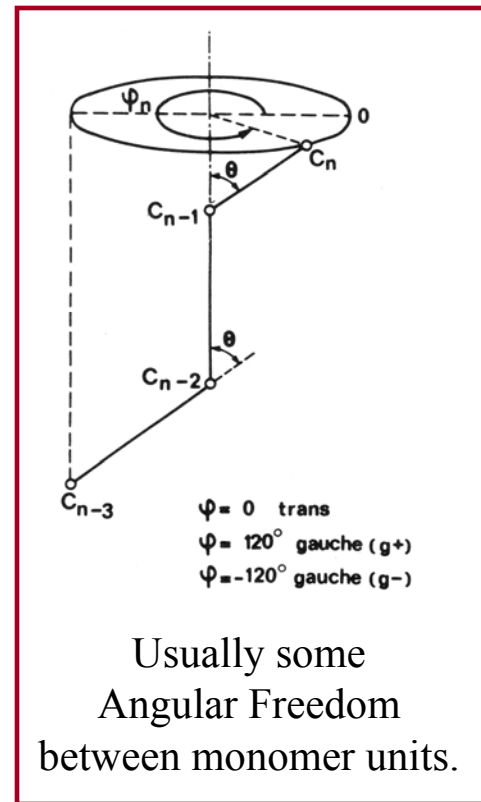
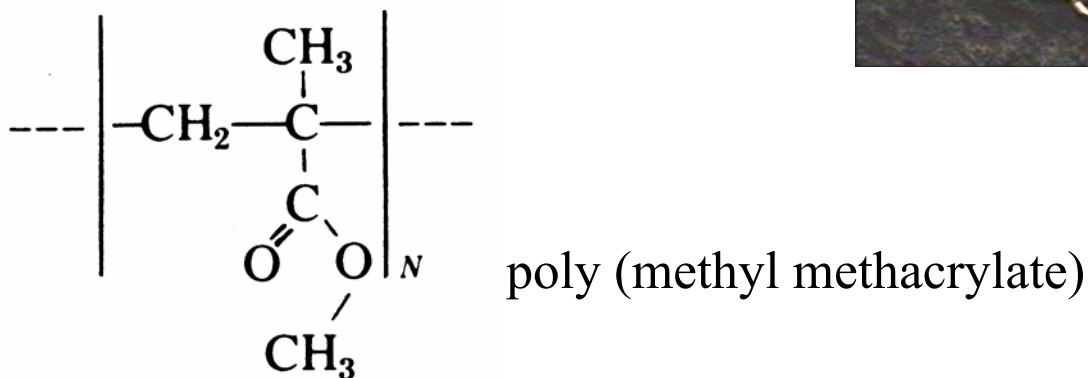
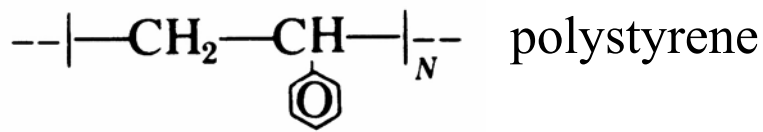


Other Examples

- **Polymers**
- **Light Diffusion**



Random Walks and Flexible Polymers

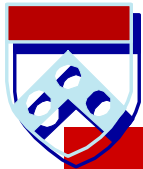


Figures from: *Scaling Concepts in Polymer Physics* (de Gennes)

Define:

Persistence length of Polymer = l = length of “straight” segments in chain.

Monomer repeat distance $< l <$ many repeat distances

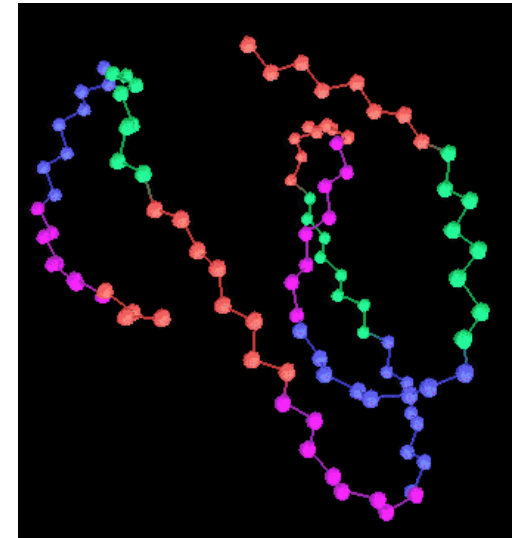
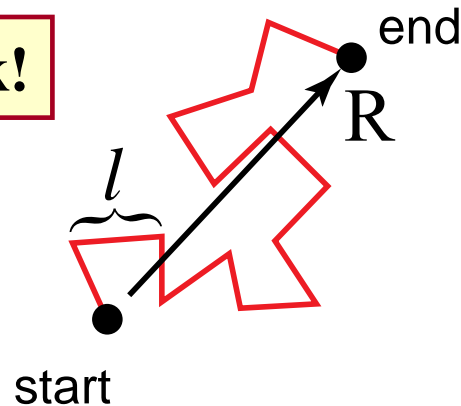


What is the “size” of Isolated Polymer Coil?

Total length of Polymer = $L \gg l$

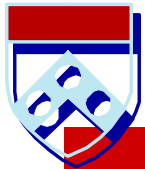
steps in Polymer coil = $N = \frac{L}{l}$; $L = Nl$

Analyze as Random Walk!



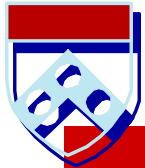
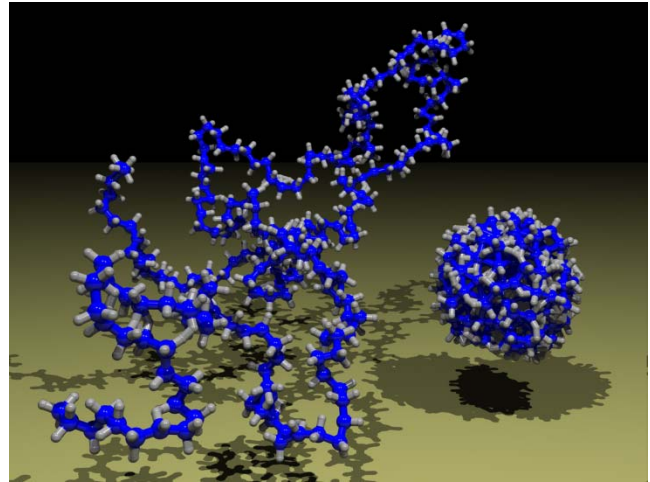
$$\sqrt{\langle R^2 \rangle} \sim \text{Coil diameter} \sim \sqrt{N}l \\ \sim \sqrt{L}l$$

Size scales as \sqrt{L} , \sqrt{N}

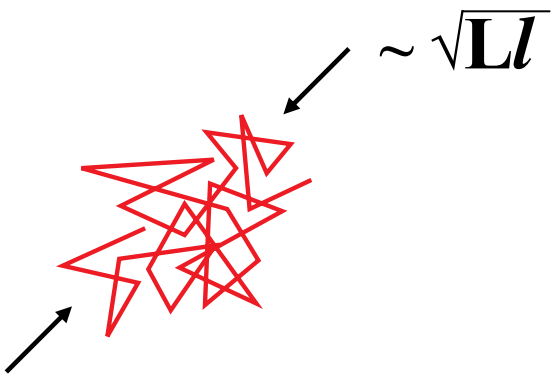


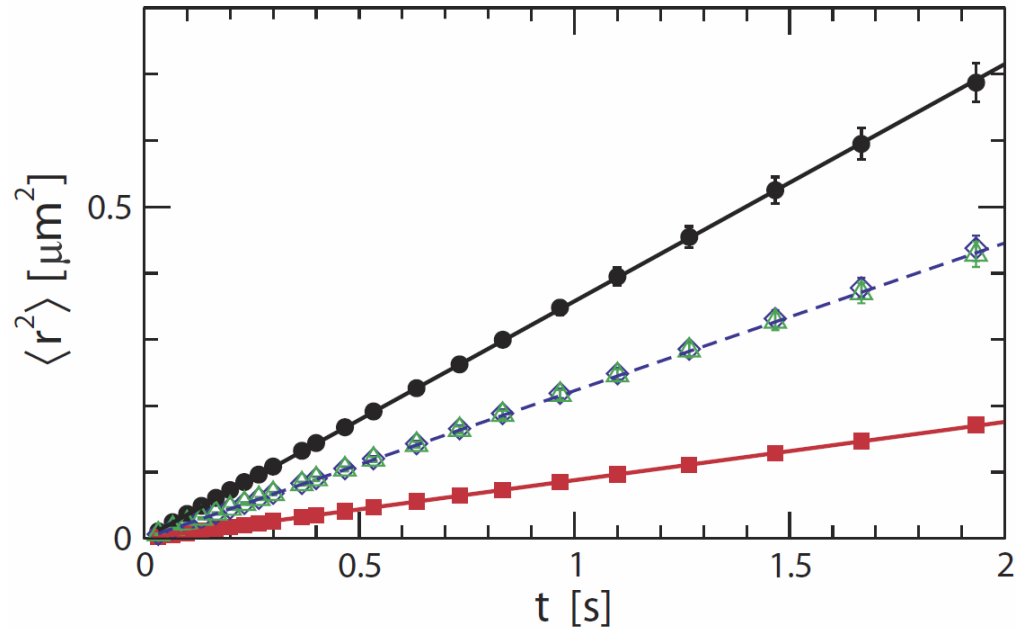
What is the “size” of Isolated Polymer Coil?

How to measure size?

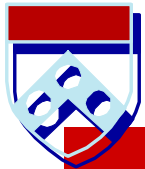


Use Brownian Motion (Diffusion) to Measure Coil Size


$$D = \frac{kT}{6 \pi \eta (\sqrt{Ll})}$$



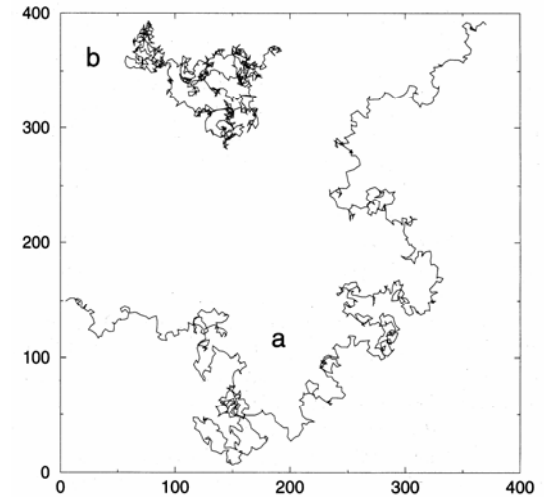
Change coil length, to confirm \sqrt{L} , \sqrt{N} dependence!



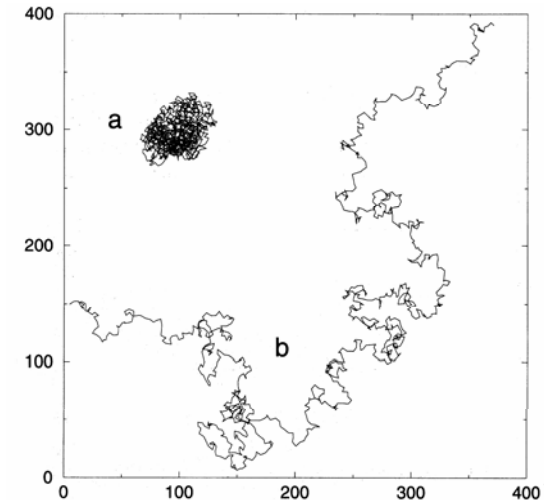
Further Complications

Interactions between links

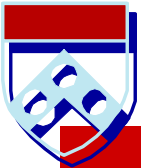
- **Self Avoidance**
 - Coil Swells $\sim N^{3/4}$ (in 2D)
 - Coil Swells Less $\sim N^{3/5}$ (in 3D)
- **Attractive interactions**
 - Coil Collapses!



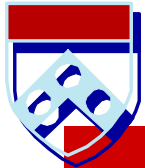
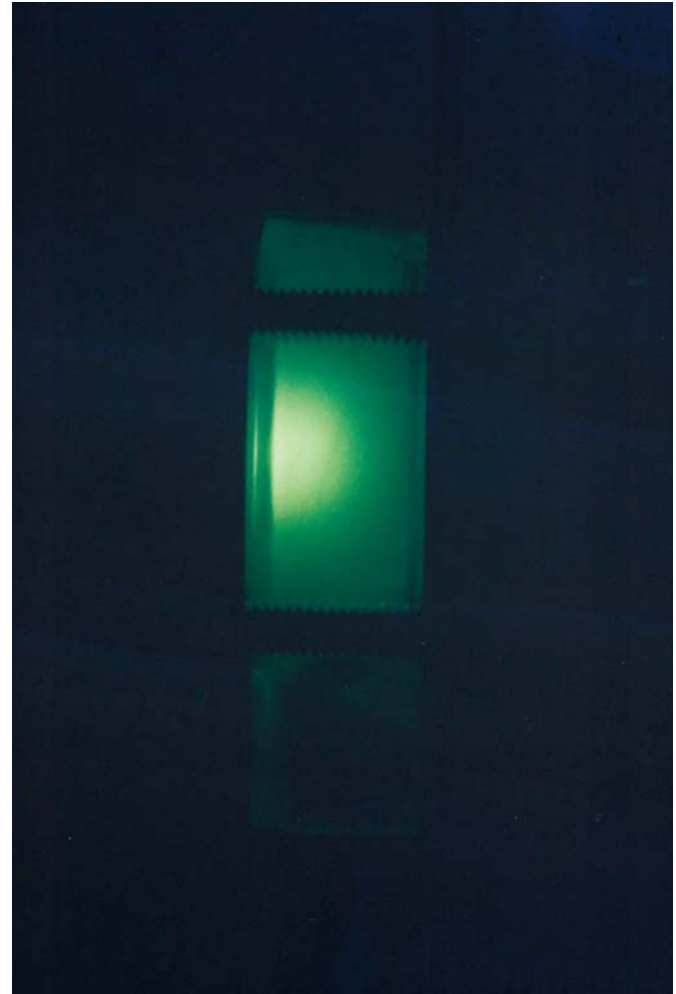
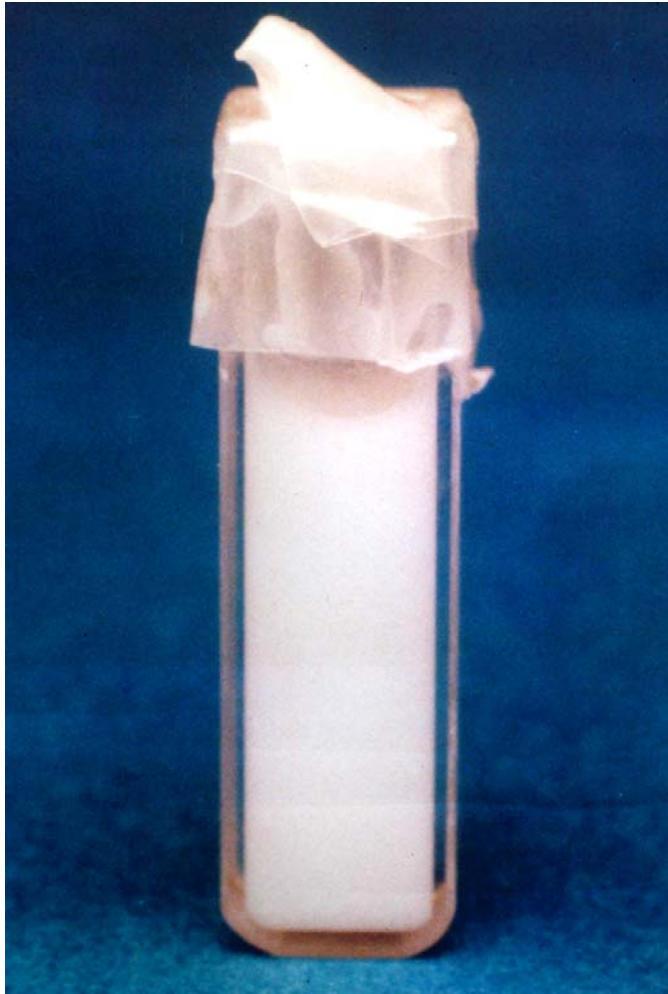
Figures from: *Giant Molecules* (Grosberg, Khokhlov)



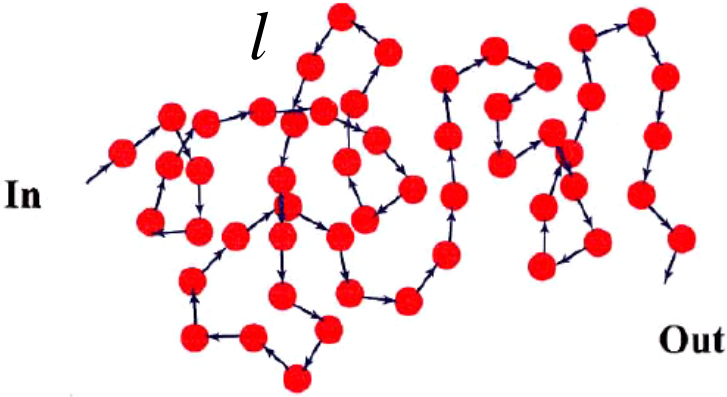
Measure using Diffusion effects.



Light Diffusion



What happens when Multiple Scattering becomes important?



l - random walk step of photon

l (Scattering)

l_a (Absorption)

Photon Concentration Obeys Diffusion Equation (with loss).

$$\frac{\partial \Phi(r, t)}{\partial t} = D \nabla^2 \Phi(r, t) - \nu \frac{1}{l_a} \Phi(r, t) + \nu S(r, t)$$

$\Phi(\vec{r}, t) \sim$ Photon Concentration

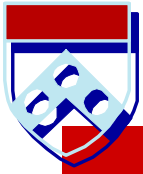
$S =$ Light Source term

$\nu =$ Speed of Light in tissue

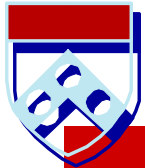
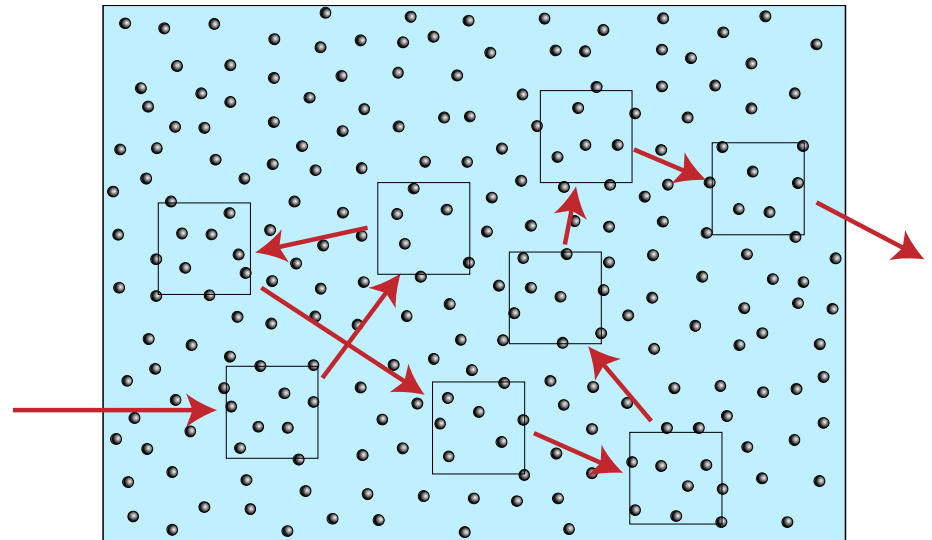
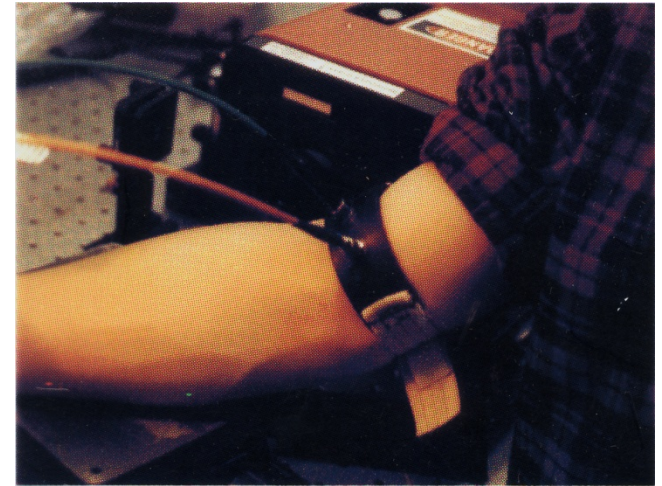
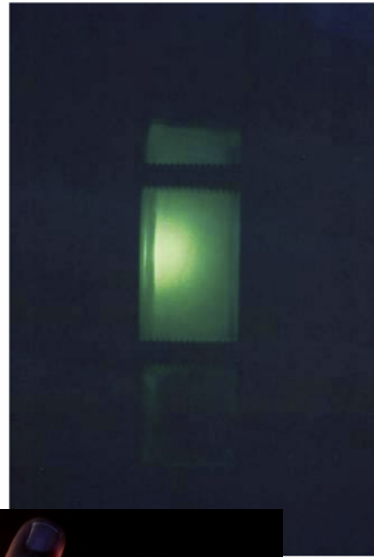
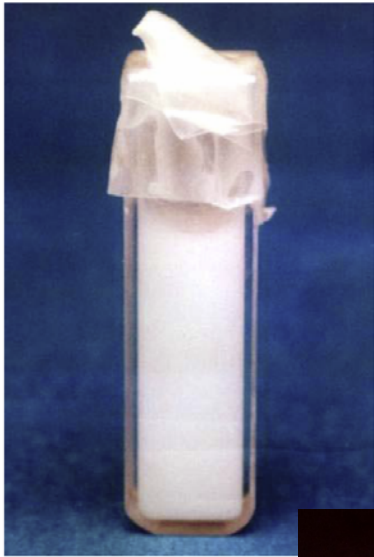
$l_a =$ Absorption Coefficient (cm^{-1})

$D = \frac{1}{3} \nu l =$ Photon Diffusion Coefficient

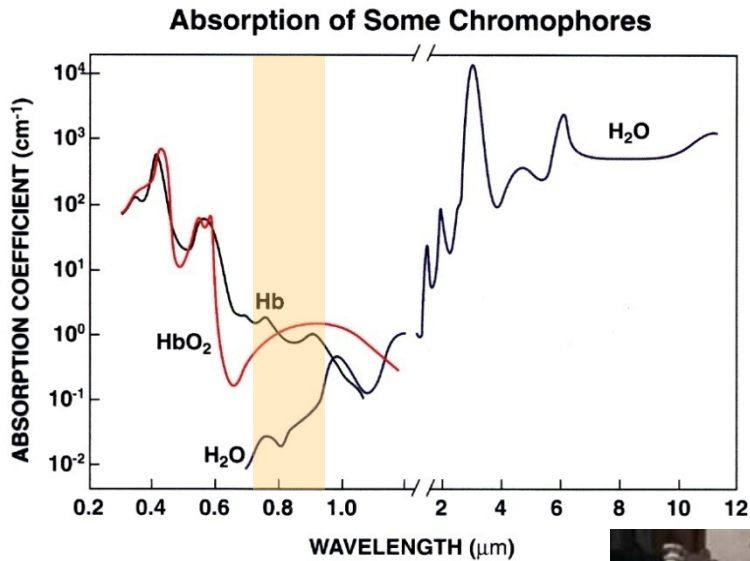
$l =$ Scattering Coefficient (cm^{-1})



Problem of Tissue: Multiple Scattering



The Dream.



Yodh and Chance
Spectroscopy &
imaging
with diffusing light,

Physics Today (1995).



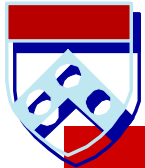
from: *Star Trek*



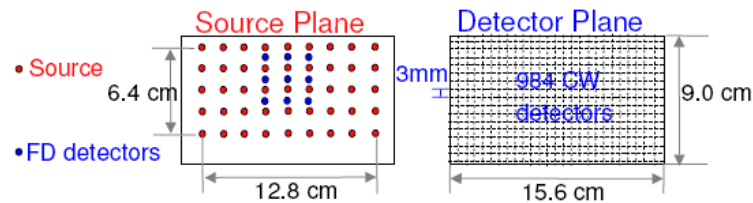
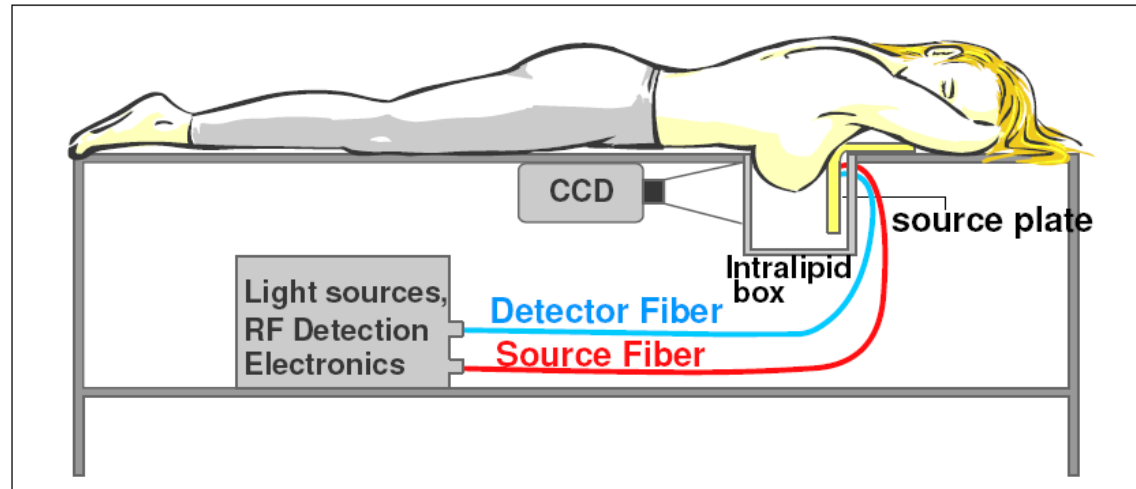
from: *Minority Report*



◆ ◆ ◆ Diffuse Optical Tomography of Breast



Diffuse Optical Tomography of Breast



Light sources

- 45 source
- 690, 750, 786, 830 nm
- 650, 905 nm

Detectors

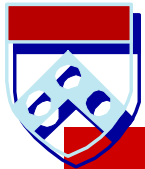
- CCD CW Transmission
- 9 FD Remission

Other features

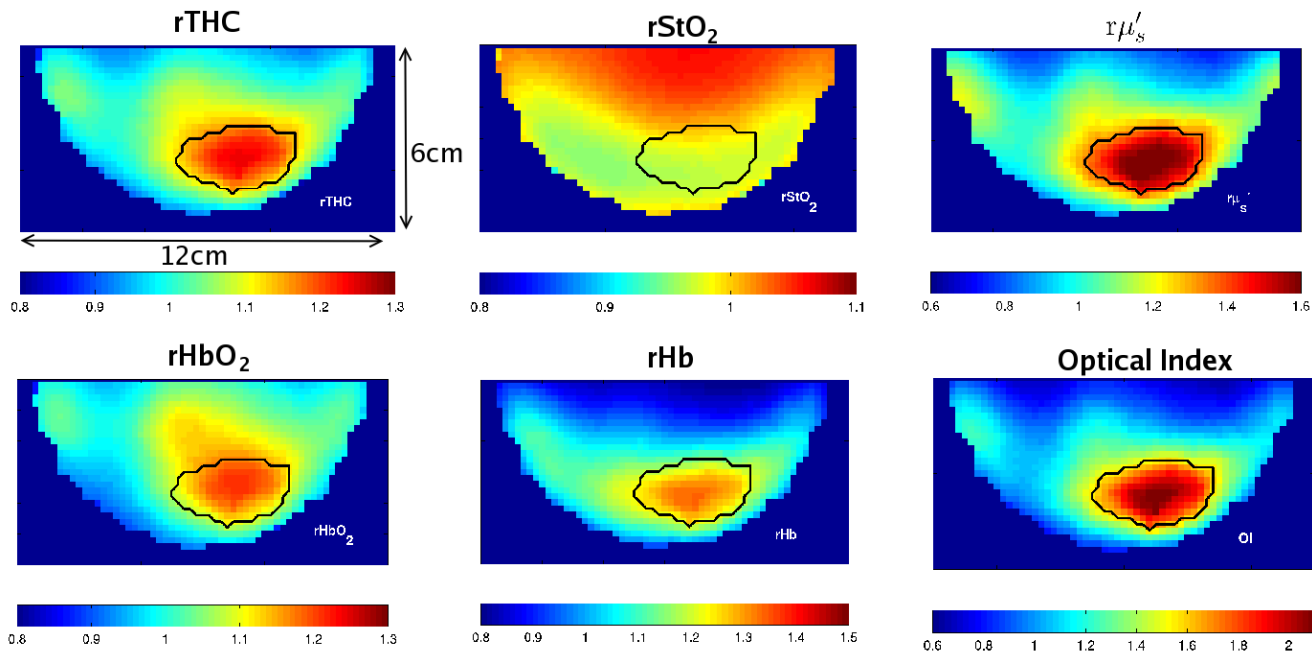
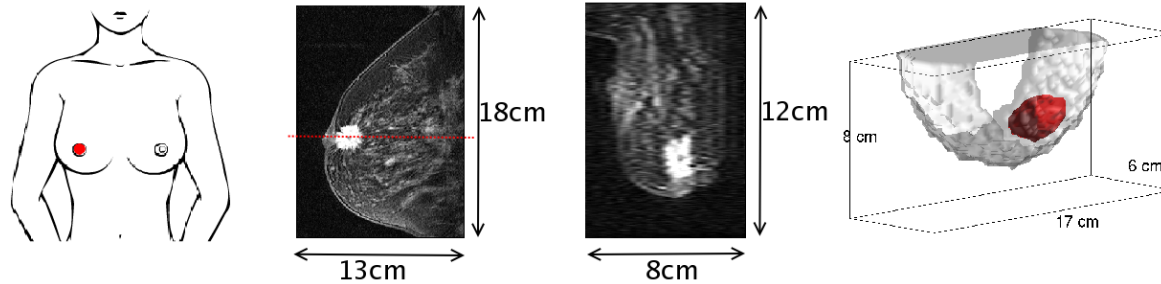
- matching fluid
- soft compression

Data set : 45 x 984 x 6 ~ 266,000

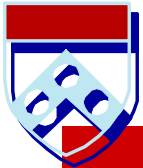
Acquisition time = 8 minutes



Solve Inverse Problem Based on Diffusion of Photons

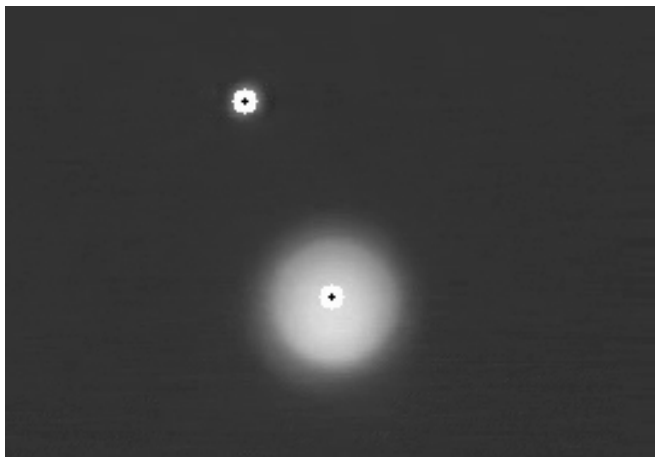


- 53-year-old post-menopausal female, 2.2 cm invasive ductal carcinoma



Summary

- Random Walks contain many deep and useful physical concepts.
- Show up in a surprisingly diverse array of physical situations.



→
trajectory

