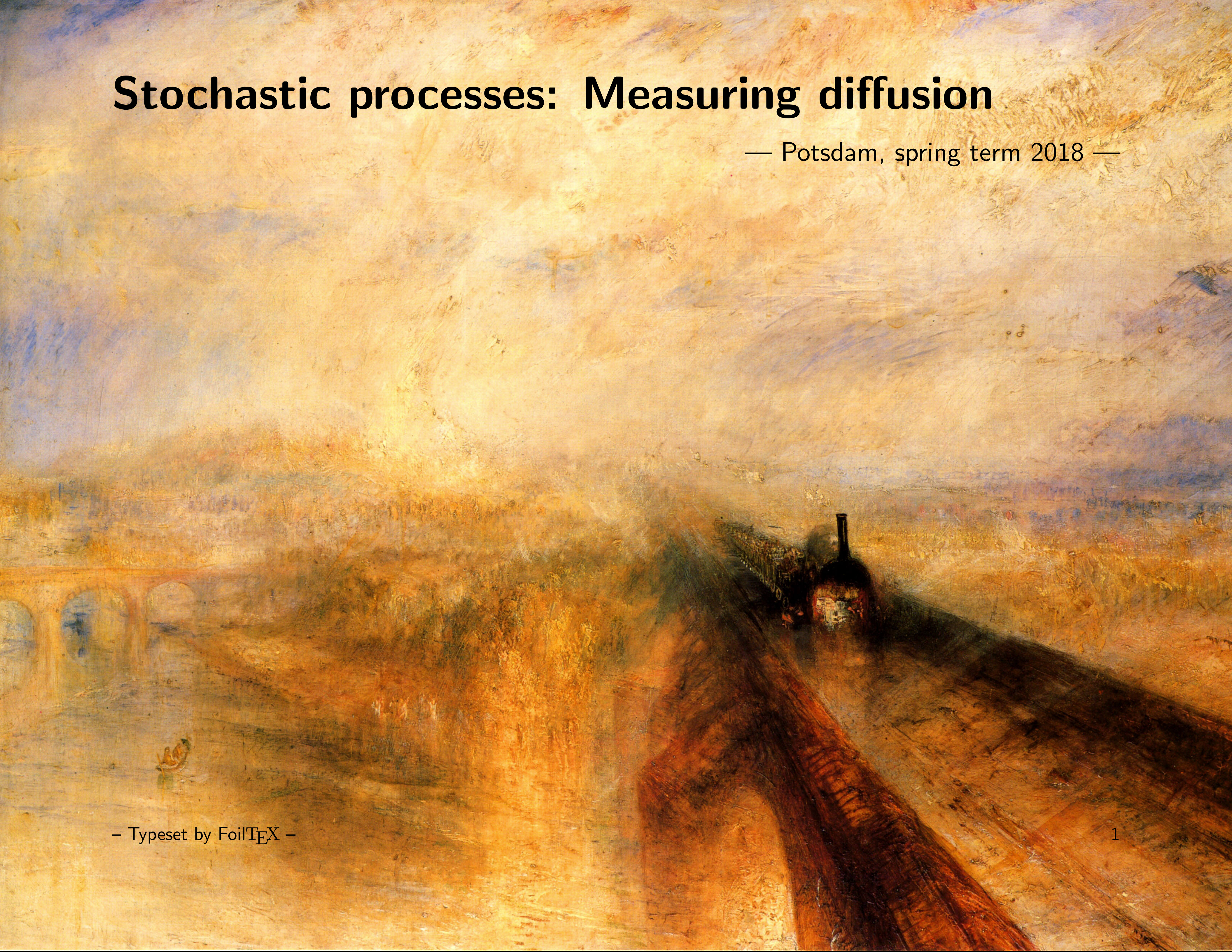


Stochastic processes: Measuring diffusion

— Potsdam, spring term 2018 —

Relaxation processes

Deborah number:

$$\daleth = \frac{\text{Relaxation time scale}}{\text{Experimental time}}$$

The tar pitch drop experiment (U Queensland):

Date	Event
1927	Setup experiment
1930	Stem cut
12/1938	1st drop fell
02/1947	2nd drop fell
04/1954	3rd drop fell
05/1962	4th drop fell
08/1970	5th drop fell
04/1979	6th drop fell
07/1988	7th drop fell
11/2000	8th drop fell

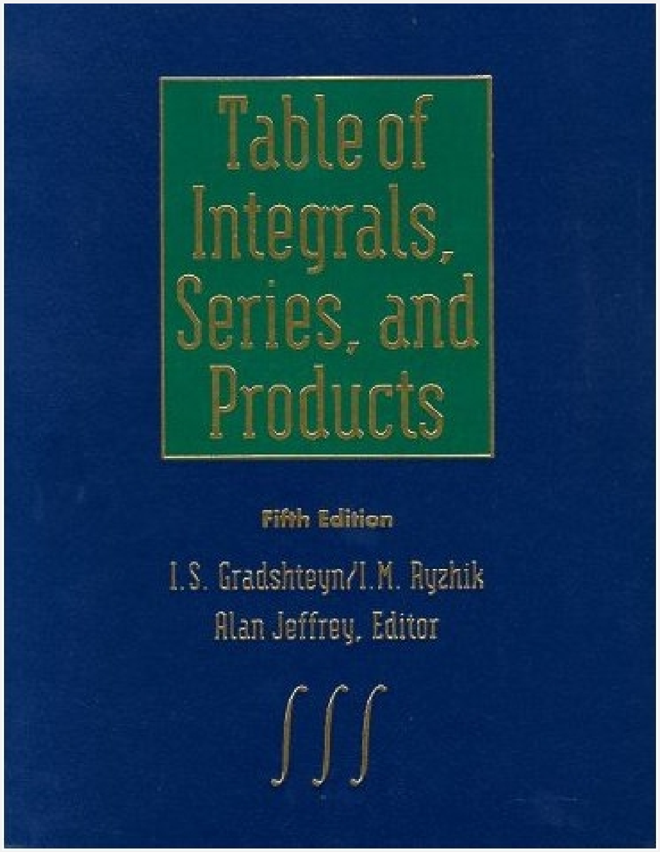
Inverse Laplace transform

With Mathematica:

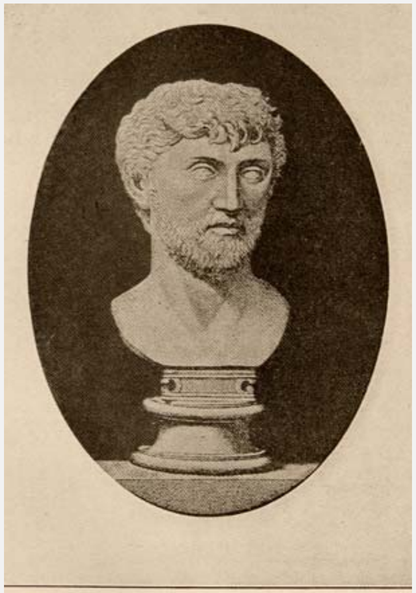
$$\texttt{In[1]:} = \texttt{InverseLaplaceTransform[phi0/(u + 1/tau), u, t]}$$

$$\texttt{Out[1]} = e^{-\frac{t}{tau}}\,\texttt{phi0}$$

With tables:



. . . for behold whenever
The sun's light and the rays, let in, pour down
Across dark halls of houses: thou wilt see
The many mites in many a manner mixed
Amid a void in the very light of the rays,
And battling on, as in eternal strife,
And in battalions contending without halt,
In meetings, partings, harried up and down.


LUCRETIUS.

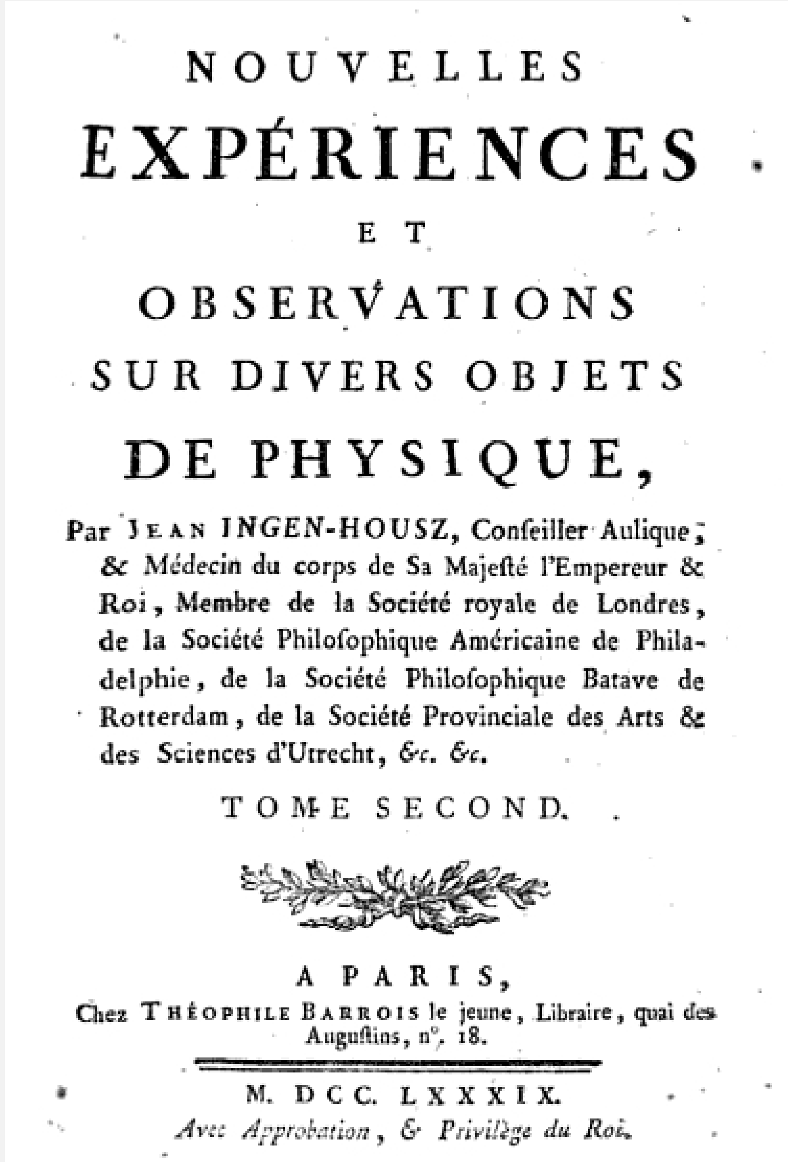
Laß in ein dunkeles Zimmer einmal die Strahlen der Sonne
Fallen durch irgendein Loch und betrachte dann näher den Lichtstrahl:
Du wirst dann in dem Strahl unzählige, winzige Stäubchen
Wimmeln sehn, die im Leeren sich mannigfach kreuzend vermischen,
Die wie in ewigem Kriege sich Schlachten und Kämpfe zu liefern
Rottenweise bemühen und keinen Moment sich verschnaufen.
Immer erregt sie der Drang zur Trennung wie zur Verbindung.

On the Nature of Things, Titus Lucretius Carus (50 BCE)

http://classics.mit.edu//Carus/nature_things.html

Dutch physician Jan Ingenhousz 1785

Described the jittery motion of coal dust on an alcohol surface



NOUVELLES

EXPÉRIENCES

ET

OBSERVATIONS

SUR DIVERS OBJETS

DE PHYSIQUE,

Par JEAN INGEN-HOUSZ, Conseiller Aulique, & Médecin du corps de Sa Majesté l'Empereur & Roi, Membre de la Société royale de Londres, de la Société Philosophique Américaine de Philadelphie, de la Société Philosophique Batave de Rotterdam, de la Société Provinciale des Arts & des Sciences d'Utrecht, &c. &c.

TOME SECOND.

A PARIS,

Chez THÉOPHILE BARROIS le jeune, Libraire, quai des Augustins, n°. 18.

M. DCC. LXXXIX.

Avec Approbation, & Privilège du Roi.

This plant was Clarkia pulchella, of which the grains of pollen, taken from antherae full grown, but before bursting, were filled with particles or granules of unusually large size, varying from nearly 1/4000th to 1/5000th of an inch in length, and of a figure between cylindrical and oblong, perhaps slightly flattened, and having rounded and equal extremities. While examining the form of these particles immersed in water, I observed many of them very evidently in motion; their motion consisting not only of a change of place in the fluid, manifested by alterations in their relative positions, but also not unfrequently of a change of form in the particle itself; a contraction or curvature taking place repeatedly about the middle of one side, accompanied by a corresponding swelling or convexity on the opposite side of the particle. In a few instances the particle was seen to turn on its longer axis. These motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the fluid, nor from its gradual evaporation, but belonged to the particle itself.—1828

Microscopical observations

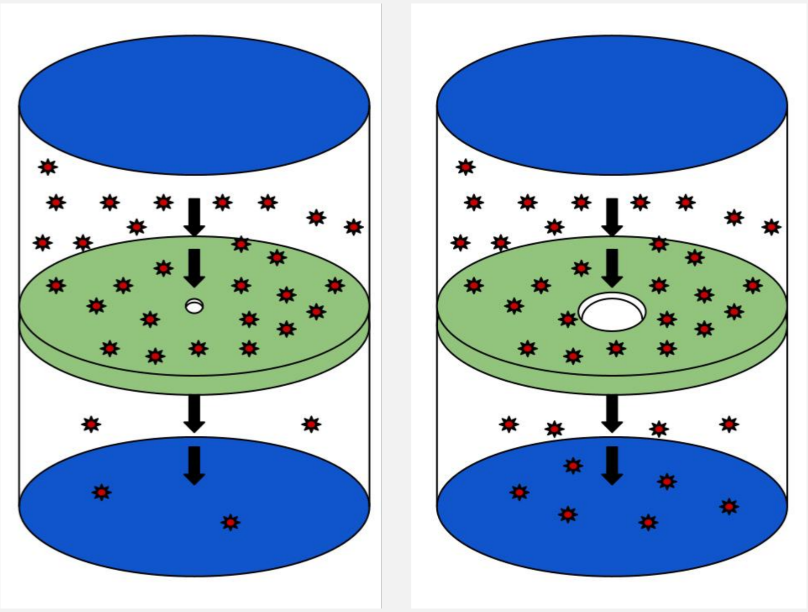
on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies

Rocks of all ages, including those in which organic remains have never been found, yielded the molecules in abundance. Their existence was ascertained in each of the constituent molecules of granite, a fragment of the Sphinx being one of the specimens examined.

R Brown, Edinburgh new Philosophical Journal 358-371 (1828)

Scottish chemist Thomas Graham 1846

Formulates a law of effusion of gases



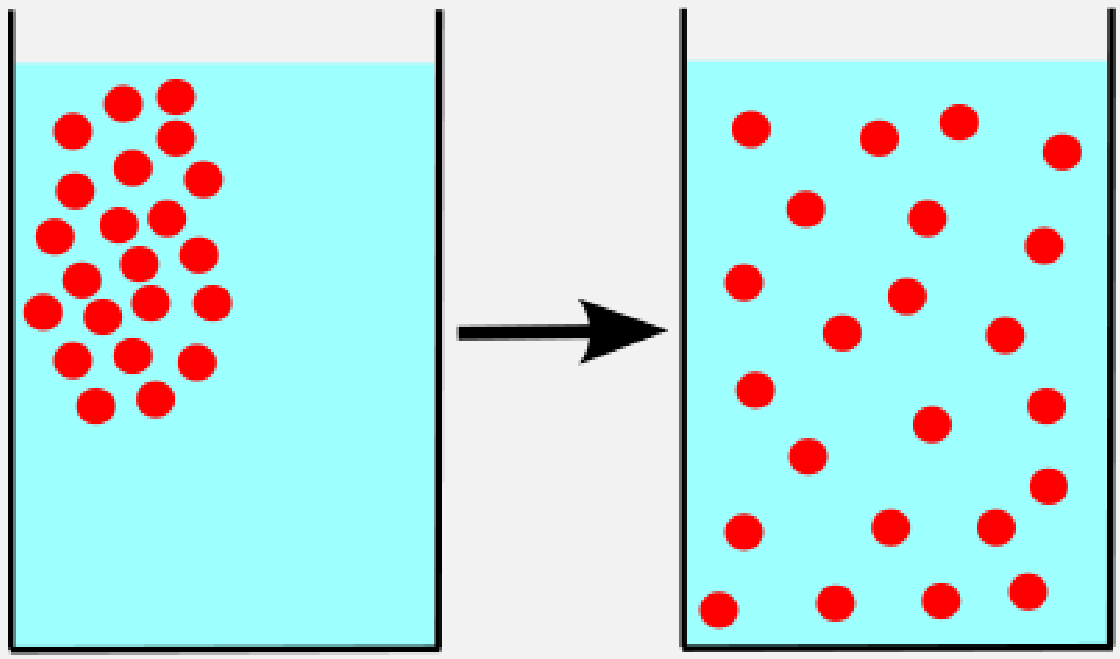
Effusion (left) vs diffusion (right)

Graham's law:

$$\frac{\text{Rate of effusion of gas 1}}{\text{Rate of effusion of gas 2}} = \sqrt{\frac{M_2}{M_1}}$$

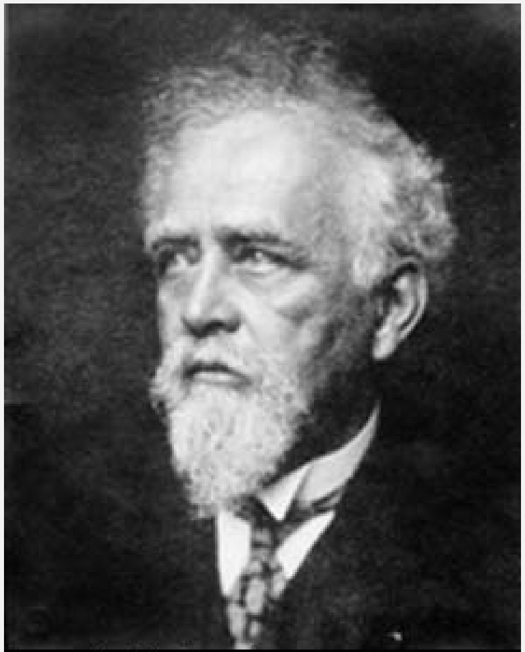
M_i: molecular mass

Diffusion, schematic idea

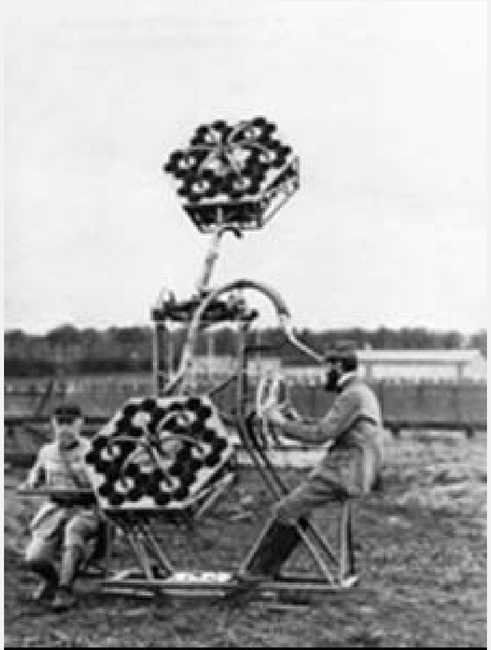


The bromine experiment

Jean Perrin

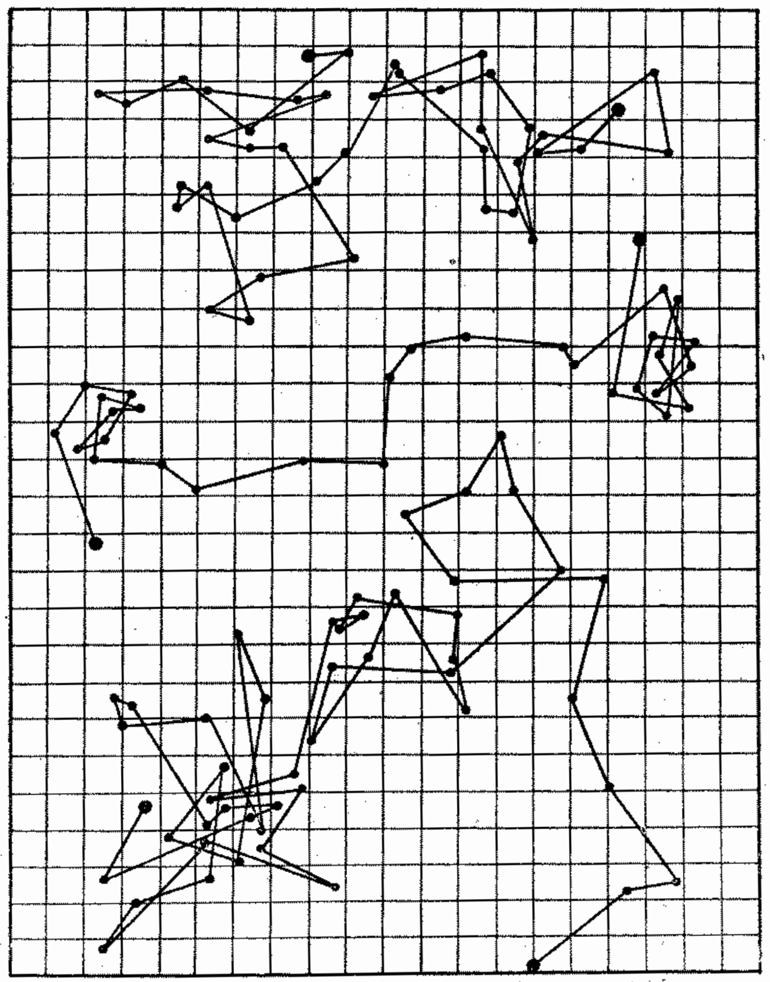

Scanned at the American Institute of Physics

Scanned at the American Institute of Physics


Scanned at the American Institute of Physics

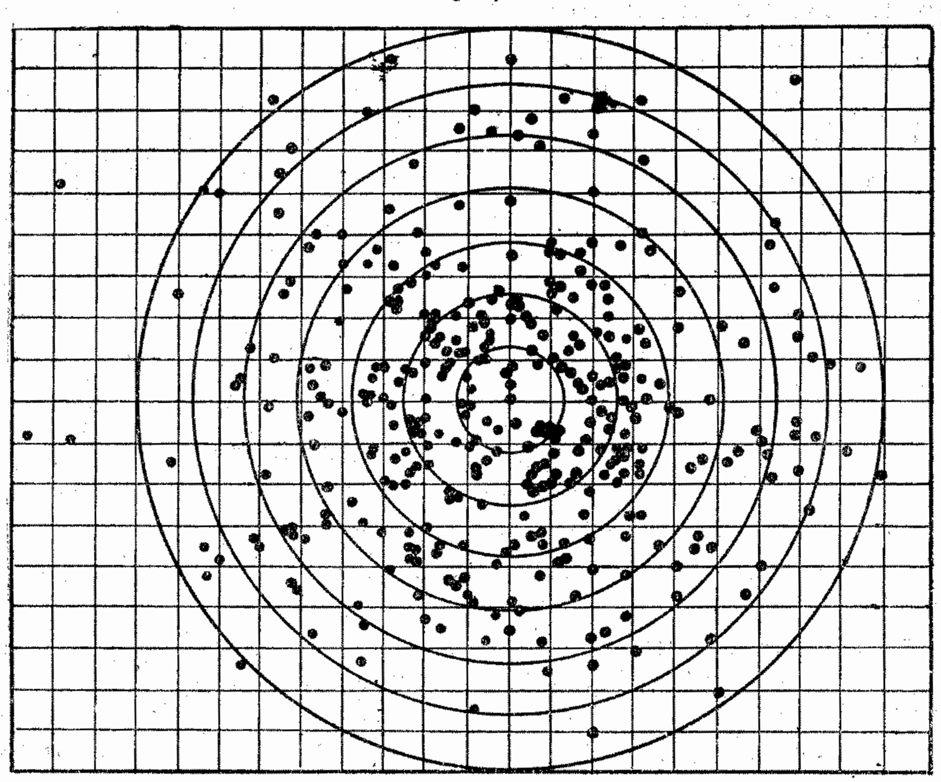
Brownian motion

Fig. 6.



Δt=30 sec

Fig. 7.



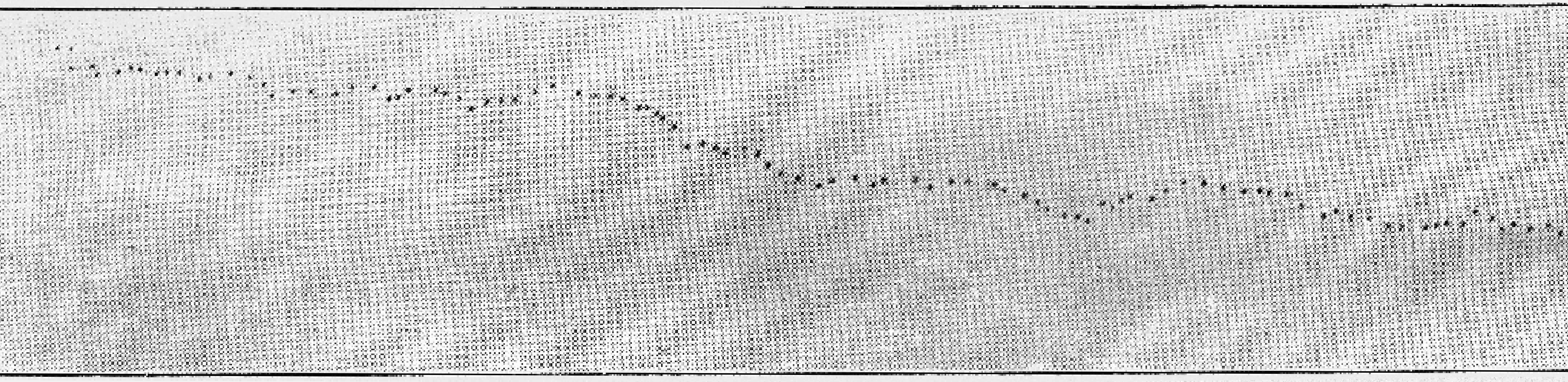
$$P(\mathbf{r}, \Delta t) = \frac{1}{(4\pi K \Delta t)^{d/2}} \exp\left(-\frac{r^2}{4K\Delta t}\right)$$

Einstein-Smoluchowski relation:

$$K = \frac{k_B T}{m\eta} = \frac{(R/N_A)T}{m\eta}$$

J Perrin, Comptes Rendus (Paris) 146 (1908) 967: $N_A = 70.5 \times 10^{22}$

Ivar Nordlund: 100 years of SPT with time series analysis



Mercury droplet in aqueous solution

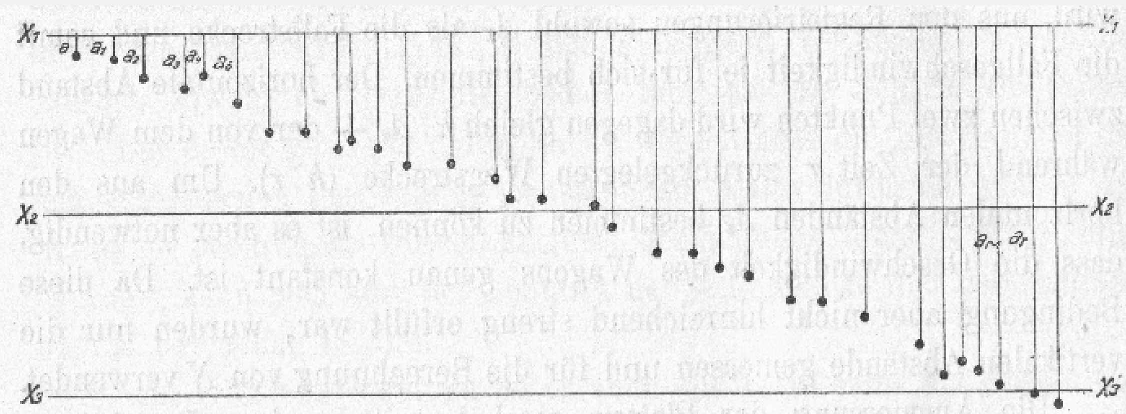


Fig. 5.

I Nordlund, Z Physik (1914): $N_A = 5.91 \times 10^{23}$

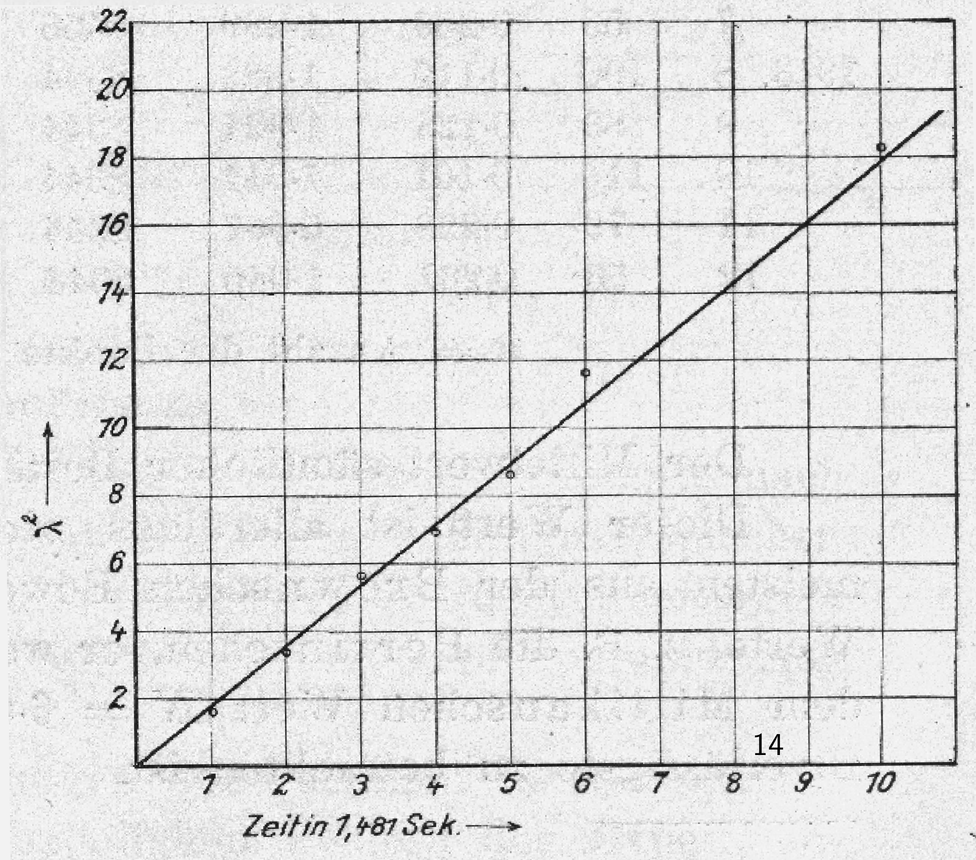
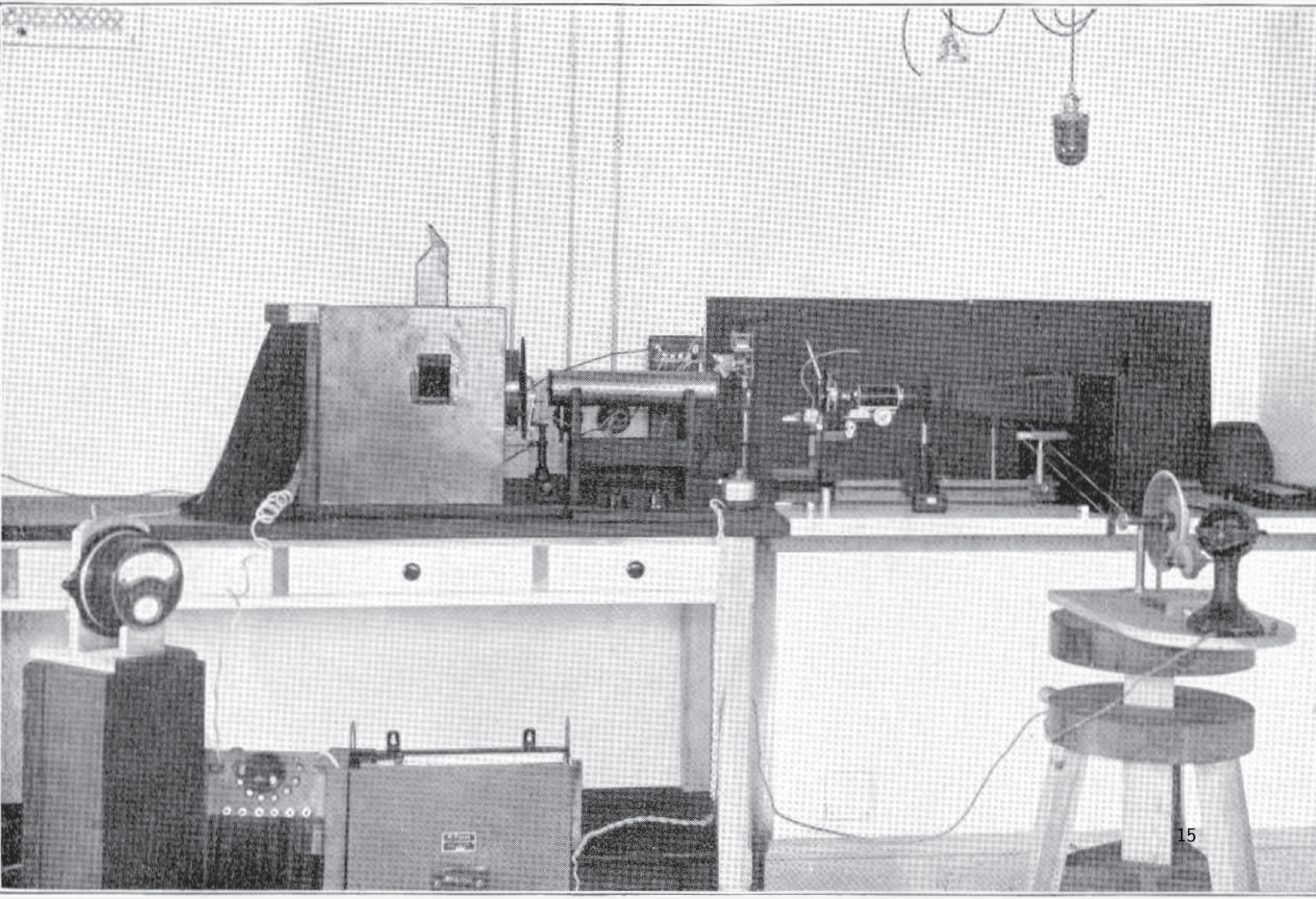


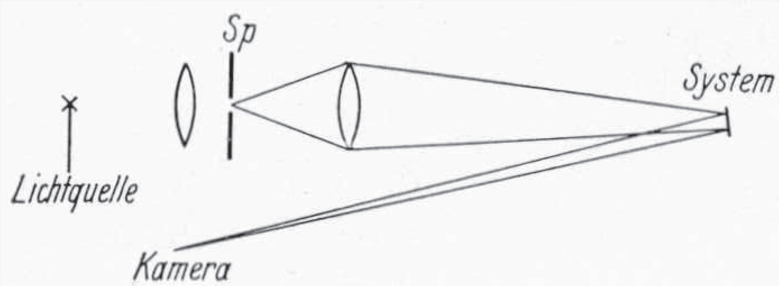
Fig. 11.



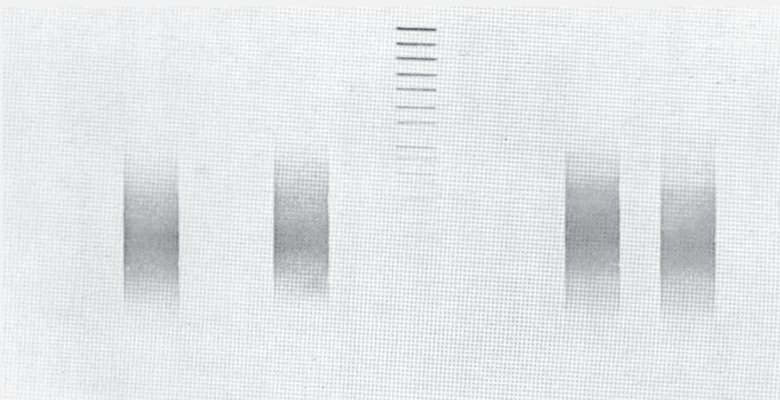
Eugen Kappler: ultimate diffusion measurements

Obiturary by L Reimer, Physikalische Blätter Feb 1978 pp 86

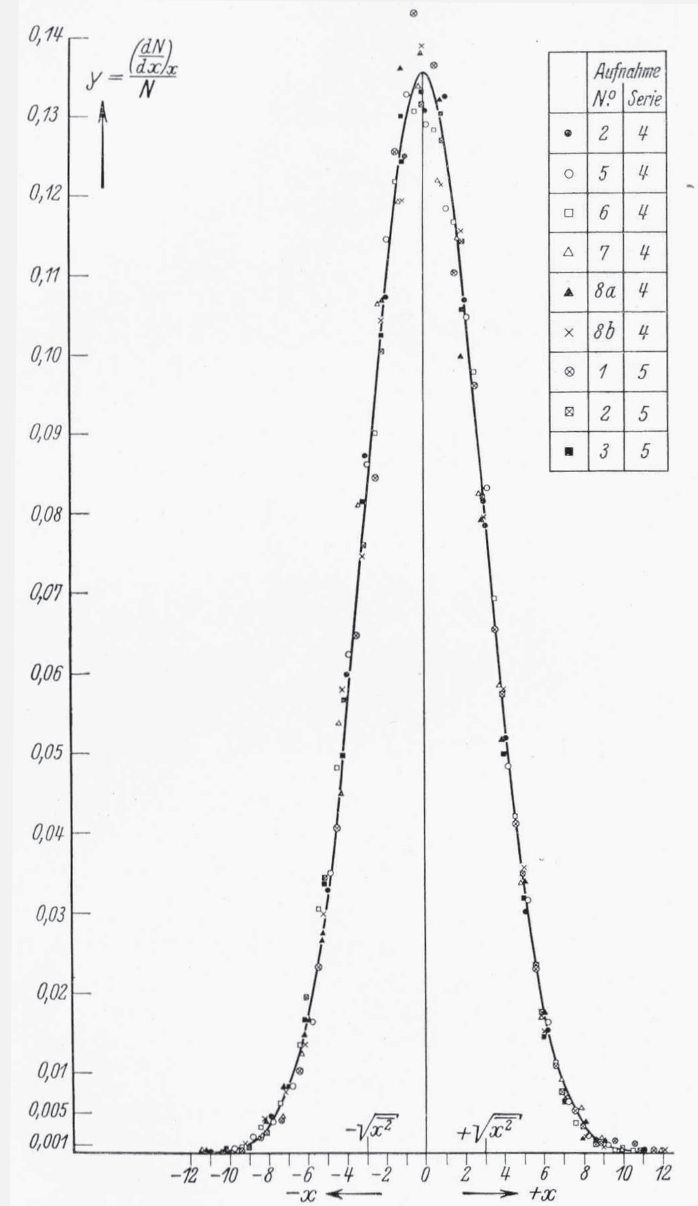
Eugen Kappler: ultimate diffusion measurements



Schema der Meßanordnung
Fig. 1

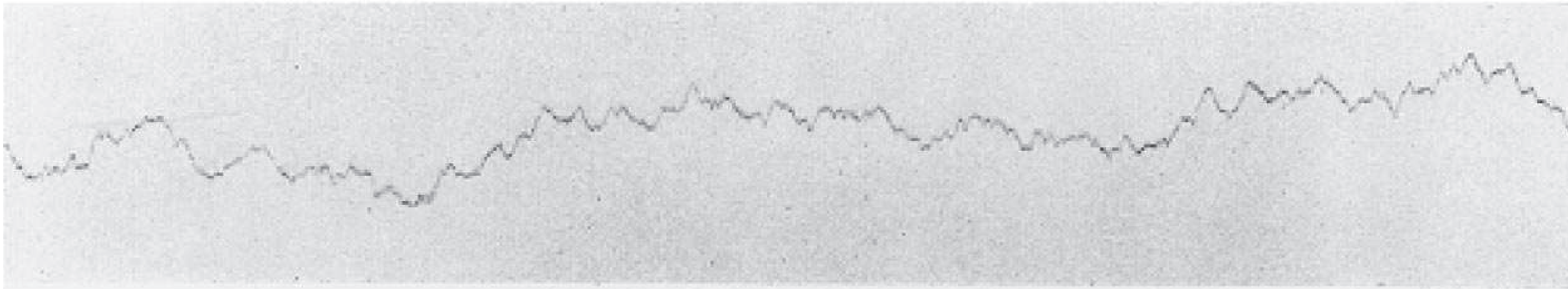


Distribution @ fixed photographic plate



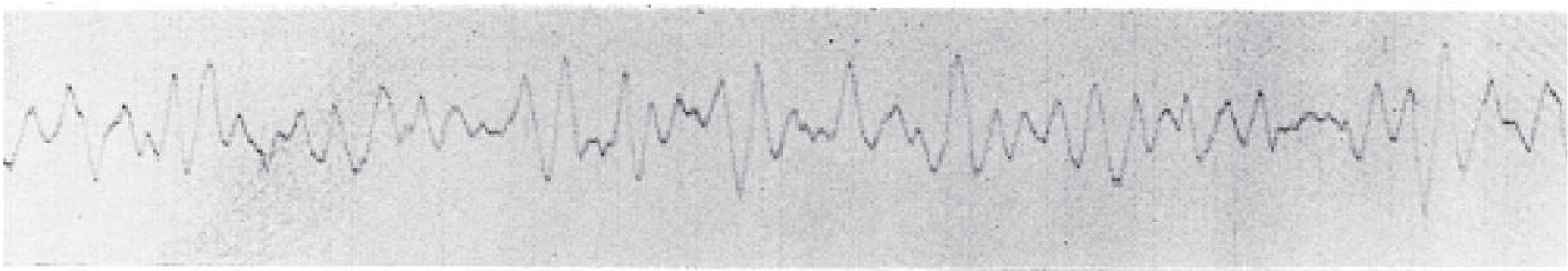
E Kappler, Ann d Physik (1931): $N_A = 60.59 \times 10^{22} \pm 1\%$

Eugen Kappler: ultimate diffusion measurements



Registrieraufnahme der Brownschen Bewegung (natürliche Größe).
Direktionskraft $9{,}428 \cdot 10^{-9}$ abs. Einh. Trägheitsmoment: $1 \cdot 10^{-7}$ abs. Einh. Abstand Spiegel–Kamera: 72,1 cm.
Zeitmarke: 30 sec $dx = 1$ mm. a) Atmosphärendruck. Temperatur 13° C

Fig. 5a

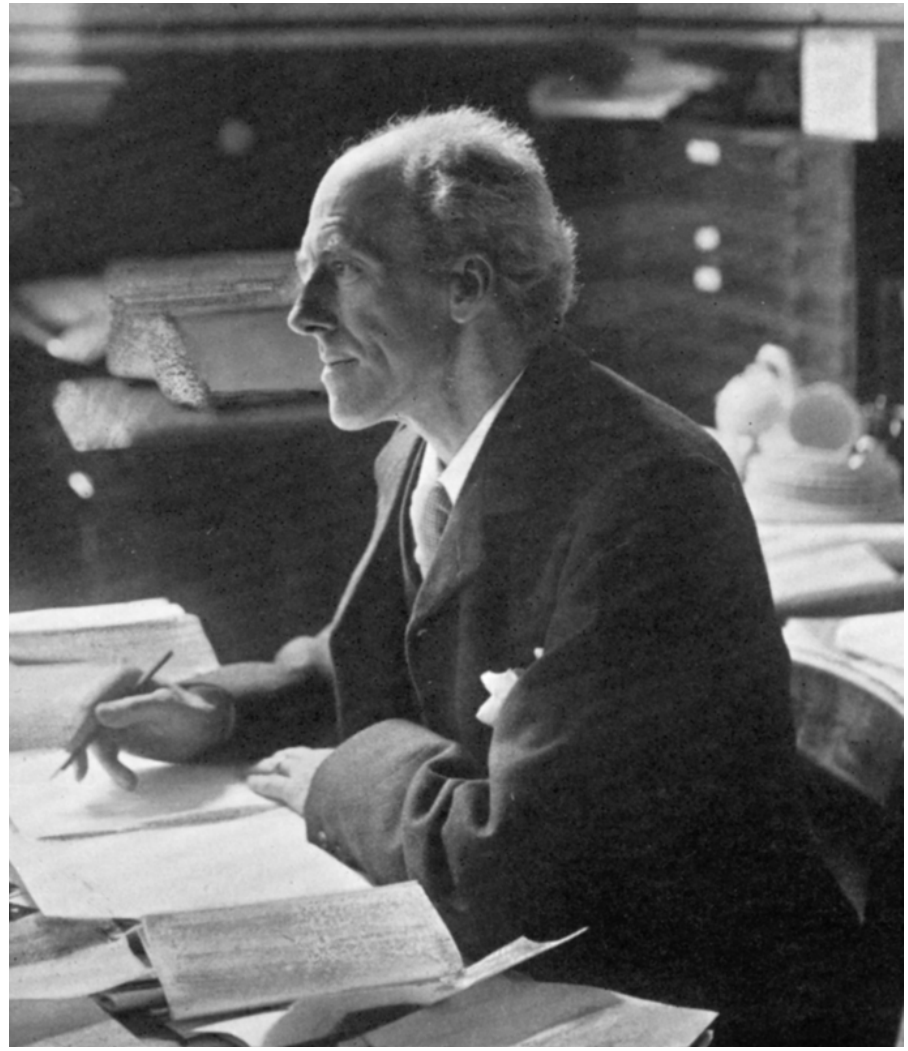


Registrieraufnahme der Brownschen Bewegung (natürliche Größe).
Direktionskraft $9{,}428 \cdot 10^{-9}$ abs. Einh. Trägheitsmoment $1 \cdot 10^{-7}$ abs. Einh. Abstand Spiegel–Kamera: 72,1 cm.
Zeitmarke: 30 sec $dx = 1$ mm. b) $1 \cdot 10^{-8}$ mm Hg. Temperatur 13° C

Fig. 5b

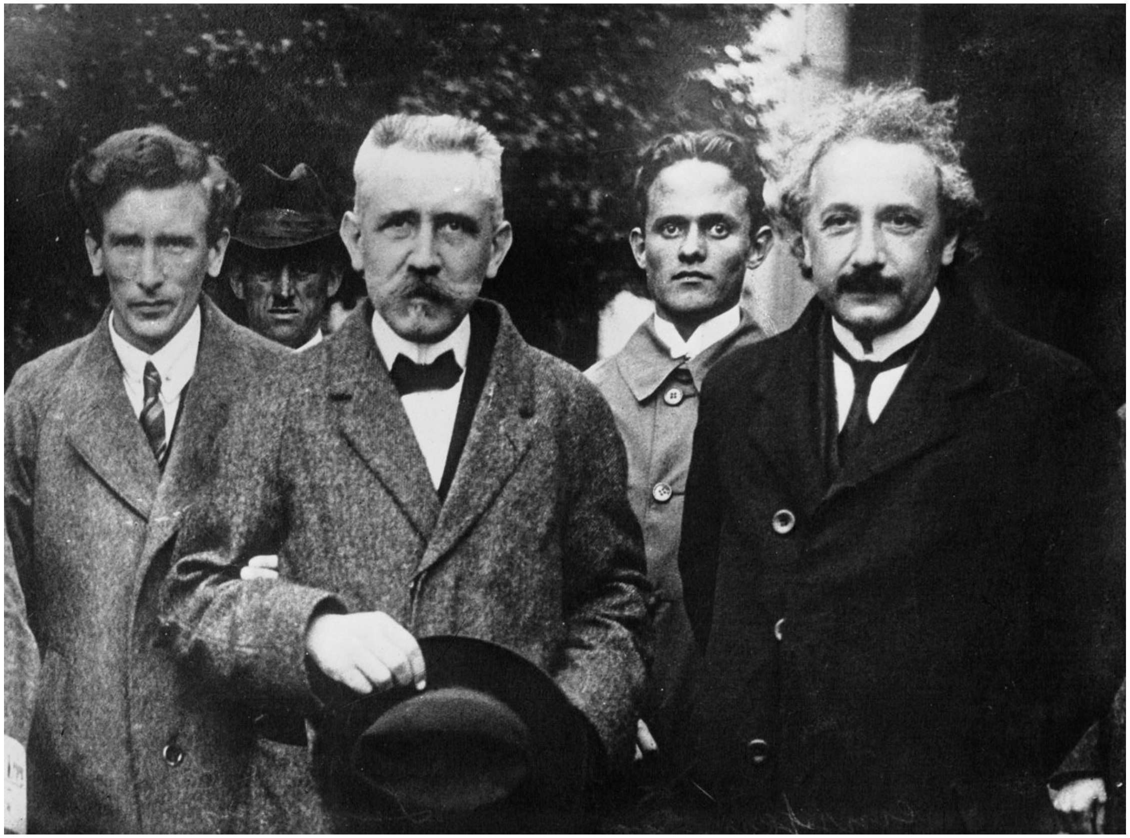
E Kappler, Ann d Physik (1931): $N_A = 60.59 \times 10^{22} \pm 1\%$

Enter the theorists...



Adolf Fick

Karl Pearson



Paul Langevin & Albert Einstein

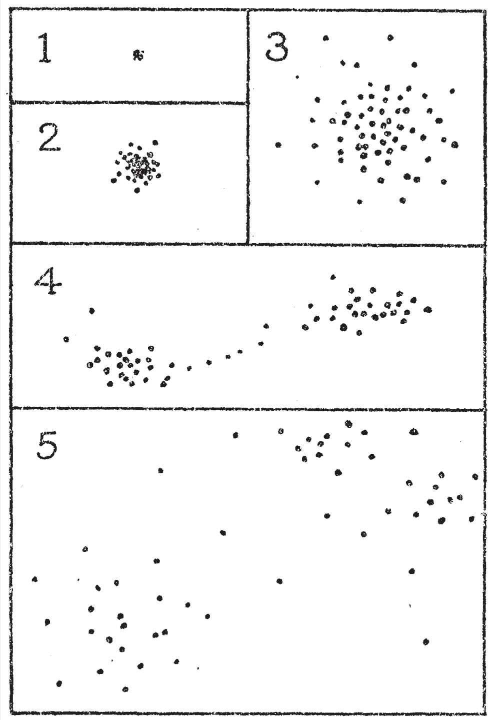
Marian Smoluchowski

William Sutherland

Lewis Frey Richardson

George Keith Batchelor

Richardson (relative) diffusion in turbulence: $\langle l^2(t)\rangle \simeq t^3$



FIGS. 1–5.

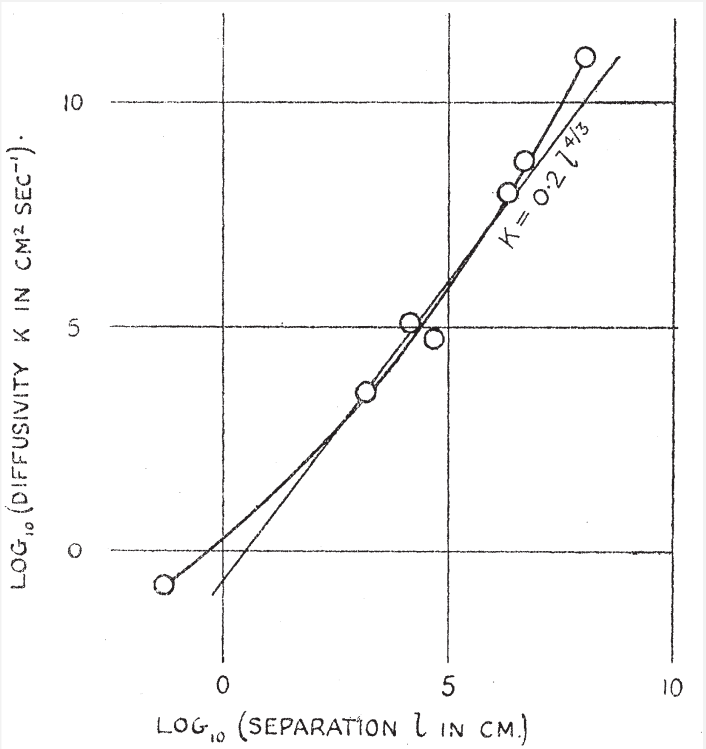


FIG. 8.

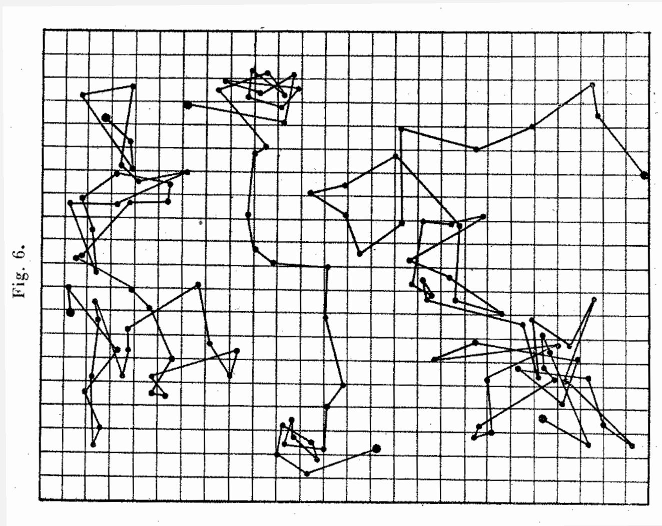
$$\frac{\partial q}{\partial t} = \varepsilon \frac{\partial}{\partial l}\left(l^{4/3} \frac{\partial q}{\partial l} \right), \quad \varepsilon \sim 0.4\,\mathrm{cm}^{2/3}\mathrm{sec}^{-1}$$ Richardson

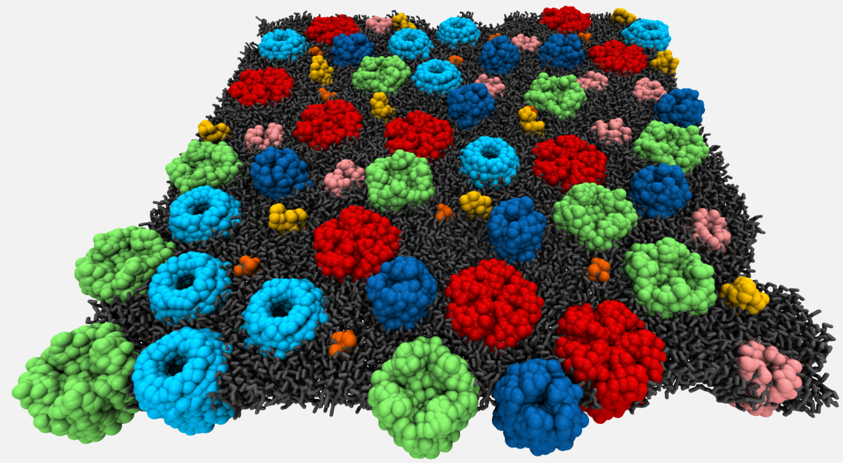
$$\frac{\partial q}{\partial t} = \overline{\varepsilon} t^2 \frac{\partial^2}{\partial l^2} q(l,t)$$ Batchelor

LF Richardson, Proc Roy Soc London Ser A (1926); GK Batchelor, Proc Cambridge Philos Soc (1952)

Stochastic processes in 2018: why should we care?

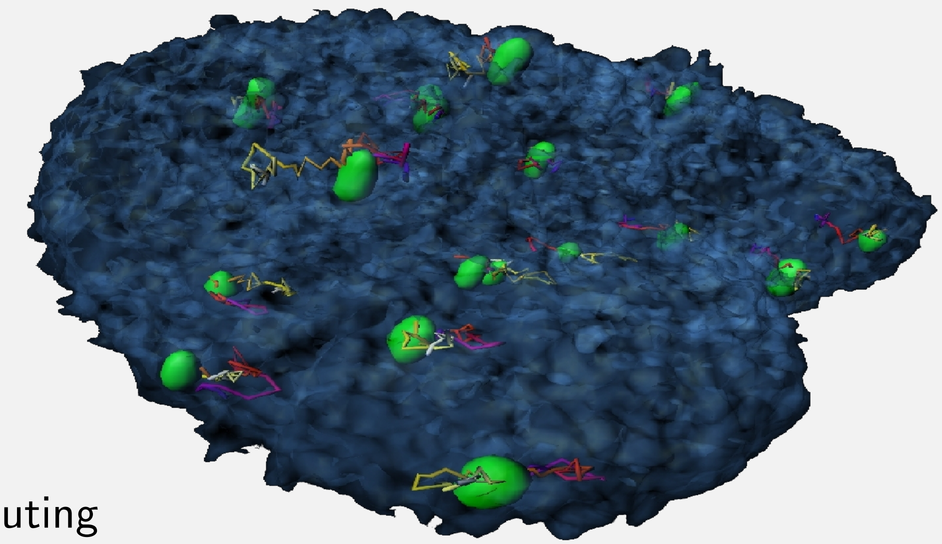
Jean Perrin (1908)





Courtesy Matti Javanainen

1905: Albert Einstein & Karl Pearson
1906: Marian Smoluchowski
1908: Paul Langevin
1914: Ivar Nordlund
1935: Eugen Kappler
Later: Skorokhod, Lévy, Mandelbrot,
Montroll, Weiss, Hänggi, etc.

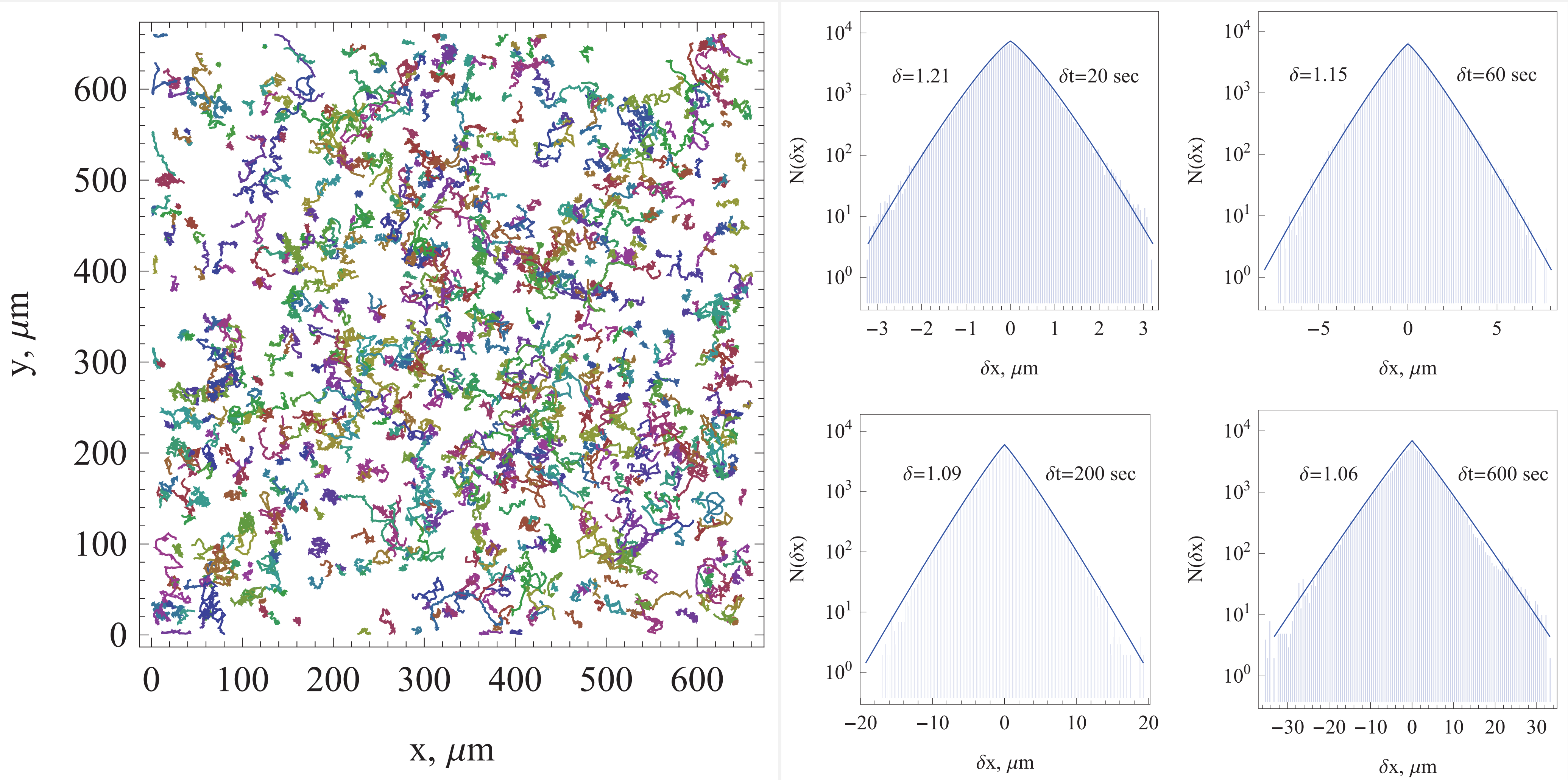


Courtesy Yuval Garini

Now: superresolution microscopy & supercomputing
$>10^6$ data points per trajectory, nm/sub-msec resolution

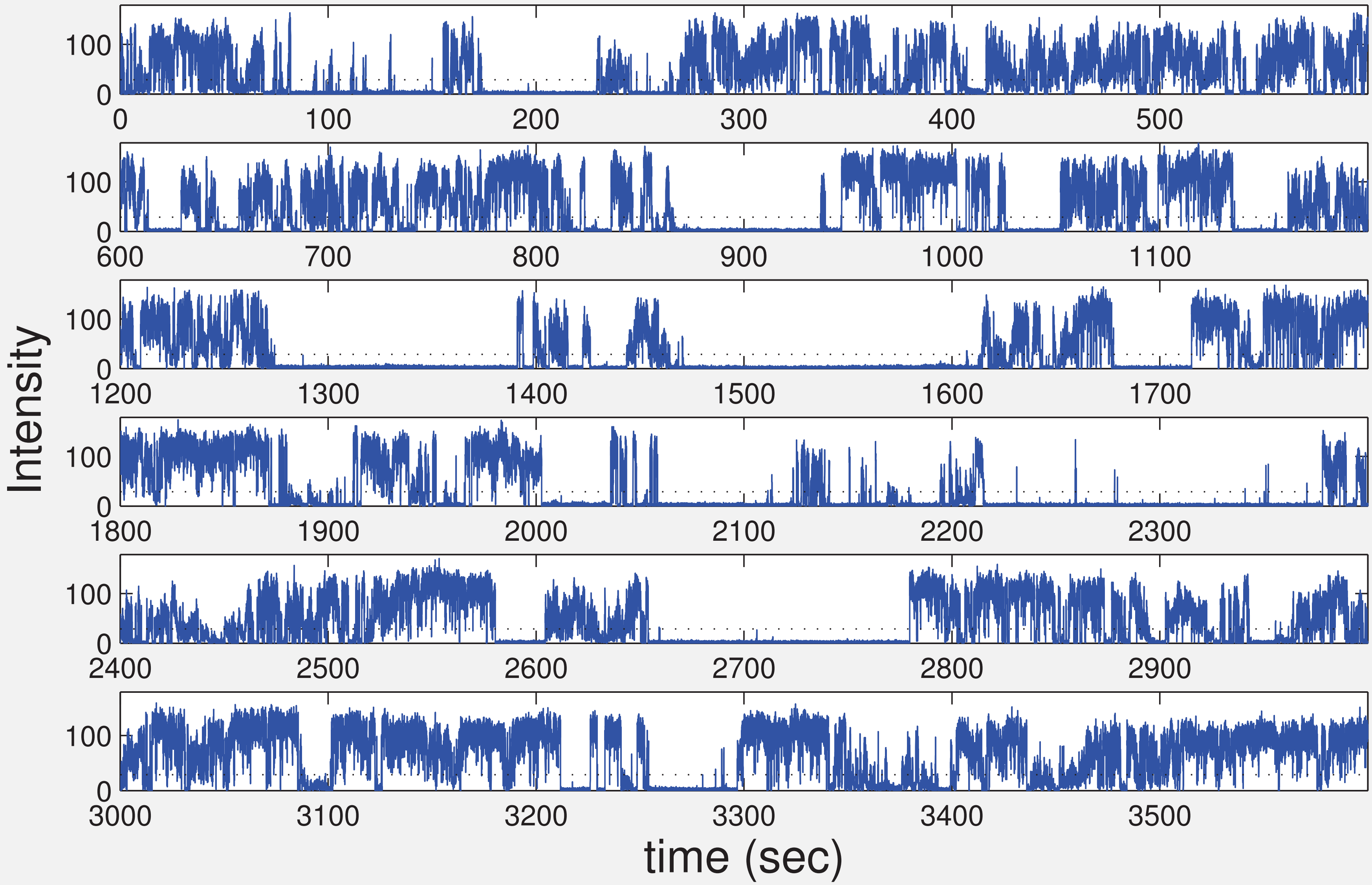
E Barkai, Y Garini & RM, Phys Today (2012)

Non-Gaussian diffusion of Dictyostelium cells



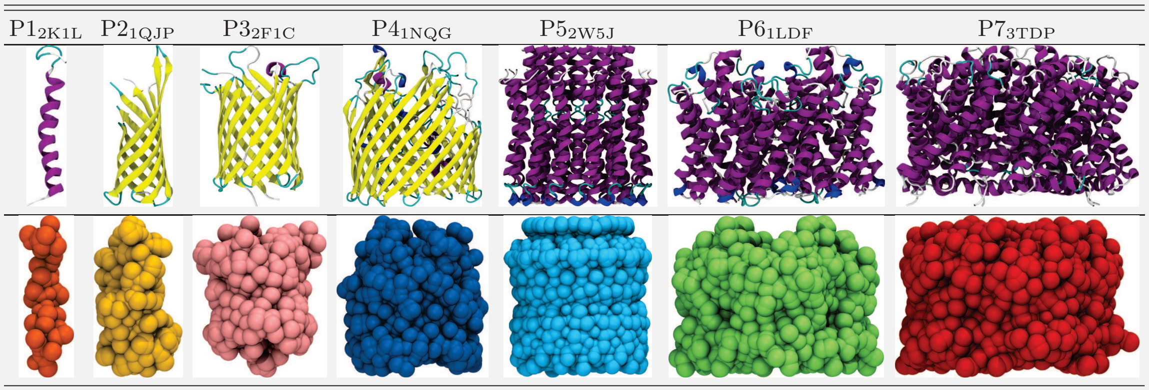
AG Cherstvy, O Nagel, C Beta & RM (2018)

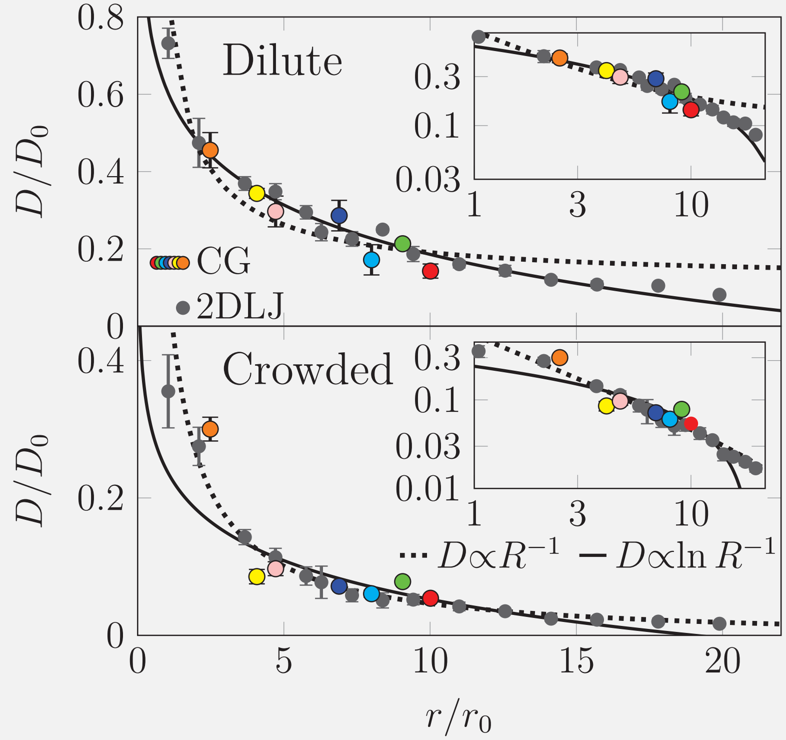
On/off blinking dynamics in quantum dots

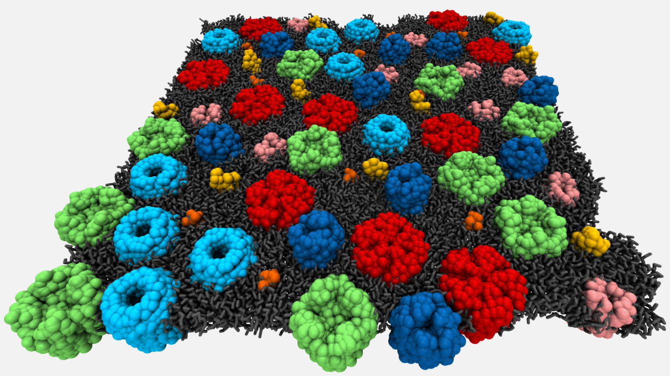


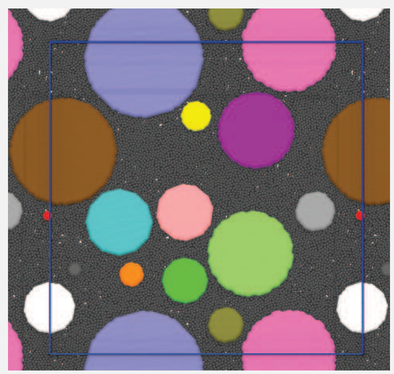
FD Stephani, JD Hoogenboom & E Barkai, Phys Today (2009)

Diffusion of proteins in crowded lipid bilayer membranes









Dilute system: Saffman-Delbrück law

$$D(R) \simeq \log(1/R)$$

Crowded membrane & 2DLJ discs:

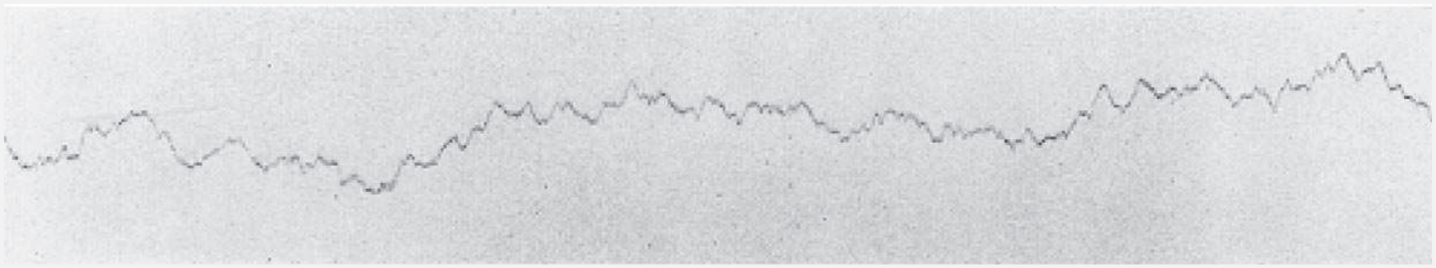
$$D(R) \simeq 1/R$$

M Javanainen, H Seara Monne, RM & I Vattulainen, JPC Lett (2017)

Anomalous diffusion, ensemble & time averaged MSD

Ensemble averaged MSD (subdiffusion: $0 < \alpha < 1$; superdiffusion: $1 < \alpha < 2$):

$$\langle \mathbf{r}^2(t) \rangle = \int \mathbf{r}^2 P(\mathbf{r}, t) d\mathbf{r} \simeq K_\alpha t^\alpha$$



E Kappler (1931)

Time averaged MSD:

$$\overline{\delta^2(\Delta)} = \frac{1}{T - \Delta} \int_0^{T-\Delta} \Big[\mathbf{r}(t + \Delta) - \mathbf{r}(t)\Big]^2 dt; \quad \left\langle \overline{\delta^2(\Delta)} \right\rangle = N^{-1} \sum_{i=1}^{N} \overline{\delta_i^2(\Delta)}$$

Ergodicity:

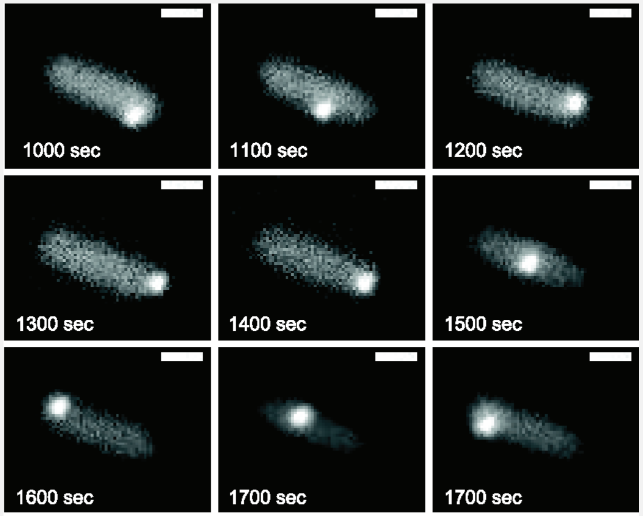
$$\langle \mathbf{r}^2(\Delta) \rangle = \lim_{T \to \infty} \overline{\delta^2(\Delta)}$$

Ergodicity breaking parameter: $\mathrm{EB} = \langle \xi^2 \rangle - 1$ with $\xi = \overline{\delta^2(\Delta)} \Big/ \left\langle \overline{\delta^2(\Delta)} \right\rangle$

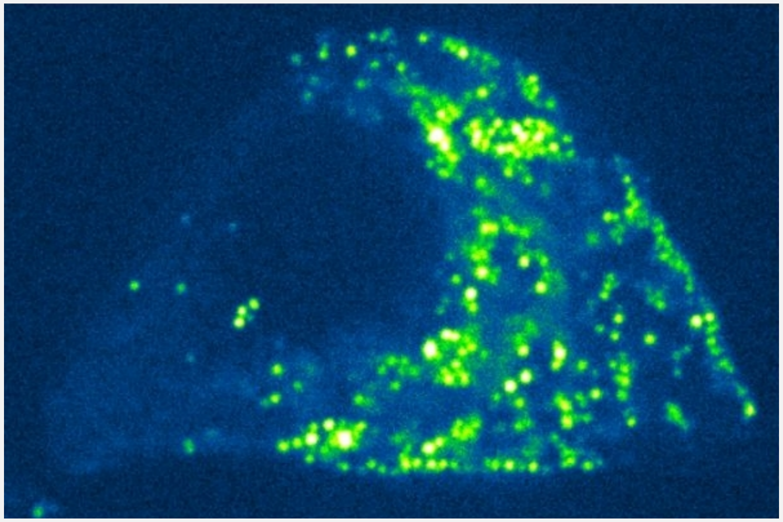
Brownian motion: $\mathrm{EB} \simeq (\Delta / T)$

RM, JH Jeon & E Barkai, PCCP (2014); C Nørregaard, RM, CM Ritter, K Berg-Sørensen & LB Oddershede, Chem Rev (2017)

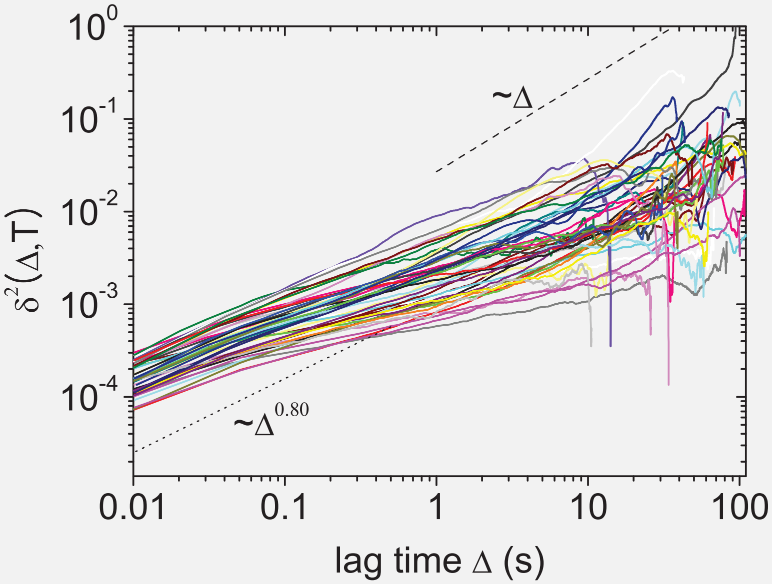
In vivo anomalous diffusion of submicron tracers: $\langle \mathbf{r}^2(t) \rangle \simeq t^\alpha$



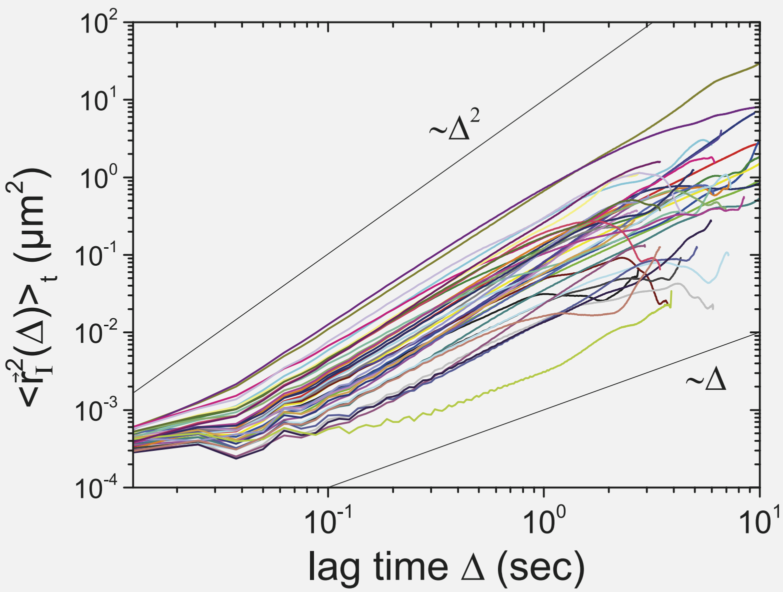
I Golding & EC Cox, PRL (2006)



SMA Tabei et al, PNAS (2013)

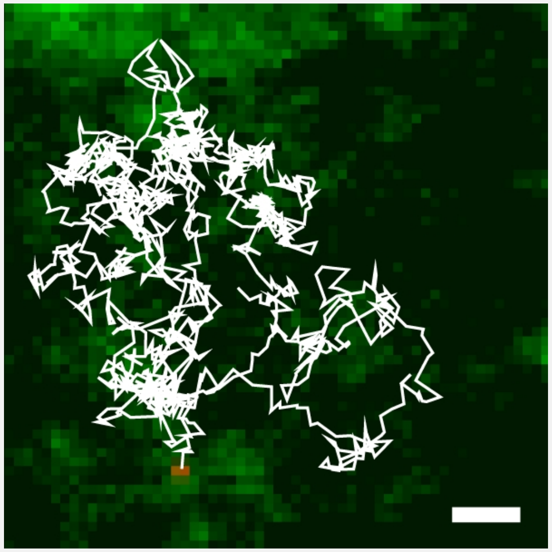


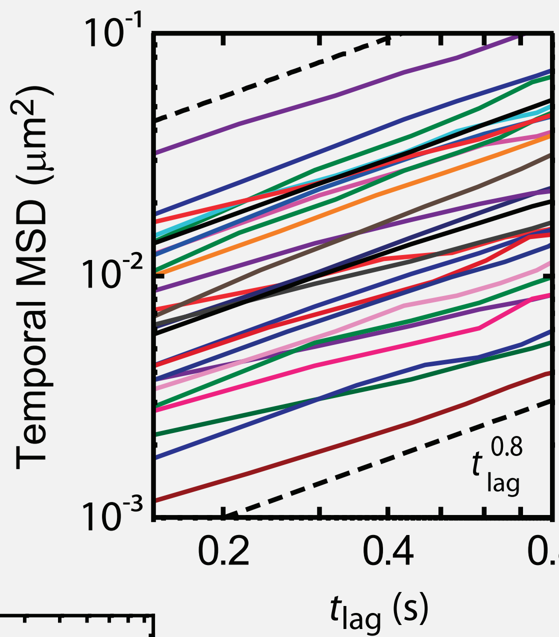
JH Jeon, . . . LB Oddershede & RM, PRL (2011)

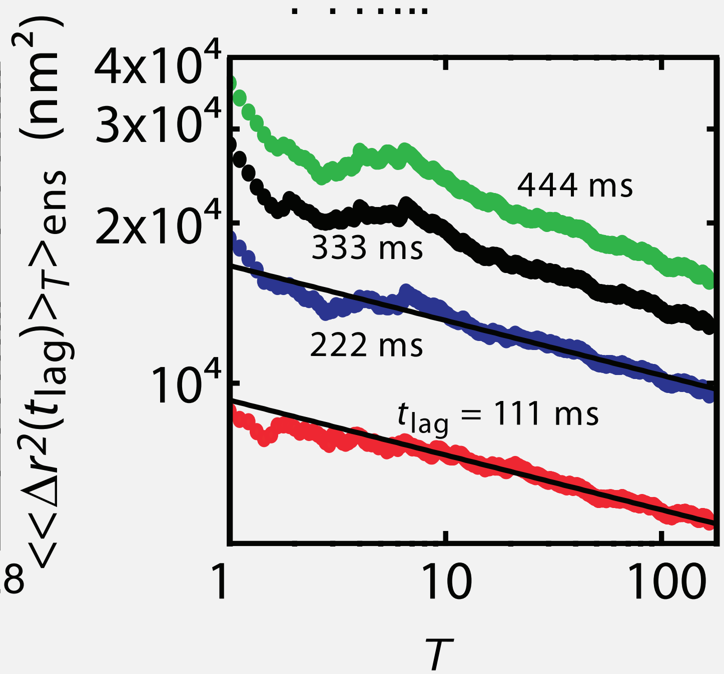


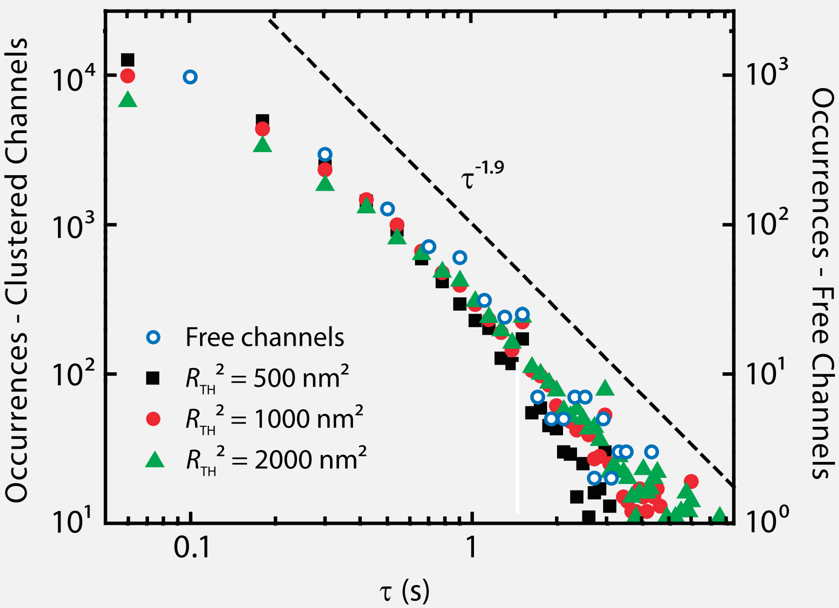
J Reverey, . . . RM & C Selhuber-Unkel, Sci Rep (2015)

Ageing motion of Ka channels in plasma membrane









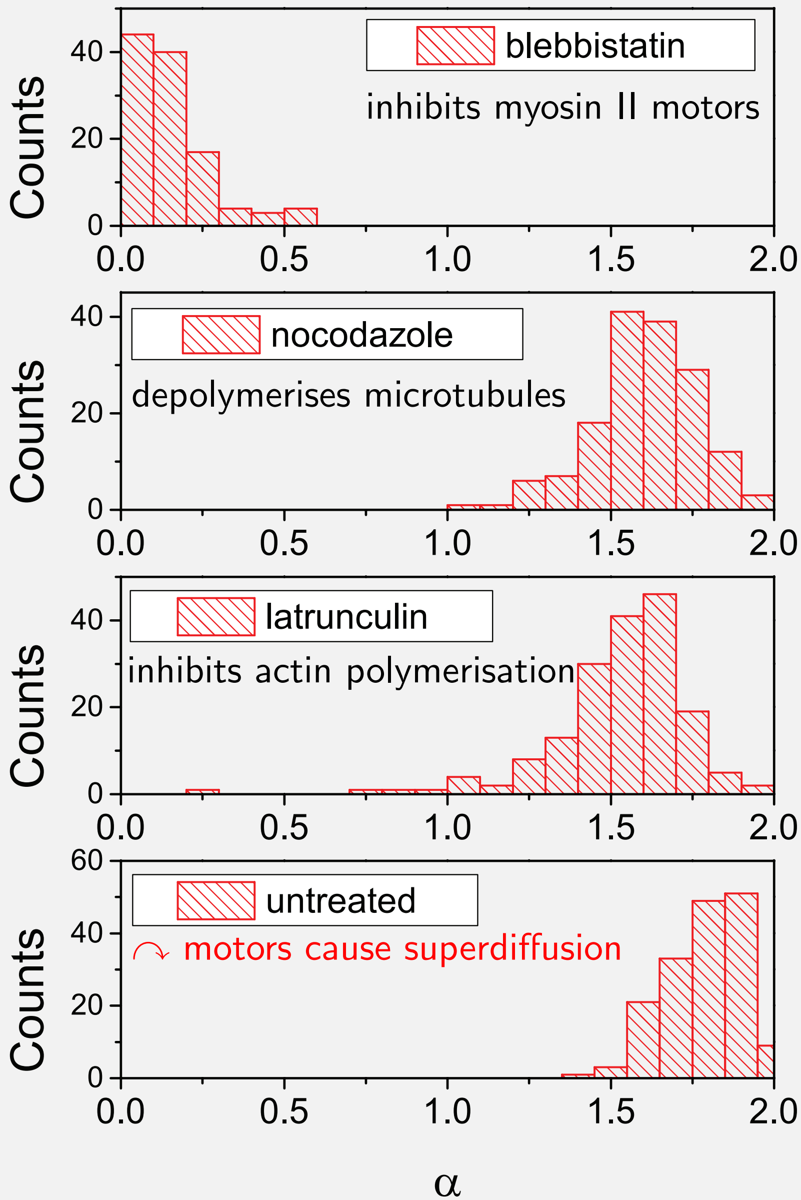
$\psi(\tau) \simeq \tau^{-1-\alpha}$ scale free

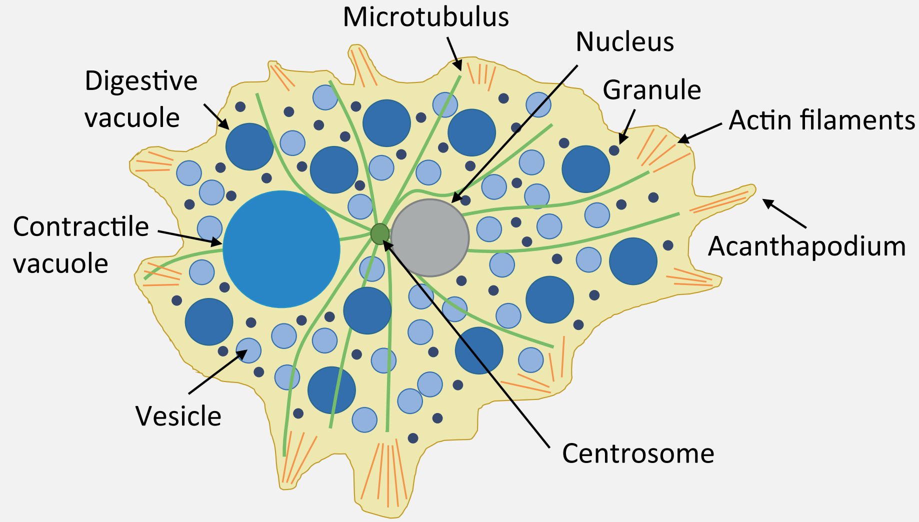
$\overline{\delta^2(\Delta)}$ apparently random

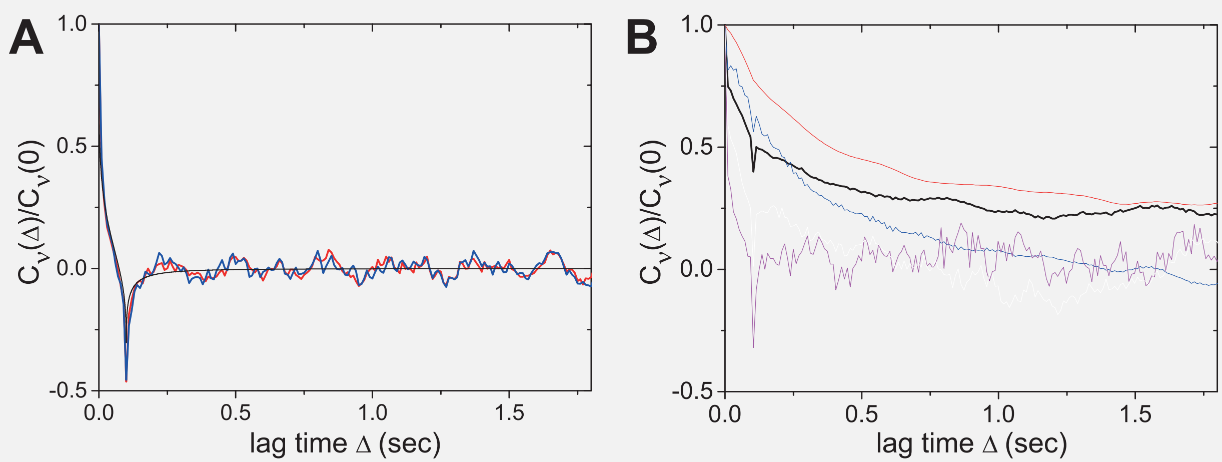
$\overline{\delta^2(\Delta)} \neq \langle \mathbf{r}^2(\Delta) \rangle$ WEB

AV Weigel, B Simon, MM Tamkun & D Krapf, PNAS (2011)

Superdiffusion in living Acanthamoeba castellani







JF Reverey, J-H Jeon, H Bao, M Leippe, RM & C Selhuber-Unkel, Sci Rep (2015)

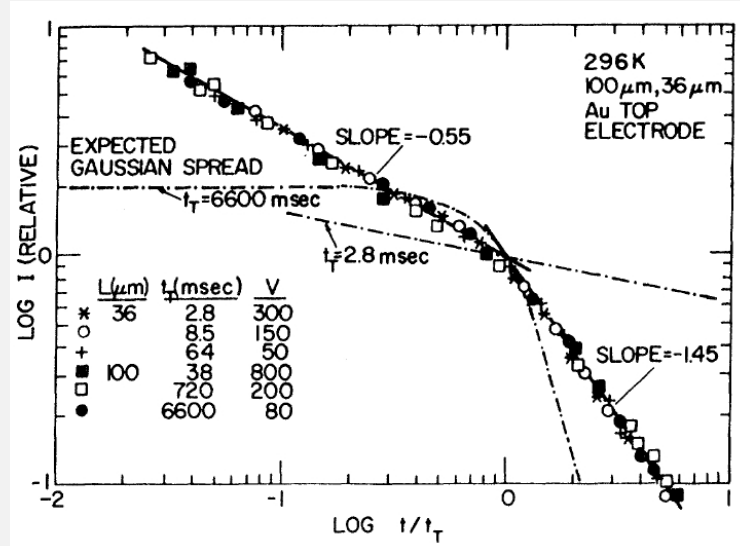
Charge carrier diffusion in amorphous semiconductors

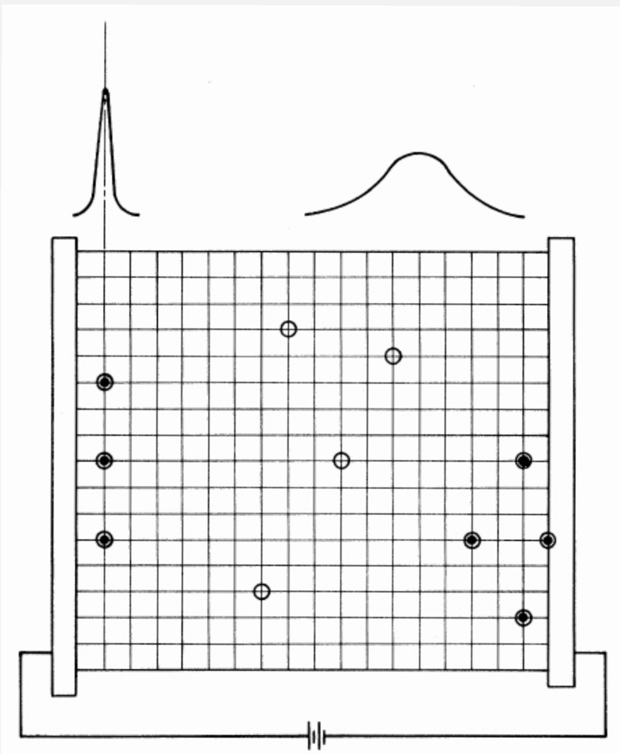
Waiting time distribution

$$\psi(t) \simeq \frac{\tau^\alpha}{t^{1+\alpha}} \Leftrightarrow \psi(u) = \exp\left(-[u\tau]^\alpha\right)$$

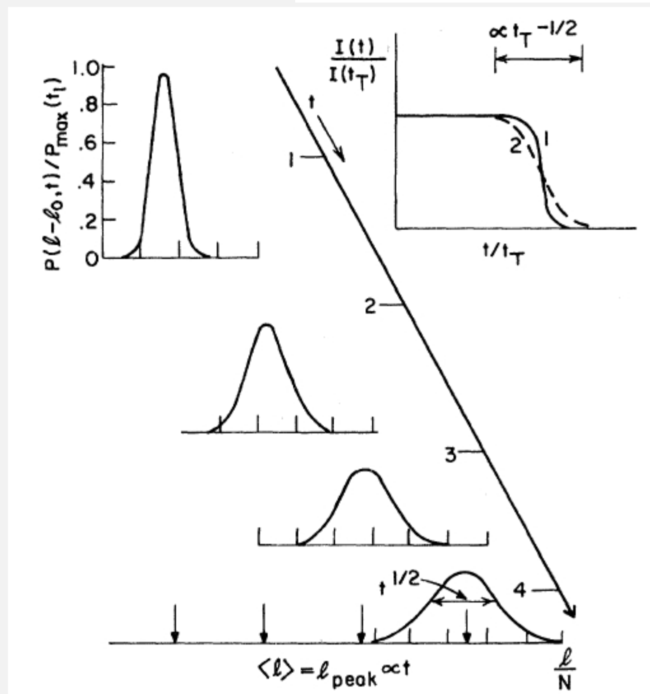
In the bias of the electrical field:

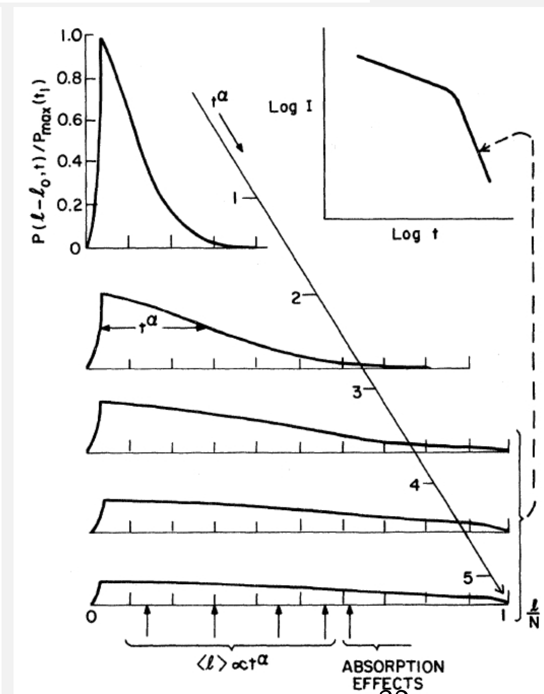
$$\frac{\sqrt{\langle(\Delta x)^2\rangle}}{\langle x(t)\rangle} \simeq t^0 \;\leftrightsquigarrow\; \underbrace{\frac{\sqrt{\langle(\Delta x)^2\rangle}}{\langle x(t)\rangle} \simeq t^{-1/2}}_{\alpha=1}$$





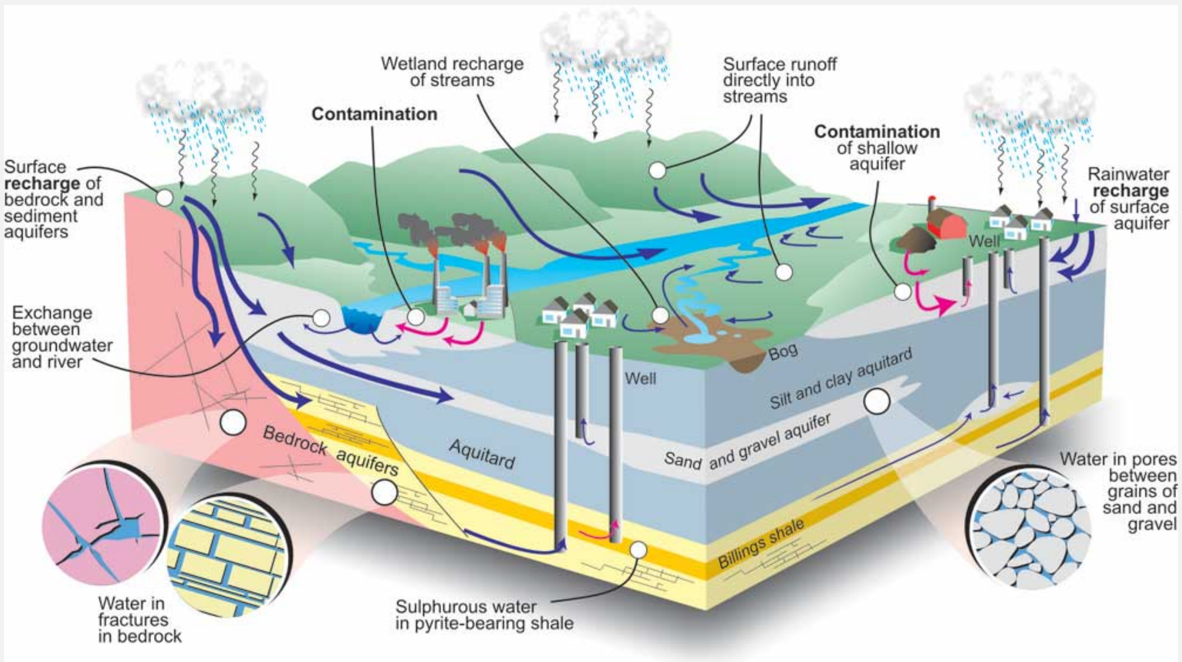
H Scher & E Montroll, PRB (1975)



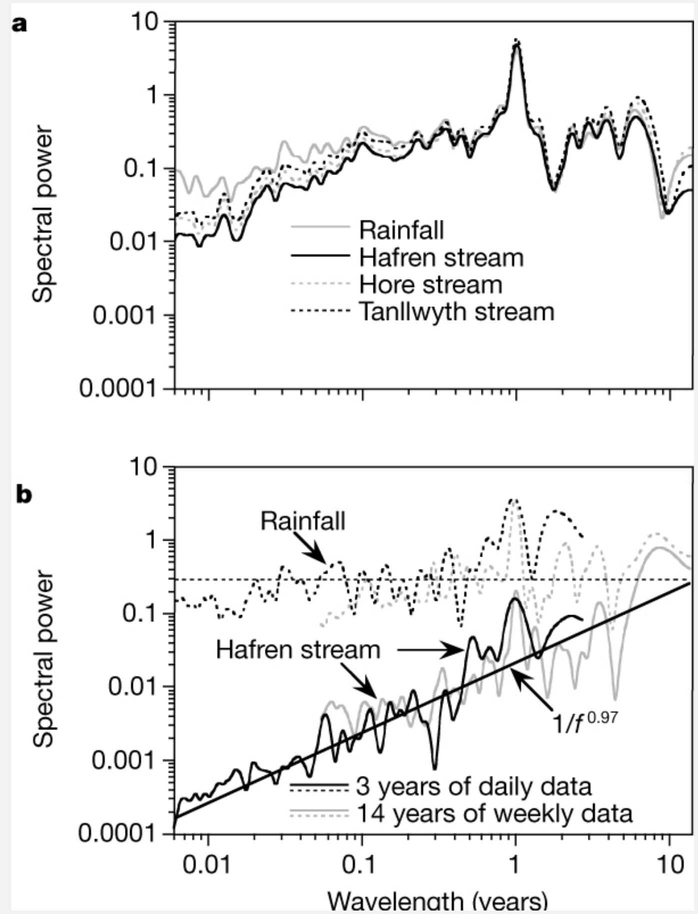


Subsurface hydrology

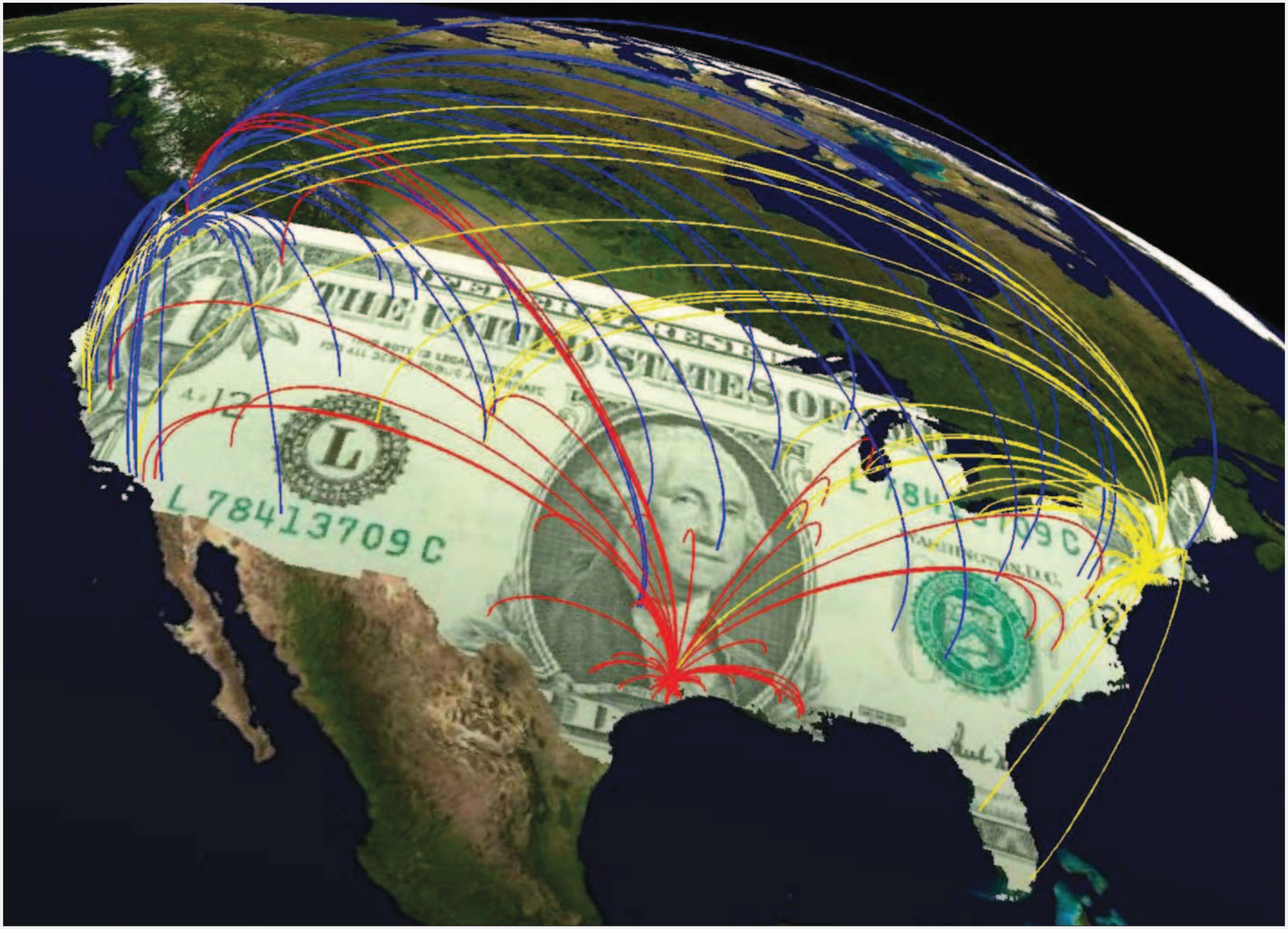
Geoscape Ottawa-Gatineau



Contaminant transport in catchments

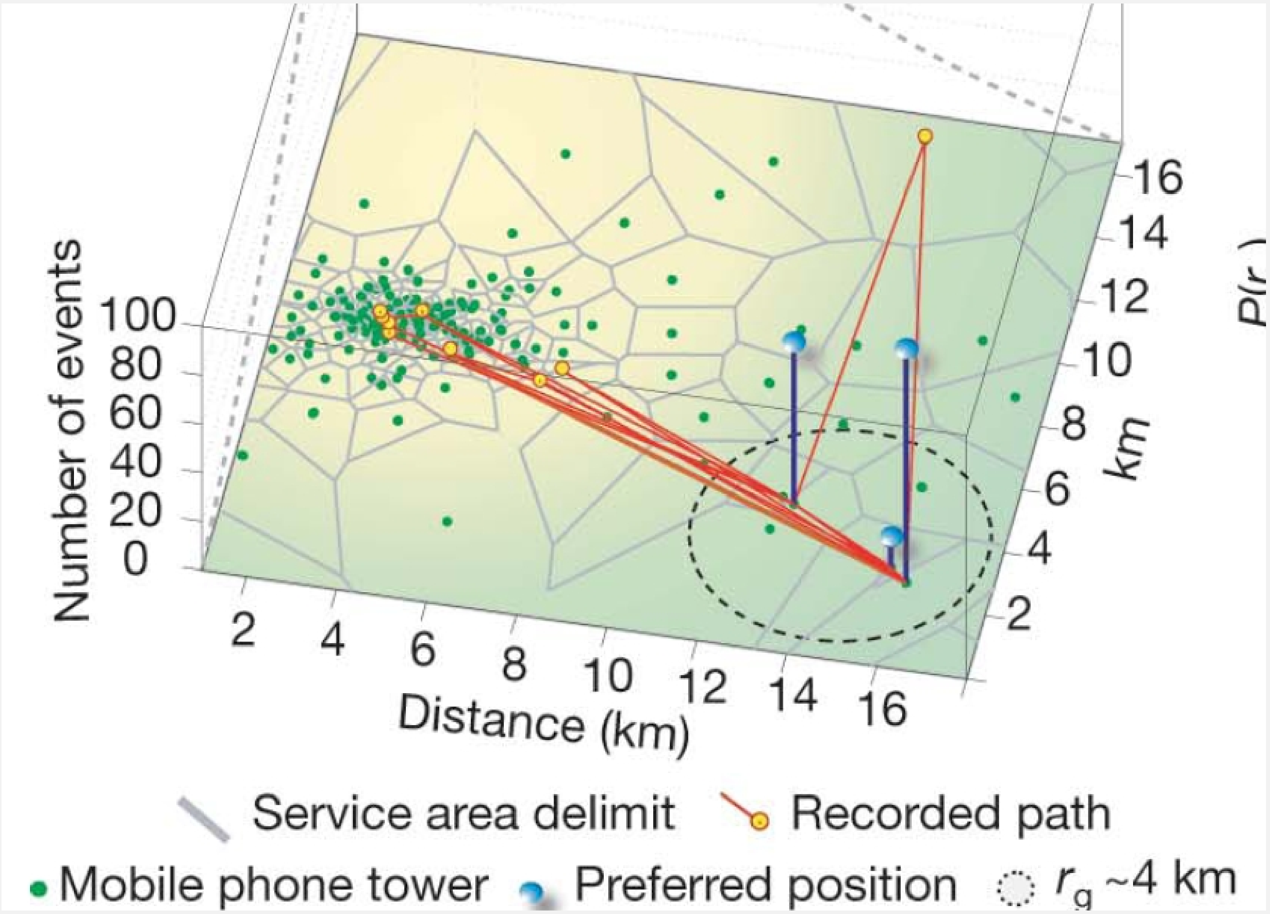


The trace of money . . .



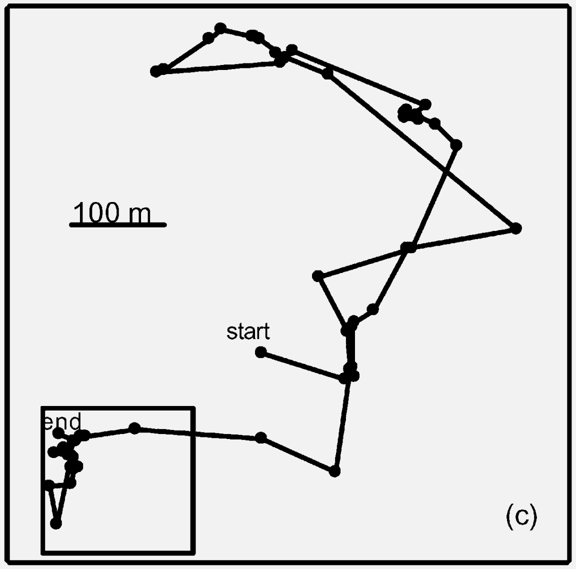
D Brockmann, Physics World (2010)

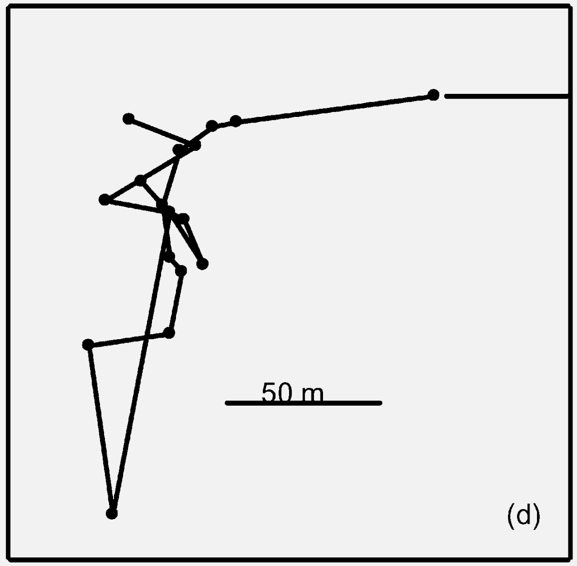
Single human motion patterns: mobile phone tracking

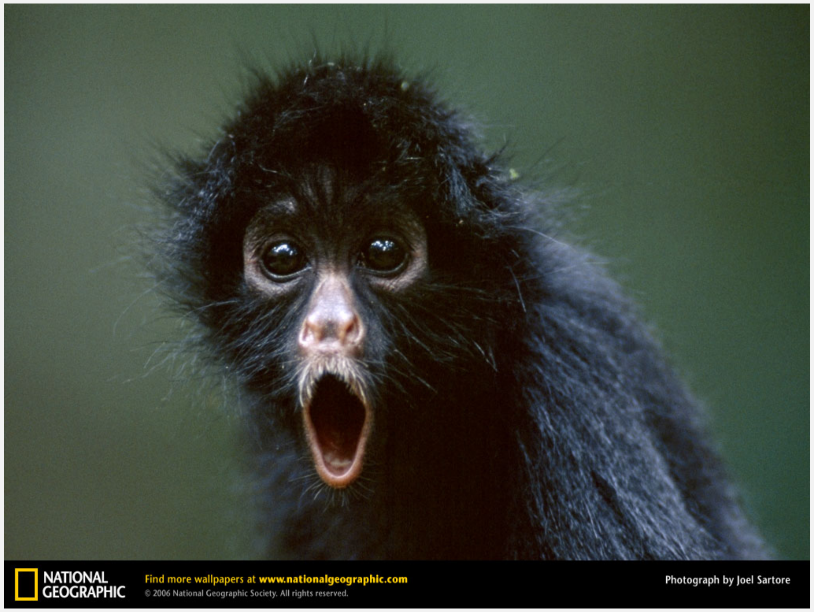


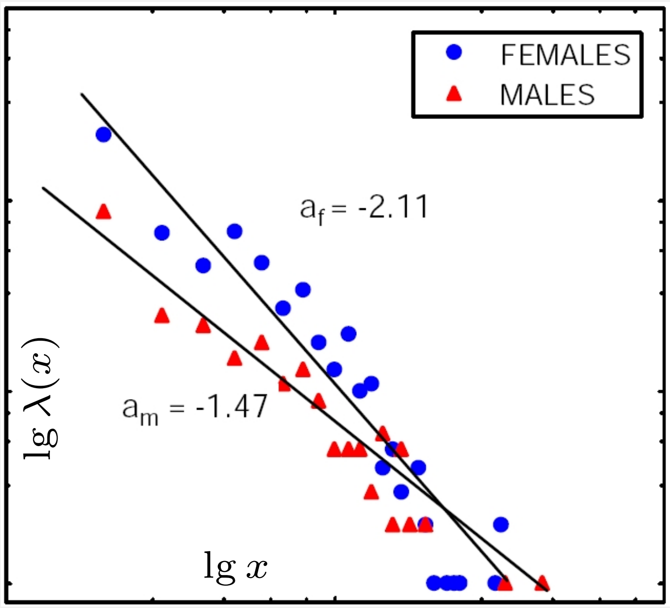
MC González, CA Hidalgo & A-L Barabási, Nature (2008)

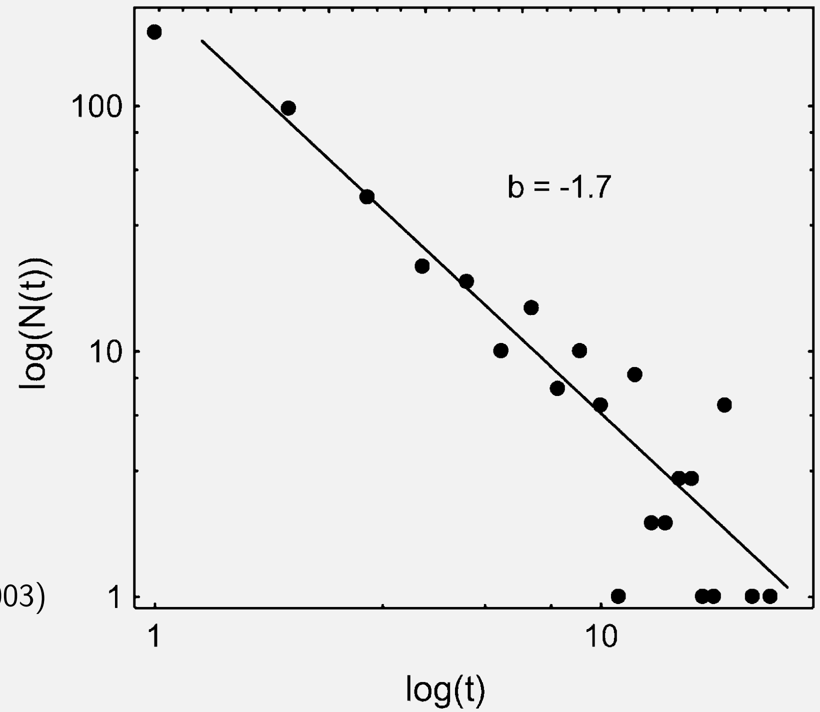
The jumps of the spider monkeys











Ramos-Fernandez et al, Behav Ecol Sociobiol (2003)