Igor Sokolov, Humboldt-Universität zu Berlin

Diffusion in complex environments: Models, properties, instruments

Nonergodicity and inhomogeneity…

Outline

- Normal diffusion
- Subdiffusion: Experiments, models, and mathemaical instruments
  - CTRW
  - Percolation
  - Slow modes of multiparticle models
- Aging and ergodicity breaking
- “The twins”: exactly solvable examples
- Conclusitons

IV. *Ueber Diffusion; von Dr. Adolf Fick,*
Prosector in Zürich.

Die Hydrodiffusion durch Membranen dürfte billig nicht blofs als einer der Elementarfactoren des organischen Lebens sondern auch als ein an sich höchst interessanter physikalischer Vorgang weit mehr Aufmerksamkeit der Physiker in Anspruch nehmen als ihr bisher zu Theil geworden ist.

Ann. der Phys. u. Chemie, **96**, 9, 59-86 (1855)

Diffusion in water confined by membranes is not only one of the basic factors of organic life, but is also an extremely interesting physical process and, as such, should attract much more attention from physicists than it has so far.

the diffusion equation

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

Emergence of normal diffusion

Einstein (1905)

Postulates:

0) $n(x,t) \rightarrow P(x,t)$

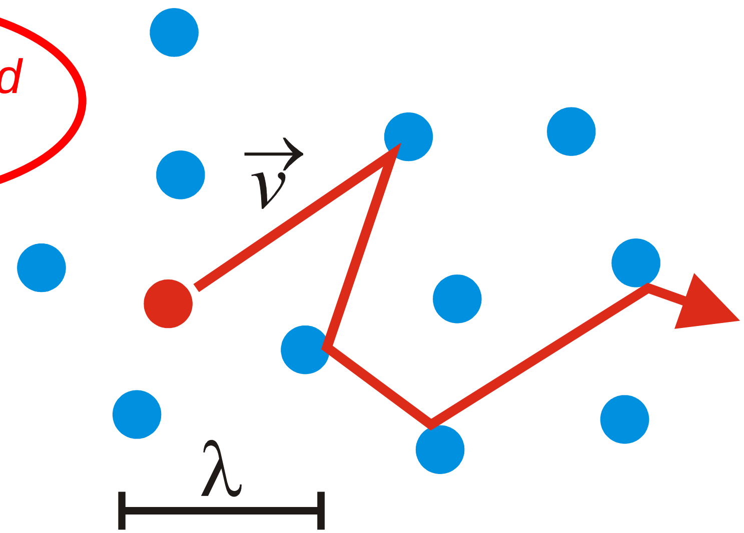
i) $\exists$ time interval $\tau < \infty$, so that the particle's motion during the two consequent intervals is *independent*

ii) The displacements s during subsequent τ-intervals are *identically distributed*.

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

iii) The second moment of s exists

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



Essentially, a 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

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

$$0 < \lambda < \infty$$

mean relaxation time

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

$$0 < \tau < \infty$$

$$N \cong t / \tau$$

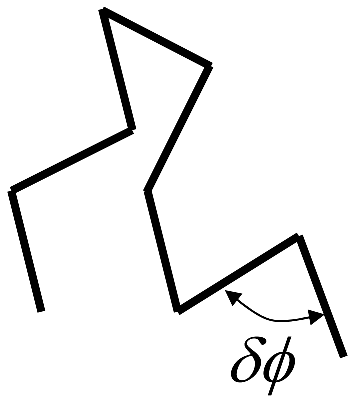
$$\langle x^2(t) \rangle = \left\langle \left(\sum_{i=1}^{N} s_i \right)^2 \right\rangle = N \langle s^2 \rangle + 2N \langle s_i s_j \rangle \quad \sim t^1$$

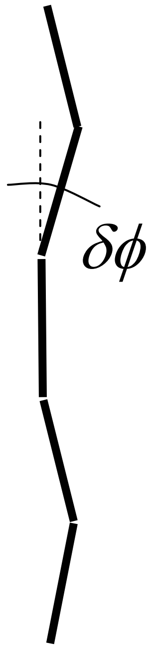
the central limit theorem (for independent steps)

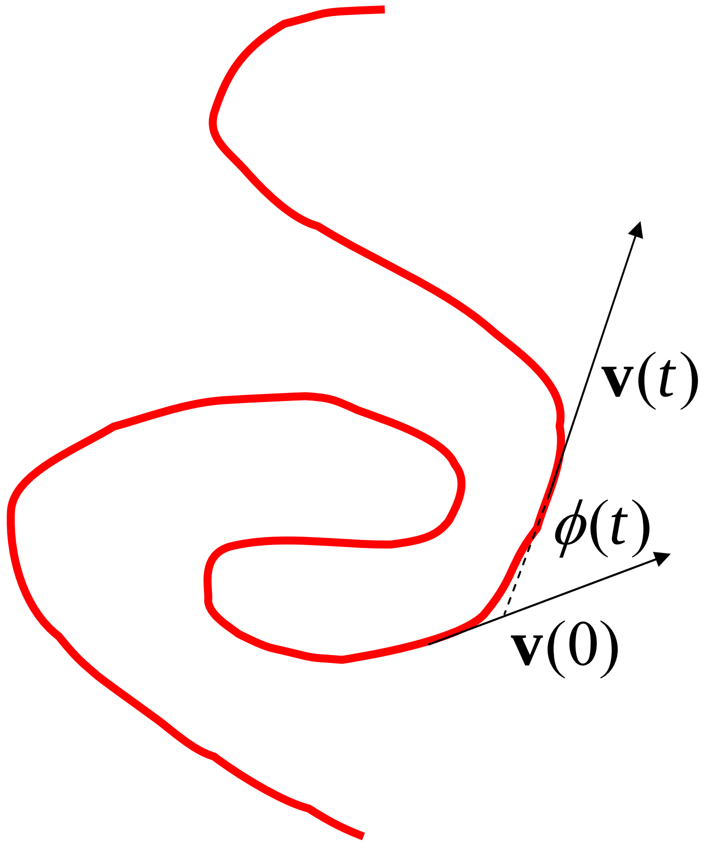
$$P(x,t) = (4\pi K t)^{-1/2} \exp\left(-\frac{x^2}{4Kt} \right)$$

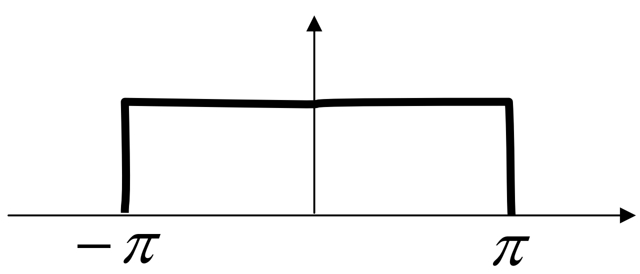
with $K \propto \langle v^2 \rangle \tau \equiv \lambda^2 / \tau$

RW models vs. continuum models









G.I. Taylor, Diffusion by continuous movements, *Phil. Trans. Roy. Soc. Lond. A* ***223***, *289 (1923).*

Autocorrelation functions

Discrete

$$\mathbf{x}_t = \sum_{i=0}^{t} \mathbf{s}_i$$

$$\langle \mathbf{x}_t^2 \rangle = \left\langle \sum_{i,j=0}^{t} \mathbf{s}_i \mathbf{s}_j \right\rangle = \sum_{i,j=0}^{t} C_{i,j}$$

Continuous

$$\mathbf{x}(t) = \int_0^t \mathbf{v}(t')dt'$$

$$\langle \mathbf{x}^2(t) \rangle = \left\langle \int_0^t \int_0^t \mathbf{v}(t')\mathbf{v}(t'')dt'dt'' \right\rangle$$

$$= \int_0^t \int_0^t C(t',t'')dt'dt''$$

Stationary velocity process → *x*-process with stationary increments

$$C(t',t'') = C(|t'-t''|), \quad \int_0^\infty C(t')dt' < \infty$$

$$\langle \mathbf{x}^2(t) \rangle = dDt$$

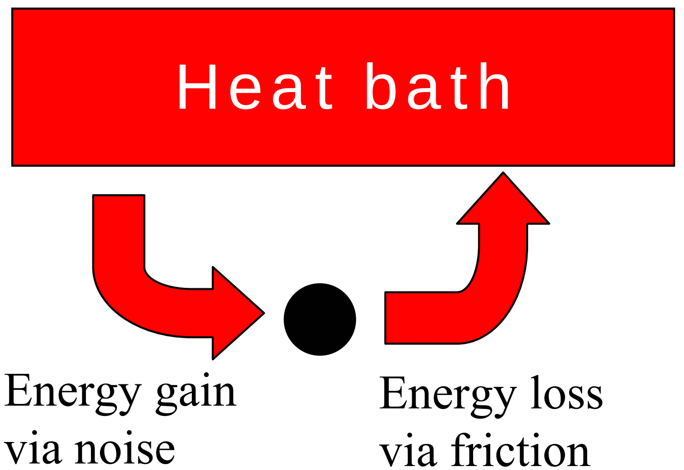
$$D = \int_0^\infty C(t')dt'$$

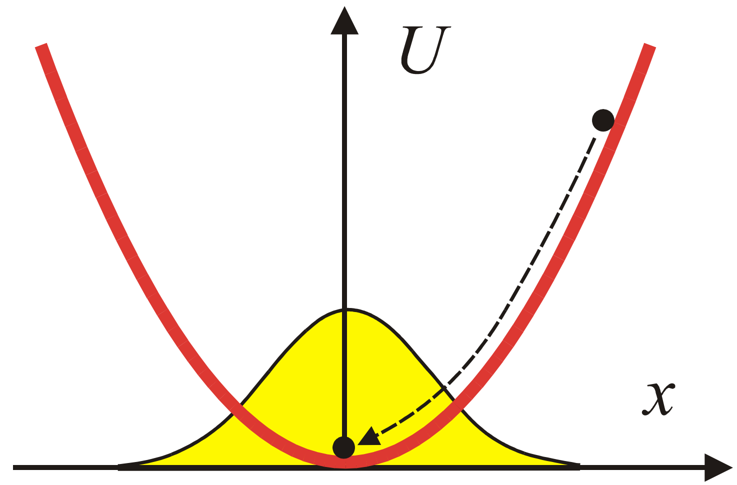
Stationarity of increments
=
Stationary (equilibrium) state
of the bath

Langevin (1908)

“infinitely simpler…”,
but equivalent approach

$$m\frac{d^2x}{dt^2} = f - \gamma\frac{dx}{dt} + \sqrt{2D}\xi(t)$$





Ornstein-Uhlenbeck Process
(linear relaxation) ⇒ Onsager

overdemped motion

$$\gamma\frac{dx}{dt} = f + \sqrt{2D}\xi(t)$$

- The mean displacement relaxes *exponentially* to its equilibrium value.
- The distribution relaxes to Boltzmann distr.
- The velocity correlations in equilibrium decay exponentially

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

$$\left\langle x^2(t) \right\rangle \propto t^{\alpha}$$

$$\alpha \neq 1$$

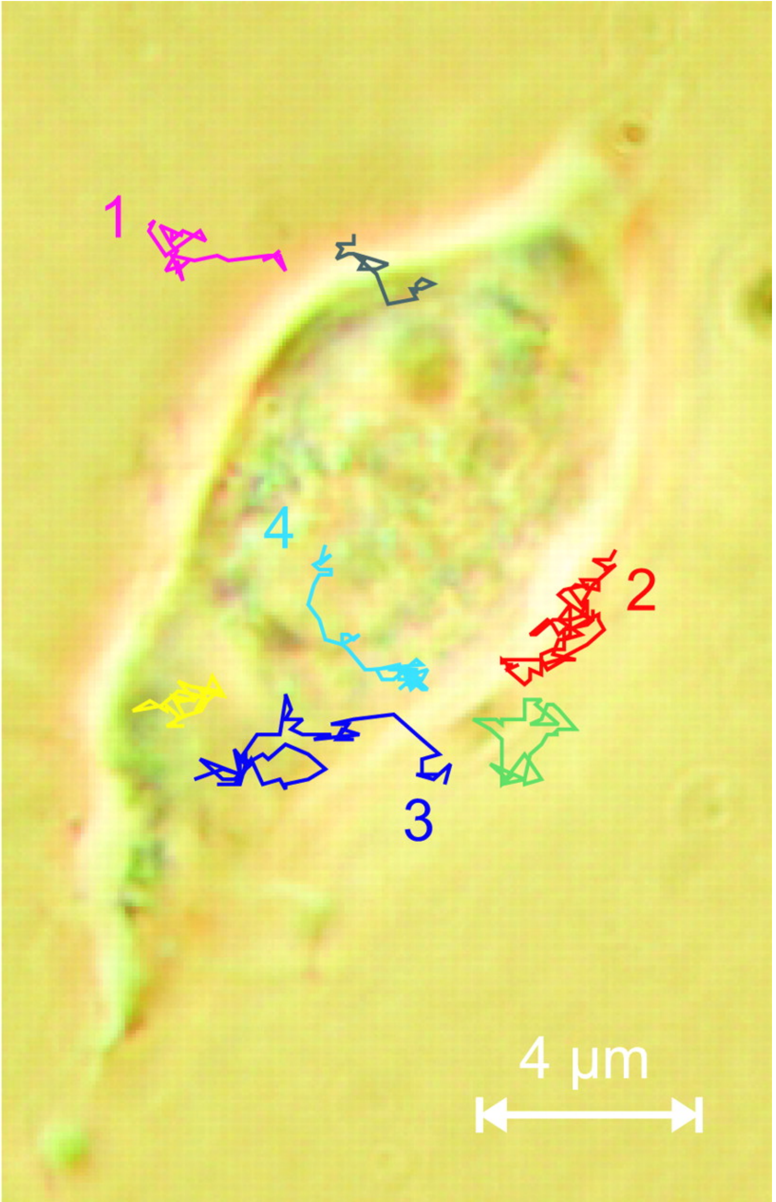
Joseph Klafter and Igor M Sokolov

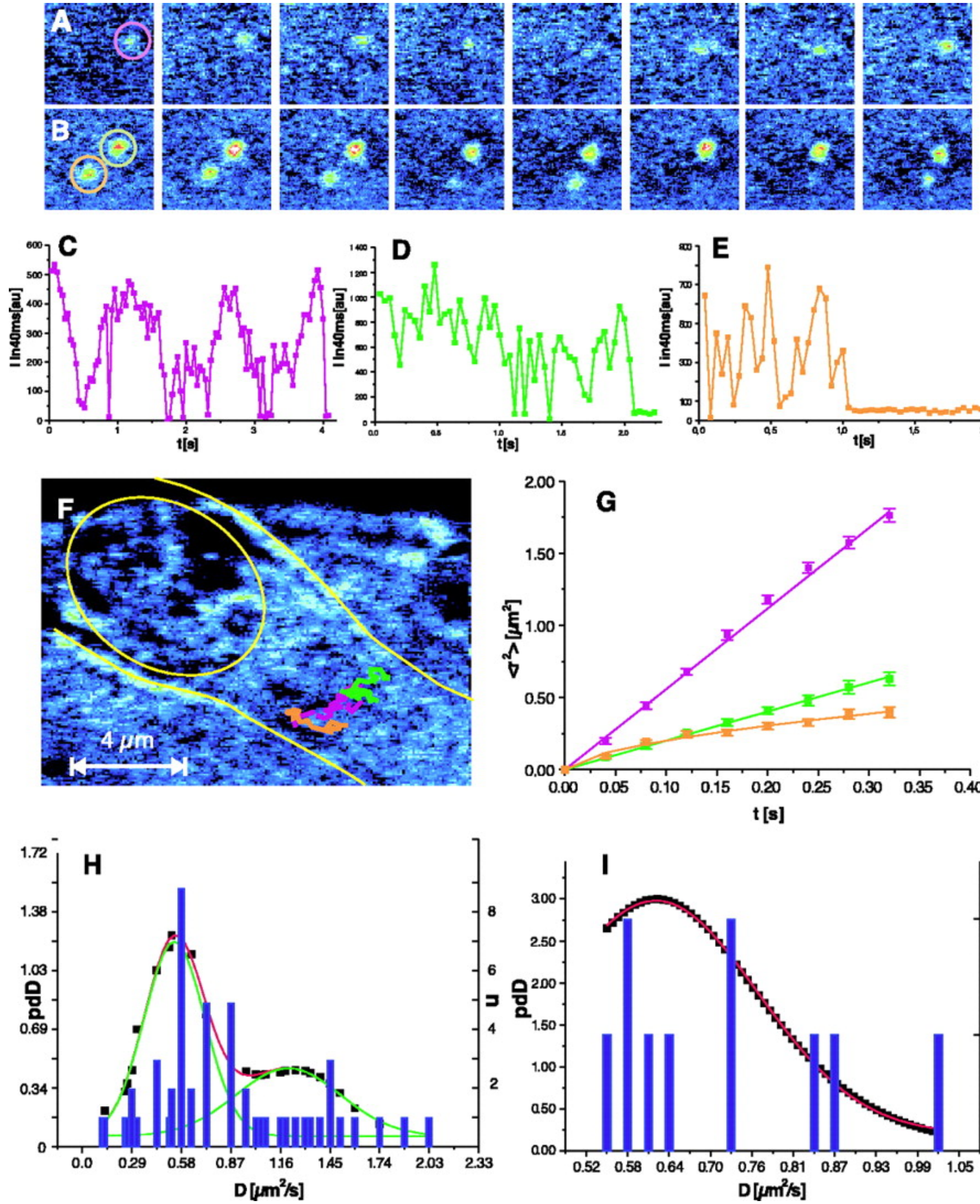
AS ALL of us are no doubt aware, this year has been declared "world year of physics" to celebrate the three remarkable breakthroughs made by Albert Einstein in 1905. However, it is not so well known that Einstein's work on Brownian motion – the random motion of tiny particles first observed and investigated 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

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



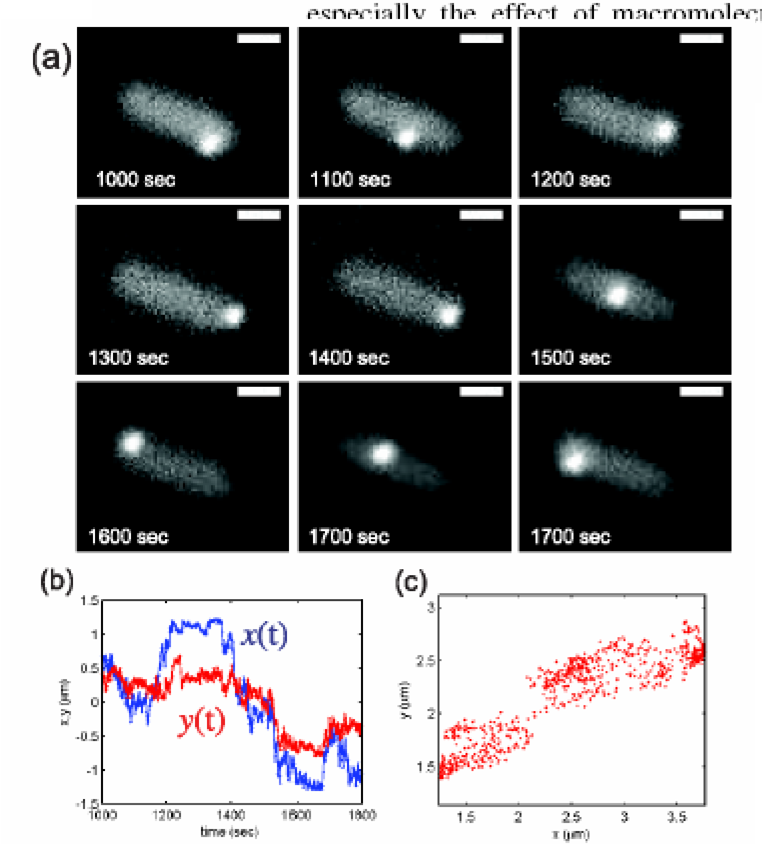


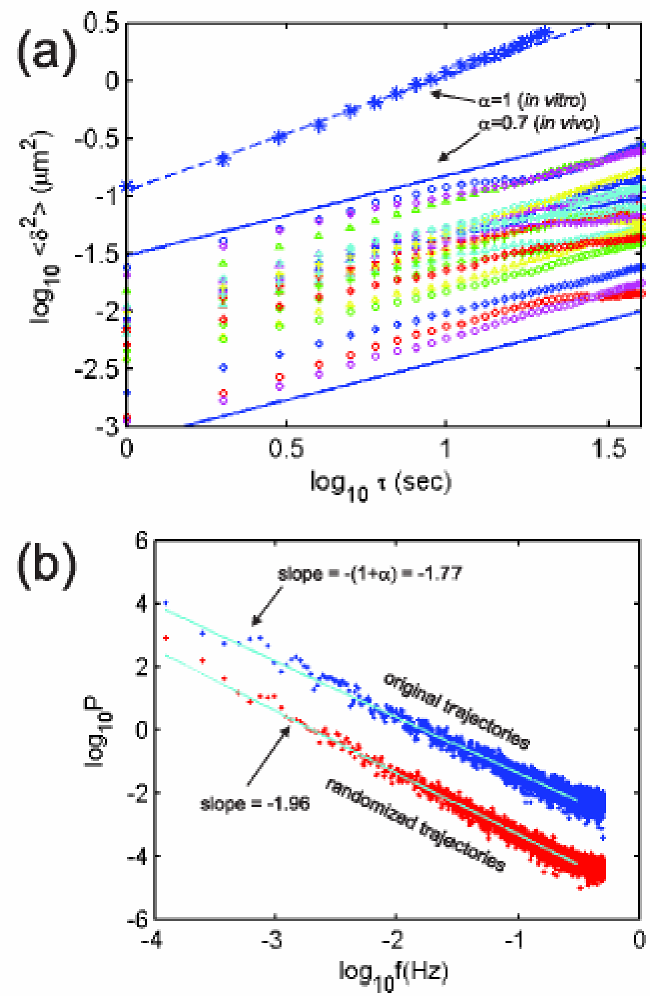
Seisenberger, G., Ried, M.U. Endreß, T., Büning, H., Hallek, M. & Bräuchle, C., Real-time single-molecule imaging of the infection pathway of an adeno-associated virus. *Sience.* **294,** 1929-1932 (2001)

Physical Nature of Bacterial Cytoplasm

Ido Golding and Edward C. Cox
Department of Molecular Biology, Princeton University, Princeton, New Jersey 08544, USA
(Received 10 November 2005; published 10 March 2006)

We track the motion of individual fluorescently labeled mI
find that the motion is subdiffusive, with an exponent that is ro
disruption of cytoskeletal elements. By modifying the parame
cell, we are able to examine the possible mechanisms tha
especially the effect of macromolecular crowding. We als
gene regulation, in par





Ergodic and nonergodic processes coexist in the plasma membrane as observed by single-molecule tracking

Aubrey V. Weigel[a], Blair Simon[b], Michael M. Tamkun[c,d], and Diego Krapf[a,b,1]

[a]School of Biomedical Engineerin
State University, Fort Collins, CO
[d]Department of Biochemistry anc

Edited* by Jennifer Lippincott-Sch

Diffusion in the plasma mem
display anomalous dynamics.
this diffusion pattern remain:

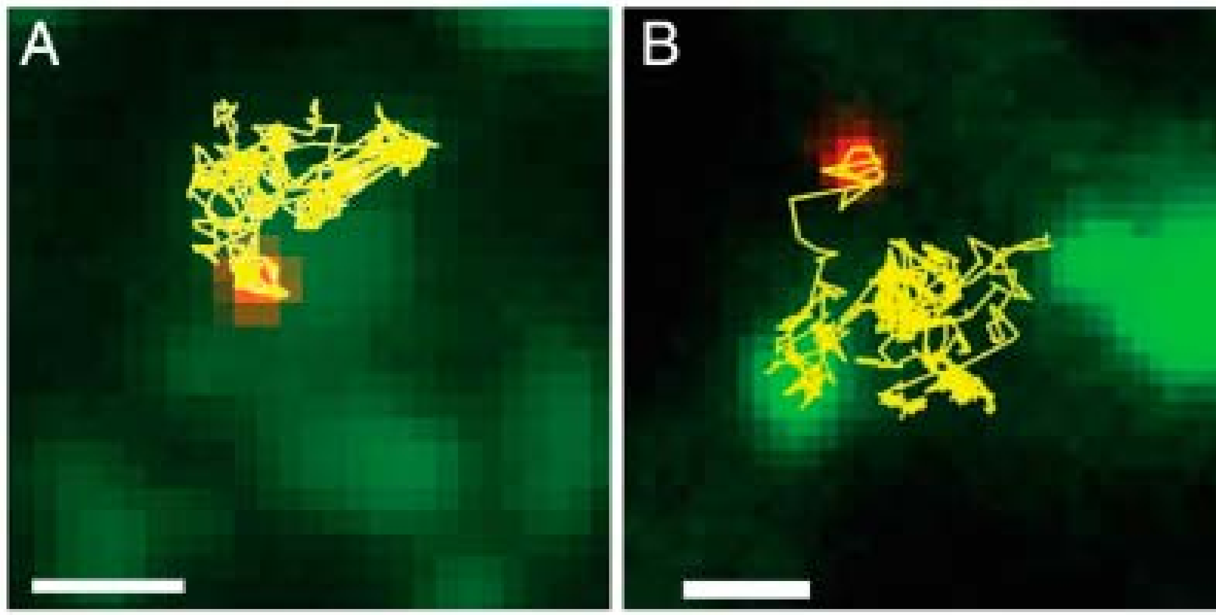


Fig. 1. Overlay image of GFP-tagged Kv2.1 clusters and individual QDs. Kv2.1 clusters are shown in green and QD-tagged channels in red. The trajectories of (*A*) a clustered and (*B*) a nonclustered (free) Kv2.1 channels are shown. Interestingly, the nonclustered channel ignores the compartment perimeters and the channel travels freely into and out of a cluster. Scale bars: 1 μm.

Experimental techniques

• Ensemble properties:

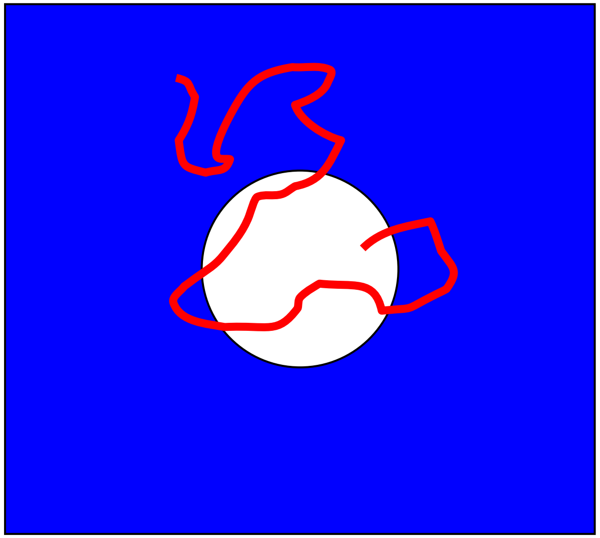
- measurements of mass transport, current or polarization
- FRAP

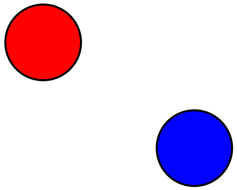
•Single-particle propertries:

•Trajectories
- single-particle tracking

•First passage times
- FRET

•Sojourn times
- FCS





"Measure and fit!"

Physical models

Possible sources of anomalous subdiffusion:

1. CTRW with power-law waiting times as arising from random potential models (*energetic disorder*, *trapping environment*) SM: i)
2. Diffusion on fractal structures, e.g. on percolation clusters (*geometrical disorder*, or *labyrinthine environment*) M: ii)
3. Temporal correlations due to *slow modes* (typical for *viscoelastic environments*). NM: iii)

The three cases correspond to different models and are described using different theoretical instruments.

Mathematical instruments

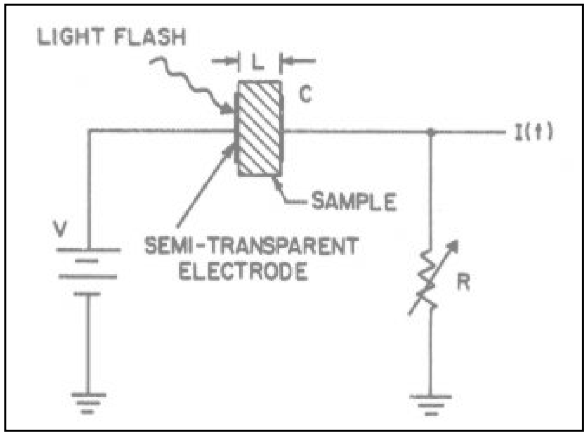
CTRW: Fractional diffusion (or Fokker-Planck) equation, or a couple of Langevin equations describing the evolution of the coordinate and of the clock time as functions of the operational time (Fogedby's approach).

Fractals: Percolation and other labyrinthine models. No equation known. Often approximately described by diffusion equations with distance-dependent diffusion coefficient.

fBm (viscoelastic models): Generalized (integrodifferential) Langevin equation. No Fokker-Planck analogue known.

sBm: "Time-dependent diffusion coefficient taken seriously": Diffusion equation with time-dependent diffusion coefficient. Often used by experimentalists for fitting of anomalous diffusion of unclear origin.

Subdiffusion: In disordered solids…



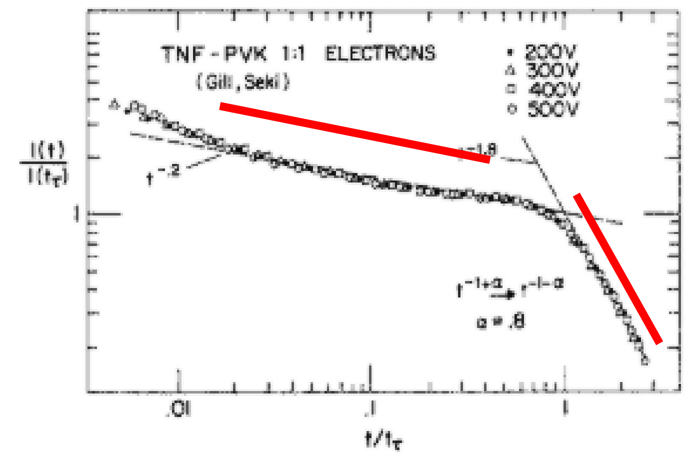
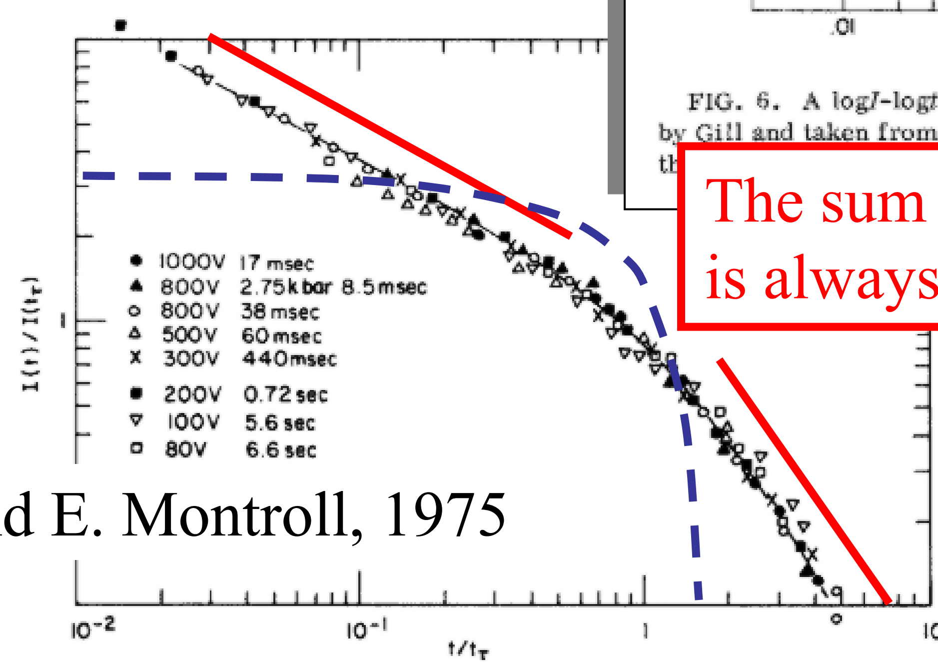


FIG. 6. A log*I*-log*t* plot for 1:1 TNF-PVK measured by Gill and taken from a paper by Seki. The slopes of th… …pectively.

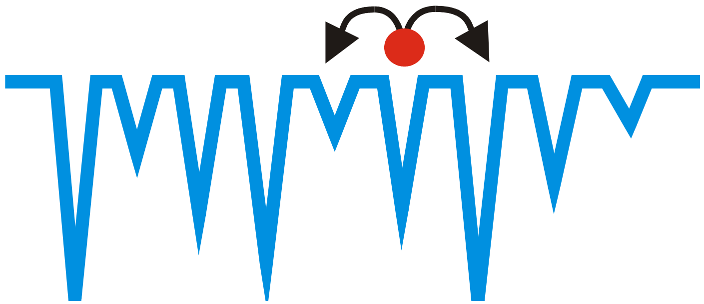
The sum of slopes is always 2



…plot …ange …n …ure- ments by Pfister also in- clude a data set at high pressure (2.75 kbar). The solid line is the theoretical curve.

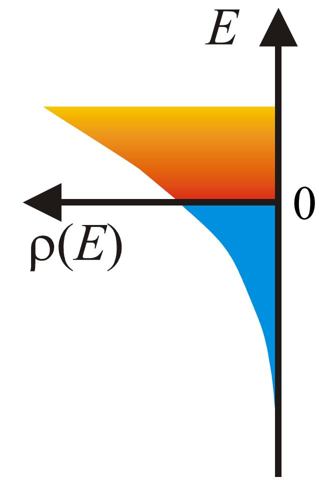
H. Scher and E. Montroll, 1975

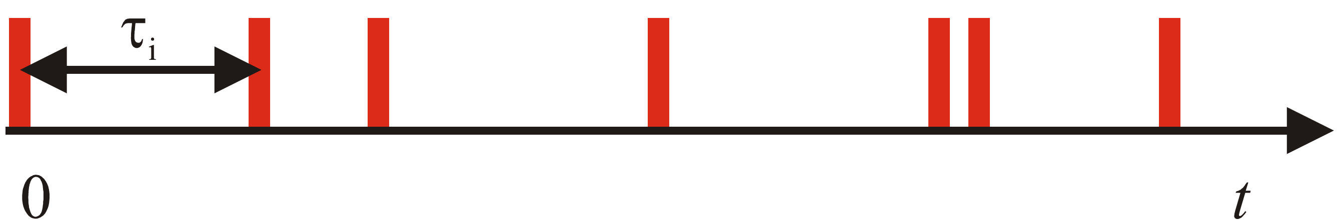
Explanation: Multple trapping and CTRW



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

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





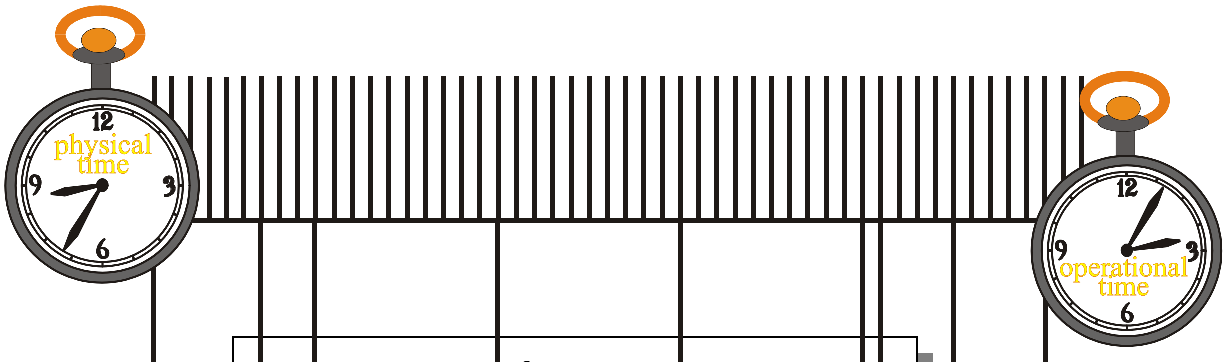
The waiting-time distribution between the two jumps $\psi(t) \propto t^{-1-\alpha}$ with $\alpha = k_B T / E_0$

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

Mean number of steps $n(t) \propto t^{\alpha}$ Mean rate of steps $M(t) = \frac{dn}{dt} \propto t^{\alpha-1}$

Mean squared displacement $\langle x^2(t) \rangle \propto t^{\alpha}$ with $\alpha < 1$

The Subordination



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

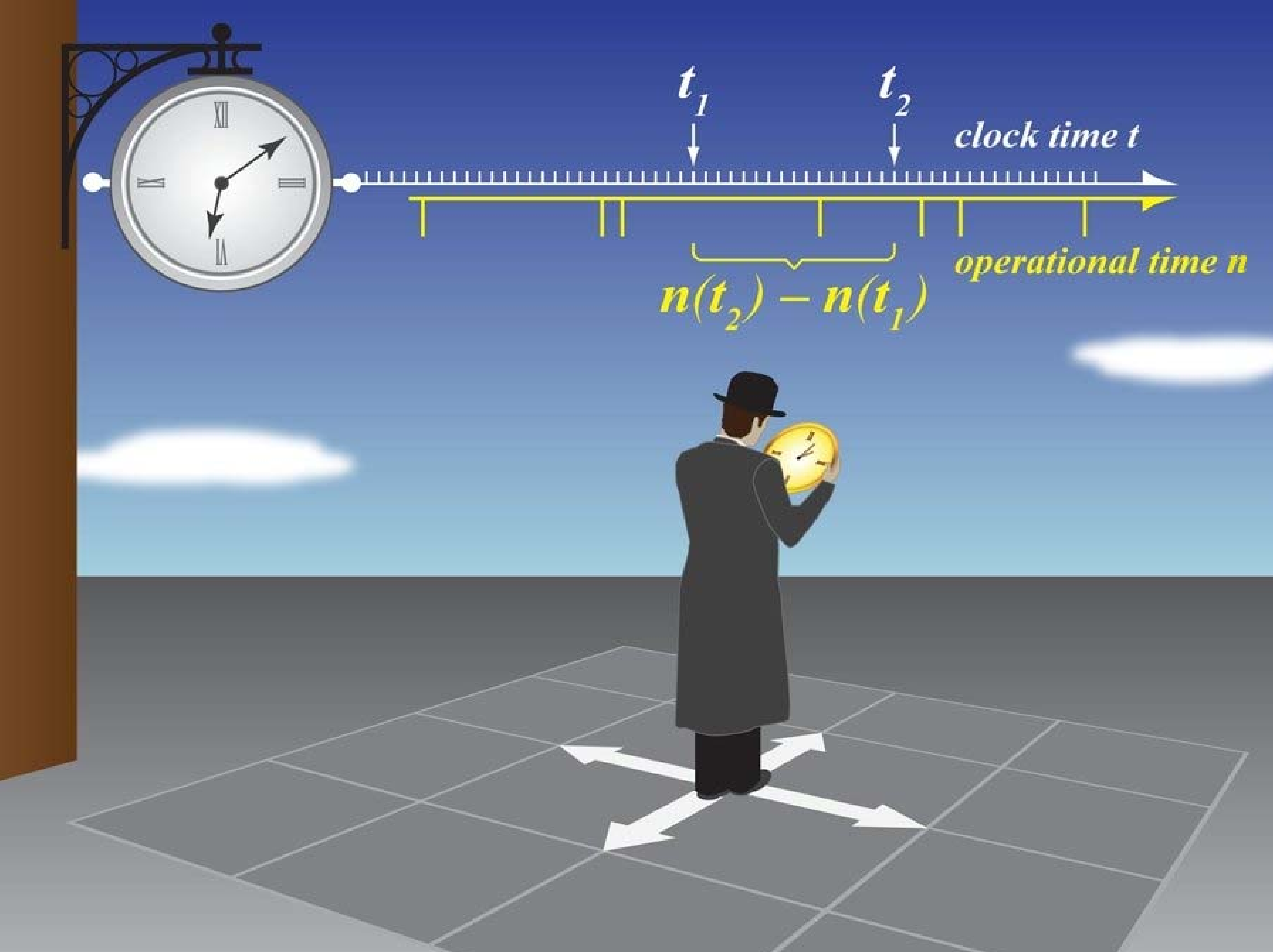
PDF of the particle's position after n steps (say, a Gaussian)

Probability to make exactly n steps up to the time t

Transition to continuum:

$$P(x,t)=\int_0^{\infty} W(x,\tau)T(\tau,t)d\tau$$

operational time


t_1
t_2
clock time t
operational time n
$n(t_2) - n(t_1)$

Short way to the result:

- Independent steps => $\langle x^2(t)\rangle = a^2\langle n(t)\rangle$
- Steps follow inhomogeneously in the physical time *t*.
- The number of steps up to the time *t* may be calculated using the renewal approach:

no steps up to time *t*: $\chi_0(t) = 1 - \int_0^t \psi(t')dt'$

1 step up to time *t*: $\chi_1(t) = \int_0^t \psi(t')\chi_0(t-t')dt'$

....

n steps up to time *t*: $\chi_n(t) = \int_0^t \psi(t')\chi_{n-1}(t-t')dt'$

$$\langle n(t)\rangle = \sum_{n=0}^{\infty} n\chi_n(t) = ?$$

After Laplace-transform: $\tilde{\chi}_n(u) = \dfrac{1-\tilde{\psi}(u)}{u}\tilde{\psi}^n(u)$

$$\langle \tilde{n}(u) \rangle = \frac{1-\tilde{\psi}(u)}{u}\sum_{n=0}^{\infty} n\tilde{\psi}^n(u) = \frac{1-\tilde{\psi}(u)}{u}\sum_{n=0}^{\infty}\tilde{\psi}(u)\frac{d}{d\tilde{\psi}}\tilde{\psi}^n(u)$$

$$= \frac{1-\tilde{\psi}(u)}{u}\tilde{\psi}(u)\frac{d}{d\tilde{\psi}}\sum_{n=0}^{\infty}\tilde{\psi}^n(u) = \frac{\tilde{\psi}(u)}{u\left[1-\tilde{\psi}(u)\right]}.$$

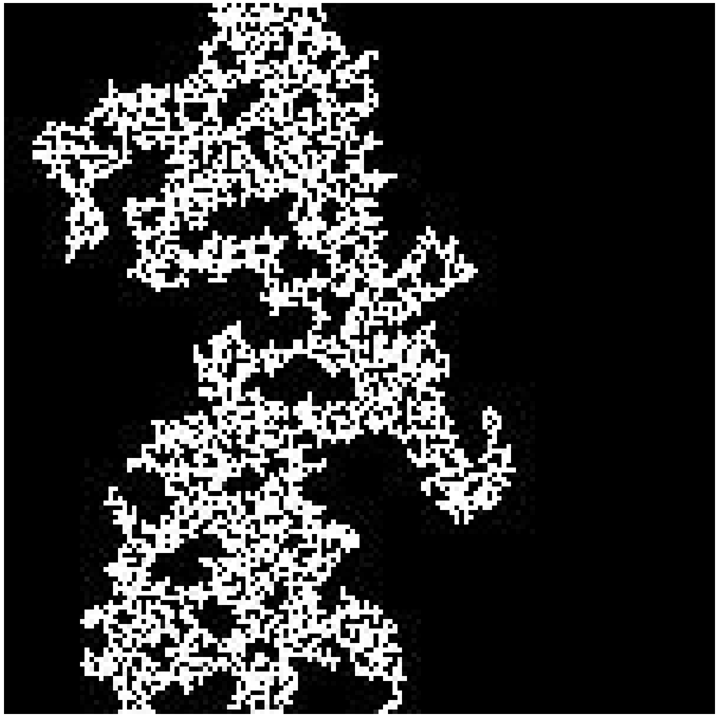
$$\boxed{\psi(t) \propto t^{-1-\alpha}} \longrightarrow \boxed{\tilde{\psi}(u) \cong 1 - cu^{\alpha} + \ldots}$$

$$\downarrow$$

$$\boxed{\langle n(t) \rangle \propto t^{\alpha}} \longleftarrow \boxed{\langle \tilde{n}(u) \rangle \cong c^{-1}u^{-1-\alpha}}$$

The the FDE can be derived from the properties of the parent process and those of subordinator (operational time)

Other relevant models: Percolation



Geometric disorder: Percolation cluster at criticality: Markovian model with non-iid steps

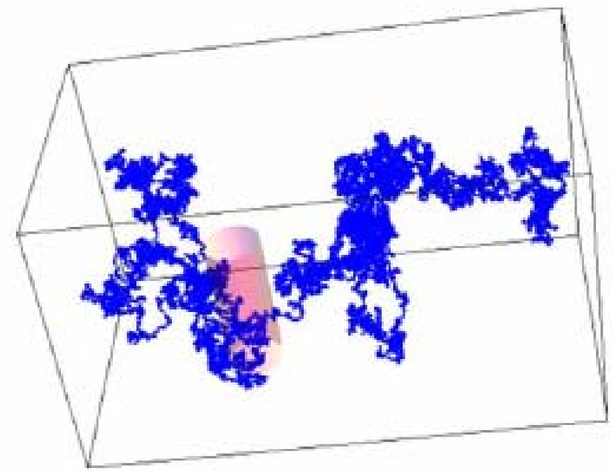


Fig. (4). The measurement system: 3D translational anomalous diffusive motion within the observation volume ΔV = 0.14 fL (in pink color). Simulation steps n=10000.

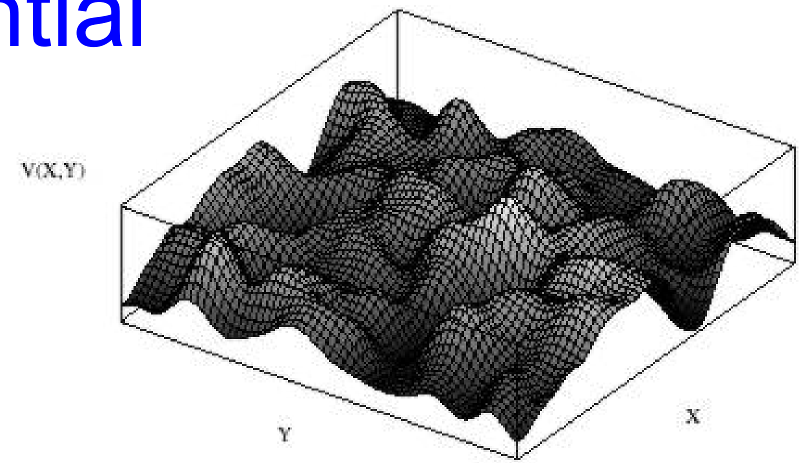
Current Pharmaceutical Biotechnology, 2010, *11*, 527-543 527

Meaningful Interpretation of Subdiffusive Measurements in Living Cells (Crowded Environment) by Fluorescence Fluctuation Microscopy

Gerd Baumann[1,*], Robert F. Place[2,3] and Zeno Földes-Papp[1,4,*]

Non-interacting particles in a random potential

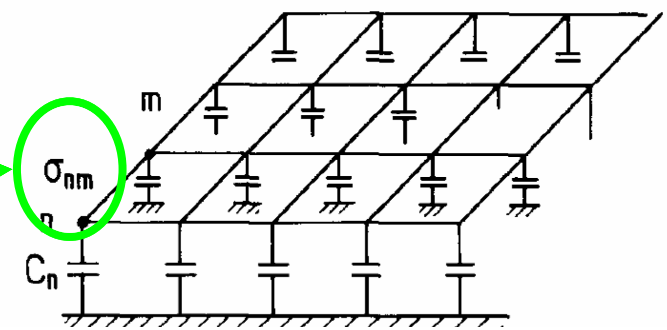
$$\dot{n}_i = \sum_j \left(w_{ij} n_j - w_{ji} n_i \right)$$



detailed balance

$$w_{ij} n_j^0 = w_{ji} n_i^0 \quad \text{with}$$

$$n_i^0 = \frac{M}{N} \exp\left(-\frac{E_i}{kT} \right)$$



$$D^* = a^2 \frac{\left\langle w_{ij} \exp\left(-\frac{E_i}{kT} \right) \right\rangle_{EM}}{\left\langle \exp\left(-\frac{E_i}{kT} \right) \right\rangle}$$

$$\sigma = \overline{n}\, e\, \overline{\mu}$$

$$\overline{\mu} = \frac{\overline{D}}{kT}$$

$$D^* = a^2 \frac{\left\langle w_{ij} \exp\left(-\frac{E_i}{kT}\right)\right\rangle_{EM}}{\left\langle \exp\left(-\frac{E_i}{kT}\right)\right\rangle}$$

• Superdiffusion is impossible: The enumerator never diverges in finite dimensions and the denominator never vanishes

Two (and only two) sources of subdiffusion in our system:

• Either $\left\langle \exp\left(-\frac{E_i}{kT}\right)\right\rangle$ diverges ("strong energetic disorder")

• or the percolation concentration in the system is unity, e.g. on the percolation threshold, in 1d, or on a finitely ramified fractal ("structural disorder"). No anomalous diffusion in random barrier models in $d > 1$.

• both can apply simultaneously ("subdiffusion of mixed origins") e.g. in 1d barrier model

F. Camboni & IMS, PRE in press

Electric analogy

$$\dot{n}_i = \sum_j \left(g_{ij} \frac{n_j}{n_j^0} - g_{ji} \frac{n_i}{n_i^0} \right)$$

$$n_i^0 \frac{d}{dt} \frac{n_i}{n_i^0} = \sum_j \left(g_{ij} \frac{n_j}{n_j^0} - g_{ji} \frac{n_i}{n_i^0} \right)$$

activity ζ_i

Electric analogy:
random resistor - capacitor model

conductivity

$\sigma_{ij} = \sigma_{ji}$

$$C_i \frac{d}{dt} \phi_i = \sum_j \left(\sigma_{ij} \phi_j - \sigma_{ji} \phi_i \right)$$

capacity

potential of site i

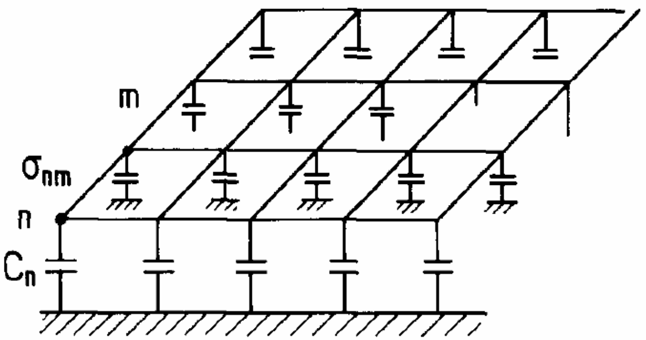
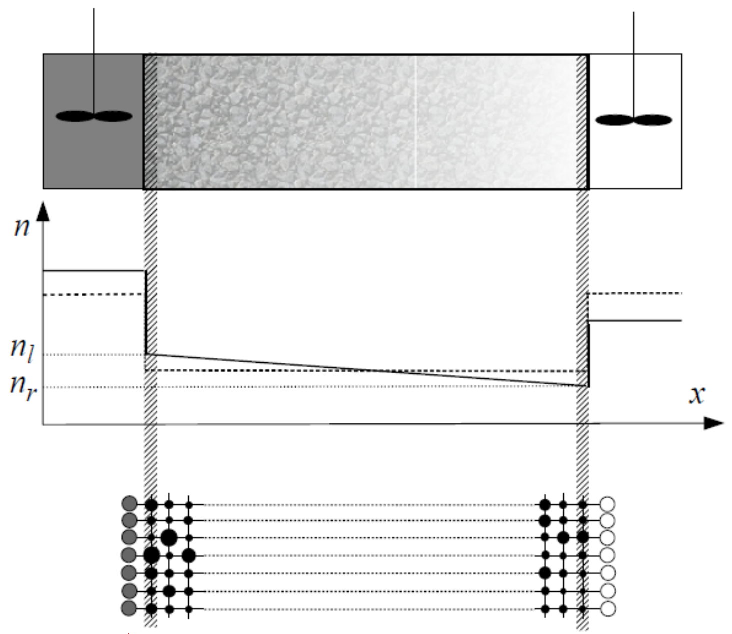


Fig 2 5 Random resistor network, with each node connected to the ground by random capacitors

(From Bouchaud & Georges)

n_i	$/ \; q_i$	conserved
$\frac{n_i}{n_i^0}$	$/ \; \phi_i$	non-conserved

Calculating D^*



well-mixed layers with infinitely strong bonds to the interior of the system. In these layers all ζ_i are the same.

$$\dot{\zeta}_i = \frac{1}{n_i^0} \sum_i g_{ij} \left[\zeta_j - \zeta_i \right]$$

In stationary state

$$\sum_i g_{ij} \left[\zeta_j - \zeta_i \right] = 0$$

In the first / last layer in the system $\zeta_i \approx \zeta_l$ resp. $\zeta_i = \zeta_r$

$$\langle n_l \rangle = \zeta_l \langle n_i^0 \rangle; \quad \langle n_r \rangle = \zeta_r \langle n_i^0 \rangle$$

$$I = \sum_{i \in \text{surface}} J_{ij} = W^{d-1} \langle J_{ij} \rangle_{\text{surface}}$$

Somewhat stronger property

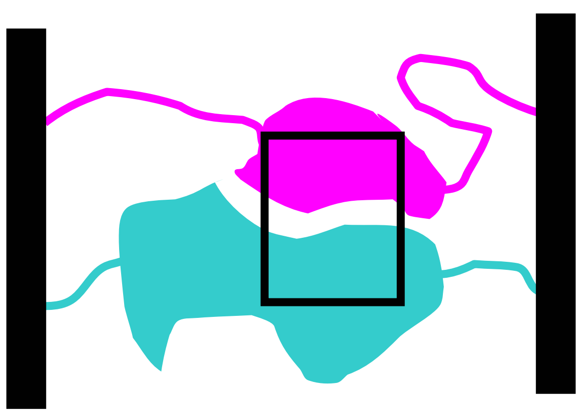
Let $\{j\}$ be the connected neighbors of site i. In a stationary state

$$\zeta_i = \sum_j g_{ij}\zeta_j \Big/ \sum_j g_{ij}$$

(i.e. ζ_i is the weighted arithmetic mean of ζ_j)

ζ_l and ζ_r are fixed, and $L \to \infty$

$\Rightarrow$ ζ_j is slowly varying ("smooth") in each connected environment of site i.



Only large connected parts of the system contribute to macroscopic diffusion / conductivity

In each such part, due to smoothness of activities, the *local activities* and the *local equilibrium* concentrations *decouple*.

Denominator

The denominator $\int_{-\infty}^{\infty} \exp\left(-\frac{E}{kT}\right) p(E)\,dE$ may diverge for $p(E)$ growing slower than $p(E) \sim \exp(-E/kT)$ for large (negative) E.

The denominator does not vanish for any proper PDF $p(E)$.

median value of $p(E)$

$$\int_{-\infty}^{\infty} \exp\left(-\frac{E}{kT}\right) p(E)\,dE = \int_{-\infty}^{E_M} \exp\left(-\frac{E}{kT}\right) p(E)\,dE + \int_{E_M}^{\infty} \exp\left(-\frac{E}{kT}\right) p(E)\,dE$$

$$= \exp\left(-\frac{E^*}{kT}\right) \int_{-\infty}^{E_M} p(E)\,dE + \int_{E_M}^{\infty} \exp\left(-\frac{E}{kT}\right) p(E)\,dE \geq \frac{1}{2} \exp\left(-\frac{E_M}{kT}\right)$$

mean value theorem

non-negative

Enumerator

Some results from percolation theory:

• The mixture of resistors of (same) finite conductivity (prob. p) and insulating bonds (prob. $1-p$) possesses zero conductance below the percolation threshold p_c and finite (non-zero) conductance above it.

Mathematically proved for Bernoulli case, ***generally believed*** even for short-range correlated cases (RG).

J.T. Chayes and L. Chayes, Comm. Math. Phys. 105, 133 (1986)

Above the percolation threshold the system homogenizes for any distribution of iid conductivities

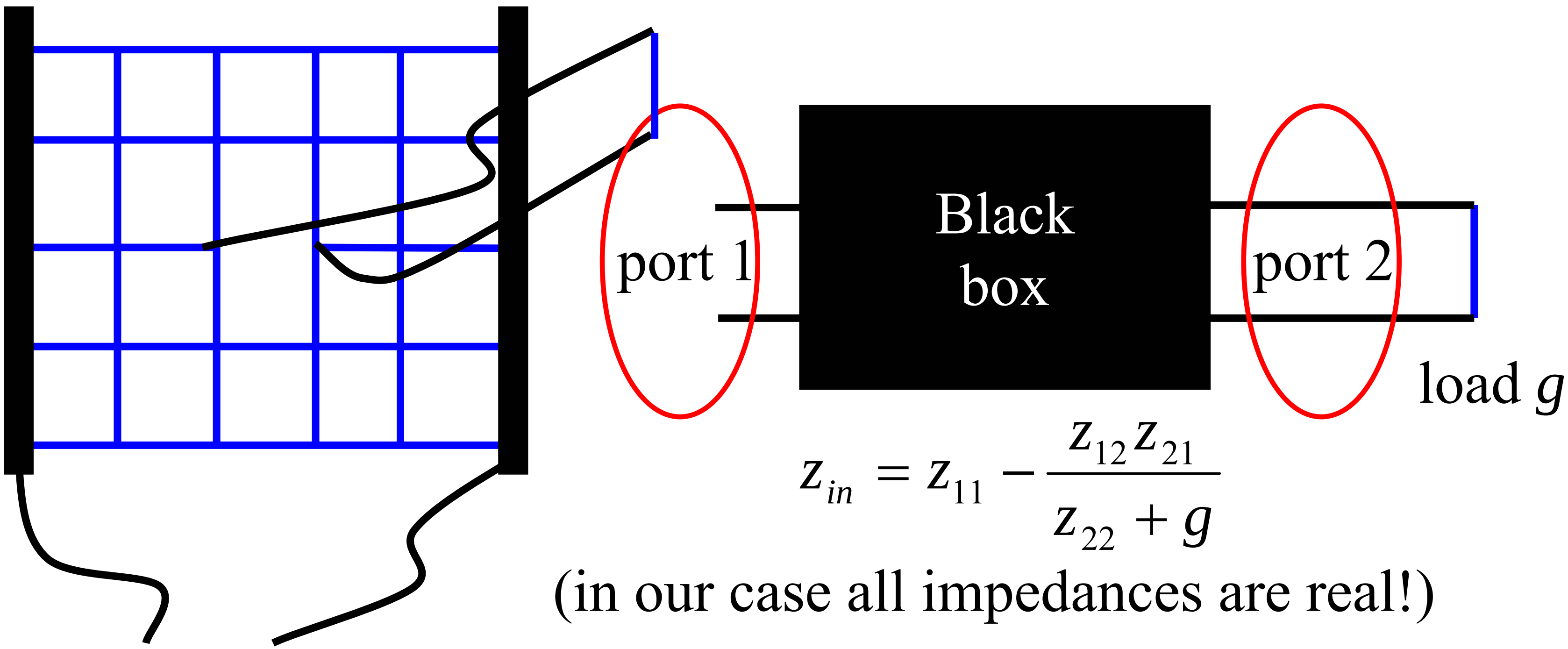
P. Mathieu, J. Stat. Phys. 130, 1025 (2008)

• p_c does depend on correlations between the bonds

•The mixture of resistors of (same) finite conductivity (prob. p) and superconducting bonds (prob. $1-p$) possesses finite conductance above the percolation threshold $p_c^s = 1 - p_c$ and infinite conductance below it.

Two-port systems

The input conductivity is a non-decaying function of load conductivity



$$z_{in} = z_{11} - \frac{z_{12} z_{21}}{z_{22} + g}$$

(in our case all impedances are real!)

$z_{11} \geq 0,\ z_{22} \geq 0,\ z_{11} z_{22} - z_{12} z_{21} \geq 0$ non-negative heat production

$z_{12} = z_{21}$ reciprocity theorem as a consequence of Kirchhoff's laws

$\Rightarrow z_{in}$ monotonically non-decaying function of g.

Consequences

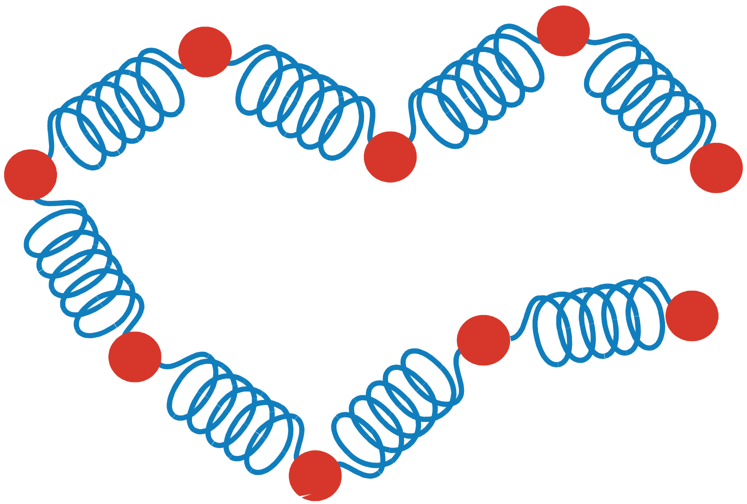
The total conductance is a non-decaying function of the conductivity of each bond.

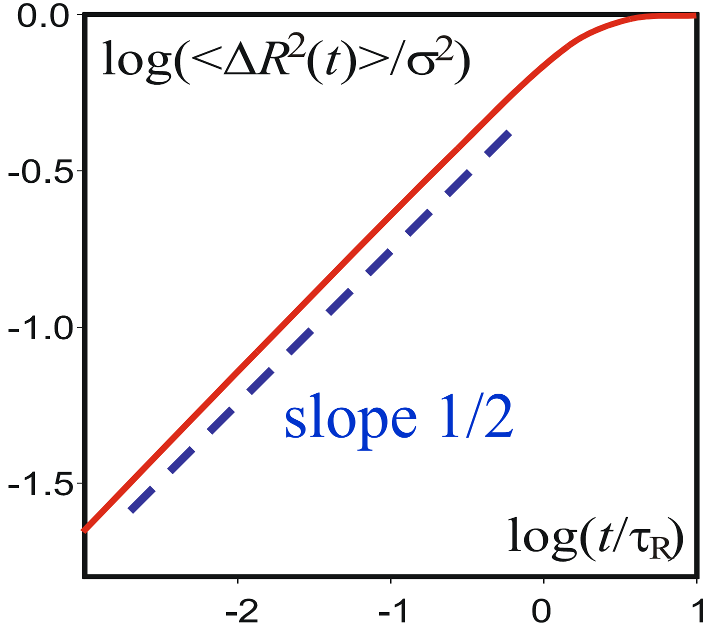
Fix some $q < 1 - p_c$ and remove the fraction q of all bonds starting from the ones with smallest conductivities, up to some σ_{max}. The remaining system still percolates and possesses the conductance which is larger than the conductance of the percolation system with $p = 1 - q$ where all conductivities are put to σ_{max}. The overall system homogenizes.

$\Rightarrow$ The enumerator can only vanish if $p_c = 1$ (i.e. at the percolation threshold, in 1d or on a finitely ramified fractal)

In the models of particles' motion in static random potentials there are two (and only two) sources of anomalous diffusion.

Other relevant models: Polymers





Slow modes: Subdiffusion in a Rouse polymer chain.
Each mode normally diffusing (OU-process).
More complex models: polymer networks,
intramolecular interactions etc.

The whole process is a non-Markovian process
with stationary arguments

- Anomalous is normal

- Happy families are all alike; every unhappy family is unhappy in its own way

Position-position correlation function

$$\phi(t,s) = \langle x(t)x(s) \rangle$$

Displacement during the time interval between s and t ($t > s$)

$$\left\langle [x(t) - x(s)]^2 \right\rangle = \left\langle x^2(t) \right\rangle + \left\langle x^2(s) \right\rangle - 2\langle x(t)x(s) \rangle$$

Anomalous diffusion with stationary increments: $\left\langle x^2(t) \right\rangle = Kt^{\alpha}$

$$\left\langle [x(t) - x(s)]^2 \right\rangle = \left\langle x^2(t-s) \right\rangle$$

$$\phi(t,s) = \frac{K}{2}\left[t^{\alpha} + s^{\alpha} - |t-s|^{\alpha} \right] \rightarrow \text{fractional Brownian Motion}$$

Process starting at t_0

$$\left\langle [x(t-t_0) - x(s-t_0)]^2 \right\rangle = \left\langle x^2(t - t_0 - s + t_0) \right\rangle = \left\langle x^2(t-s) \right\rangle$$

No age,
no aging!

Processes with uncorrelated increments

$$\phi(t,s)=\langle x(t)x(s)\rangle=\langle x(s)x(s)\rangle+\langle \Delta x(t-s)x(s)\rangle=\langle x^2(s)\rangle$$

Displacement during the time interval between *s* and *t* (*t* > *s*)

$$\langle [x(t)-x(s)]^2\rangle=\langle x^2(t)\rangle+\langle x^2(s)\rangle-2\langle x(t)x(s)\rangle=\langle x^2(t)\rangle-\langle x^2(s)\rangle$$

Anomalous diffusion: $\langle x^2(t)\rangle=Kt^\alpha$

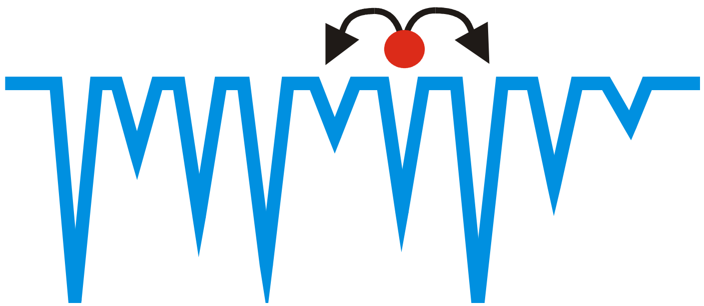
$$\langle [x(t)-x(s)]^2\rangle=Kt^\alpha-Ks^\alpha$$

Process starting at t_0

$$\langle [x(t-t_0)-x(s-t_0)]^2\rangle=K(t-t_0)^\alpha-K(s-t_0)^\alpha$$

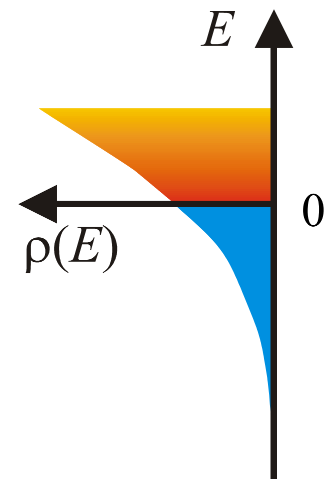
Age $s-t_0$ at beginning of observation can be determined for $\alpha\neq 1$

Resampling of CTRW

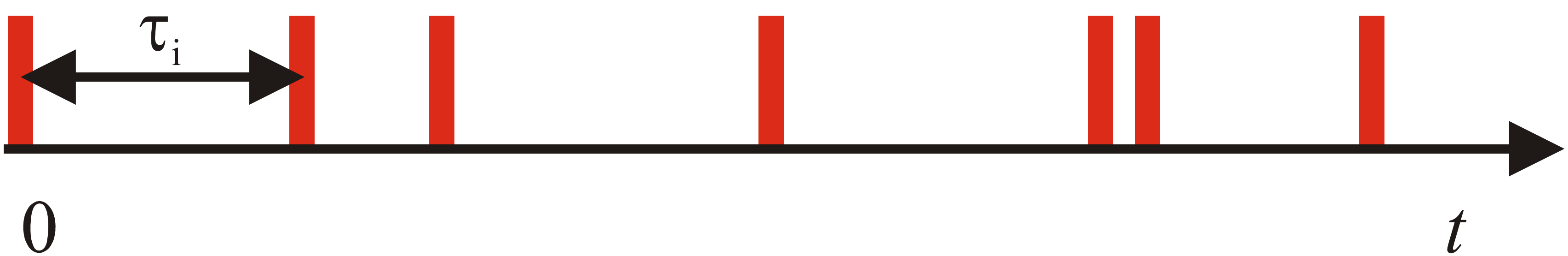


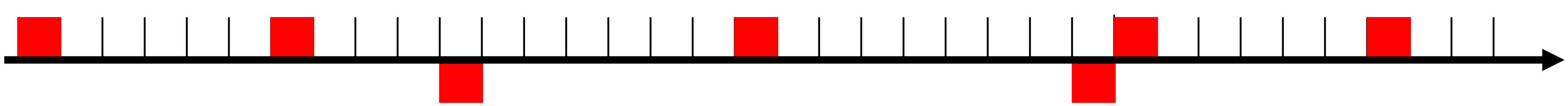
$$\rho(E_i) \propto \exp(E_i / E_0)$$

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



CTRW as a process with dependent, uncorrelated increments



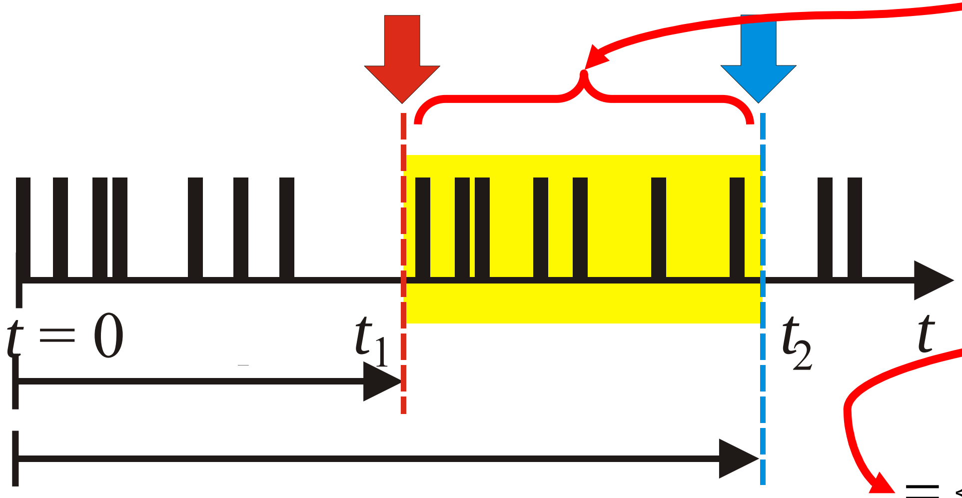


Aging properties in CTRW

In normal diffusion: $\left\langle [x(t_2)-x(t_1)]^2 \right\rangle = \left\langle x^2(t_1-t_2) \right\rangle = 2D(t_1-t_2)$

Explanation: Since $\left\langle n(t) \right\rangle = t/\tau, \left\langle n(t_2) \right\rangle - \left\langle n(t_1) \right\rangle = \left\langle n(t_2-t_1) \right\rangle$

In CTRW $\left\langle [x(t_2)-x(t_1)]^2 \right\rangle \propto \left\langle n \right\rangle = \left\langle n(t_2) \right\rangle - \left\langle n(t_1) \right\rangle$



$\propto t_2^{\alpha} - t_1^{\alpha}$

$$= \begin{cases} t_2^{\alpha} & t_2 - t_1 >> t_1 \\ t_1^{\alpha-1}(t_2 - t_1) & t_2 - t_1 << t_1 \end{cases}$$

The process ***ages***.

Moving time average

$$\langle n(t)\rangle_{\text{ens}} \cong At^{\alpha}$$

$$\langle x^2(t)\rangle = a^2\langle n(t)\rangle_{ens}$$

$$\left\langle [x(t_2)-x(t_1)]^2\right\rangle_{\text{ens}} = a^2\left[\langle n(t_2)\rangle_{\text{ens}} - \langle n(t_1)\rangle_{\text{ens}}\right]$$

•Ensemble average of moving time averages

= moving time average of ensemble av.

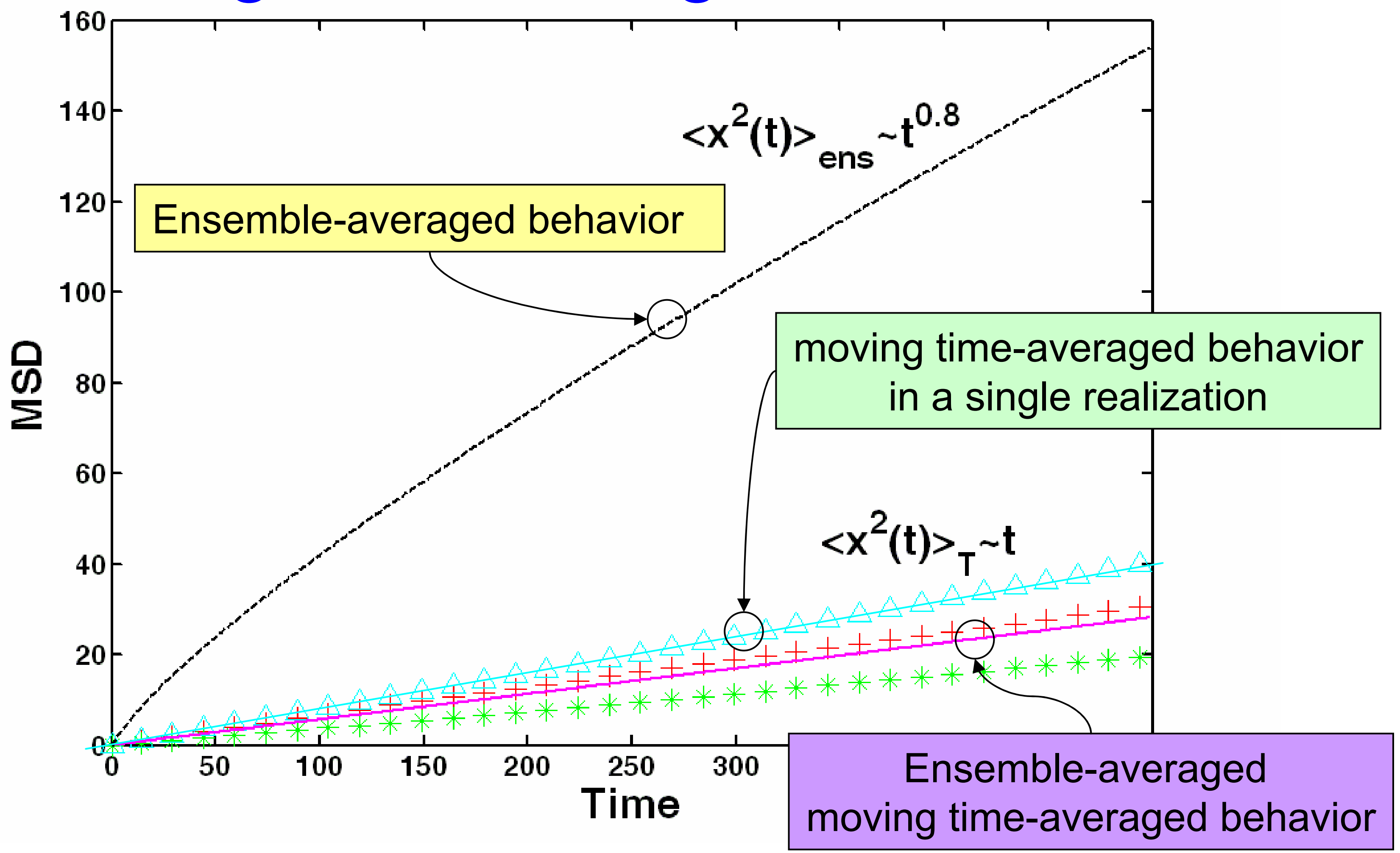
$$\left\langle\langle x^2(t)\rangle_T\right\rangle_{\text{ens}} = a^2\frac{1}{T}\int_0^T\left[\langle n(t'+t)\rangle_{\text{ens}} - \langle n(t')\rangle_{\text{ens}}\right]dt' = \frac{a^2A}{T}\int_0^T\left[(t'+t)^{\alpha} - t'^{\alpha}\right]dt'$$

•For $t << T$ one gets: $\left\langle\langle x^2(t)\rangle_T\right\rangle_{\text{ens}} = a^2AT^{\alpha-1}t$

•**Prediction:** time dependent mean diffusion coefficient

$$K_{\text{eff}}(T) = a^2AT^{\alpha-1}/2$$

Moving time averages in CTRW



Some numerical results for the case $\psi(t) \sim t^{-1.8}$

A. Lubelski, IMS, J. Klafter, PRL **100**, 250602 (2008)

Y. He, S. Burov, R. Metzler and E. Barkai, PRL **101**, 058101 (2008)

Elucidating the Origin of Anomalous Diffusion in Crowded Fluids

Jedrzej Szymanski and Matthias Weiss
Cellular Biophysics Group (BIOMS), German Cancer Research Center, Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany
(Received 12 December 2008; published 15 July 2009)

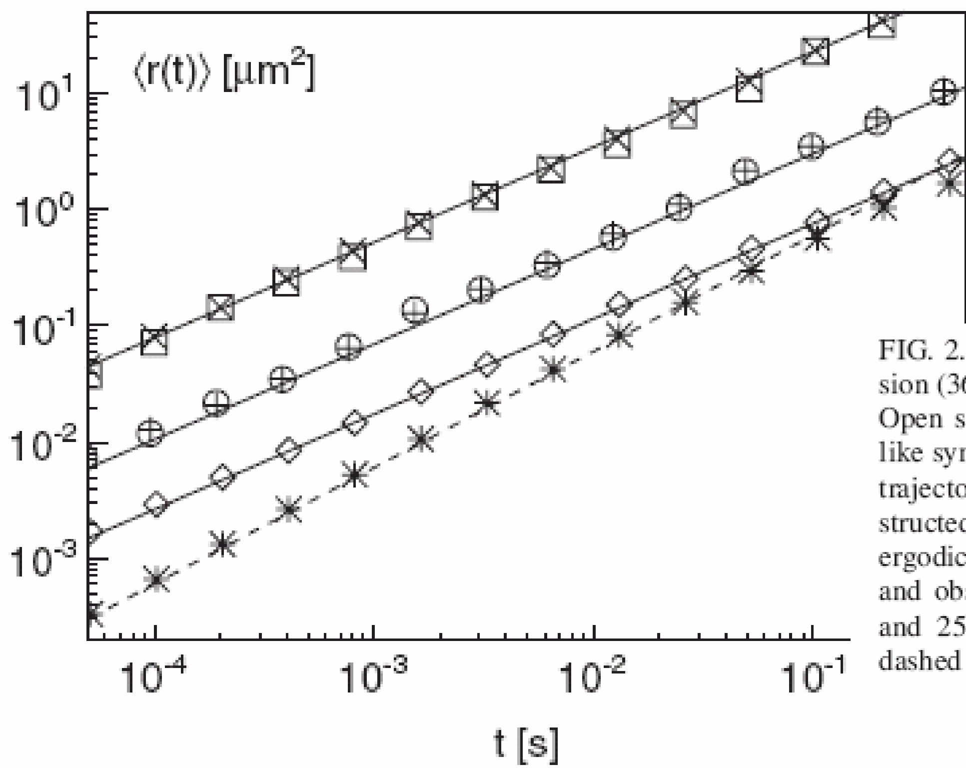


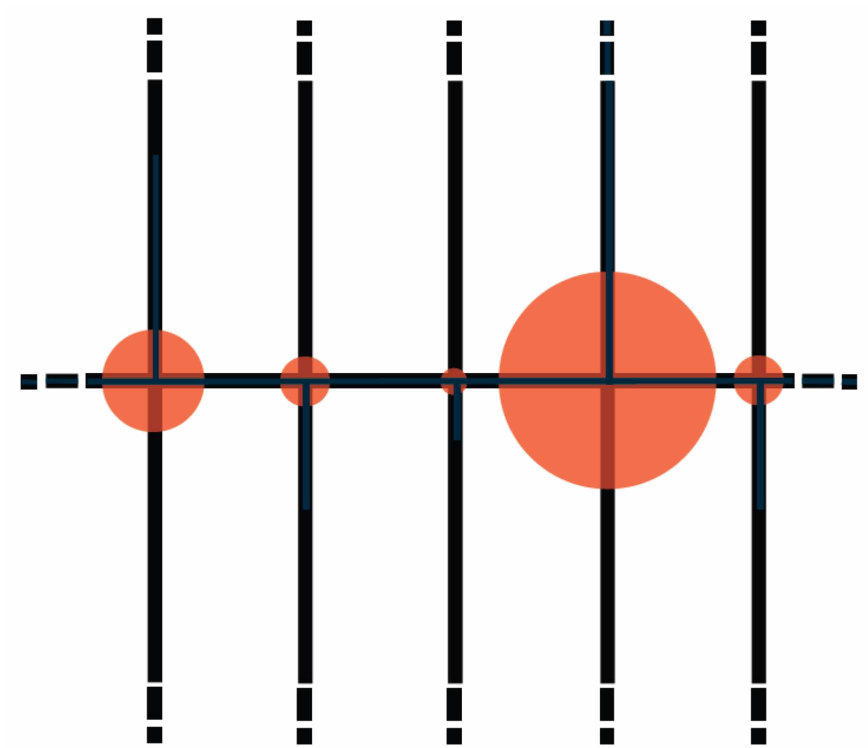
FIG. 2. Mean square displacement $\langle r(t)^2 \rangle$ for obstructed diffusion (36% obstacle concentration), FBM, and CTRW (from top). Open symbols denote the ensemble-averaged MSD, and cross-like symbols denote the time-averaged MSD for a representative trajectory. While both approaches coincide for FBM and obstructed diffusion, the curves differ for the CTRW due to weak ergodicity breaking. For better visibility, MSD curves for FBM and obstructed diffusion have been shifted upwards (factor 50 and 250, respectively). Full lines scale as $\langle r(t)^2 \rangle \sim t^{0.82}$; the dashed line is linear in time.

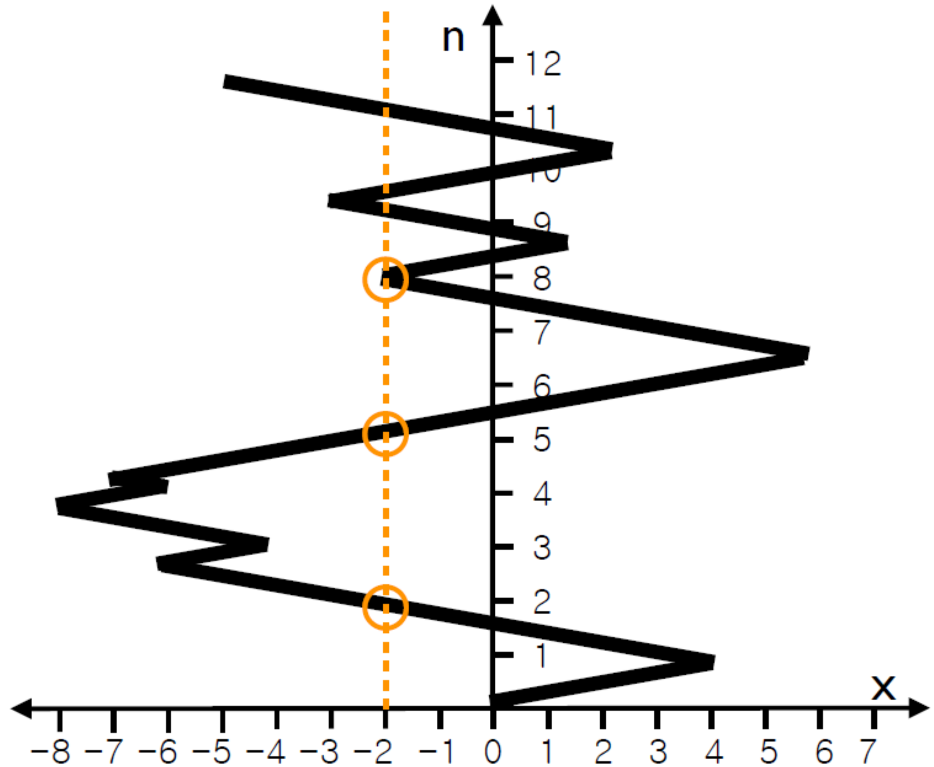
Properties of the most popular models of subdiffusion

Environment	Model	Correlations	Aging prop.	Moving time av.	PDF
trapping	CTRW	none	aging	normal	non-Gauss.
labyrinthine	fractal	antipersistent	equilibr.	anomal.	non-Gauss.
“changing”	sBm	none	aging	normal	Gaussian
viscoelastic	fBm	antipersistent	equilibr.	anomal.	Gaussian

The (unequal) twins

Y. Meroz, IMS and J. Klafter, PRL **107,** 260601 (2011)



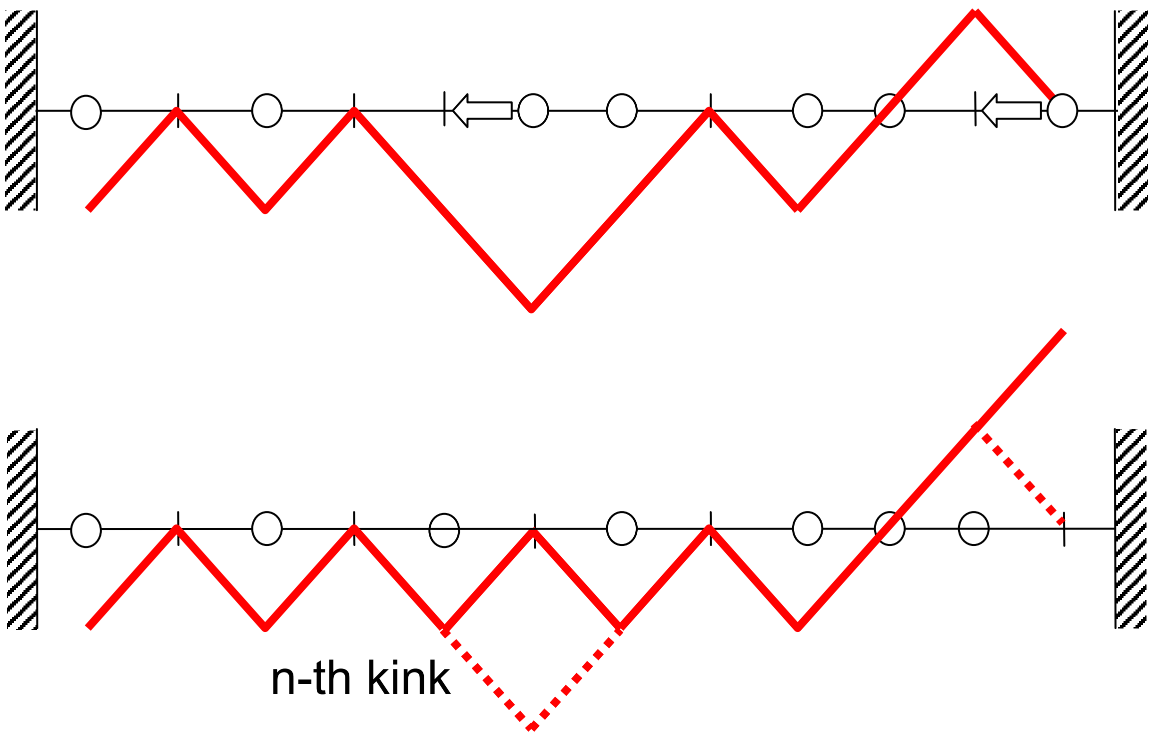


x

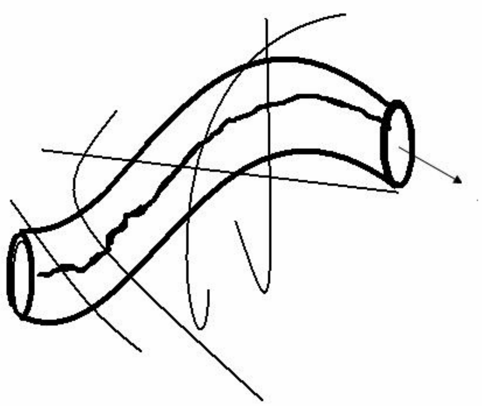
G. H. Weiss and S. Havlin, Physica A 134, 474 (1986)

K. W. Kehr and R. Kutner, Physica A 110, 535 (1982)

RWRW, single file diffusion and freely jointed chain



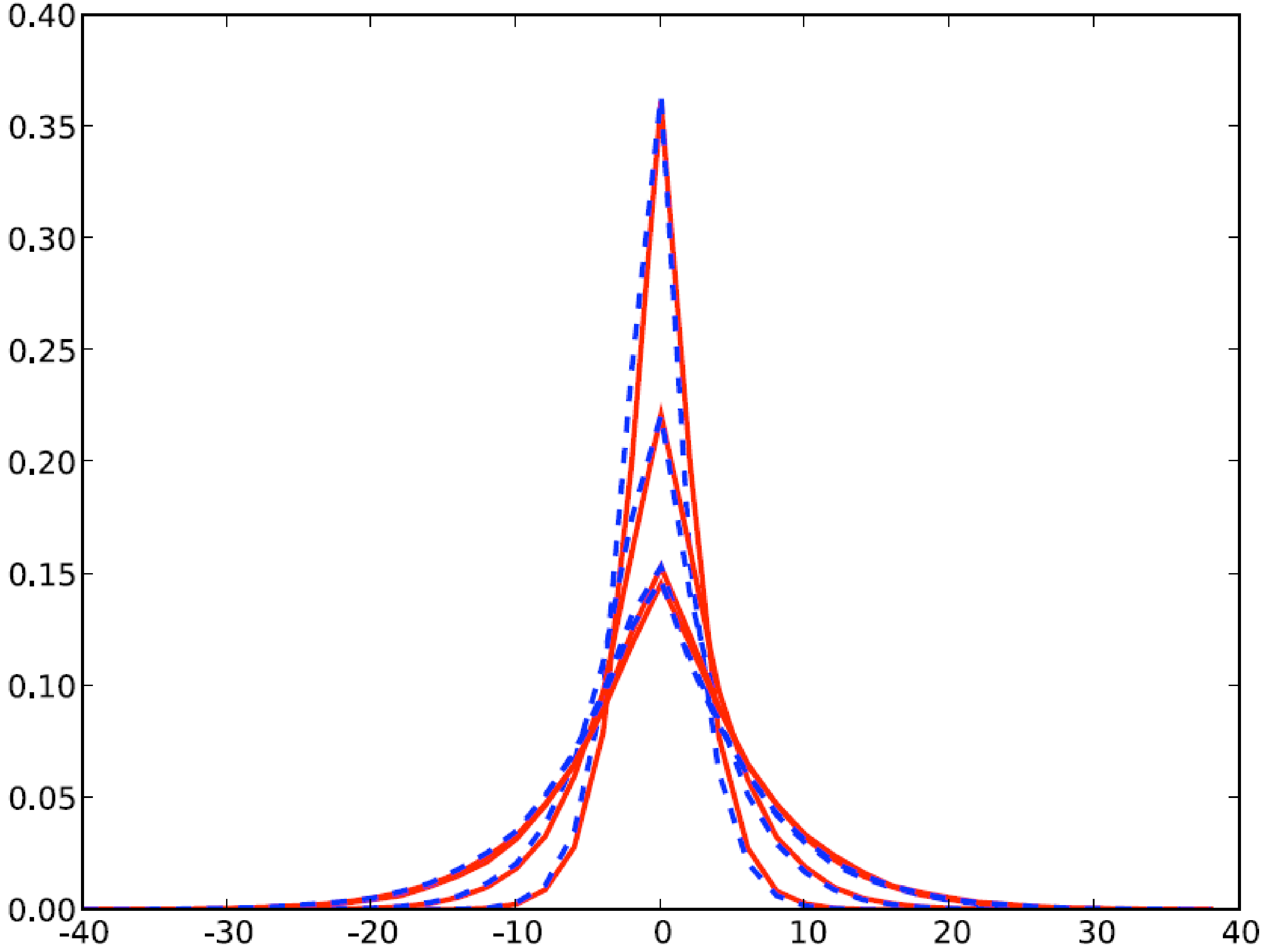
RWRW as intermediate
Regime of reptation



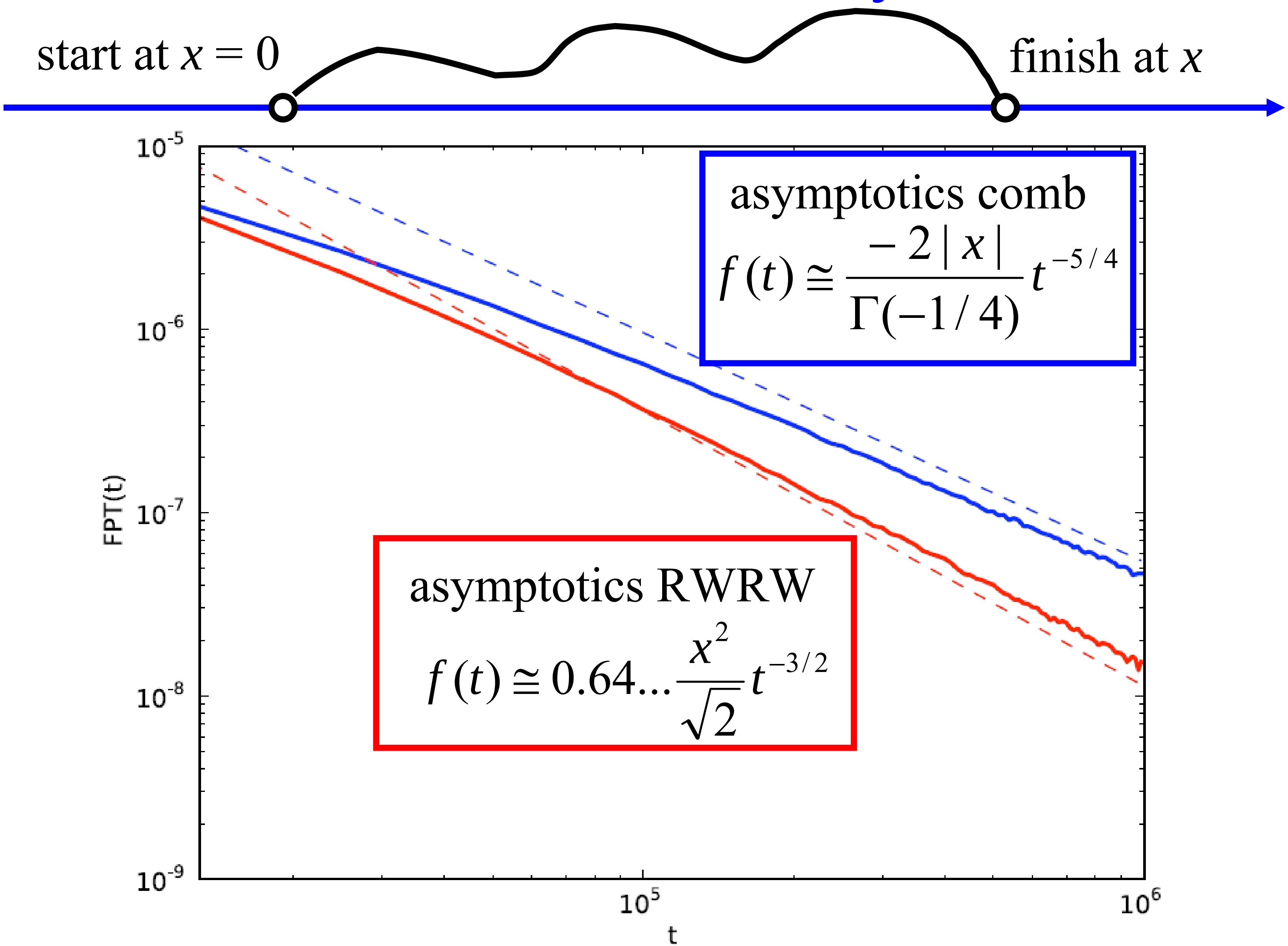
Single file diffusion and 1d kink-flip-model

$$\left\langle x^2(t) \right\rangle \propto t^{1/2}$$

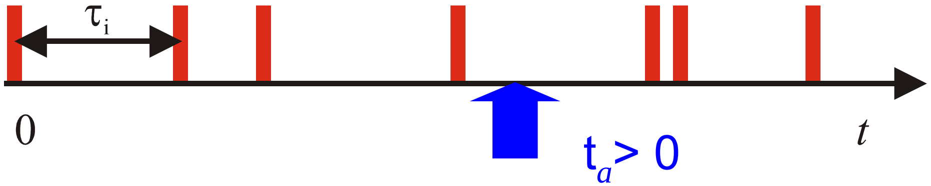
The PDFs



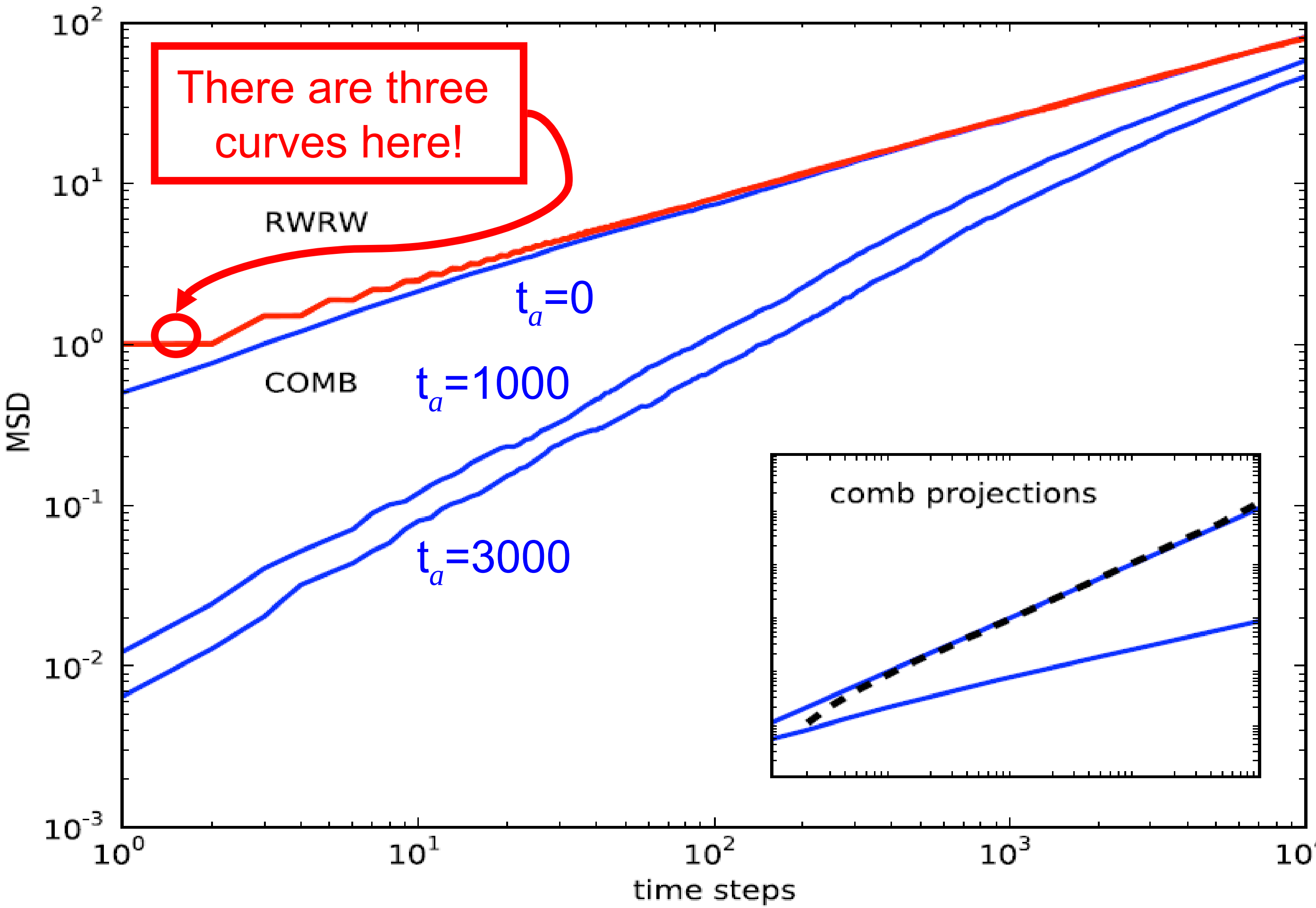
The FPT density

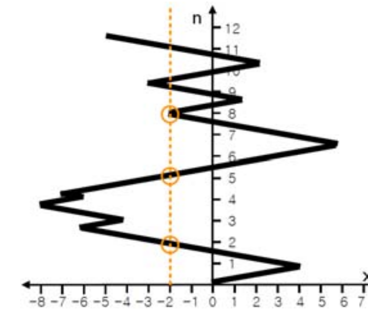


Aging properties

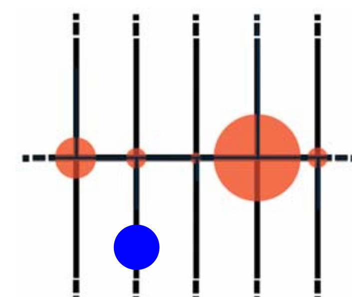


$$\left\langle x^2(t)\,|_{t_a} \right\rangle = \left\langle \left[x(t_a + t) - x(t_a)\right]^2 \right\rangle$$





stationary

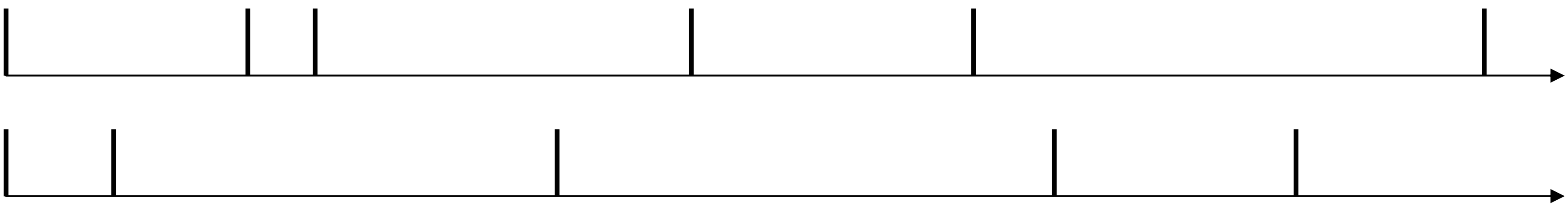


non-stationary

sBm as a mean filed approximation for CTRW

$$\frac{\partial}{\partial t}P(x,t) = {}_0D_t^{1-\alpha} K \frac{\partial^2}{\partial x^2}P(x,t)$$

$N >> 1$ random walkers



…….

Pooling: A Poisson process with $\lambda(t) \propto M(t) \propto t^{\alpha-1}$

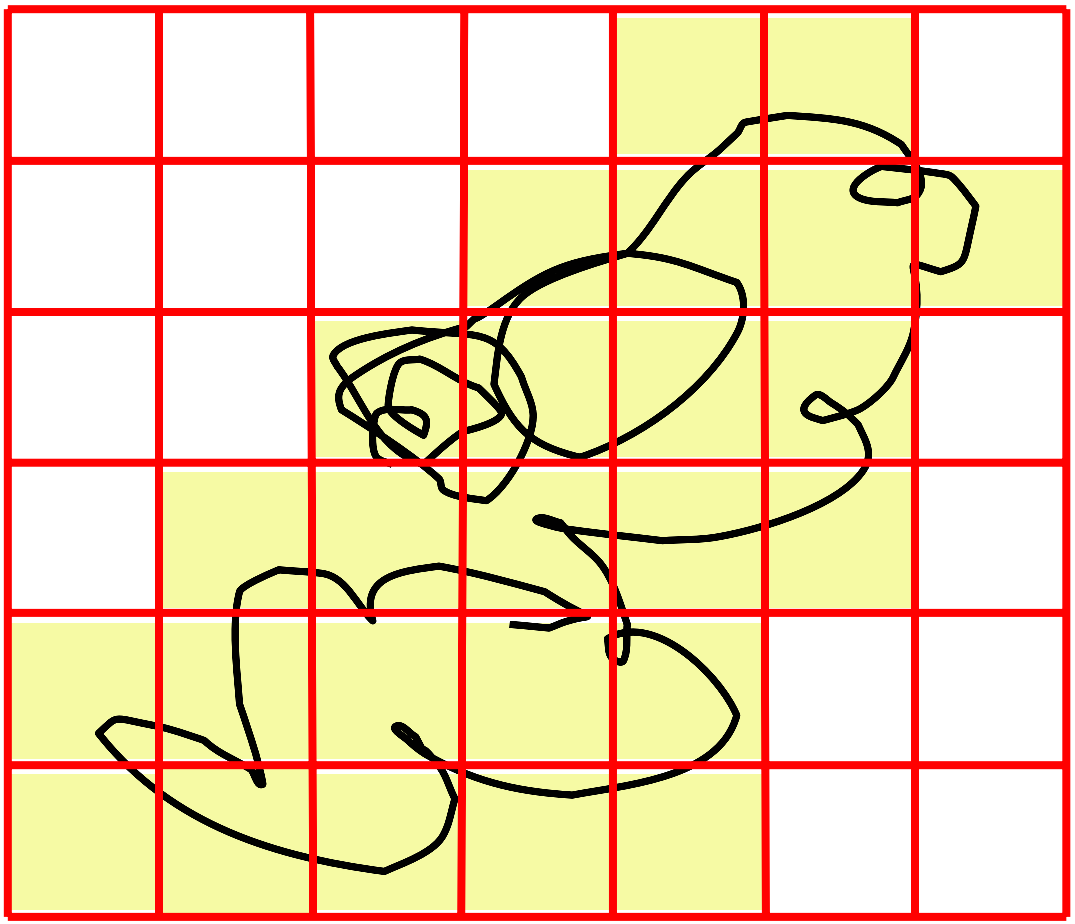
PDF of the CM coord. of $N >> 1$ random walkers

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

Same for Fractal / fBm

Distinguishing fBm/Percolation

Use space-filling properties
(spatial inhomogeneity of a fractal substrate)



n – # of cells visited
S_n – # of different cells visited

Test statistics in 2d:

$$\frac{S_n(t)}{< r^2(t) >}$$

(together with Yossi Klafter
And Yasmine Meroz)

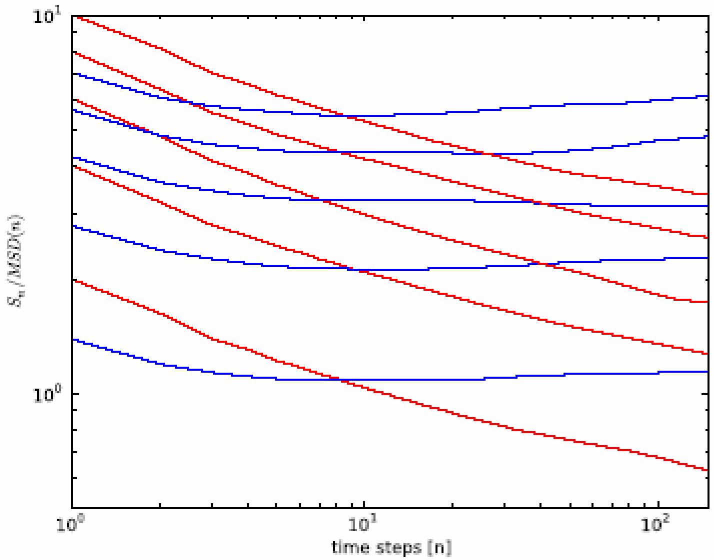


FIG. 1: (color online) Participation function divided by the MSD (Sn/MSD(n)) temporally averaged with a moving window of $0 < \tau < 150$ for 5 trajectories created with fBm (blue, flatten out) and 5 trajectories created with a RW on a percolation cluster (red, with a clear negative slope). All trajectories are 40000 time steps long.

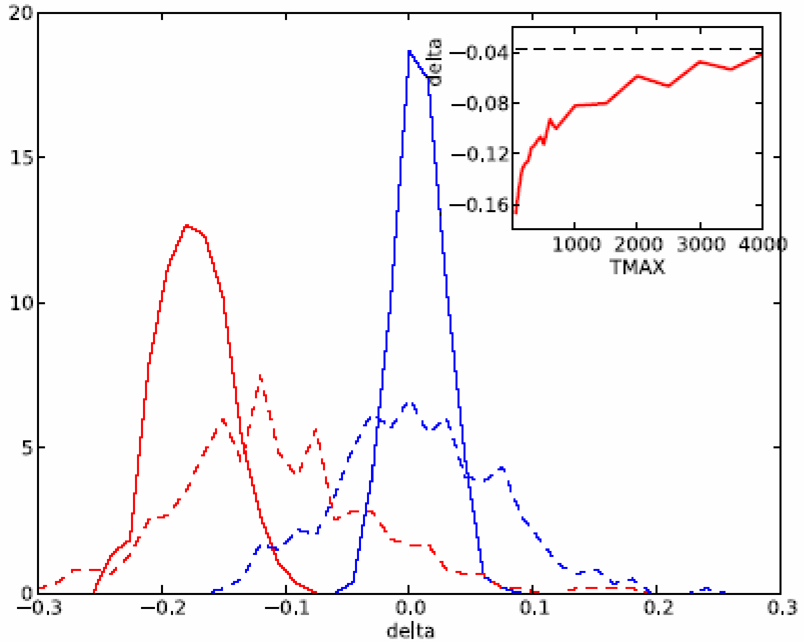


FIG. 2: (color online) Distribution of δ, the Sn/MSD slope, of 400 fBm trajectories (blue peaks on the right) and 400 trajectories of RW on a percolation cluster (red peaks on the left). The trajectories are temporally averaged once with a time window of TMAX=50 time steps (solid line), and once with TMAX=550 (dashed line). It is immediately obvious that the fBm distribution stays centered at the expected value of 0, while the percolation distribution starts far off (≈ -0.18 for TMAX=50) converges to the expected value of -0.037. This convergence as a function of TMAX is demonstrated in the inset, where the expected value is shown as a guide for the eye. Moreso, it is clear that the two distributions are well divided for small averaging time windows.

Take home messages

- Anomalous is normal
- Happy families are all alike; every unhappy family is unhappy in its own way
- Knowledge of the PDF as a function of time (and even of an equation for this function) is not too much
- The most important distinction has to be made between models with stationary increments and models with uncorrelated increments. The rest are prefactors!
- Models of mixed origin make the situation even more complex

Of course, this is only a first approximation...