From Diffusion to Anomalous Diffusion:
A Century After Einstein

M.F. Shlesinger (ONR)
A. Blumen (Freiburg)
G. Zumofen (ETH)
J. Drager (Hamburg)
E. Barkai (Notre Dame)
R. Metzler (Nordita)
S. Denisov (Dresden)
O. Flomenbom (TAU)
I.M. Sokolov (Berlin)
A. Chechkin (Kharkov)
A. Lubelski (TAU)

The Diffusion Equation

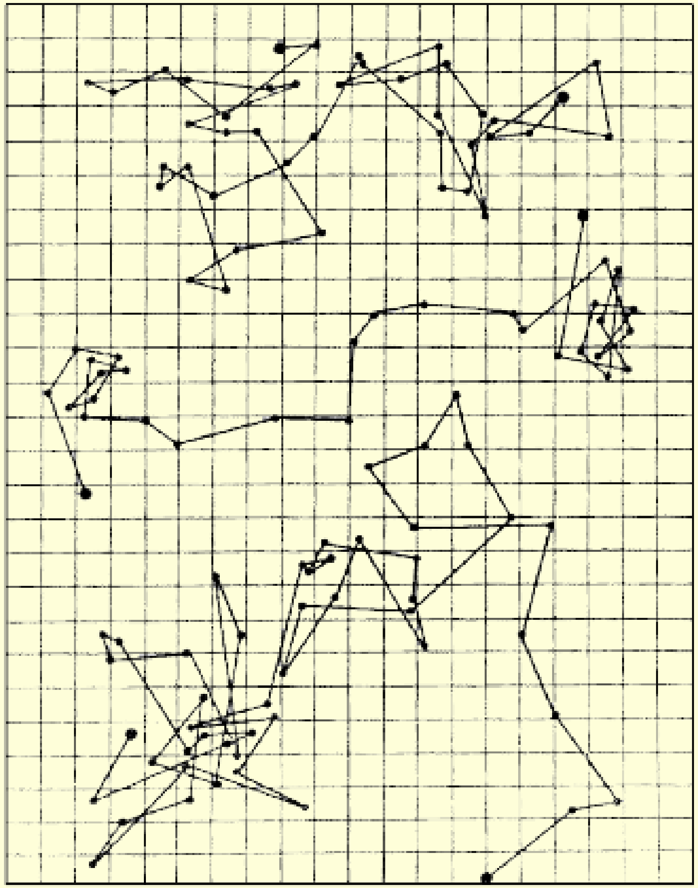
A. Fick

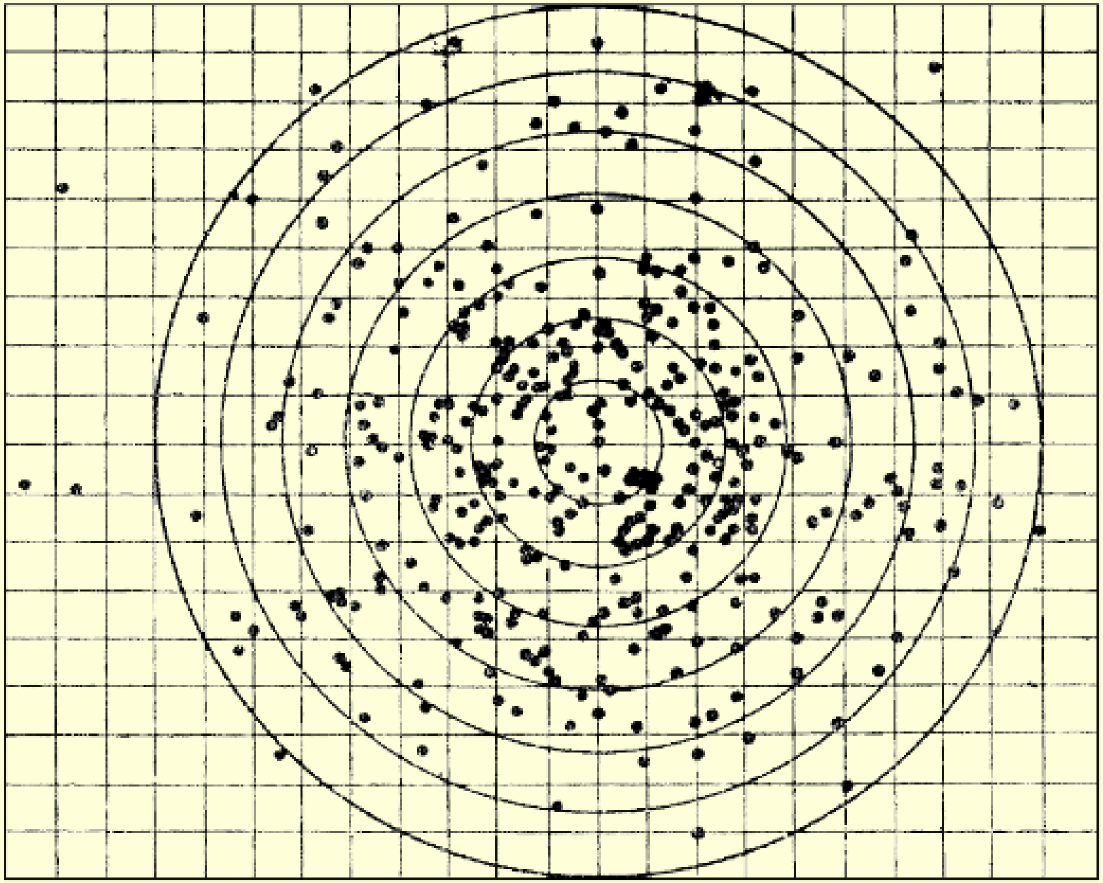
M. Smoluchowski

A. Einstein

$$\frac{\partial}{\partial t} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t)$$

Brownian Motion





The Diffusion Equation (1855)

Continuity

$$\frac{\partial}{\partial t} n(\vec{x},t) = -\mathrm{div}\,\vec{j}(\vec{x},t)$$

+ linear response

$$\vec{j}(\vec{x},t) = -K\,\mathrm{grad}\,n(\vec{x},t)$$

=> the diffusion equation

$$\frac{\partial}{\partial t} n(\vec{x},t) = K\Delta n(\vec{x},t)$$

(1914,1915,1918)

$$+\mu n(\vec{x},t)\vec{f}(\vec{x},t)$$

$$-\nabla\left(\mu\vec{f}(\vec{x},t)n(\vec{x},t)\right)$$

the Green's function solution

$$n(\vec{x},t) = (4\pi K t)^{-d/2} \exp\left(-\frac{\vec{x}^2}{4Kt}\right)$$

Essentially an equation for the pdf: $n(\vec{x},t) \rightarrow P(\vec{x},t)$

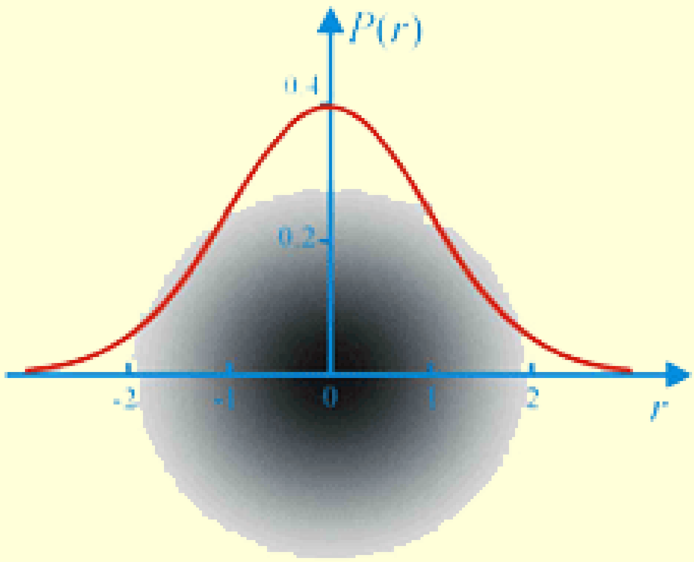
“The problem of the random walk”

“Can any of you readers refer me to a work wherein I should find a solution of the following problem, or failing the knowledge of any existing solution provide me with an original one? I should be extremely grateful for the aid in the matter. A man starts from the point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. Inquire the probability that after n stretches he is at a distance between r and r + δr from his starting point O”.

Karl Pearson

Nature, 1905

Pearson’s random walk



Emergence of Normal Diffusion

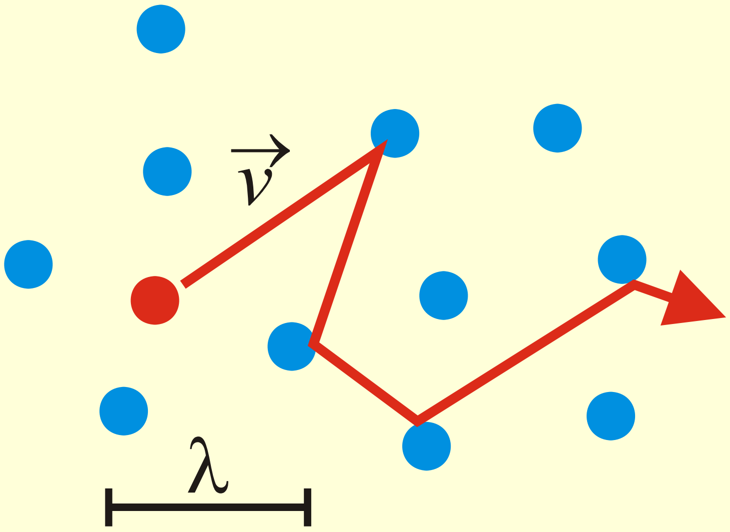
Einstein, 1905

Postulates:

i) Independent particles

ii) The particle's motion during two consequent intervals is independent

iii) The displacement during t is s.



For unbiased diffusion: $\phi(s) = \phi(-s)$

Moreover, $$\lambda^2 = \int_{-\infty}^{\infty} s^2 \phi(s) ds < \infty$$

Essentially the Random Walk Model (1880, 1900, 1905×2)

Motion as a sum of small independent increments: $x(t) = \sum_{i=1}^{N} s_i$

mean free path

$$\lambda = \left\langle s_i^2 \right\rangle^{1/2}$$

$$0 < \lambda < \infty$$

mean relaxation time

$$\tau \propto \lambda / \left\langle v^2 \right\rangle^{1/2}$$

$$0 < \tau < \infty$$

$$N \cong t / \tau$$

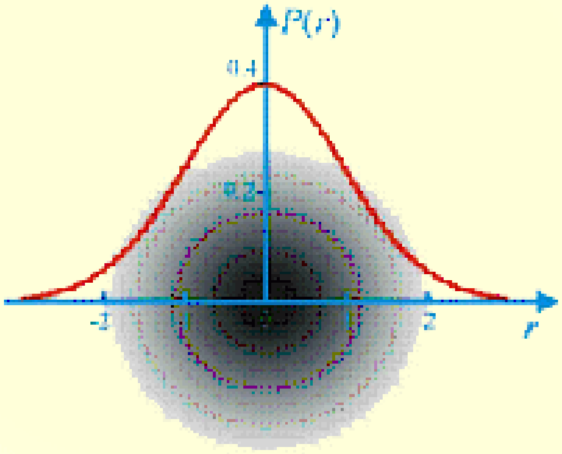
$$\left\langle x^2(t) \right\rangle = \left\langle \left(\sum_{i=1}^{N} s_i \right)^2 \right\rangle = N \left\langle s^2 \right\rangle + \cancel{2N \left\langle s_i s_j \right\rangle}$$

the central limit theorem

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

with $K \propto \left\langle v^2 \right\rangle \tau \equiv \lambda^2 / \tau$

Brownian motion (simple random walk)



$$< r^2(t) > \sim Kt$$; K is the diffusion coefficient

Anomalous diffusion

(a) $< r^2(t) > \sim t^{\alpha}$

$\alpha < 1$ Subdiffusion (dispersive)
$\alpha > 1$ Superdiffusion

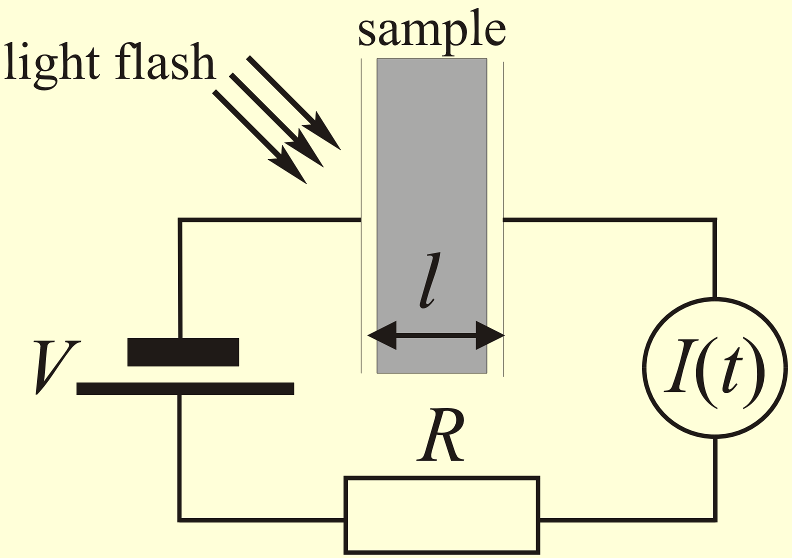
(b) $< r^2(t) > \sim \log^{\beta}(t)$

strong anomaly, ultraslow

Aim: creating framework for treating anomaly and strong anomaly in diffusion.

Physics of Disorder- Subdiffusion

H. Scher and E. Montroll, 1975



in crystalline solids

$$I(t) = \frac{dP}{dt} = \frac{d}{dt}\int_0^L n(l,t)\,dl$$

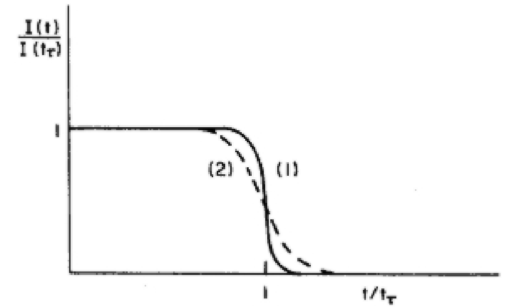


FIG. 10. Normalized current trace $I(t)/I(t_\tau)$ vs t/t_τ expected for a propagating Gaussian packet. Curve (1) corresponds to the longer t_τ and curve (2) corresponds to the shorter t_τ. This figure illustrates the incompatibility of a Gaussian with the universality of $I(t)$.

In disordered solids (no matter organic or inorganic...)

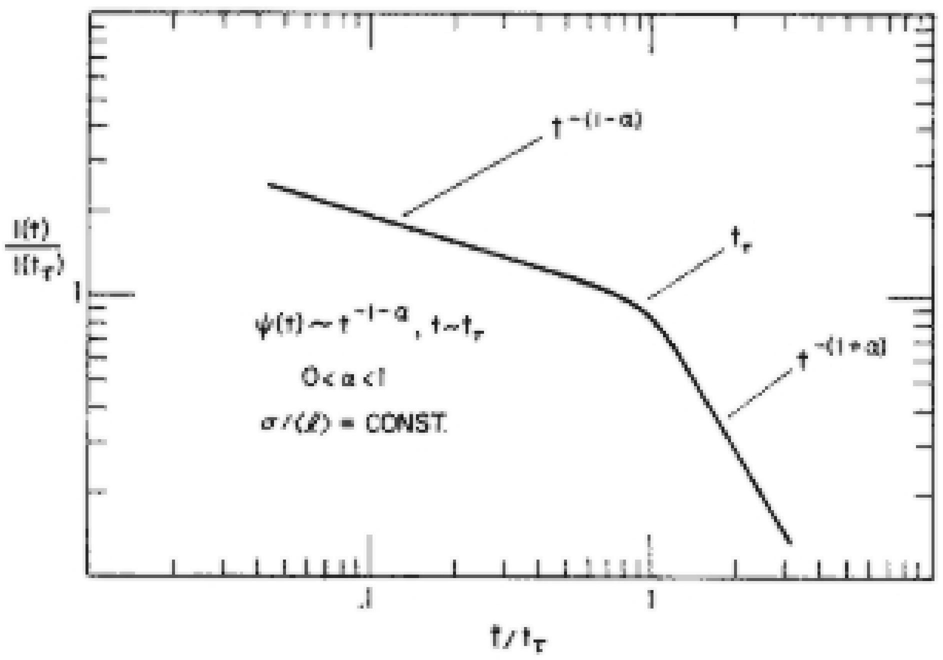
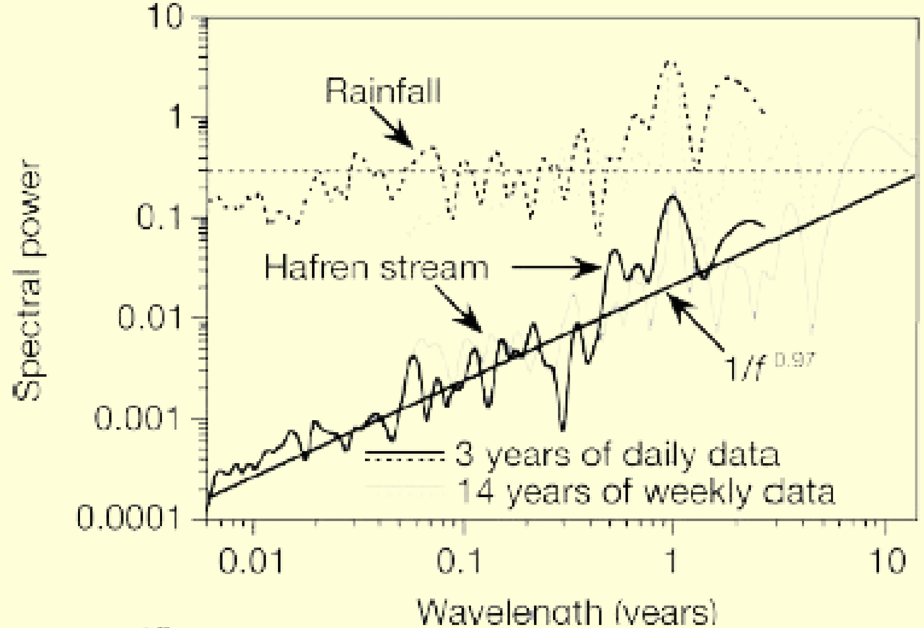
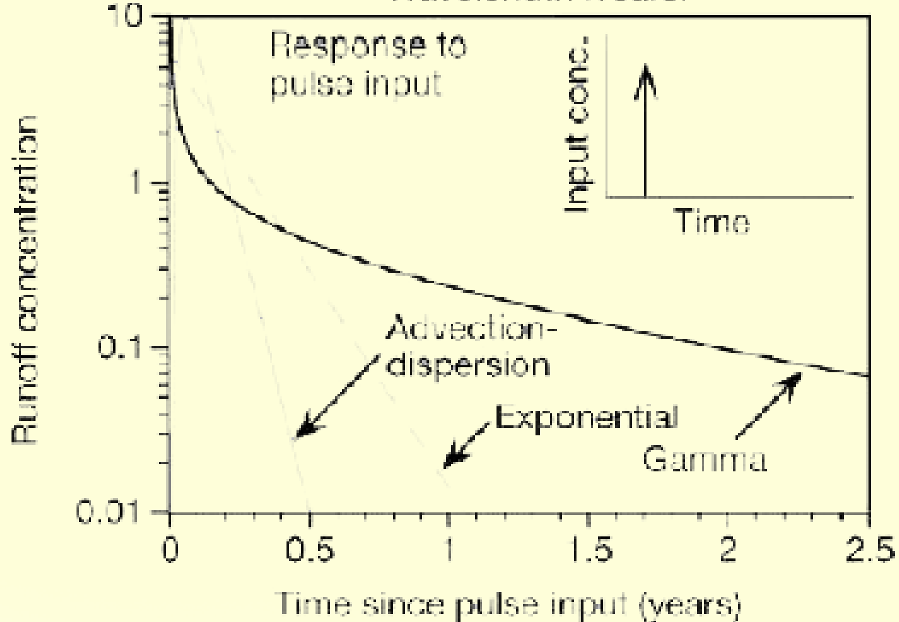


FIG. 7. A log$I$–log$t$ plot indicating the current $I(t)$ associated with a packet of carriers moving, in an electric field, with a hopping-time distribution function $\psi(t) \sim t^{-1-\alpha}$, $0 < \alpha < 1$, towards an absorbing barrier at the sample surface.

Dispersion of Contaminants



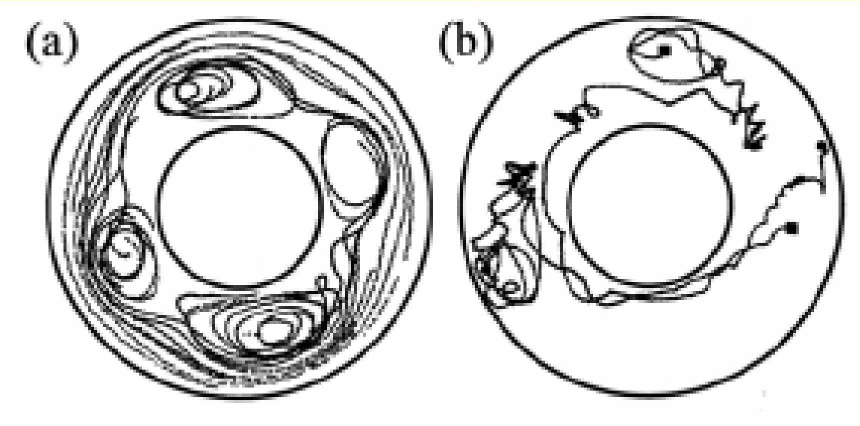


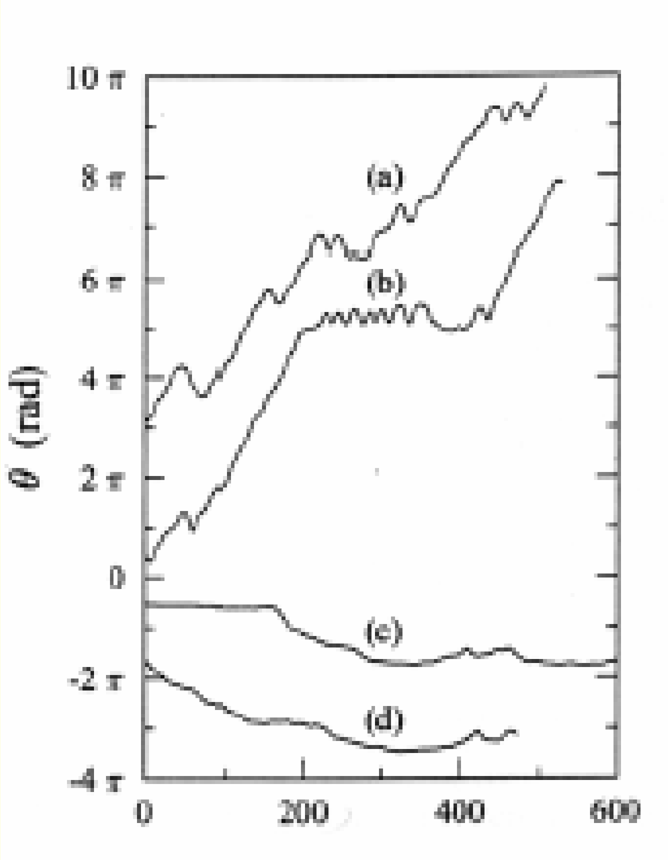
Diffusion of tracers in fluid flows.

Large scale structures (eddies, jets or convection rolls) dominate the transport.
Example. Experiments in a rapidly rotating annulus (Swinney et al.).

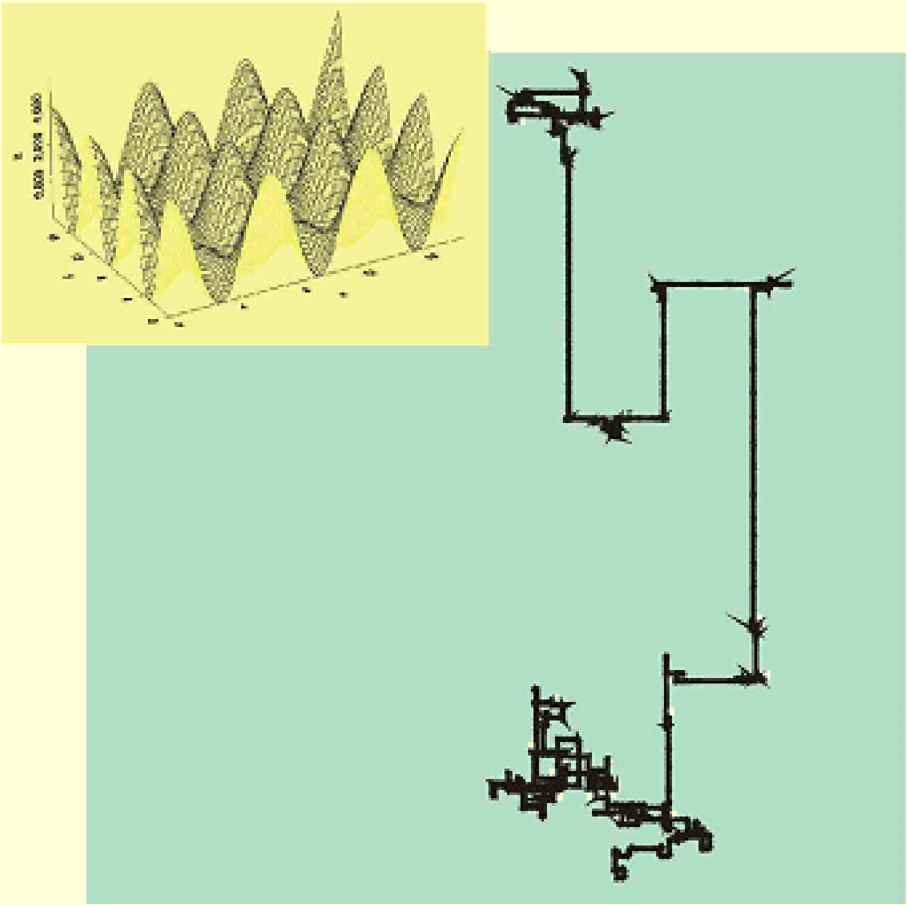
Ordered flow:
Levy diffusion
(flights and traps)

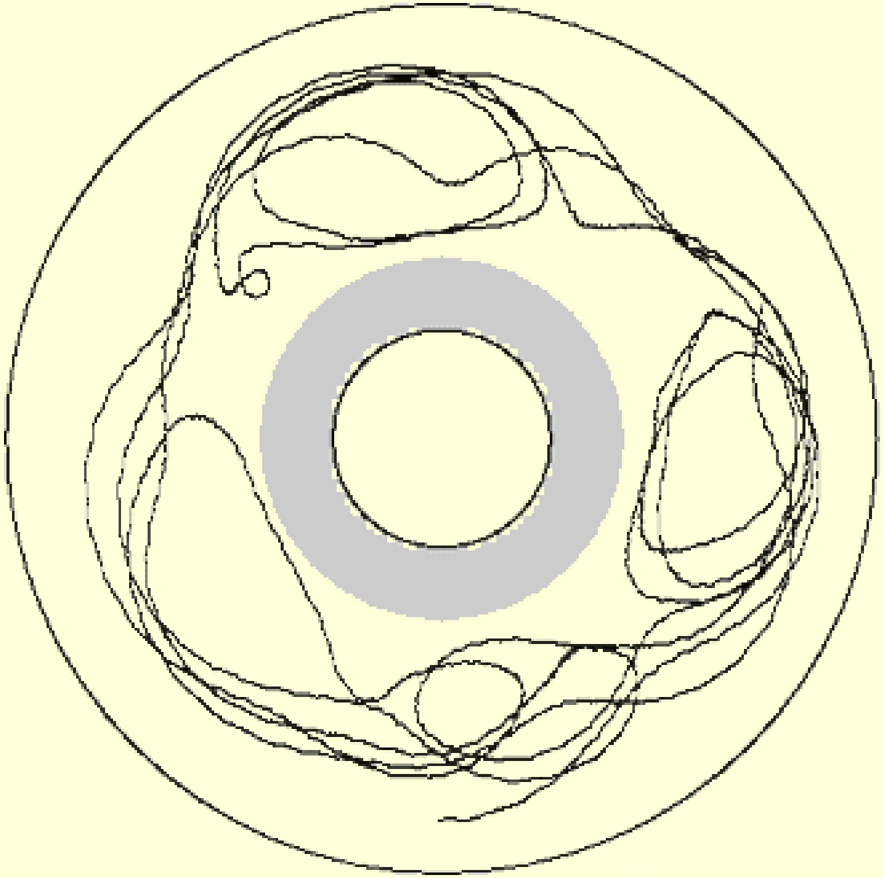
Weakly turbulent flow:
Gaussian diffusion



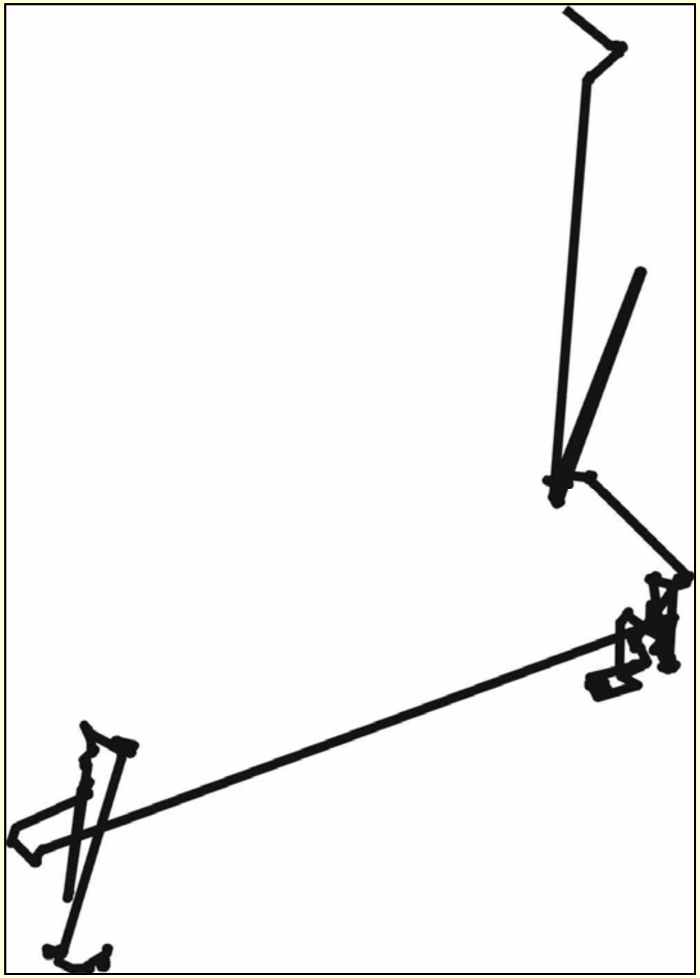


Superdiffusion

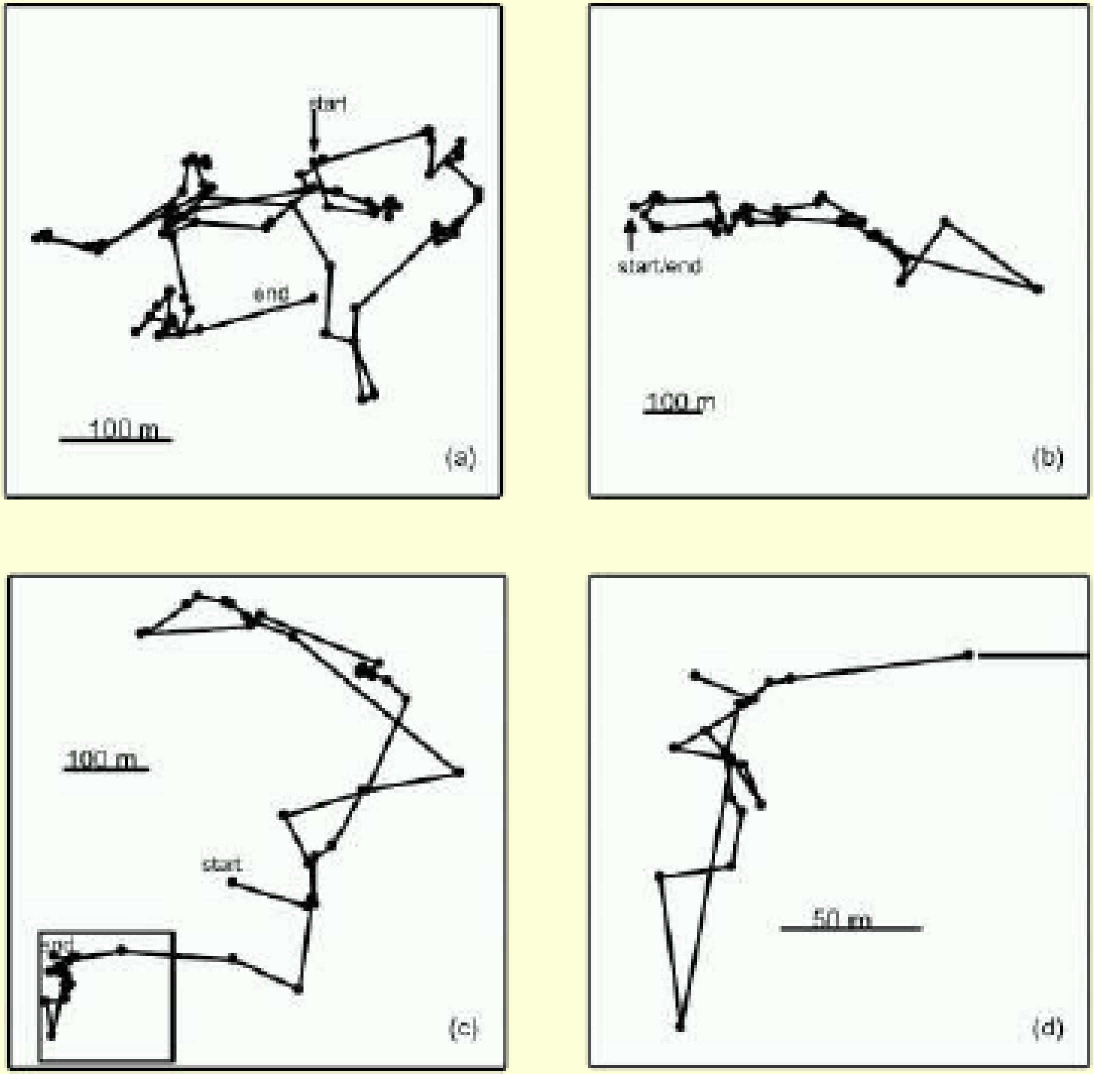




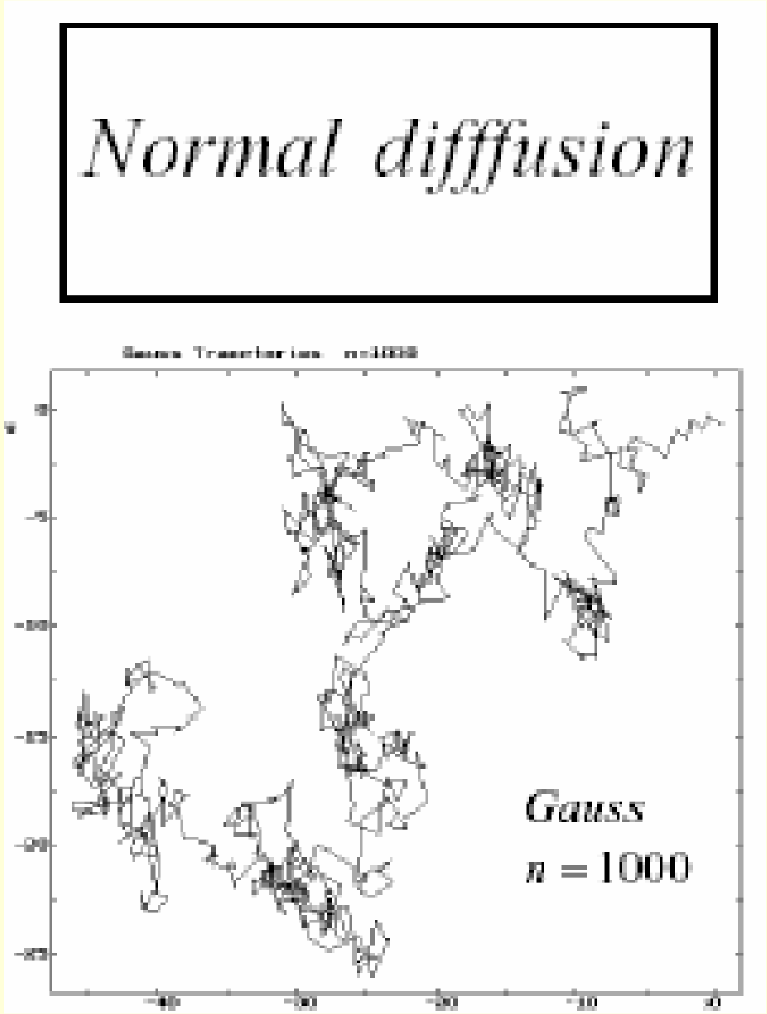
The Flight of the Albatross

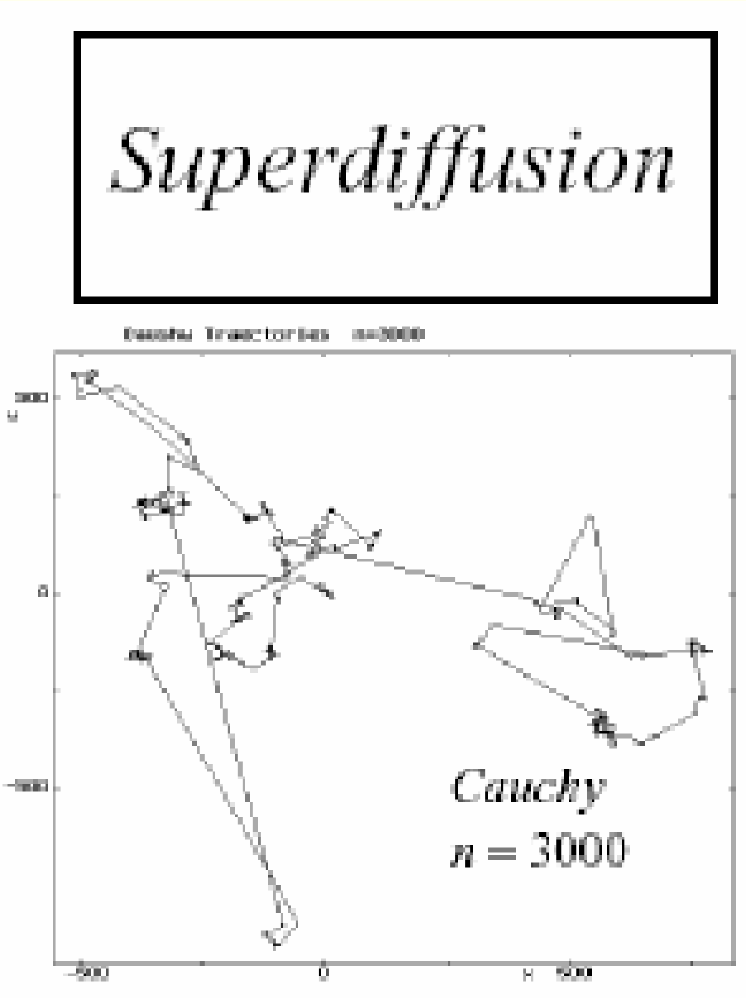


Searching for Food

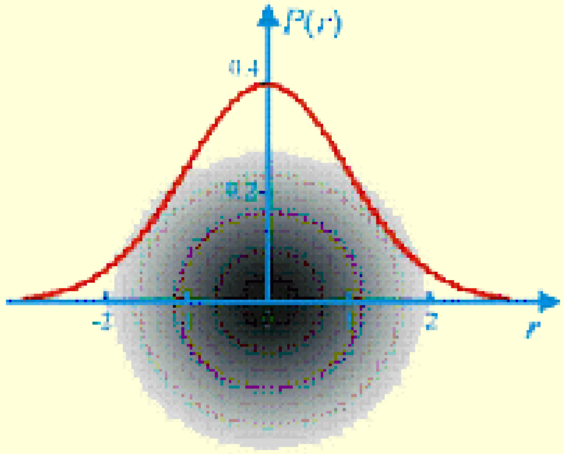


Normal vs. Anomalous Diffusion





Anomalous is Normal...

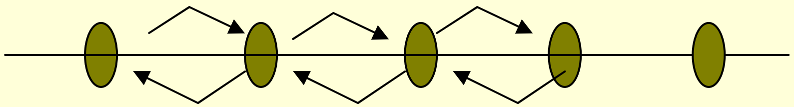


CTRW Frameworks

1. $\psi(r,t) =$ Probability distribution to make a step *r* in time *t*.

   Single motion event

2. Jump Model

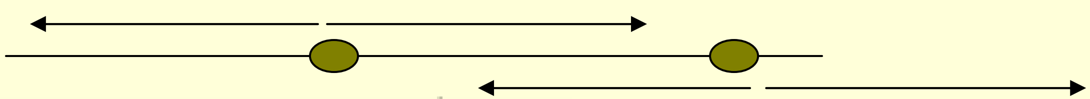


$P(r,t) =$ p.d. of being at *r* at time *t*.

$P(k,u) = \dfrac{\phi(u)}{1-\psi(k,u)}$ Fourier-Laplace

3. $\psi(r,t) = p(r)\psi(t)$, decoupling

4. Velocity model:



$$P(r,t) = \int \eta(r-r',t-\tau)\widetilde{\Psi}(r',\tau)dr'd\tau$$

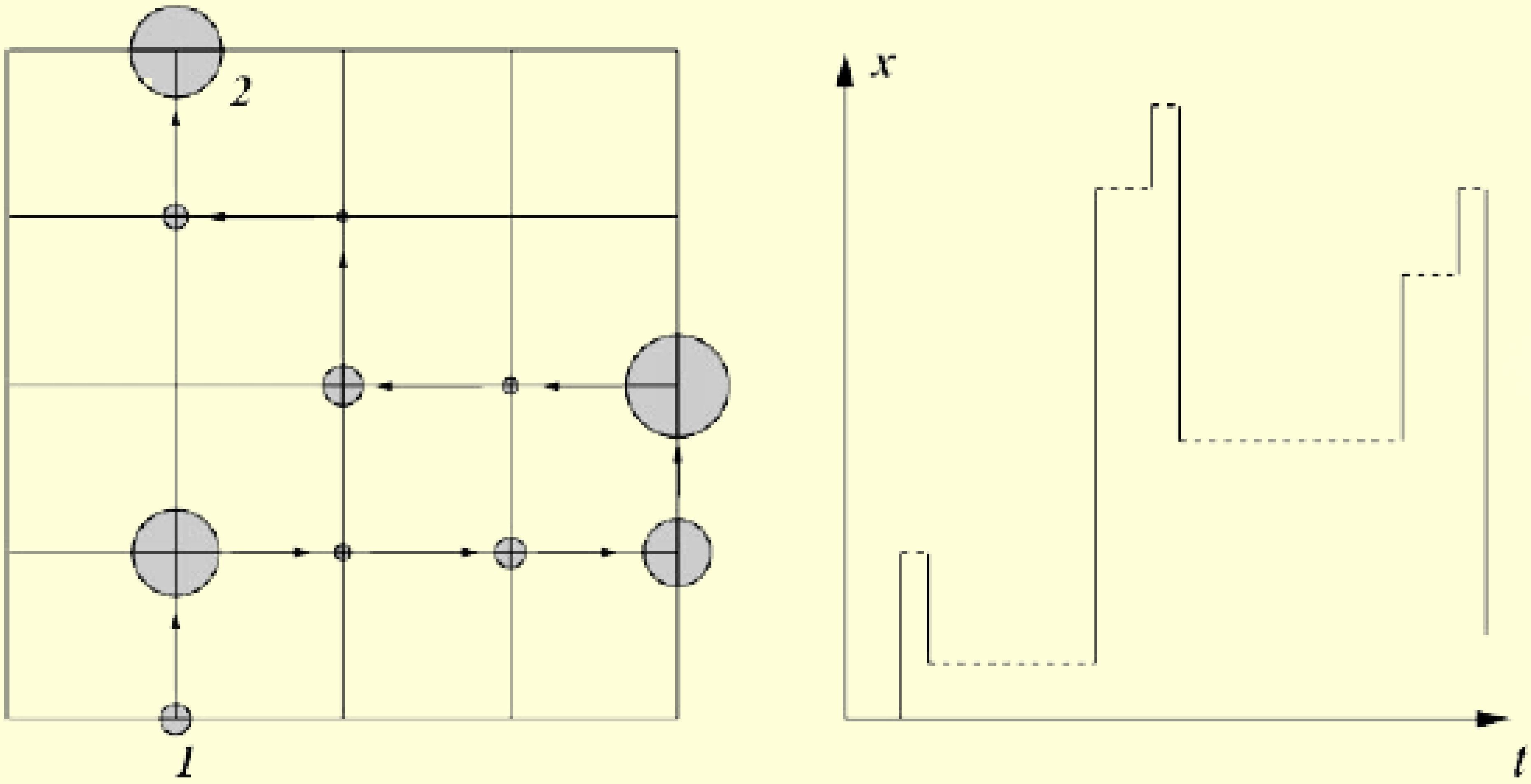
$$P(k,s) = \frac{\widetilde{\Psi}(k,s)}{1-\psi(k,s)}$$

Probability to move distance *r'* at τ

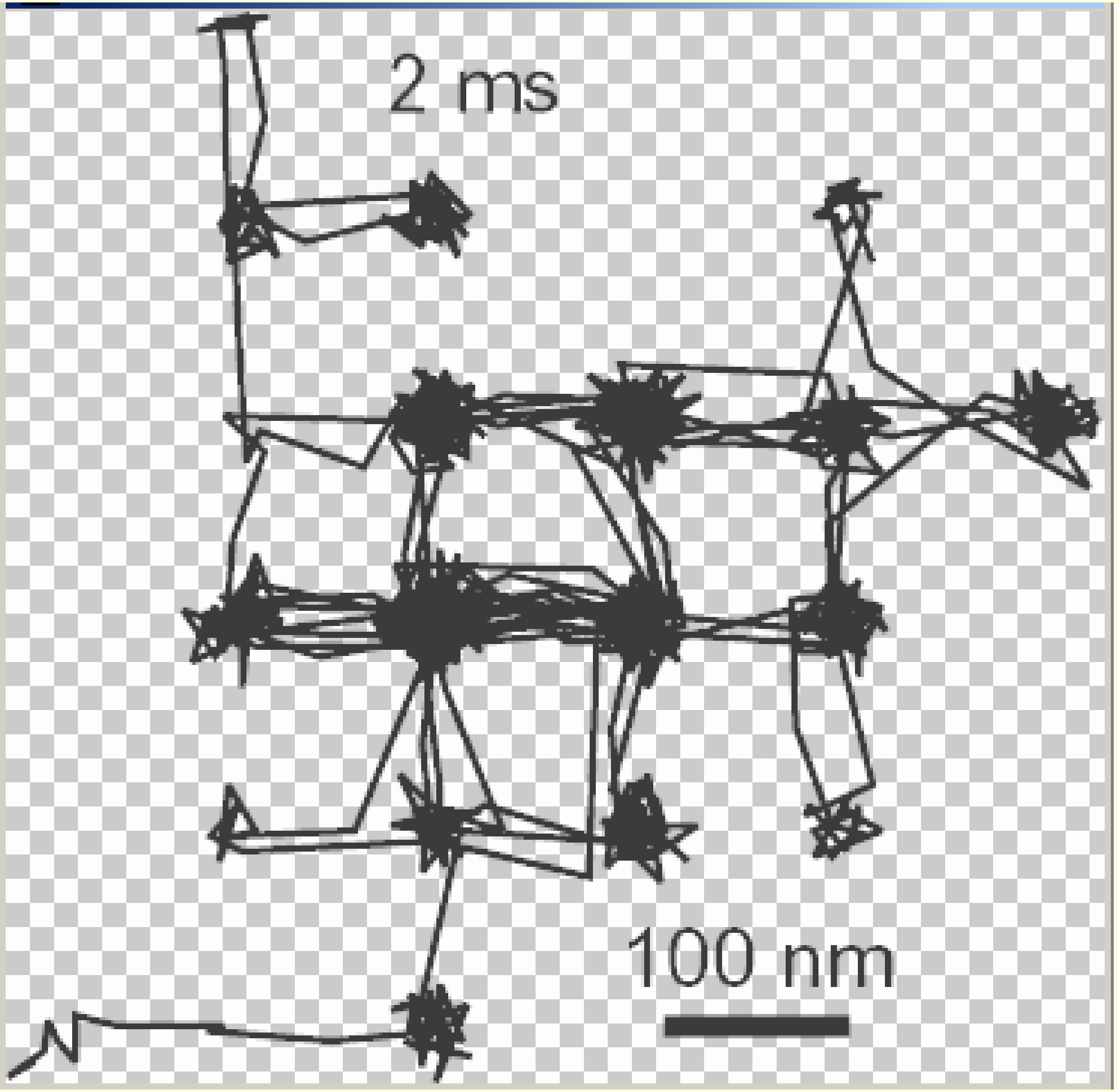
5. <u>Possible generalizations:</u>
   Distribution of velocities
   Coupled models
   Distance dependent velocities

6. $$\tilde{\Psi}(r,t) \sim \delta(|r| - vt)\int_{t}^{\infty} \psi(t')dt'$$

Waiting Times



Continuous time random walk (CTRW) model.


2 ms
100 nm

CTRW

1. Within the random walk framework:
   (a) Small changes in step length or time **not** enough
   (b) Need for processes on **all** scales;
   broad distribution
   no moments

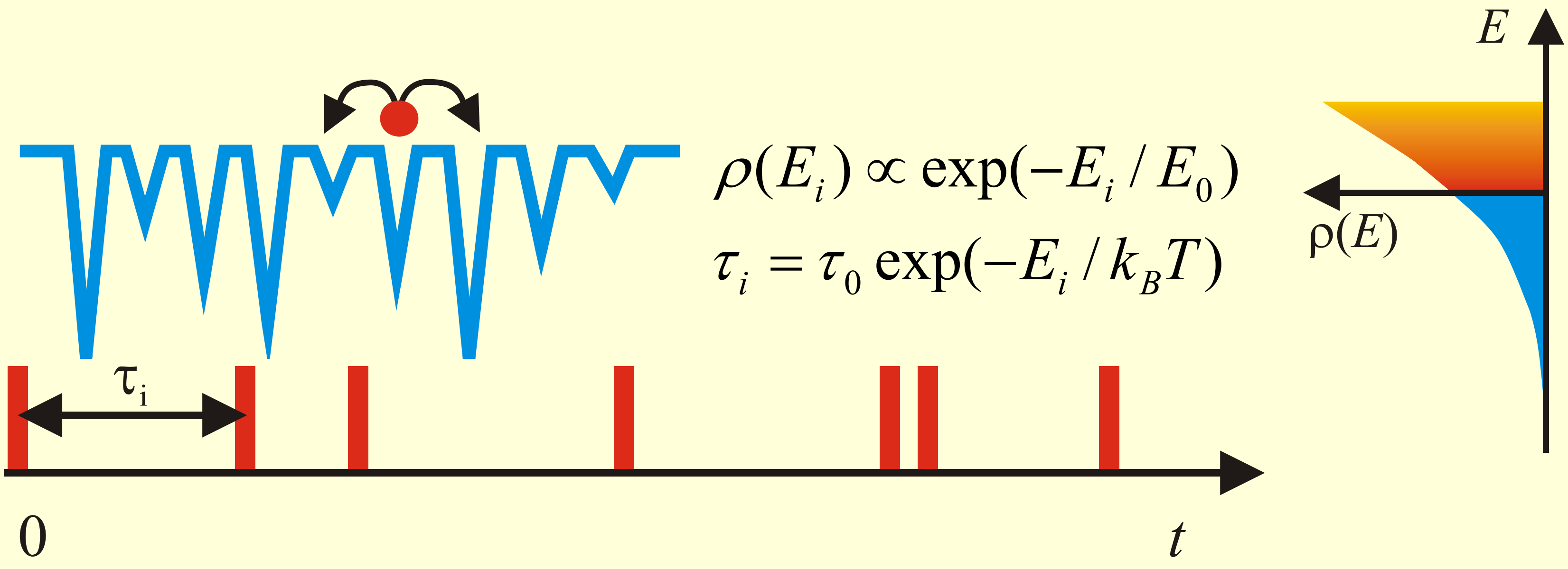
2. $$< r^2(t) > \sim Kt^{\alpha}$$

   Broad distributions

   Simple distributions

3. Long tailed distributions
   temporal (subdiffusion)
   spatial (superdiffusion)

Explanation: The CTRW



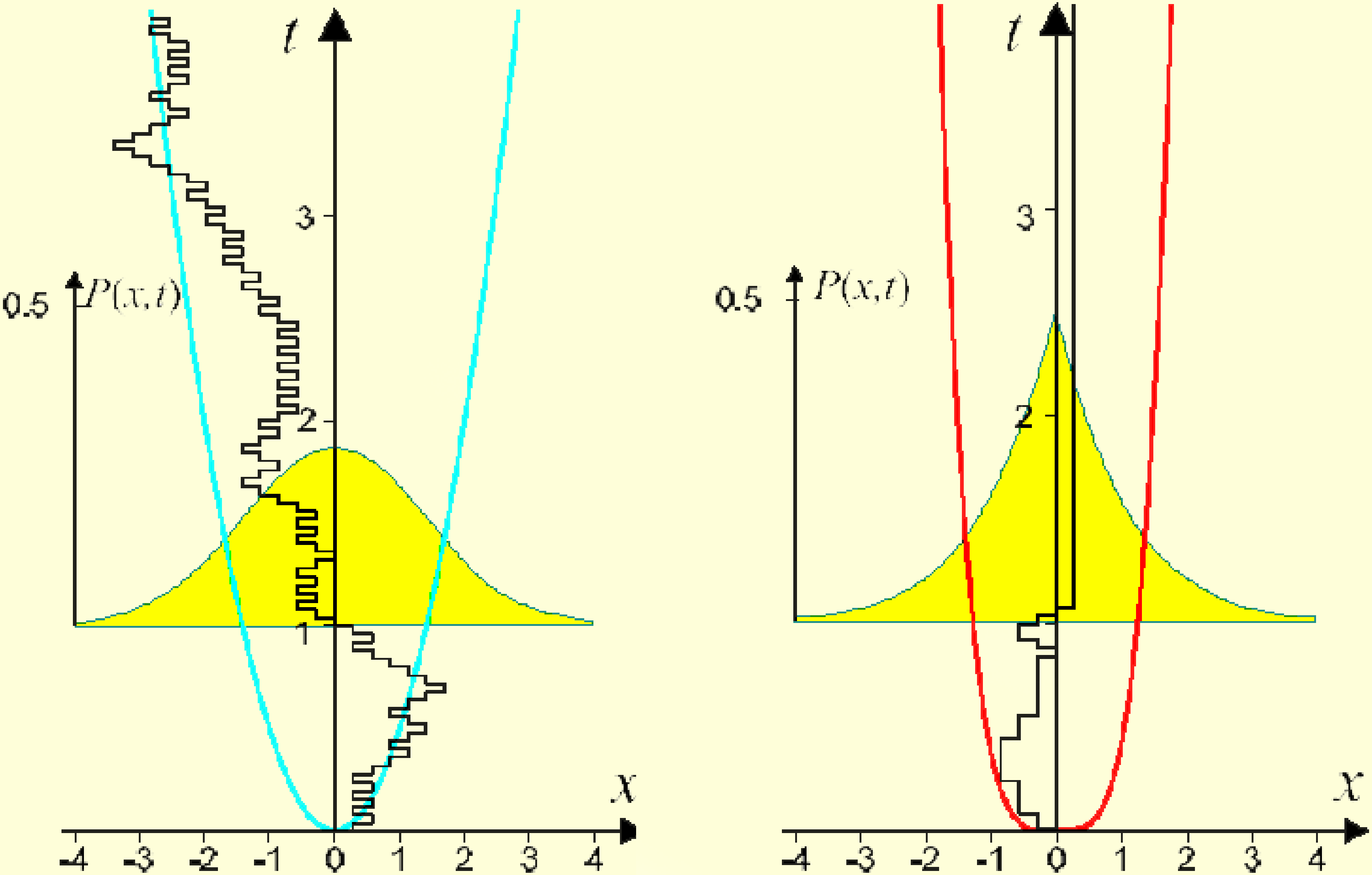
$$\rho(E_i) \propto \exp(-E_i / E_0)$$

$$\tau_i = \tau_0 \exp(-E_i / k_B T)$$

The waiting-time distribution between the two jumps $\psi(t) \propto t^{-1-\alpha}$
with $\alpha = k_B T / E_0$

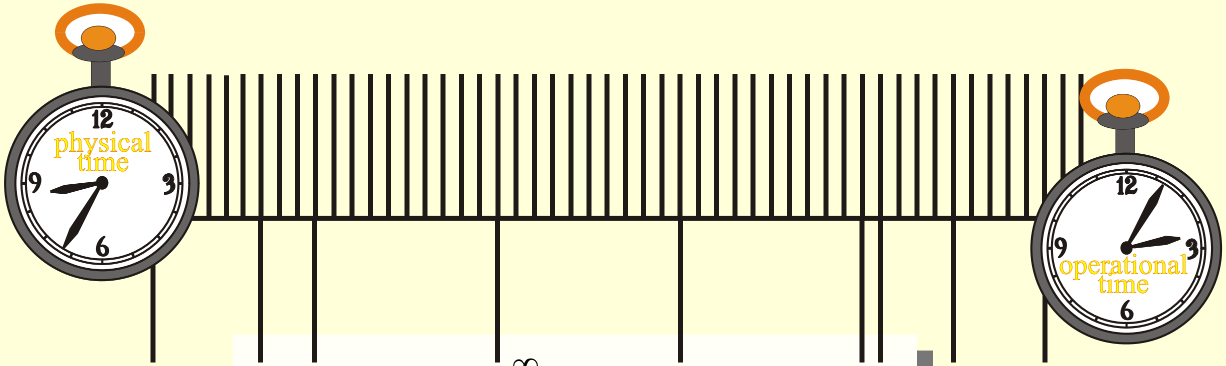
Diffusion anomalies for $0 < \alpha < 1$: the mean waiting time diverges!

Note: The CTRW processes with the power-law waiting times (with $0 < \alpha < 1$) are **always** nonstationary!



t
3
2
1
0.5
$P(x,t)$
x
-4 -3 -2 -1 0 1 2 3 4
t
3
2
0.5
$P(x,t)$
x
-4 -3 -2 -1 0 1 2 3 4

The Subordination



$$P(x,t) = \sum_{n=0}^{\infty} F(x,n)\,\chi_n(t)$$

PDF of the particle's position after n steps (say, a Gaussian)

Probability to make exactly n steps up to the time t

the limiting form of the characteristic function in Laplace representation

$$\hat{\tilde{f}}(k,u) = \frac{1-\tilde{\psi}(u)}{u}\,\frac{1}{1-(1-\lambda^2 k^2)\tilde{\psi}(u)}$$

$\psi(t) \propto t^{-1-\alpha} \;\Rightarrow\; \psi(u) \cong 1 - Au^{\alpha}$ The second moment $\langle x^2(t)\rangle \propto t^{\alpha}$

An increasing number of natural phenomena do not fit into the relatively simple description of diffusion developed by Einstein a century ago

Anomalous diffusion spreads its wings

Joseph Klafter and Igor M Sokolov

AS ALL of us are no doubt aware, this year has been declared "world year of physics" to celebrate the three remarkable breakthroughs made by Albert Einstein in 1905. However, it is not so well known that Einstein's work on Brownian motion – the random motion of tiny particles first observed and investigated by the botanist Robert Brown in 1827 – has been cited more times in the scientific literature than his more famous papers on special relativity and the quantum nature of light. In a series of publications that included his doctoral thesis, Einstein derived an equation for Brownian motion from microscopic principles – a feat that ultimately enabled Jean Perrin and others to prove the existence of atoms (see *Physics World* January pp19–22).

Einstein was not the only person thinking about this type of problem. The 27 July 1905 issue of *Nature* contained a letter with the title "The problem of the random walk", in which the British statistician Karl Pearson proposed the following: "A

Strange behaviour – albatrosses fly by the rules of anomalous diffusion.

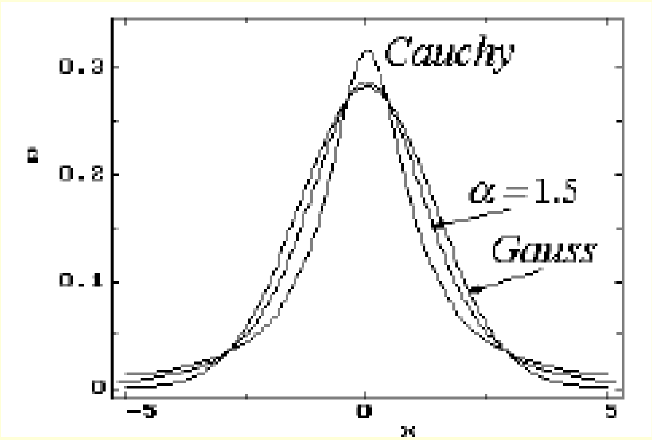
in living organisms. In 1855 Fick published the famous diffusion equation, which, when written in terms of probability, is $\partial p/\partial t = D\partial^2 p/\partial x^2$, where p gives the probability of finding an object at a certain position x, at a time t, and D is the diffusion coefficient. Fick went on to show that the mean-squared displacement of an object undergoing diffusion is $2Dt$.

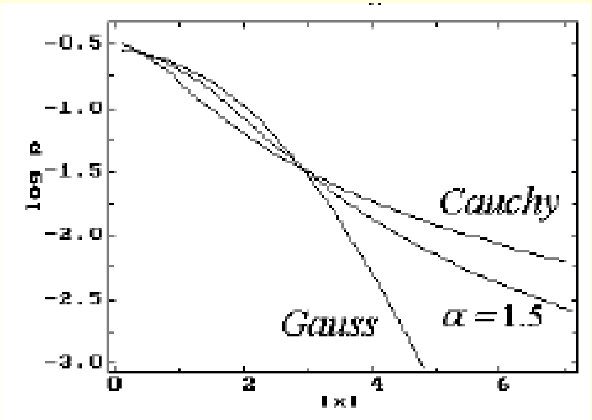
However, Fick's approach was purely phenomenological, based on an analogy with Fourier's heat equation – it took Einstein to derive the diffusion equation from first principles as part of his work on Brownian motion. He did this by assuming that the direction of motion of a particle gets "forgotten" after a certain time, and that the mean-squared displacement during this time is finite. When Einstein combined the diffusion equation with the Boltzmann distribution for a system in thermal equilibrium, he was able to predict the properties of the unceasing motion of Brownian particles in

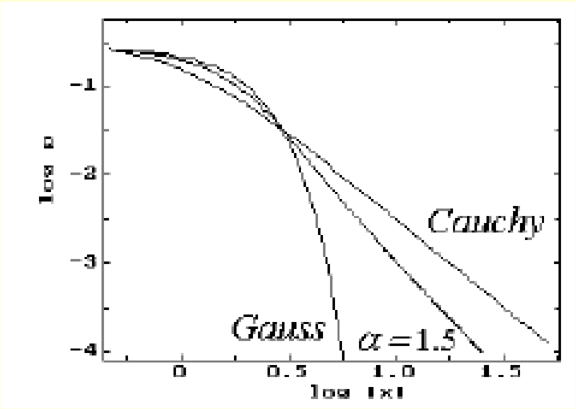
Forms of stable distributions (Levy)

$$P_\alpha(x \to \infty) \sim \frac{1}{|x|^{1+\alpha}} \qquad P_\alpha(x \to \infty) \sim \frac{1}{x^{1+\alpha}}$$

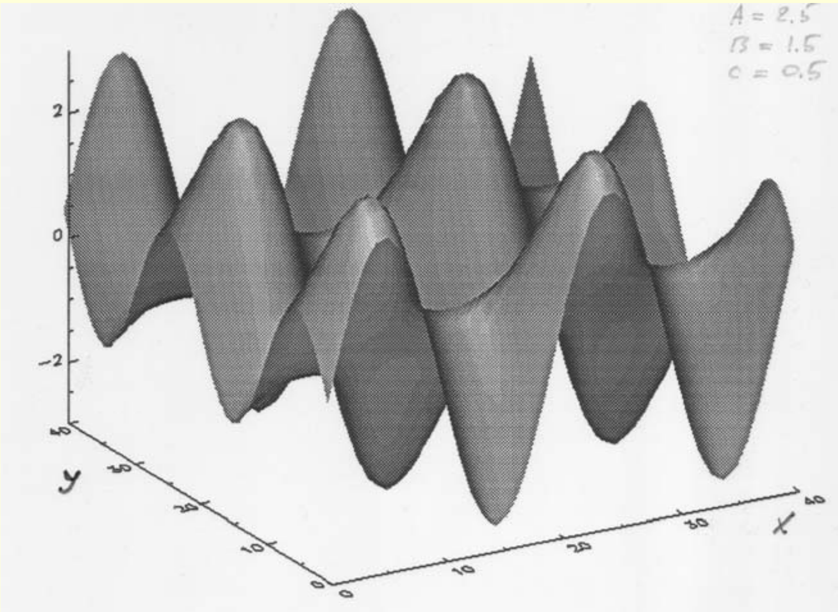
$$0 < \alpha < 2 \qquad\qquad 0 < \alpha < 1$$

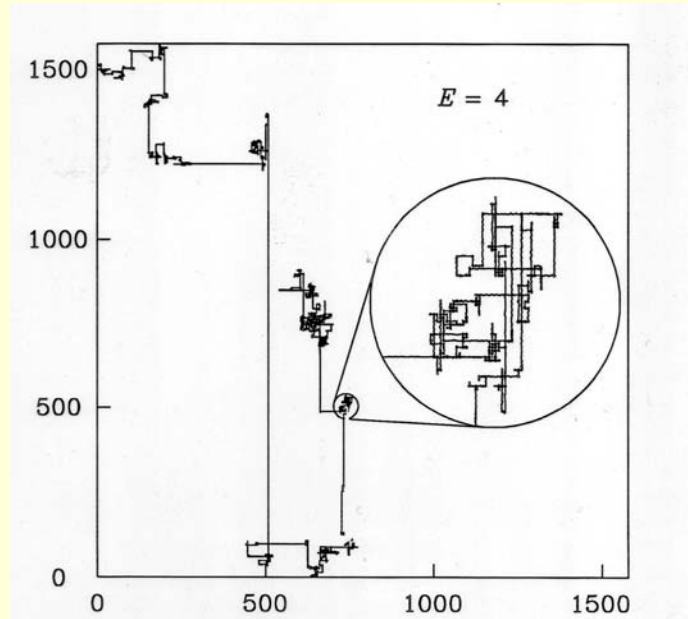


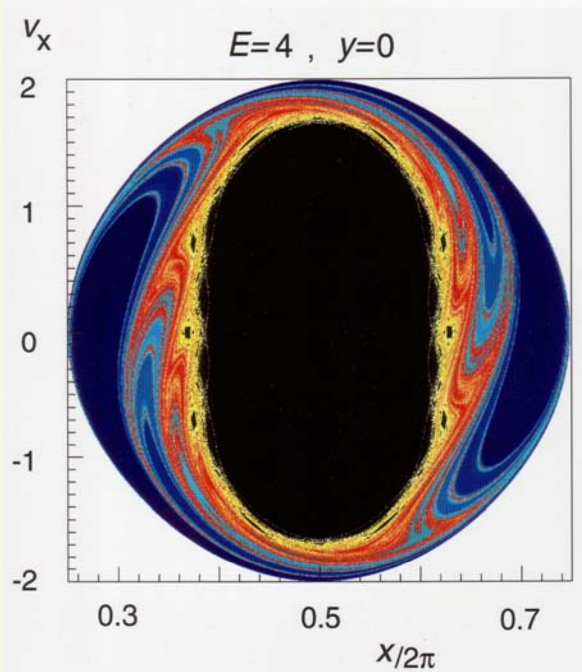


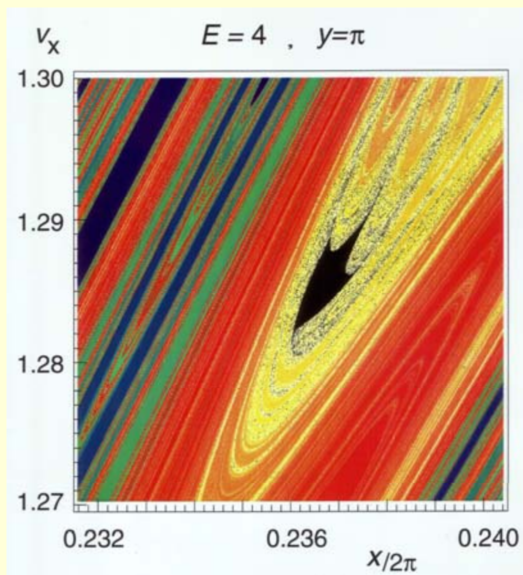


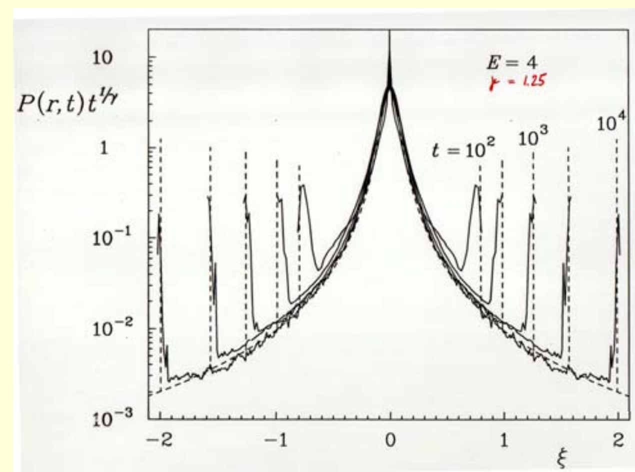
$$V(x, y) = A + B(\cos x + \sin y) + C\cos x\cos y$$





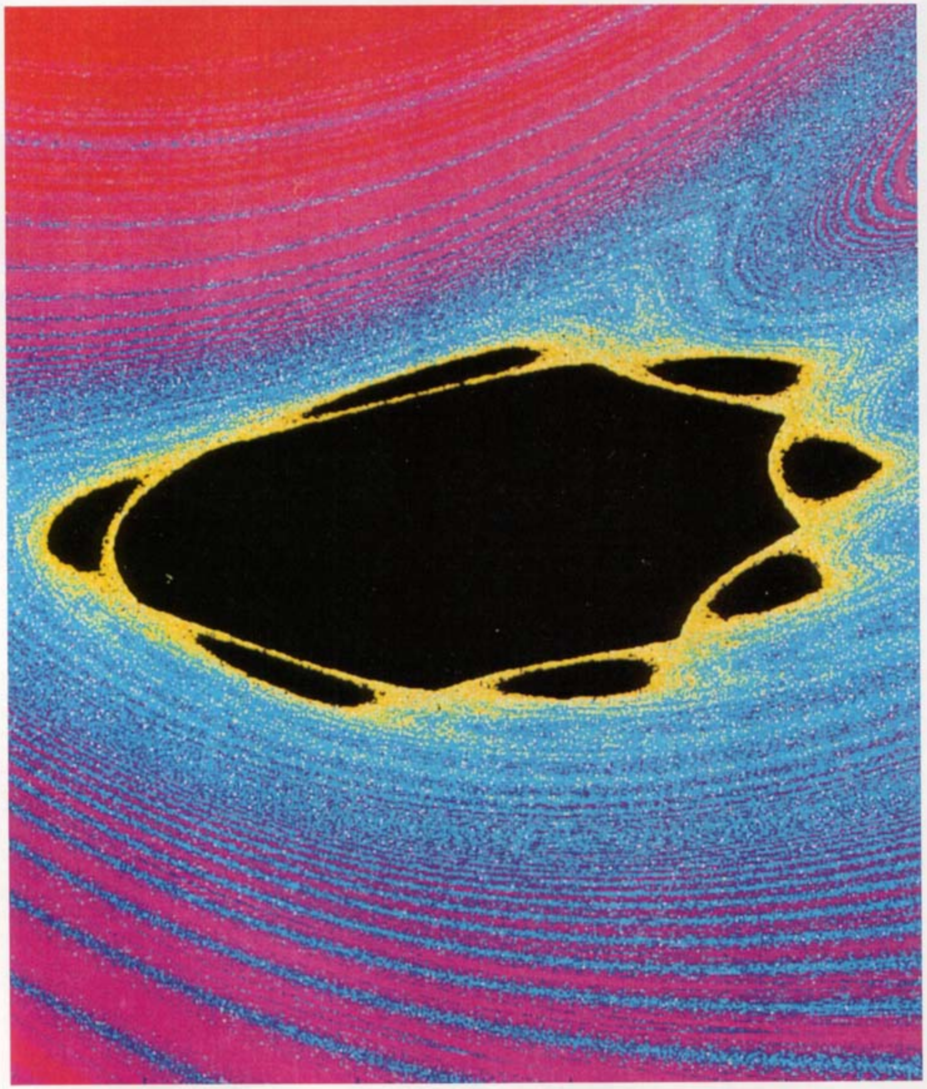






PHYSICS TODAY

FEBRUARY 1996



FLYING BEYOND BROWNIAN MOTION

Questions:

- Can Anomalous diffusion be described on the **same level** of description as simple diffusion?
- How does anomalous diffusion modify **reactions** and first passage times?
- Can we use a generalization of:

$$\frac{\partial}{\partial t}P(x,t)=K\frac{\partial^2}{\partial x^2}P(x,t)$$

Fractional Diffusion Equations

- Following scaling arguments one can postulate equations which are of non-integer order in time or in space, e.g.

$$\frac{\partial^\alpha}{\partial t^\alpha} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t)$$

or

$$\frac{\partial}{\partial t} P(x,t) = K \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} P(x,t)$$

Such equations allow for :

- easier introduction of external forces
- introduction of boundary conditions
- using the methods of solutions known for “normal” PDEs

Fractional Derivatives

1695 Leibnitz - de l'Hospital

$$\frac{d^n}{dt^n} t^m = \frac{m!}{(m-n)!} t^{m-n} \equiv \frac{\Gamma(1+m)}{\Gamma(1+m-n)} t^{m-n}$$

Trivial generalization:

$$\frac{d^\nu}{dt^\nu} t^\mu = {}_0 D_t^\nu t^\mu = \frac{\Gamma(1+\mu)}{\Gamma(1+\mu-\nu)} t^{\mu-\nu}$$

Interesting:

$${}_0 D_t^\nu 1 = \frac{1}{\Gamma(1-\nu)} t^{-\nu}$$

This definition is enough to handle the functions which can be expanded into Taylor series, but obscures the nature of the fractional differentiation operator.

All modern definitions are based on generalizations of the repeated integration formula:

$$ {}_aD_x^{-n} f(x) = \int_a^x \int_a^{y_1} \ldots \int_a^{y_{n-1}} f(y_n) dy_n \ldots dy_1 = \frac{1}{(n-1)!} \int_a^x (x-y)^{n-1} f(y) dy $$

Its generalization is: The fractional integral

$$ {}_{t_0}D_t^{-p} f(t) = \frac{1}{\Gamma(p)} \int_{t_0}^{t} \frac{f(t')}{(t-t')^{1-p}} \qquad (0 < p < 1) $$

Fractional derivatives may be defined through additional differentiation:

$$ {}_{t_0}D_t^{q} f(t) = \frac{d^n}{dt^n} {}_{t_0}D_t^{-(n-q)} f(t) \qquad (n = [q+1]) $$

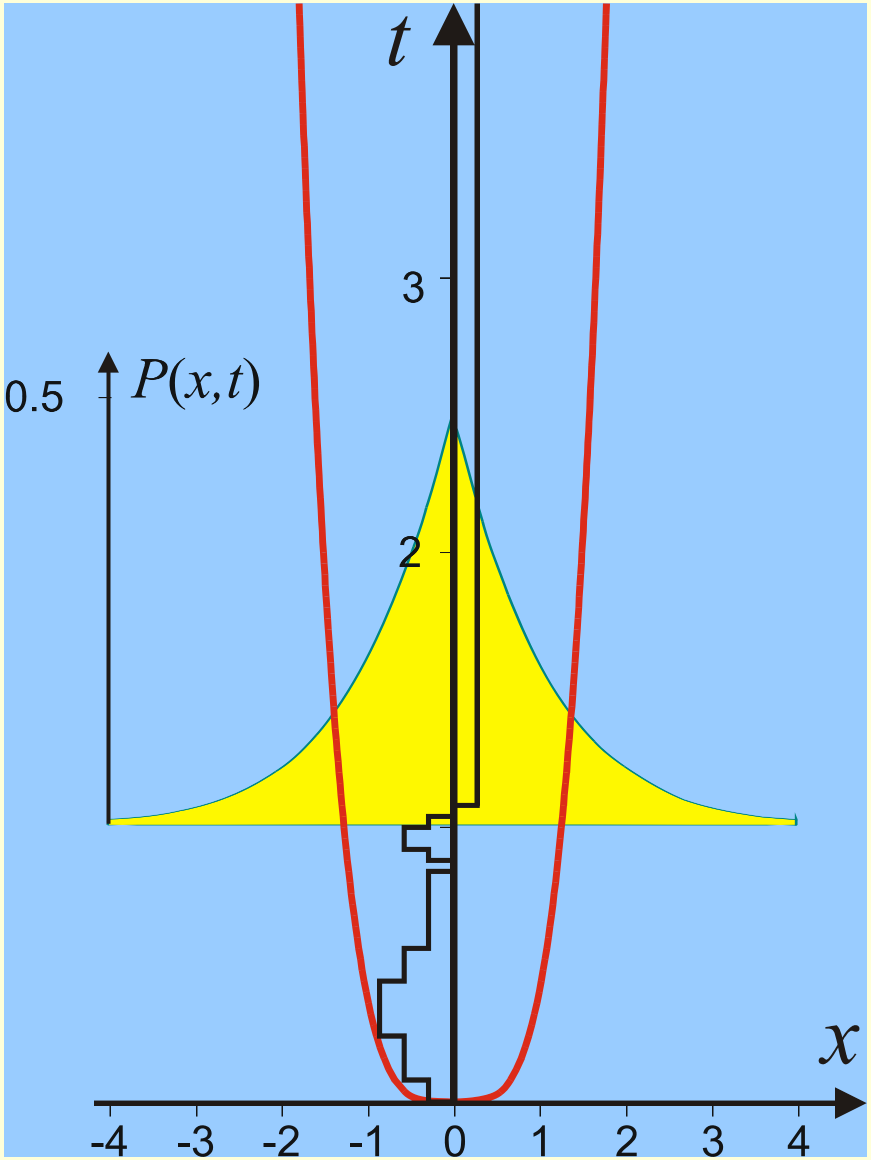
Fractional derivatives are nonlocal integral operators and are best suited for the description of nonlocalities in space (long jumps) or time (memory effects)

Examples of Fractional Calculus with $\alpha = \pm 1/2$

Semi-integral	Function	Semi-derivative
${}_0D_x^{-1/2} f(x) = \dfrac{d^{-1/2}}{dx^{-1/2}} f(x)$	$f(x)$	${}_0D_x^{1/2} f(x) = \dfrac{d^{1/2}}{dx^{1/2}} f(x)$
$2C\sqrt{x/\pi}$	C, any constant	$C/\sqrt{\pi x}$
$\sqrt{\pi}$	$1/\sqrt{x}$	0
$x\sqrt{\pi}/2$	$\sqrt{x}$	$\sqrt{\pi}/2$
$4x^{3/2}/3\sqrt{\pi}$	x	$2\sqrt{x/\pi}$
$\dfrac{\Gamma(\mu+1)}{\Gamma(\mu+3/2)} x^{\mu+1/2}$	$x^{\mu}, \ \mu > -1$	$\dfrac{\Gamma(\mu+1)}{\Gamma(\mu+1/2)} x^{\mu-1/2}$
$\exp(x)\,\mathrm{erf}(\sqrt{x})$	$\exp(x)$	$1/\sqrt{\pi x} + \exp(x)\,\mathrm{erf}(\sqrt{x})$
$2\sqrt{\pi/x}\,[\ln(4x) - 2]$	$\ln x$	$\ln(4x)/\sqrt{\pi x}$

$$\frac{\partial}{\partial t}P(x,t) = {}_tD_0^{\,1-\alpha} K \frac{\partial^2}{\partial x^2} P(x,t')$$

$$\boxed{{}_tD_0^{\,1-\alpha} f(t) = \frac{\partial}{\partial t}\frac{1}{\Gamma(1-\alpha)}\int_0^t \frac{1}{(t-t')^{\alpha}} f(t')dt'}$$



The Fractional Fokker-Planck Equation

$$\boxed{\dot{P}(x,t) = {}_0D_t^{1-\alpha}\left[\frac{\partial}{\partial x}\frac{V'(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2}\right]P(x,t)}$$

$$[\eta_\alpha] = \sec^{\alpha-2}$$

- Force-free mean squared displacement

$$< x^2(t) >_0 = \frac{2K_\alpha}{\Gamma(1+\alpha)} t^\alpha$$

- Stationary solution

$$P_{st} \propto \exp\left(-\frac{V(x)}{k_B T}\right)$$

$$K_\alpha = \frac{k_B T}{m\eta_\alpha}$$ **Generalized Einstein-Stokes relation**

Not all systems obey the fractional Fokker-Planck Equation

- Fractional Langevin equation

$$m\frac{d^2}{dt^2}x(t)+m\eta_\alpha\,{}_0D_t^\alpha x(t)=T(t)$$

$T(t)$ = Gaussian random noise

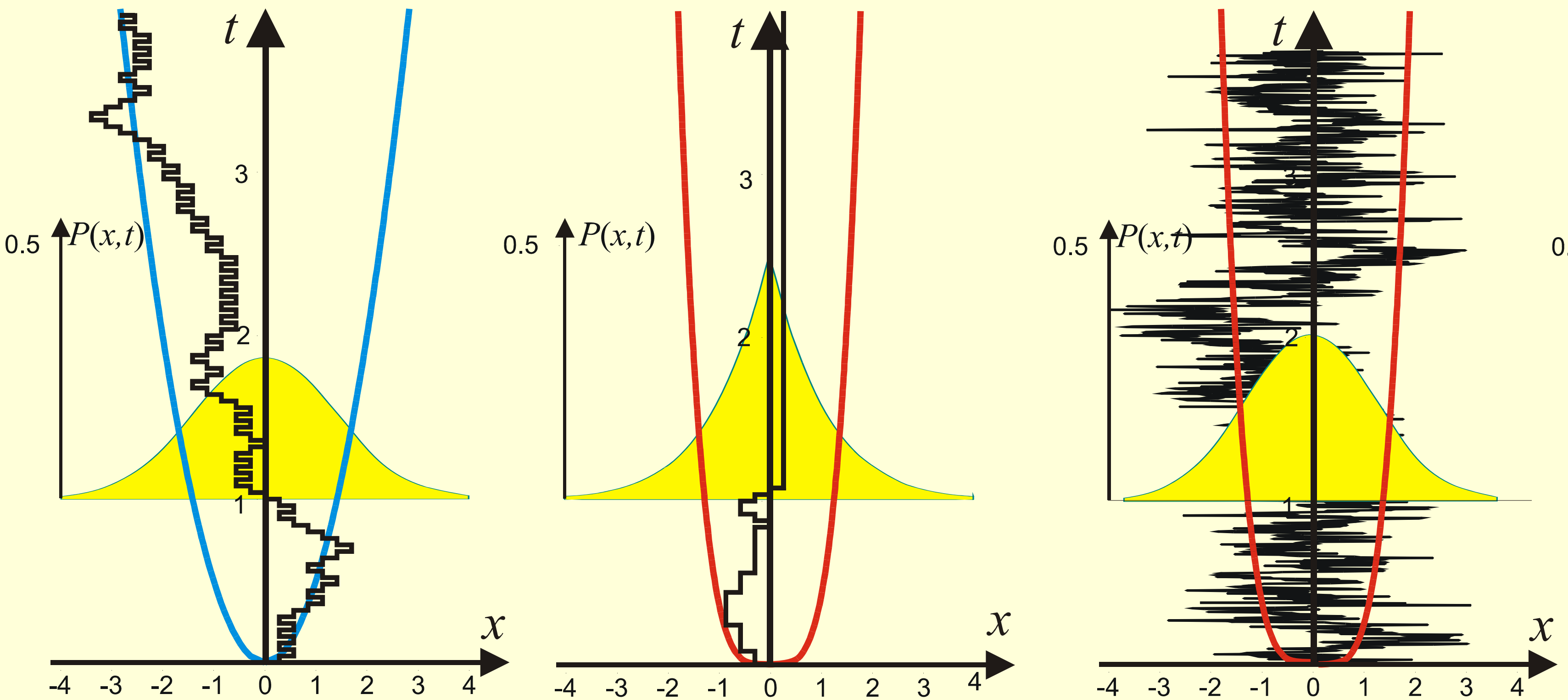
$$\langle T(t)T(0)\rangle \sim t^{-\alpha}$$

- The corresponding diffusion equation is:

$$\frac{\partial}{\partial t}P_{\mathrm{FBM}}(x,t)=\alpha K_\alpha t^{\alpha-1}\frac{\partial^2}{\partial x^2}P_{\mathrm{FBM}}(x,t)$$

Local in time

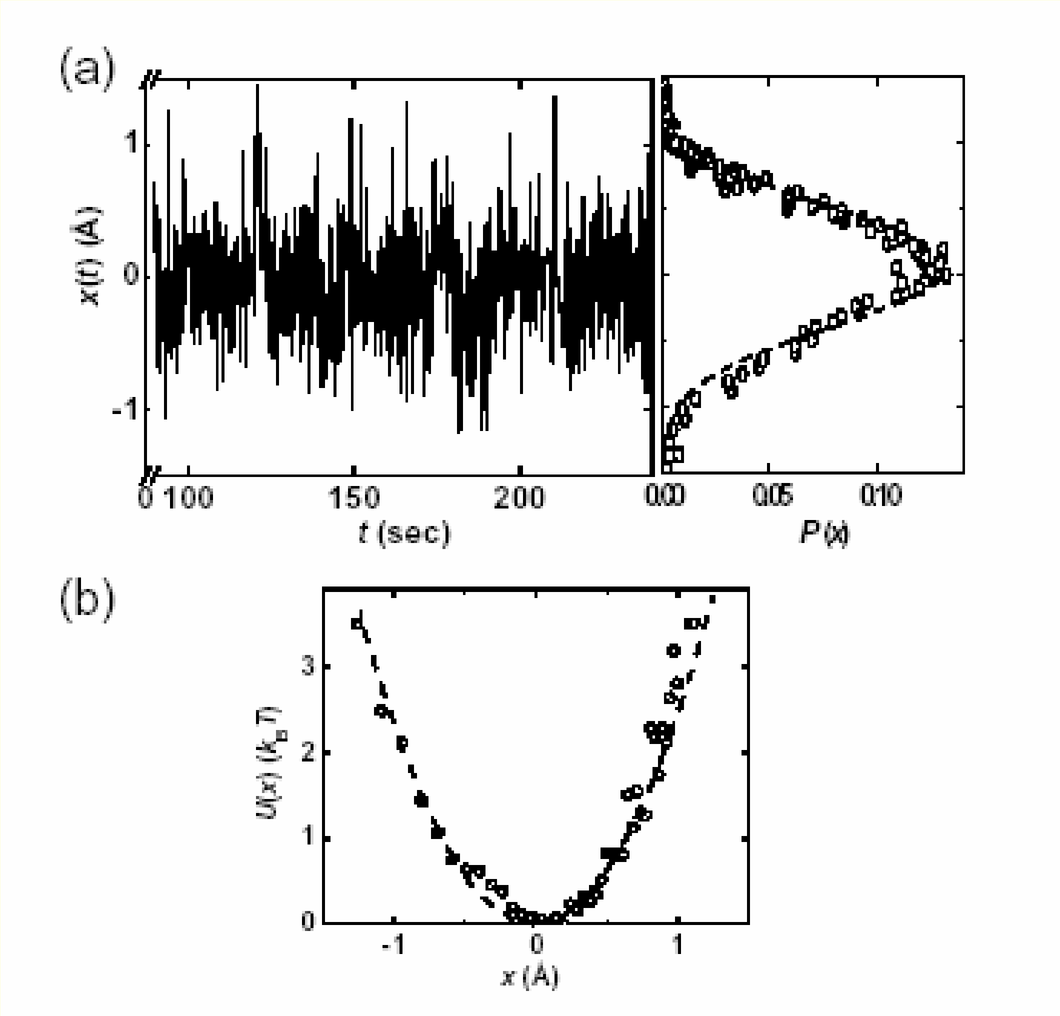
The fractional Brownian motion

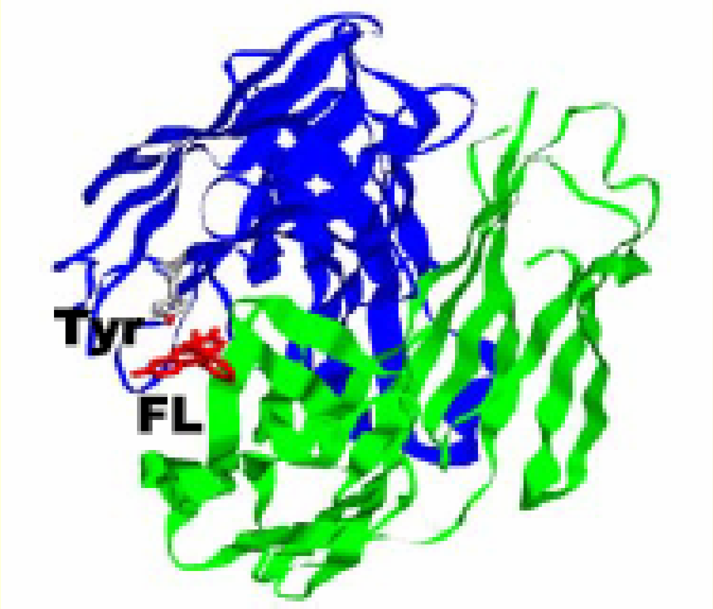


t
3
2
1
0.5
P(x,t)
x
-4 -3 -2 -1 0 1 2 3 4
t
3
2
0.5
P(x,t)
x
-4 -3 -2 -1 0 1 2 3 4
t
3
2
1
0.5
P(x,t)
0.5
x
-4 -3 -2 -1 0 1 2 3 4

Single molecule experiments in proteins

- Fluorescence resonant energy transfer (tens of angstroms).
- Photo-induced electron transfer (a few angstroms)





$$x(t) = X(t) - X_{\mathbf{eq}}$$

S. C. Kou and X. S. Xie, PRL (2004)
W. Min et al., PRL (2005)

Not all diffusion processes lead to power-law scaling

Prominent examples are:

•Simple crossover models in CTRW: Waiting-time distributions with exponential cutoff

•Sinai diffusion: Retarding subdiffusion typically with logarithmic scaling $\left\langle x^2(t)\right\rangle \propto \ln^\alpha t$ (genuine model corresponds to α = 4).

•Retarding superdiffusion: Truncated Lévy flights.

Although such examples can easily be formulated within the framework of (continuous time) random walks, they can not be described through the fractional diffusion equations.

$\Rightarrow$ We need generalizations of the FDE scheme.

Distributed-Order Diffusion Eqns.

Example: The equation with the distributed-order Caputo derivative in the l.h.s.

$$\int_0^1 d\beta \tau^{\beta-1} p(\beta) \frac{\partial^\beta P}{\partial t^\beta} = K \frac{\partial^2 P}{\partial x^2}$$

The Fourier-Laplace representation of the Green's function

$$\tilde{\hat{f}}(k,s) = \frac{1}{s} \frac{I(s\tau)}{I(s\tau) + k^2 K \tau} \quad \text{with} \quad I(s\tau) = \int_0^1 d\beta \, (s\tau)^\beta \, p(\beta)$$

shows that a process *may be* subordinated to a Wiener process:

$$P(x,t) = \int_0^\infty d\omega \frac{e^{-x^2/4\omega}}{\sqrt{4\pi\omega}} T(\omega,t) \text{ with } \tilde{T}(\omega,s) = \frac{I(s\tau)}{s} e^{-\omega I(s\tau)}$$

References:

“Beyond Brownian Motion”
Physics Today, **49**, 33 (1996).

“Strange Kinetics”
Nature **363**, 31 (1993).

“The Random Walk Guide…”
Physics reports **339**, 1 (2000).

“Fractional Kinetics”
Physics Today **55**, 48 (2002).

“The Restaurant at the End of the Random Walk….”
Journal Physics A **37**, R161 (2004).

“Anomalous Diffusion Spreads its Wings”
Physics World **18**, 29 August (2005).

Simple Example: A Crossover

Two different β-values: $p(\beta) = B_1\delta(\beta-\beta_1) + B_2\delta(\beta-\beta_2)$

with $\beta_1 < \beta_2$

$$I(s\tau) = \int_0^1 d\beta\,(s\tau)^\beta\,p(\beta) = \underbrace{B_1\tau^{\beta_1}}_{b_1} s^{\beta_1} + \underbrace{B_2\tau^{\beta_2}}_{b_2} s^{\beta_2}$$

$$\langle x^2(t)\rangle = 2K\tau\mathcal{L}_s^{-1}\left\{\frac{1}{sI(s\tau)}\right\} = \frac{2K\tau}{b_2} t^{\beta_2} E_{\beta_2-\beta_1,\beta_2+1}\left(-\frac{b_1}{b_2}t^{\beta_2-\beta_1}\right)$$

From the asymptotics of the generalized Mittag-Leffler function at small / large negative arguments one gets

$$\langle x^2\rangle \approx \frac{2D\tau}{B_2\Gamma(\beta_2+1)}\left(\frac{t}{\tau}\right)^{\beta_2} \propto t^{\beta_2}$$

small t

$$\langle x^2\rangle \approx \frac{2D\tau}{B_1\Gamma(\beta_1+1)}\left(\frac{t}{\tau}\right)^{\beta_1} \propto t^{\beta_1}$$

large t

The process described is a decelerating subdiffusion

Example: Sinai-like Diffusion

The Sinai-like models correspond to $p(\beta) = \nu\beta^{\nu-1}$ so that

$$I(s\tau) = \int_0^1 d\beta\,(s\tau)^{\beta}\,p(\beta) \approx \begin{cases} \nu s\tau / \ln s\tau, & s\tau >> 1 \\ \Gamma(\nu+1)/\left[\ln\left(1/s\tau\right)\right]^{\nu}, & s\tau << 1 \end{cases}$$

The long-time behavior of the pdf $(t/\tau >> 1)$:

$$P(x,t) \approx \frac{1}{\sqrt{4D\tau}}\left[\frac{\Gamma(\nu+1)}{\ln^{\nu}(t/\tau)}\right]^{1/2} \exp\left\{-\left(\frac{\Gamma(\nu+1)}{K\tau}\right)^{1/2} \frac{|x|}{\ln^{\nu/2}(t/\tau)}\right\}$$

Note the characteristic tent-like shape of the pdf with

$$\left\langle x^2(t)\right\rangle \cong \frac{2K\tau}{\Gamma(\nu+1)} \ln^{\nu}(t/\tau)$$

Riemann-Liouville DODE for subdiffusion

$$\frac{\partial P(x,t)}{\partial t} = \int_0^1 d\beta p(\beta) K \tau^{1-\beta} {}_0D_t^{1-\beta} \frac{\partial^2}{\partial x^2} P(x,t)$$

The Laplace transform of the characteristic function:

$$f(k,s) = \frac{1}{sI_{RL}(s)\left(\left[I_{RL}(s)\right] + k^2 K\tau\right)} \quad \text{with} \quad I_{RL}(s) = \int_0^1 d\beta p(\beta)(s\tau)^{-\beta}$$

The solution in a subordination form:

$$P(x,t) = \int_0^\infty d\omega \frac{e^{-x^2/4\omega}}{\sqrt{4\pi\omega}} T_{RL}(\omega,t) \, \text{with} \, \widetilde{T}_{RL}(\omega,s) = \frac{1}{sI_{RL}(s)} e^{-\omega/I(s)}$$

The crossover model for subdiffusion

Two different β-values: $p(\beta) = B_1\delta(\beta - \beta_1) + B_2\delta(\beta - \beta_2)$

with $\beta_1 < \beta_2$

$$I(s\tau) = \int_0^1 d\beta\, (s\tau)^\beta\, p(\beta) = B_1 \tau^{\beta_1} s^{\beta_1} + B_2 \tau^{\beta_2} s^{\beta_2}$$

$$\left\langle x^2(t) \right\rangle = D\tau L_s^{-1}\left\{ \frac{2I_{RL}(s\tau)}{s} \right\} = \frac{2B_1 K\tau}{\Gamma(1+\beta_1)}\left(\frac{t}{\tau}\right)^{\beta_1} + \frac{2B_2 K\tau}{\Gamma(1+\beta_2)}\left(\frac{t}{\tau}\right)^{\beta_2}$$

$$\left\langle x^2 \right\rangle \approx \frac{2K\tau}{B_1\Gamma(1+\beta_1)}\left(\frac{t}{\tau}\right)^{\beta_1} \propto t^{\beta_1}$$

small t

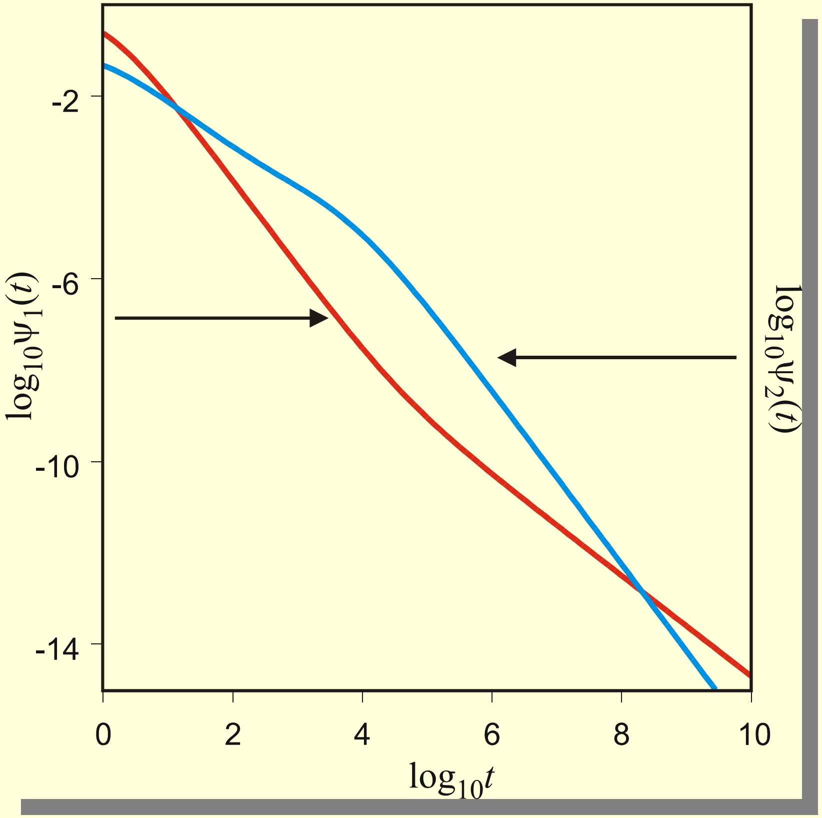
$$\left\langle x^2 \right\rangle \approx \frac{2B_2 K\tau}{\Gamma(1+\beta_2)}\left(\frac{t}{\tau}\right)^{\beta_2} \propto t^{\beta_2}$$

large t

The process described is an accelerated subdiffusion

Example: A simple crossover

Easier to start from cumulative functions:



$$\Psi_1(t) = 1 - \frac{a}{t^{\alpha}} - \frac{b}{t^{\beta}}$$

$$\psi_1(t) \cong \frac{\alpha a}{t^{\alpha+1}} + \frac{\beta b}{t^{\beta+1}}$$

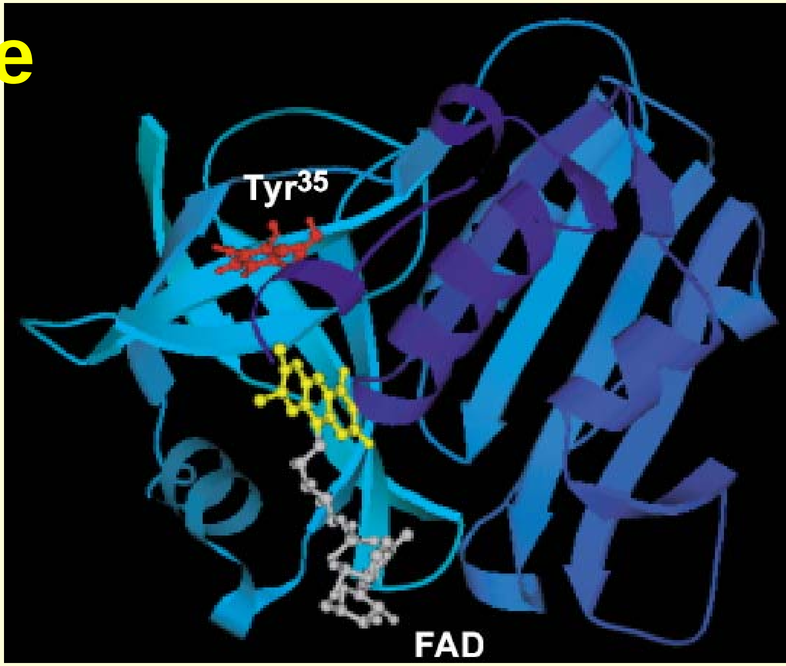
Slowing down process

Accelerating process

$$\Psi_2(t) = 1 - \frac{1}{ct^{\alpha} + dt^{\beta}}$$

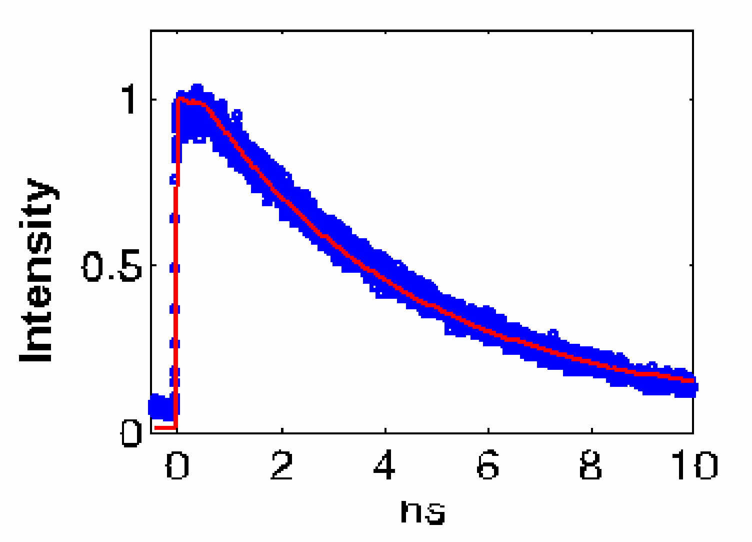
$$\psi_2(t) \cong \frac{c\alpha t^{\alpha-1} + d\beta t^{\beta-1}}{(ct^{\alpha} + dt^{\beta})^2}$$

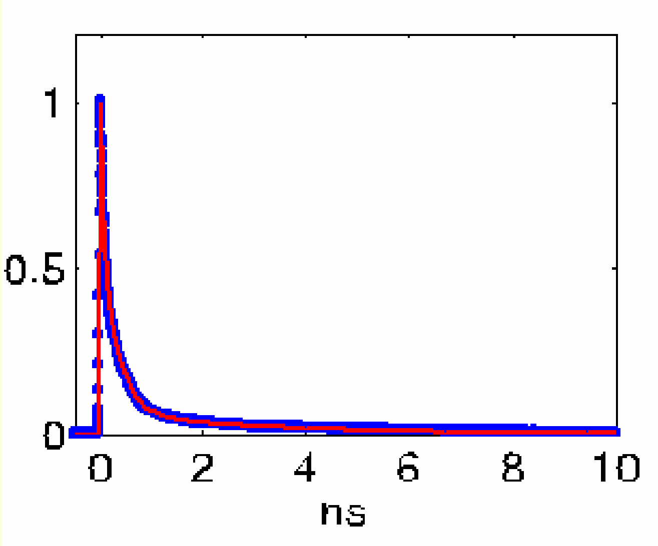
NADH:Flavin Oxidoreductase from *E. Coli*



The fluorescence lifetime of flavin is shortened upon binding to the protein.

Free FLavin in water → Flavin bound in FRE





Long and single exponential → Shortened and multi-exponential

Rules of Thumb

The equations with the distributed-order fractional derivative on the "***proper***" side describe the processes getting **more anomalous** in the course of time.

The equations with the distributed-order fractional derivative on the "***wrong***" side describe the processes getting **less anomalous** in the course of time.

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Derivation of the Continuous-Time Random-Walk Equation

J. Klafter and R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 15 October 1979)

The transport of electrons or excitations on a lattice randomly occupied by guests is considered. The equation governing the transport in any configuration is assumed to be the master equation. A projection operator technique is used to derive the exact equation governing the transport averaged over all configurations, which can be written as either a generalized master equation or the continuous-time random-walk equations (CTRW), establishing the correctness of the CTRW for these problems.

Levy Flights

1. Consider a random walker each of whose steps is an identically distributed random variable with pdf p(x).

2. When can *Pn(x)*, the pdf of being at *x* after *n* steps, be the same as *p(x)*?

3. $P_n(k) = \exp[-n|k|^{\gamma}]$ $\qquad 0 < \gamma \le 2$

   $\lim_{x\to\infty} P_n(x) \sim n|x|^{-1-\gamma}$ $\qquad 0 < \gamma < 2$

4. $\gamma = 2$, Gaussian;
   $< x^2(n) >\sim n$ (finite)

   $\gamma < 2$, $\lim_{k\to 0} P_n(k) \sim 1 - c|k|^{\gamma}$

   $$< x^2(n) >= \int dx P_n(x) x^2 = -\partial^2 P_n(k)/\partial k^2 \Big|_{k=0} \to \infty$$

Spatial derivatives

Riesz-Weil symmetric derivative:

$$\frac{d^{\alpha}}{d|x|^{\alpha}}\phi(x)=\begin{cases}-\dfrac{1}{2\cos(\pi\alpha/2)}\left[{}_{-\infty}D_x^{\alpha}\phi+{}_xD_{\infty}^{\alpha}\phi\right],\ \alpha\neq 1\\ -\dfrac{d}{dx}H\phi,\ \alpha=1\end{cases}$$

with *H* being a Hilbert-transform.

In the Fourier-representation

$$\hat{\Phi}\left(\frac{d^{\alpha}\phi}{d\,|\,x\,|^{\alpha}}\right)=-\,|\,k\,|^{\alpha}\ \hat{\phi}$$

Possible positions of derivatives:

Normal forms:	Modified forms:
$\frac{\partial^{\alpha}}{\partial t^{\alpha}}P(x,t)=K\frac{\partial^2}{\partial x^2}P(x,t)$	$\frac{\partial}{\partial t}P(x,t)=\frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}}K\frac{\partial^2}{\partial x^2}P(x,t)$
Caputo derivative on the "correct" side (l.h.s.)	Riemann-Liouville derivative on the "wrong" side (r.h.s.)
$\frac{\partial}{\partial t}P(x,t)=K\frac{\partial^{2\beta}}{\partial x^{2\beta}}P(x,t)$	$-\frac{\partial^{2-2\beta}}{\partial x^{2-2\beta}}\frac{\partial}{\partial t}P(x,t)=K\frac{\partial^2}{\partial x^2}P(x,t)$
Riesz-Weyl derivative on the "correct" side (r.h.s.)	Riesz-Weyl derivative on the "wrong" side (l.h.s.)

The Fractional Fokker-Planck Equation

$$\boxed{\dot{P}(x,t) = {}_0D_t^{1-\alpha}\left[\frac{\partial}{\partial x}\frac{V'(x)}{m\eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2}\right]P(x,t)}$$

$$[\eta_\alpha] = \sec^{\alpha-2}$$

- Force-free mean squared displacement

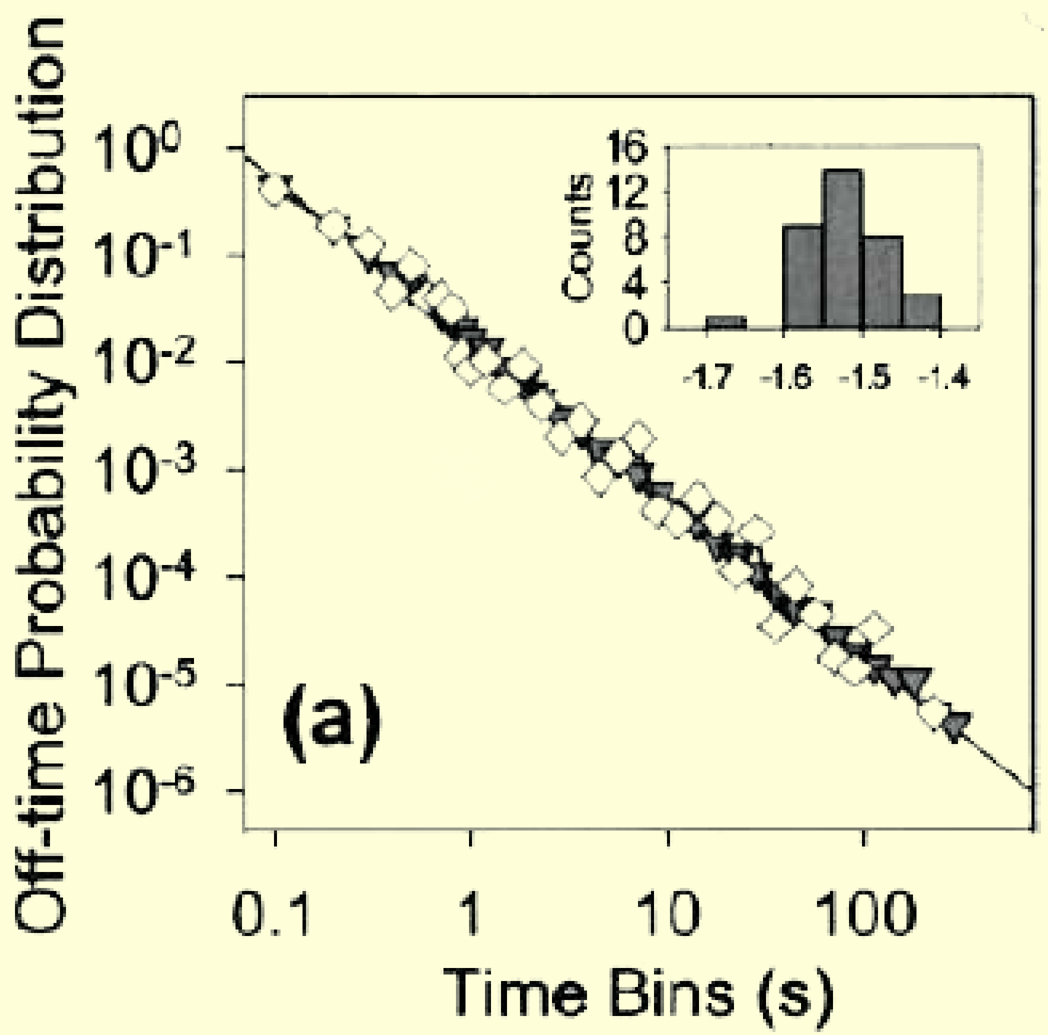
$$< x^2(t) >_0 = \frac{2K_\alpha}{\Gamma(1+\alpha)} t^\alpha$$

- Stationary solution

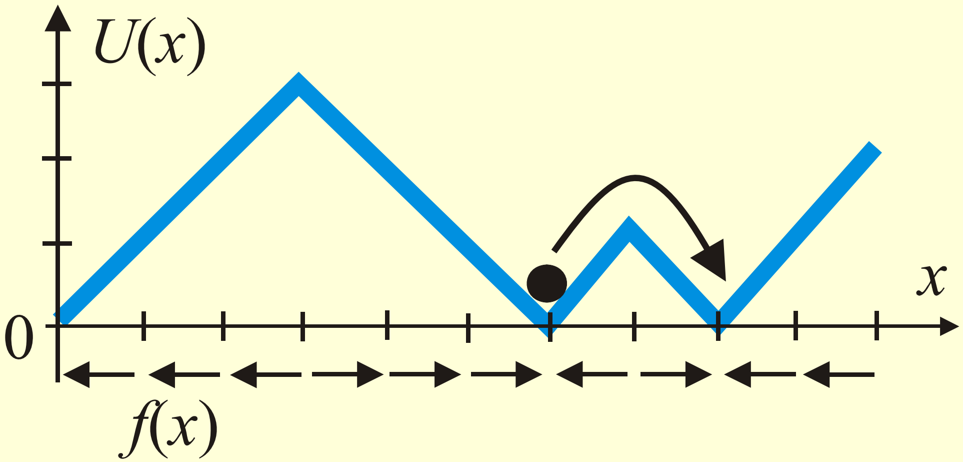
$$P_{st} \propto \exp\left(-\frac{V(x)}{k_B T}\right)$$

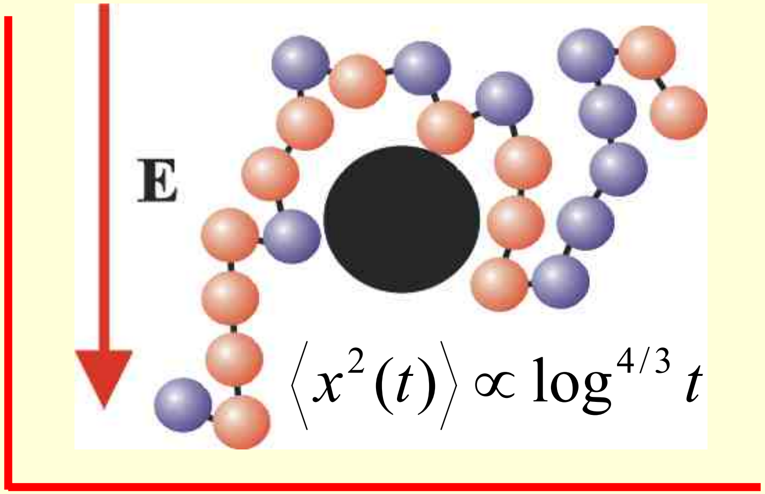
$$K_\alpha = \frac{k_B T}{m\eta_\alpha}$$ **Generalized Einstein-Stokes relation**

Blinking Quantum Dots



Ultraslow Diffusion: The Sinai Model





Scaling considerations: $U_{\max}(|\Delta x|) \propto (|\Delta x|)^{1/2}$

$$t(|\Delta x|) \cong \tau_0 \exp\left(\frac{U_{\max}(|\Delta x|)}{k_B T}\right) \propto \tau_0 \exp\left(const \cdot (|\Delta x|)^{1/2}\right)$$

Inverting this relation we get: $|\Delta x| \propto \log^2 t$ or $\langle \Delta x^2 \rangle \propto \log^4 t$

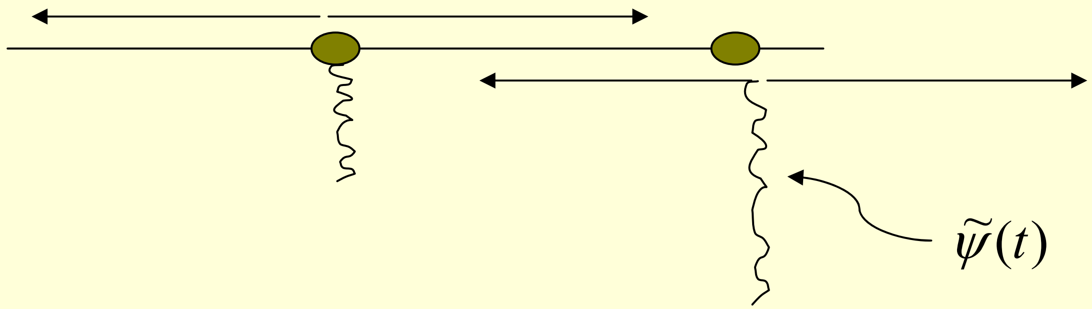
The PDF of Δx is approximately double-sided exponential

Frameworks for anomalous diffusion

1. Generalized diffusion equation
2. Fractional Brownian motion
3. Random velocity fields
4. Self avoiding walks
5. Fractional Fokker Planck Equation (FFPE)
6. Continuous Time Random Walk (CTRW)
7. Sinai diffusion

Coupled model

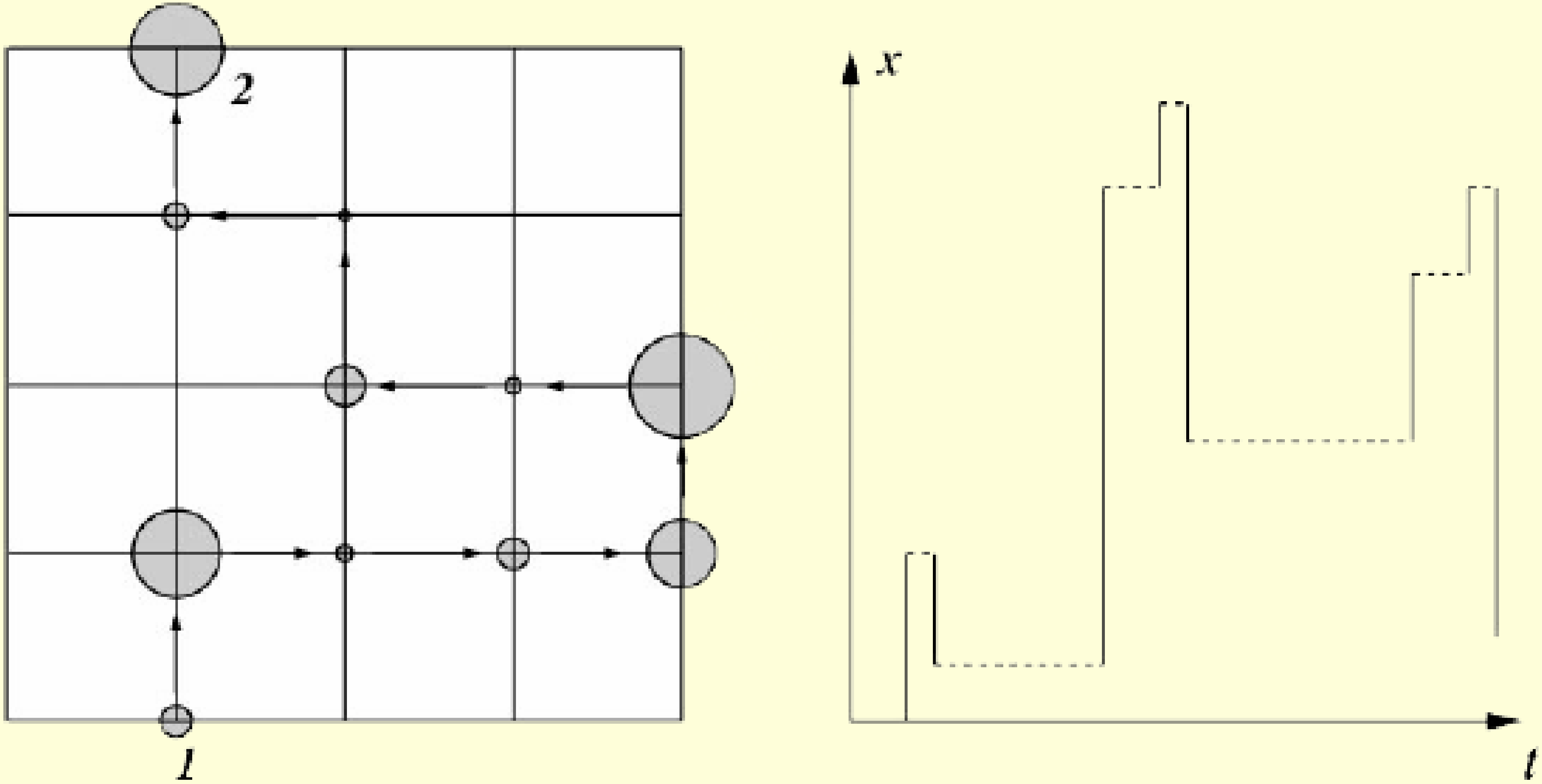
Possibility to include within the velocity model, interruptions by spatial localization (jump model)



$$P(r,t) = \Psi(r,t) + \int_0^t \psi(r,t')\tilde{\Phi}(t-t')dt' + \int_{-\infty}^{\infty} dr' \int_0^t dt' \int_0^{t'} dt' \psi(r',t'')\tilde{\psi}(t'-t'')\Psi(r-r',t-t') + \ldots..$$

$$P(k,u) = \frac{\Psi(k,u) + \tilde{\Phi}(u)\psi(k,u)}{1-\psi(k,u)\tilde{\psi}(u)}$$

Waiting Times



Continuous time random walk (CTRW) model.

Subdiffusion (dispersive transport)

$$t^{\alpha}, \quad \alpha < 1$$

1. Jump Model

   $\psi(r,t) = p(r)\psi(t)$, decoupling

   $p(r)$ well behaved

   $\psi(t) \sim t^{-\alpha-1}, \quad 0 < \alpha < 1$

   $< t >= \infty$ no time scale

2. From CTRW:

   $< r^2(t) > \sim t^{\alpha}, \quad 0 < \alpha < 1$

Subdiffusion (dispersive transport)

$$t^{\alpha}, \quad \alpha < 1$$

3. $P(r,t) \sim t^{-\alpha/2} f(\xi)$ one dimension

$$\xi = r / t^{\alpha/2}$$

$$f(\xi) \sim \begin{cases} \exp(-a_1\xi - a_2\xi^2) & \textbf{small } \xi \\ \exp(-b\xi^{\delta}), & \textbf{large } \xi, \quad \delta = \mathbf{2/(2 - }\alpha) \end{cases}$$

"Stretched" Gaussian

P(r,t)

1. Brownian motion

$$P(r,t) \sim t^{-1/2} f(\xi)$$

$$f(\xi) = \exp(-c\xi^2),\ \xi = x/t^{1/2}$$

Gaussian $< x^2(t) > \sim t$

2. Subdiffusion

$$P(r,t) \sim t^{-\alpha/2} f(\xi)$$

$$\xi = r/t^{\alpha/2}$$

$$f(\xi) \sim \begin{cases} \exp(-a_1\xi - a_2\xi^2) & \textbf{small } \xi \\ \exp(-b\xi^\delta), & \textbf{large } \xi,\ \delta = \mathbf{2/(2-}\alpha\mathbf{)} \end{cases}$$

"Stretched" Gaussian $< x^2(t) > \sim t^\alpha$

Equivalence of the forms

- RL-Form

$$\frac{\partial W}{\partial t} = K_\beta \, {}_0D_t^{1-\beta} \frac{\partial^2 W}{\partial x^2}$$

- C-form

$${}_0D_t^{1-\beta} W = K_\beta \frac{\partial^2 W}{\partial x^2}$$

under the initial condition $f(x,0) = \delta(x)$

Under the Laplace-transform the equations take the same form:

$$s^\beta \tilde{p}(x,s) - s^{\beta-1} p(x,0) = K_\beta \frac{\partial^2}{\partial x^2} \tilde{p}(x,s)$$

The two forms of fractional spatial equations show their equivalence under the Fourier transform

Definitions of derivatives: Temporal derivatives

RL derivative $${}_0D_t^{1-\beta} f = \frac{1}{\Gamma(1-\mu)} \frac{\partial}{\partial t} \int_0^t dt' \frac{f(t')}{(t-t')^{\mu}} \qquad 0 \le \mu < 1$$

Caputo derivative $${}_0D_{*t}^{1-\beta} f = \frac{1}{\Gamma(1-\mu)} \int_0^t dt' \frac{1}{(t-t')^{\mu}} \frac{\partial}{\partial t} f(t') \qquad 0 \le \mu < 1$$

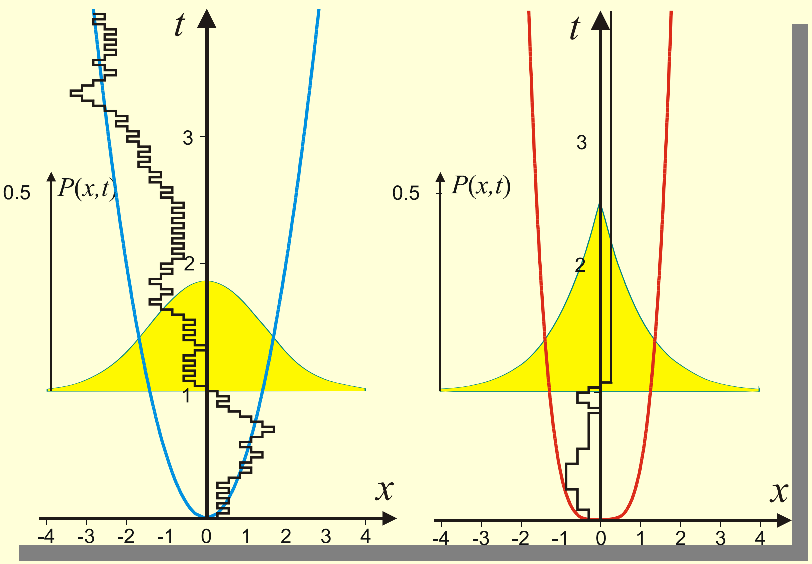
Relation between RL- and C-forms: $$D_t^{\mu} f(t) = D_{*t}^{\mu} f(t) + \frac{t^{-\mu}}{\Gamma(1-\mu)} f(0)$$

Under Laplace-transform

$$L\left\{{}_0D_t^{\mu} f(t)\right\} = s^{\mu} \widetilde{f}(s)$$

$$L\left\{{}_0D_{*t}^{\mu} f(t)\right\} = s^{\mu} \widetilde{f}(s) - s^{\mu-1} f(0)$$

Some Solutions



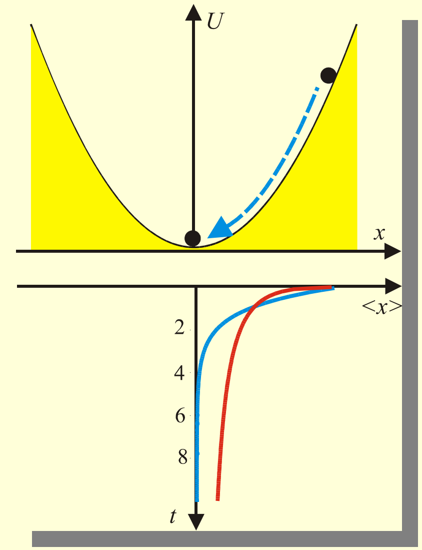
Free diffusion:

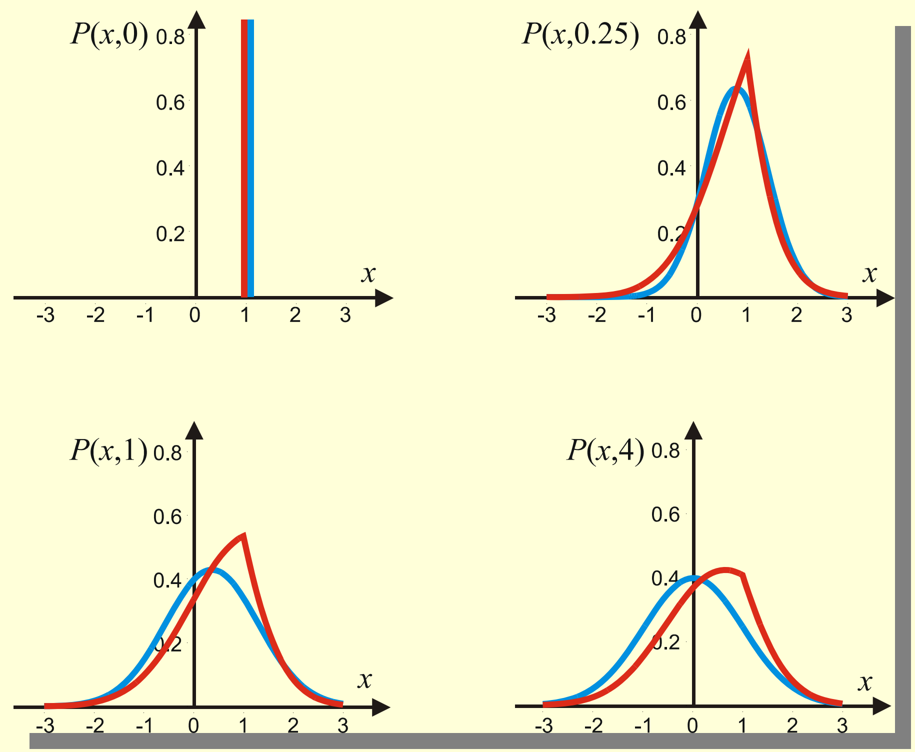
Left: Normal diffusion

Right: Subdiffusion with α = 1/2

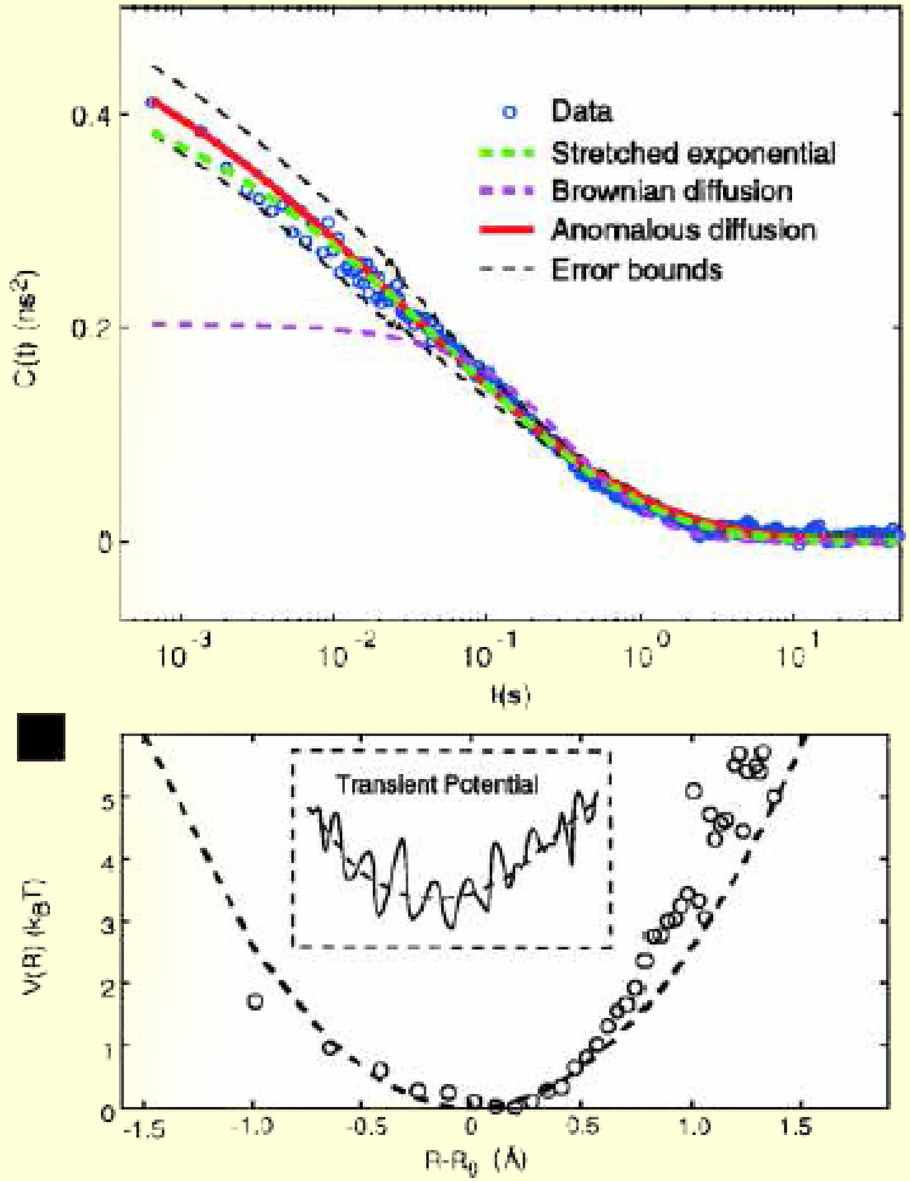
I.M. Sokolov, J. Klafter and A. Blumen, Fractional Kinetics , *Physics Today*, November 2002, p.48

Ornstein-Uhlenbeck process: Diffusion in a harmonic potential

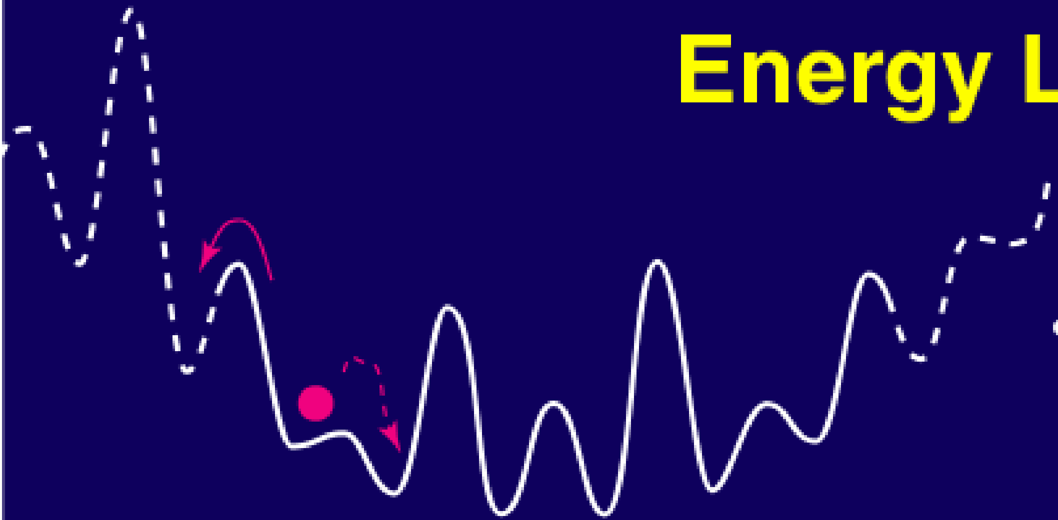




Fluctuating Enzymes

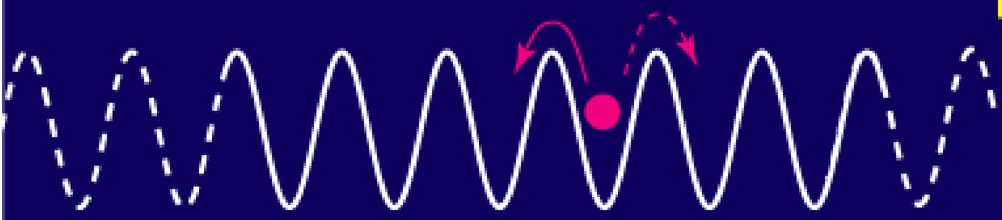


Energy Landscape Picture

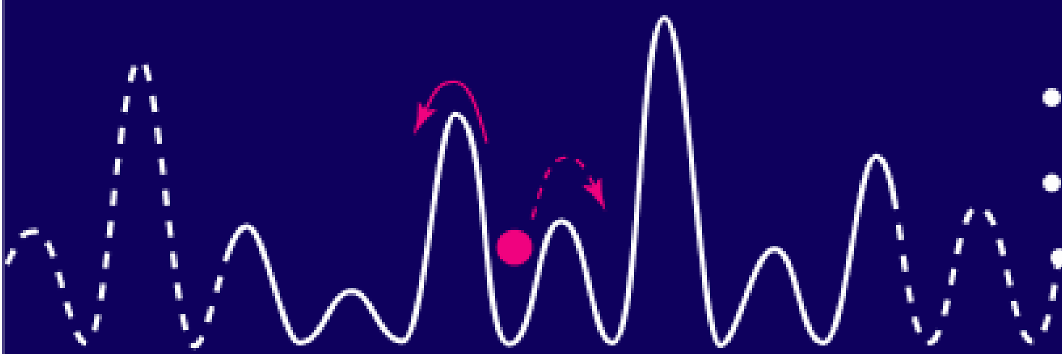


- A distribution of confromation
- Barrier heights unknown

Brownian Diffusion



- Equal barrier heights
- $\langle(\Delta x)^2\rangle \propto t$
- The distribution of waiting time in each well is exponential.



- A distribution of barrier heights
- Subdiffusion $\langle(\Delta x)^2\rangle \propto t^{\alpha}$, $0<\alpha<1$
- The waiting time between "hops" follows power law distribution, $w(t) \sim \tau^{\alpha} / t^{1+\alpha}$.

Anomalous Diffusion

no finite first moment

Broad distributions; Long range correlations;
Tails

Generalization of the central limit theorem
(Levy stable distributions)

The Diffusion Equation (1855)

Continuity

$$\frac{\partial}{\partial t} n(\vec{x},t) = -\mathrm{div}\,\vec{j}(\vec{x},t)$$

+ linear response

$$\vec{j}(\vec{x},t) = -K\,\mathrm{grad}\,n(\vec{x},t)$$

=> the diffusion equation

$$\frac{\partial}{\partial t} n(\vec{x},t) = K\Delta n(\vec{x},t)$$

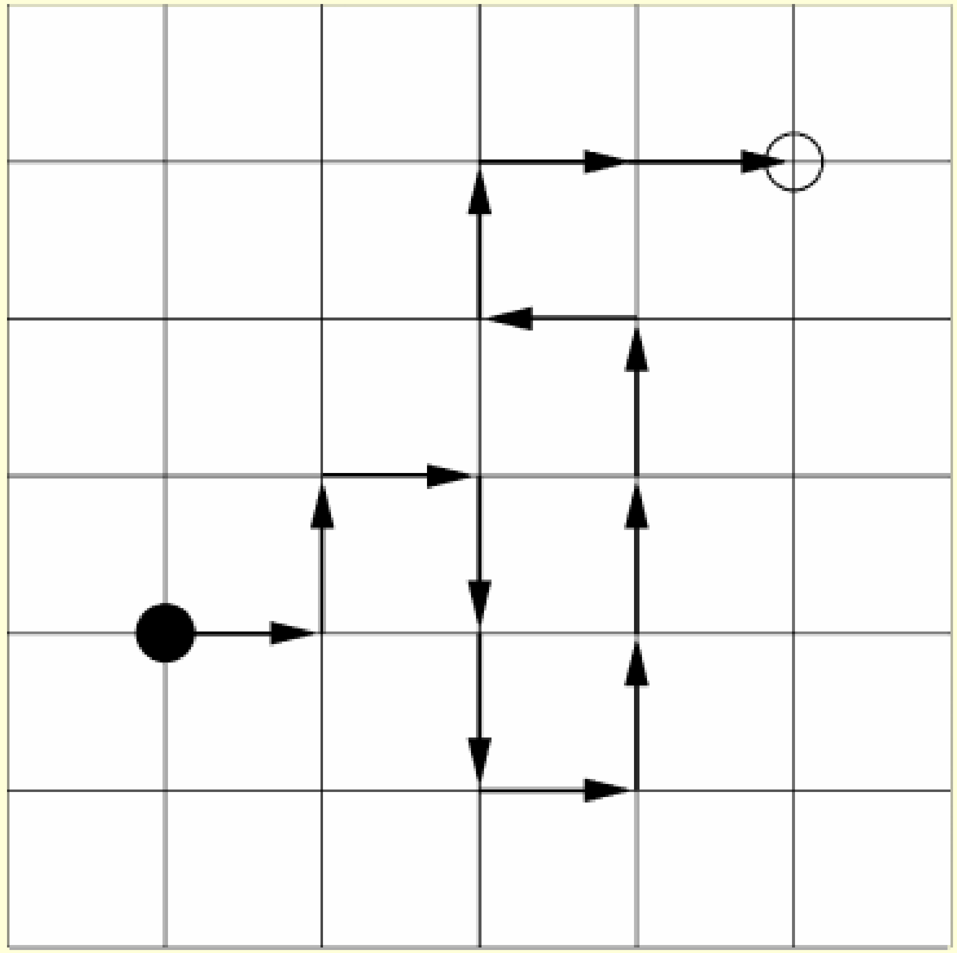
---

the Green's function solution

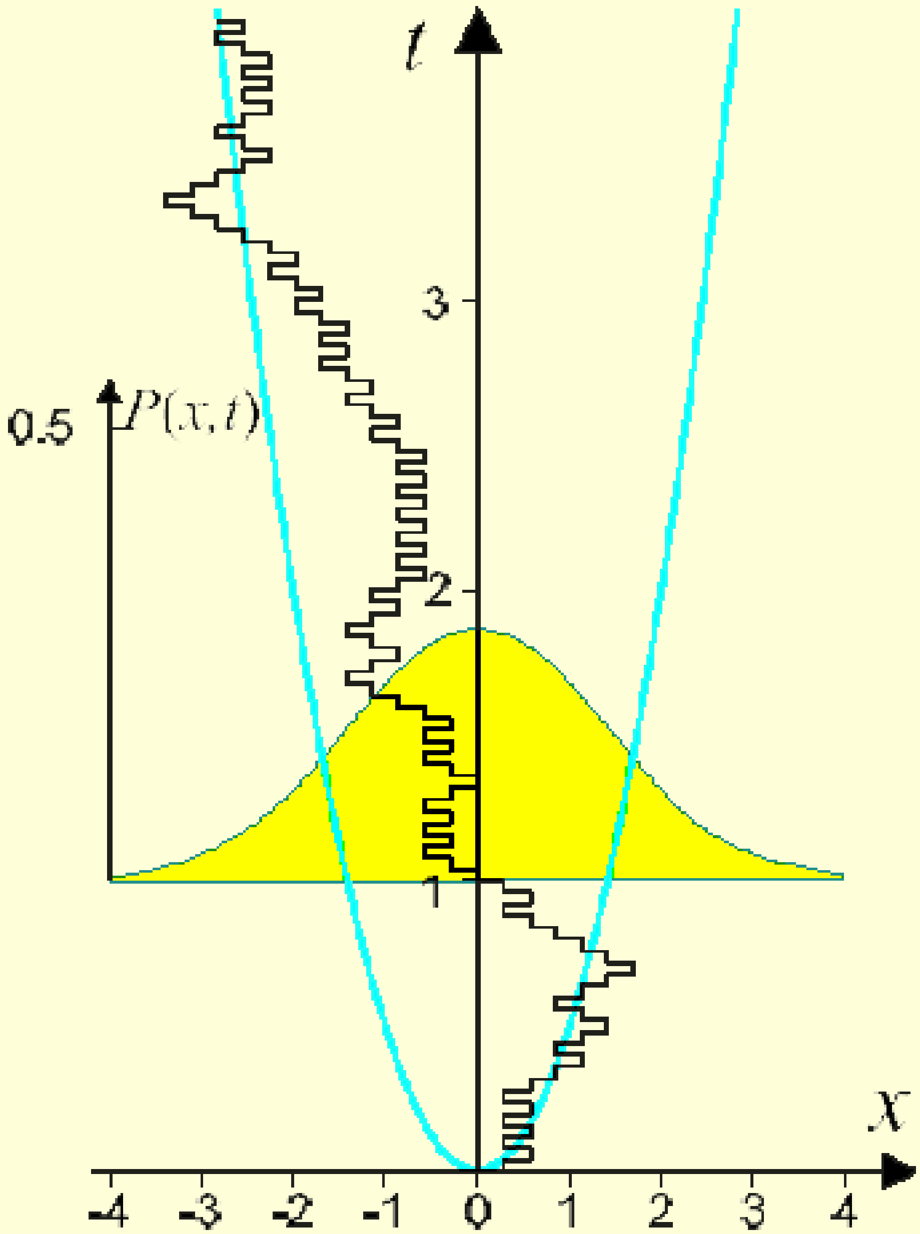
$$n(\vec{x},t) = (4\pi K t)^{-d/2} \exp\left(-\frac{\vec{x}^{\,2}}{4Kt}\right)$$

Essentially an equation for the pdf: $n(\vec{x},t) \to P(\vec{x},t)$

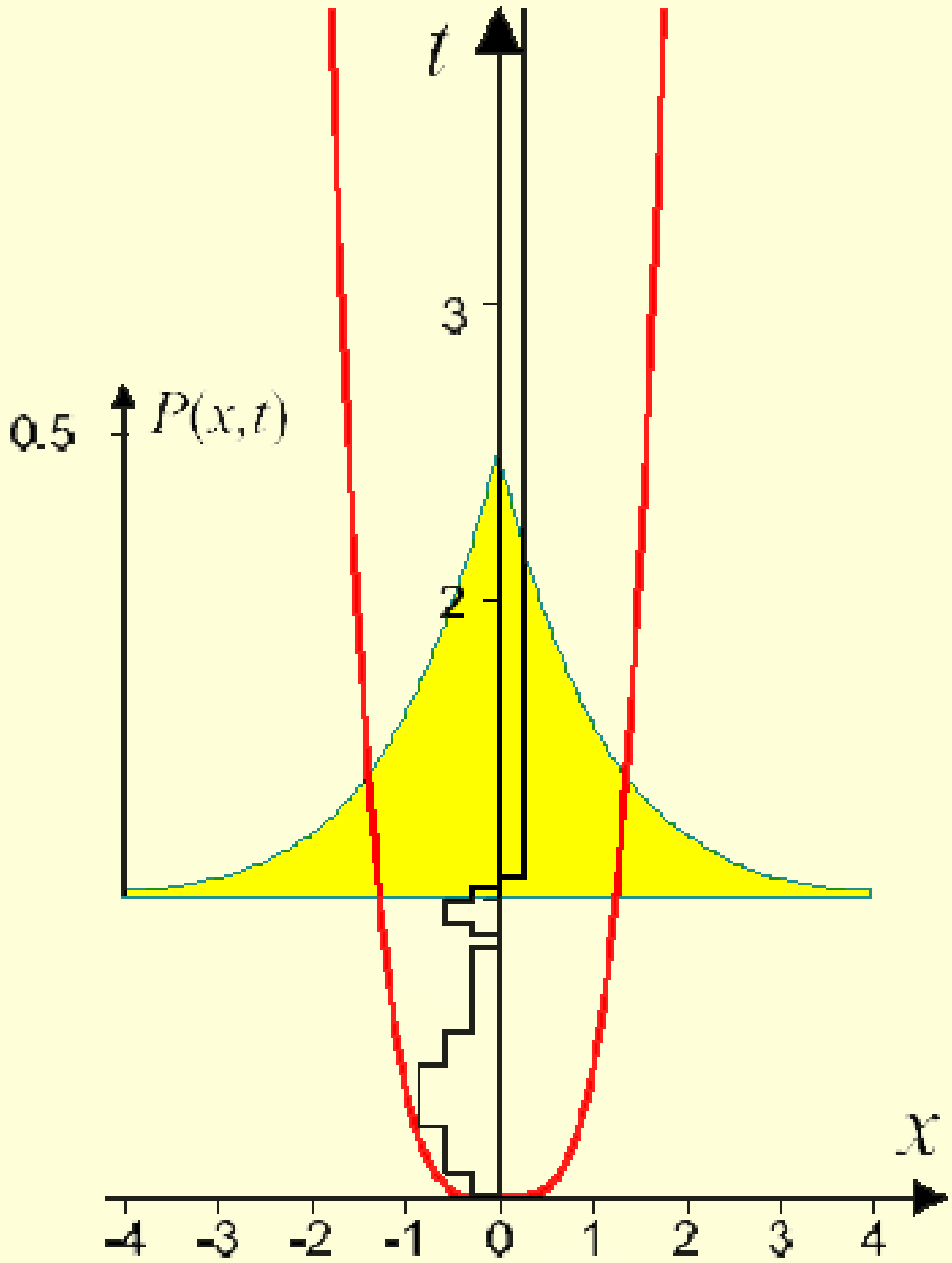
Simple Random Walk



Schematic representation of a Brownian random walk. The walker jumps at each time step to a randomly selected direction.



t
3
2
1
0.5
P(x,t)
x
-4
-3
-2
-1
0
1
2
3
4



t
3
2
0.5
P(x,t)
x
-4
-3
-2
-1
0
1
2
3
4

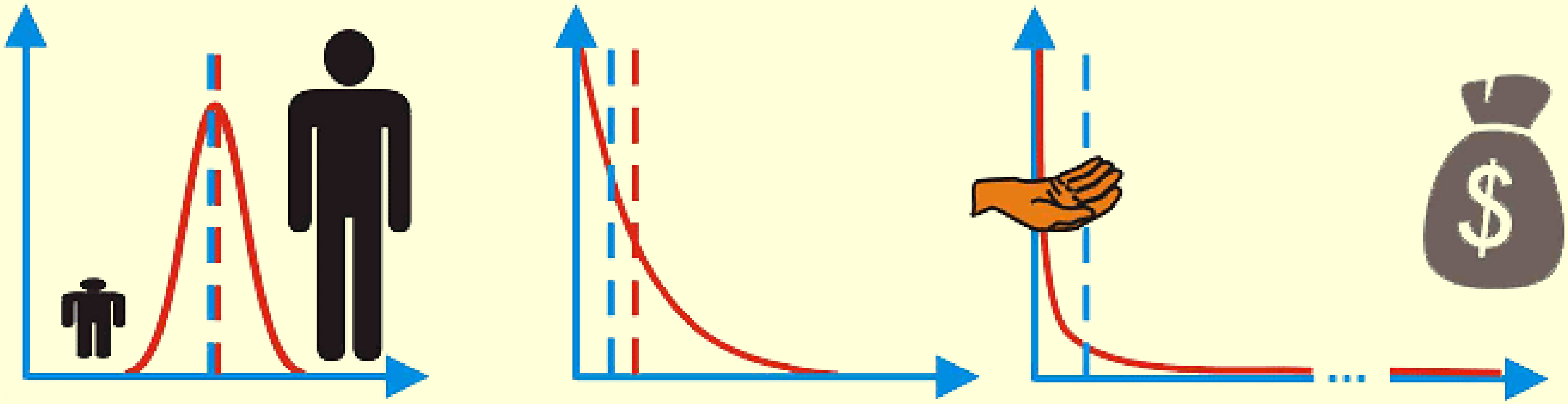
$$P(x,t) = (4\pi Kt)^{-1/2} \exp\left(-\frac{x^2}{4Kt} \right)$$

with $K \propto \left\langle v^2 \right\rangle \tau \equiv \lambda^2 / \tau$

1. Normal is anomalous

2. Anomalous is normal

Gaussian, Exponential and Pareto Distributions

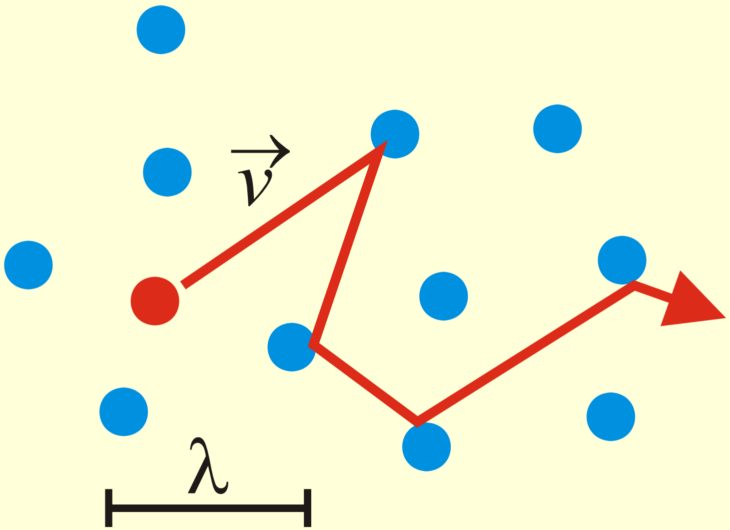


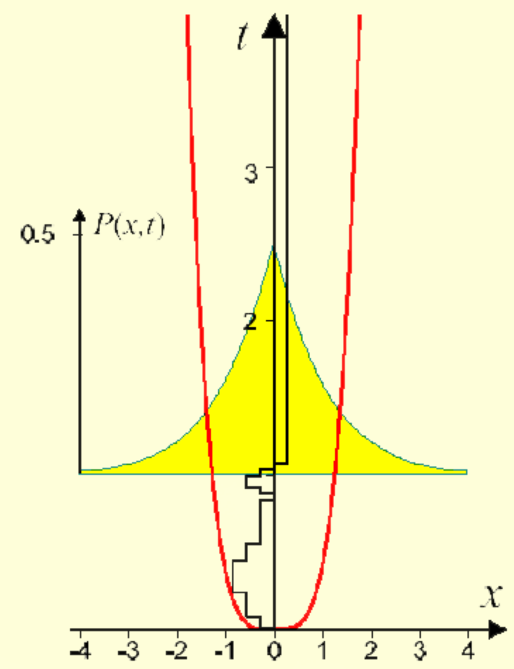
Levy-Pareto

- Self similarity (fractals)
  $< t > = \infty$
  or
  $< x^2(n) > = \infty$

- Modifying the 1905 assumptions
  $\tau \longrightarrow \infty$
  $\lambda \longrightarrow \infty$

- Memory or "Funicity" (after "Funes the memorious" by Jorge Luis Borges)

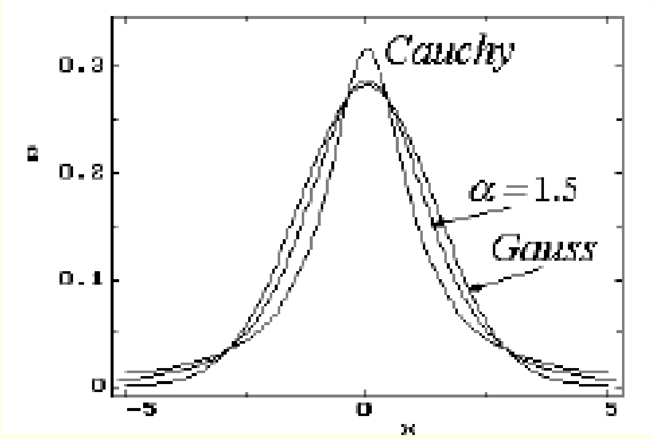


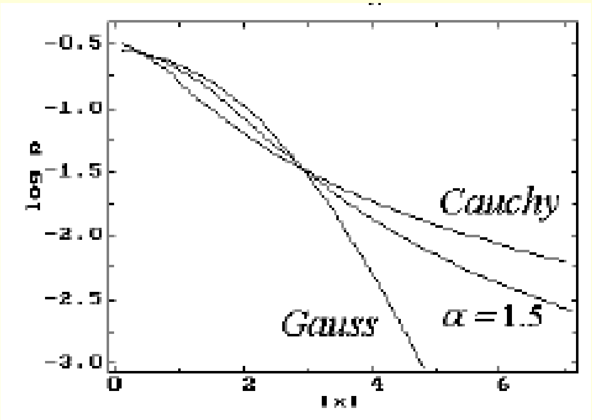


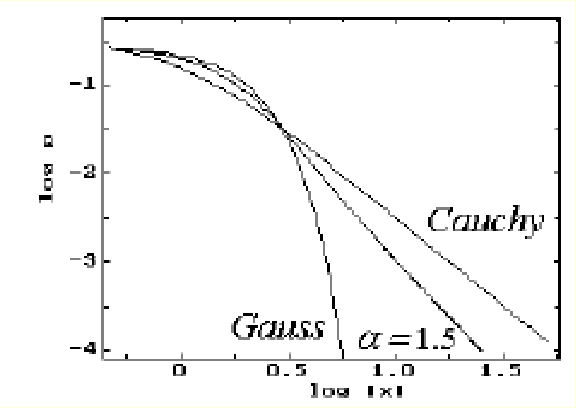
Forms of stable distributions (Levy)

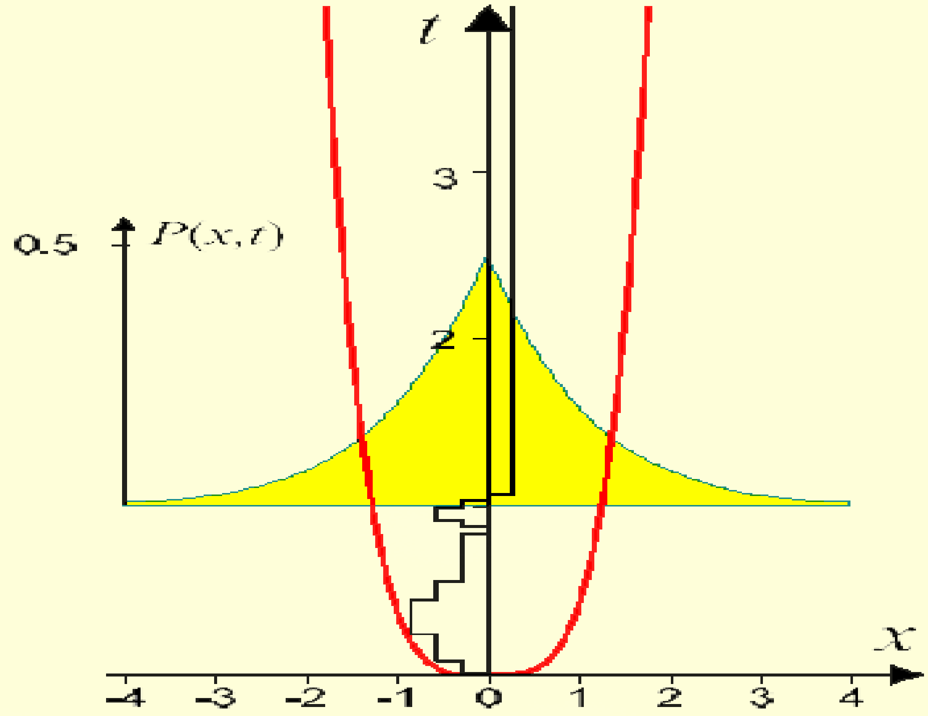
$$P_\alpha(x \to \infty) \sim \frac{1}{|x|^{1+\alpha}} \qquad P_\alpha(x \to \infty) \sim \frac{1}{x^{1+\alpha}}$$

$$0 < \alpha < 2 \qquad\qquad 0 < \alpha < 1$$







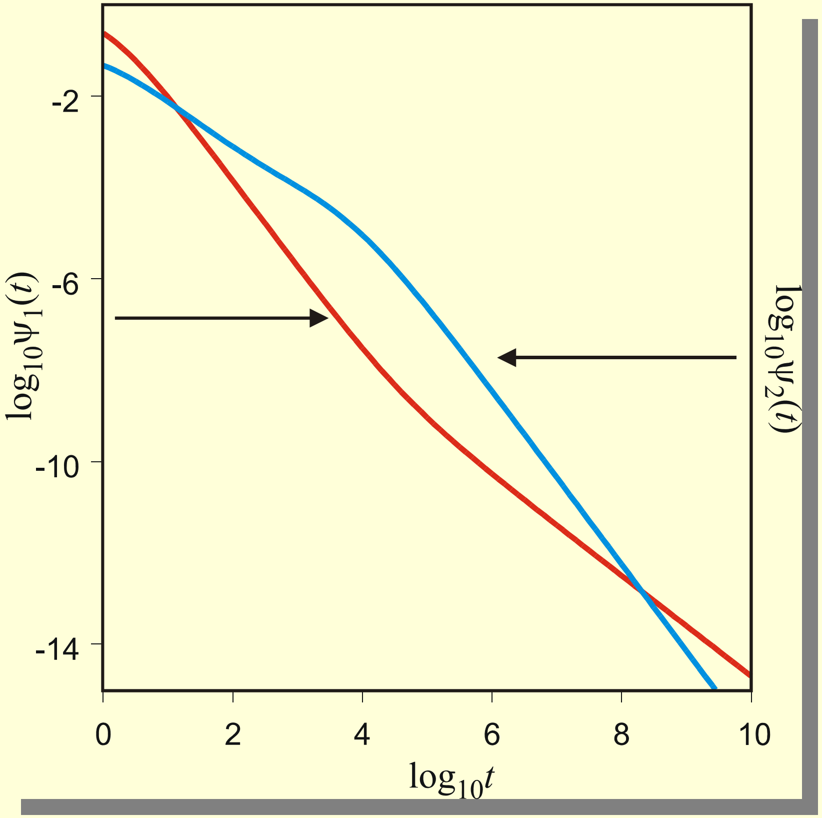


“I do not believe a word he is saying, but I am afraid that one day I will have to learn it”

Bob Silbey, 1983

Example: A simple crossover

Easier to start from cumulative functions:



$$\Psi_1(t) = 1 - \frac{a}{t^\alpha} - \frac{b}{t^\beta}$$

$$\psi_1(t) \cong \frac{\alpha a}{t^{\alpha+1}} + \frac{\beta b}{t^{\beta+1}}$$

Slowing down process

Accelerating process

$$\Psi_2(t) = 1 - \frac{1}{ct^\alpha + dt^\beta}$$

$$\psi_2(t) \cong \frac{c\alpha t^{\alpha-1} + d\beta t^{\beta-1}}{(ct^\alpha + dt^\beta)^2}$$

Slowing down process

$$\psi_1(t) \cong \frac{\alpha a}{t^{\alpha+1}} + \frac{\beta b}{t^{\beta+1}}$$

$$\langle n_1(t) \rangle \cong \frac{1}{At^{-\alpha} + Bt^{-\beta}}$$

$$C_1(t) = \frac{a}{t^{\alpha}} + \frac{b}{t^{\beta}}$$

a very simple form, a sum of 2 fractional Caputo operators

$$\Phi_2(t) \approx \frac{1}{\tilde{a} t^{\alpha} + \tilde{b} t^{\beta}}$$

does not resemble any fractional diff. operator

Accelerating process

$$\psi_2(t) \cong \frac{c\alpha t^{\alpha-1} + d\beta t^{\beta-1}}{(ct^{\alpha} + dt^{\beta})^2}$$

$$\langle n_2(t) \rangle \cong Ct^{\alpha} + Dt^{\beta}$$

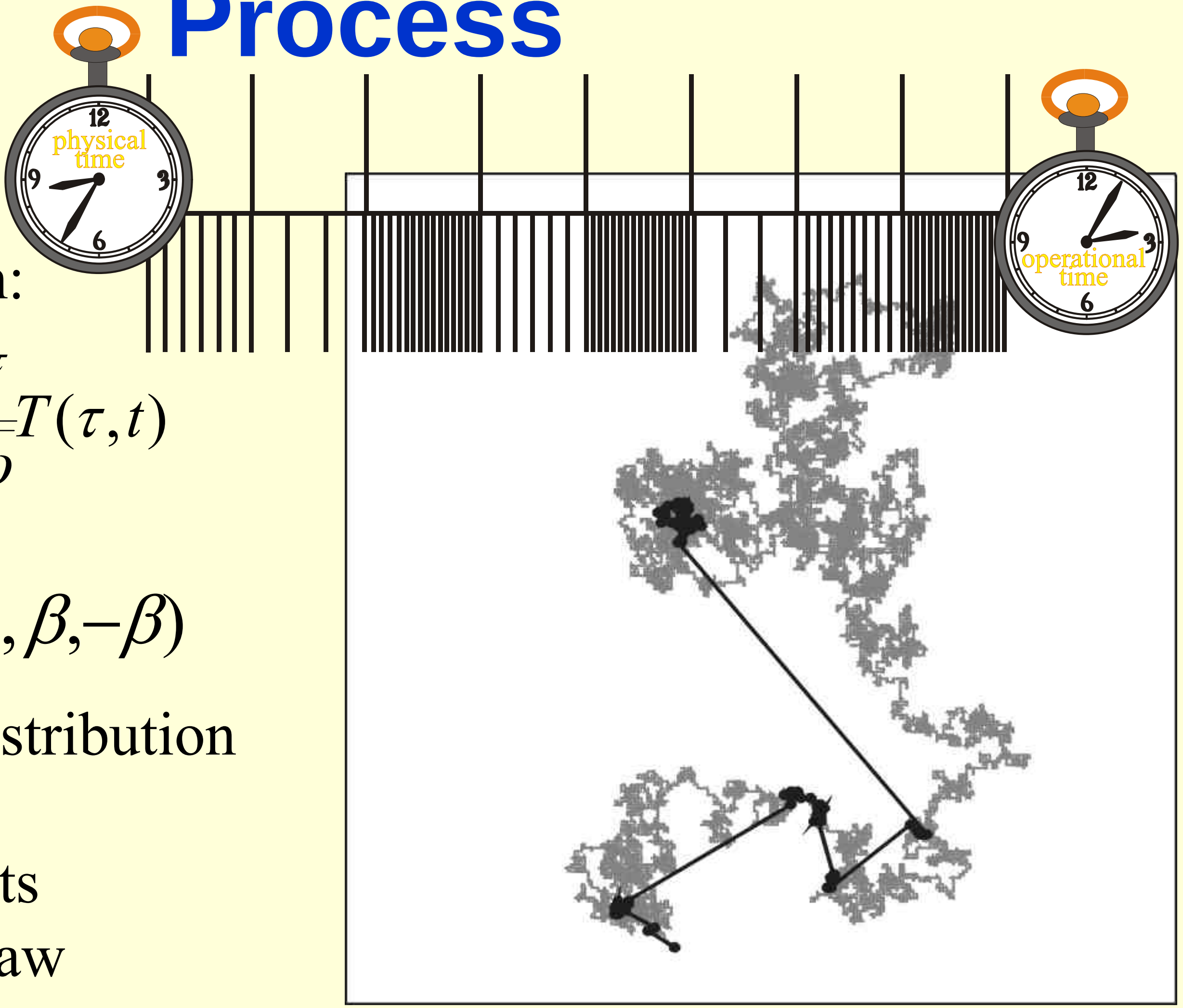
$$C_2(t) = \frac{1}{ct^{\alpha} + dt^{\beta}}$$

does not resemble any fractional diff. operator

$$\Phi_2(t) = \frac{\tilde{c}}{t^{\alpha}} + \frac{\tilde{d}}{t^{\beta}}$$

a very simple form, a sum of 2 fractional RL-operators

Superdiffusion and a Wiener Process



Subordination form:

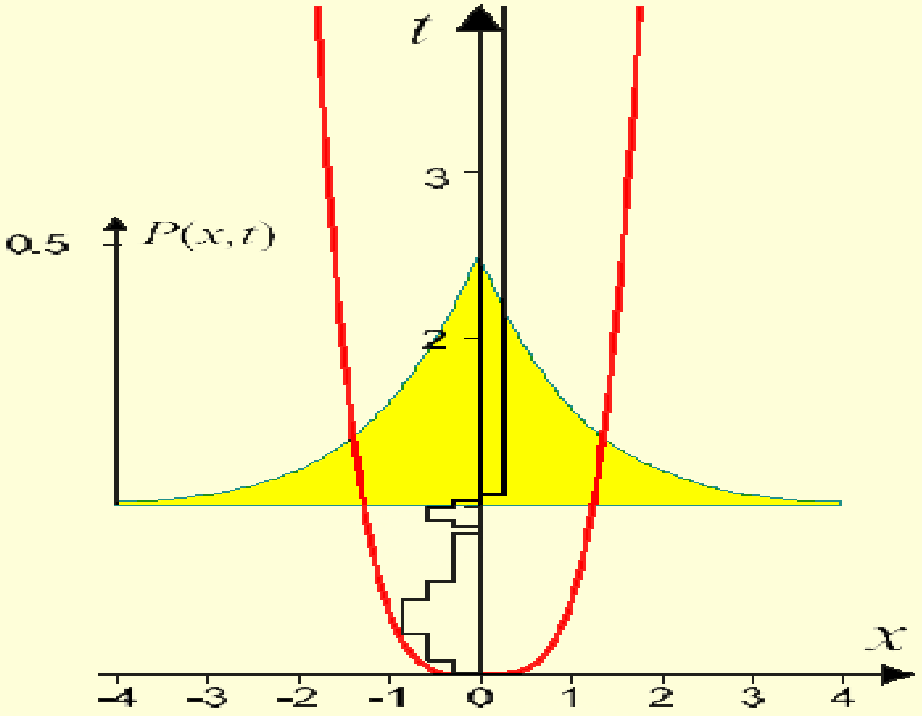
$$P(x,t)=\int_0^\infty d\omega \frac{e^{-x^2/4\tau}}{\sqrt{4\pi\omega}}T(\tau,t)$$

with

$$T(\tau,t)=t^{-\beta}L(\tau/t^{\beta},\beta,-\beta)$$

The waiting-time distribution cannot be defined.
The density of events follows the power-law

$$p(\rho)\propto\rho^{-1-\beta}$$



"I do not believe a word he is saying, but I am afraid that one day I will have to learn it"

Bob Silbey, 1983


25 μs

”I used a waiting time distribution that had such a long time tail that the mean time of it did not exist.
That was the step!
Everything fell into place.”

Harvey Scher

Fractional Diffusion Equations (1985, 1989)

- In many physical situations $X(t) \propto t^{\alpha}, \quad \alpha \neq 1/2$ holds (non-Fickian diffusion)

- Following scaling arguments one can postulate (and sometimes derive) fractional equations for anomalous diffusion:

$$\frac{\partial}{\partial t} P(x,t) = K \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} P(x,t)$$

or

$$\frac{\partial}{\partial t} P(x,t) = K \frac{\partial^{2\beta}}{\partial x^{2\beta}} P(x,t)$$

Such equations allow for

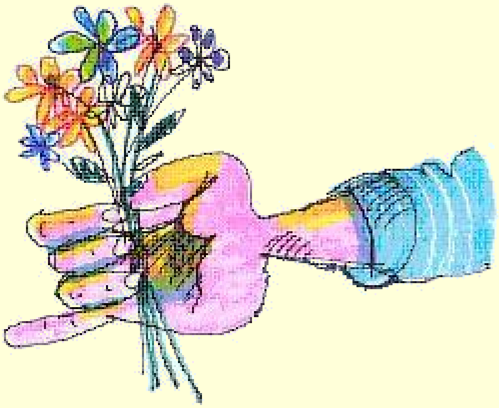
- easier introduction of external forces
- introduction of boundary conditions
- using the methods of solutions known for "normal" PDEs

Reasonable values of the orders of derivatives:

$0 < \alpha < 1$ for subdiffusion; $0 < \beta < 1$ for superdiffusion.

Congratulations

Bob



An increasing number of natural phenomena do not fit into the relatively simple description of diffusion developed by Einstein a century ago

Anomalous diffusion spreads its wings

Joseph Klafter and Igor M Sokolov

AS ALL of us are no doubt aware, this year has been declared "world year of physics" to celebrate the three remarkable breakthroughs made by Albert Einstein in 1905. However, it is not so well known that Einstein's work on Brownian motion – the random motion of tiny particles first observed and investigated by the botanist Robert Brown in 1827 – has been cited more times in the scientific literature than his more famous papers on special relativity and the quantum nature of light. In a series of publications that included his doctoral thesis, Einstein derived an equation for Brownian motion from microscopic principles – a feat that ultimately enabled Jean Perrin and others to prove the existence of atoms (see *Physics World* January pp 19–22).

Strange behaviour – albatrosses fly by the rules of anomalous diffusion.

Einstein was not the only person thinking about this type of problem. The 27 July 1905 issue of *Nature* contained a letter with the title "The problem of the random walk", in which the British statistician Karl Pearson proposed the following: "A man starts from the point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. I require the probability that after n stretches he is at a distance between r and $r + \delta r$ from his starting point O."

Pearson was interested in the way that mosquitoes spread malaria, which he showed was described by the well-known diffusion equation. As such, the displacement of a mosquito from its initial position is proportional to the square root of time, and the distribution of the positions of many such "random walkers" starting from the same origin is Gaussian in form. The random walk has since turned out to be intimately linked to Einstein's work on Brownian motion, and has become a major tool for understanding diffusive processes in nature.

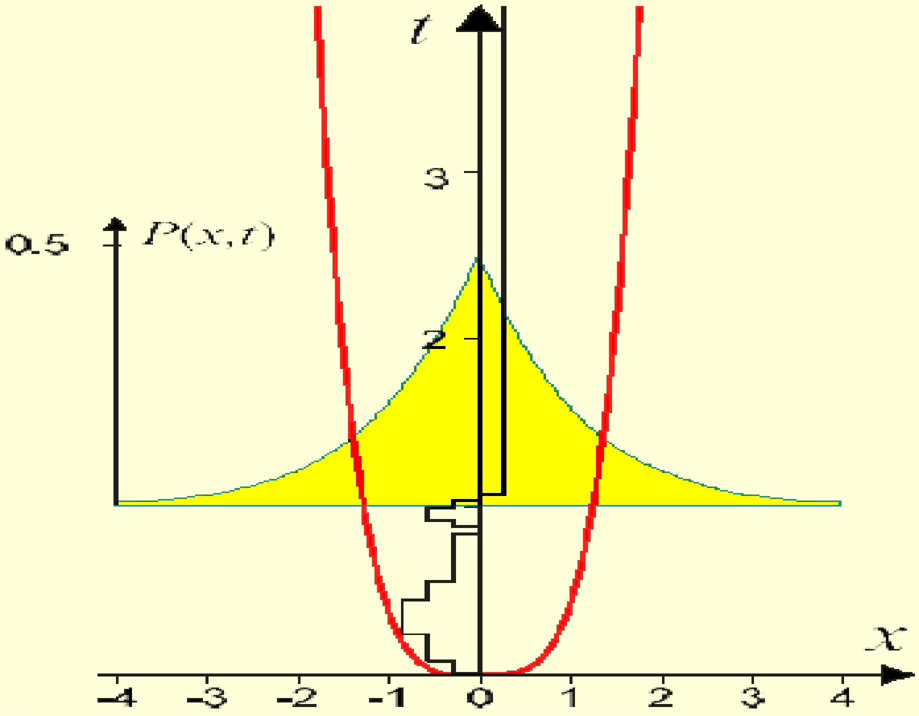
When the mean is missing

In fact, the first person to address the problem of diffusion was the German physiologist Adolf Fick, who was interested in the way that water and nutrients travel through membranes in living organisms. In 1855 Fick published the famous diffusion equation, which, when written in terms of probability, is $\partial p/\partial t = D\partial^2 p/\partial x^2$, where p gives the probability of finding an object at a certain position x, at a time t, and D is the diffusion coefficient. Fick went on to show that the mean-squared displacement of an object undergoing diffusion is $2Dt$.

However, Fick's approach was purely phenomenological, based on an analogy with Fourier's heat equation – it took Einstein to derive the diffusion equation from first principles as part of his work on Brownian motion. He did this by assuming that the direction of motion of a particle gets "forgotten" after a certain time, and that the mean-squared displacement during this time is finite. When Einstein combined the diffusion equation with the Boltzmann distribution for a system in thermal equilibrium, he was able to predict the properties of the unceasing motion of Brownian particles in terms of collisions with surrounding liquid molecules. This was the breakthrough that ultimately led to scientists believing in the reality of atoms.

The fact that Einstein's explanation of diffusion and Pearson's random walk are both based on the same two assumptions – the existence of a mean free path (the length l in Pearson's model and the distance between collisions in Einstein's description) and of a mean time taken to perform a step or between collisions – revealed just how ubiquitous diffusion processes are in nature. However, by the mid-1970s researchers had started to pay attention to situations in which the assumptions made by Einstein and Pearson do not hold. Surprisingly, perhaps, the way that photocopier machines operated played a major role in these developments.

Today, an increasing number of processes can be described by this "anomalous diffusion". From the signalling of biological cells to the foraging behaviour of animals, it seems that the overall motion of an object is better described by steps that are not independent and that can take vastly different times to perform.



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