Title: "Diffusing diffusivity": A model of "anomalous yet Brownian" diffusion

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Abstract: Wang et al.
[PNAS 106 (2009) 15160] have found that in several systems, the linear time dependence of mean-square displacement (MSD) of diffusing colloidal particles, typical of normal diffusion, is accompanied by a non-Gaussian displacement distribution (DD), with roughly exponential tails at short times, a situation termed â€œanomalous yet Brownianâ€• diffusion. We point out that lack of â€œdirection memoryâ€• in the particle trajectory (a jump in a particular direction does not change the probability of subsequent jumps in that direction) is sufficient for a strictly linear MSD (assuming that the system is pre-equilibrated), but if at the same time there is â€œdiffusivity memoryâ€• (a particle diffusing faster than average is likely to keep diffusing faster for some time), the DD will be non-Gaussian at short times. A gradual change in diffusivity can be due to the environment of the particle changing slowly on its own, the particle moving between different environments, or both. In our model, this is represented by the particle diffusivity itself undergoing a (perhaps biased) random walk (â€œdiffusing diffusivityâ€•). Roughly exponential tails of the DD, as in experiment, are observed in several variants of the model.

“Diffusing diffusivity”:

A model of "anomalous yet Brownian" diffusion

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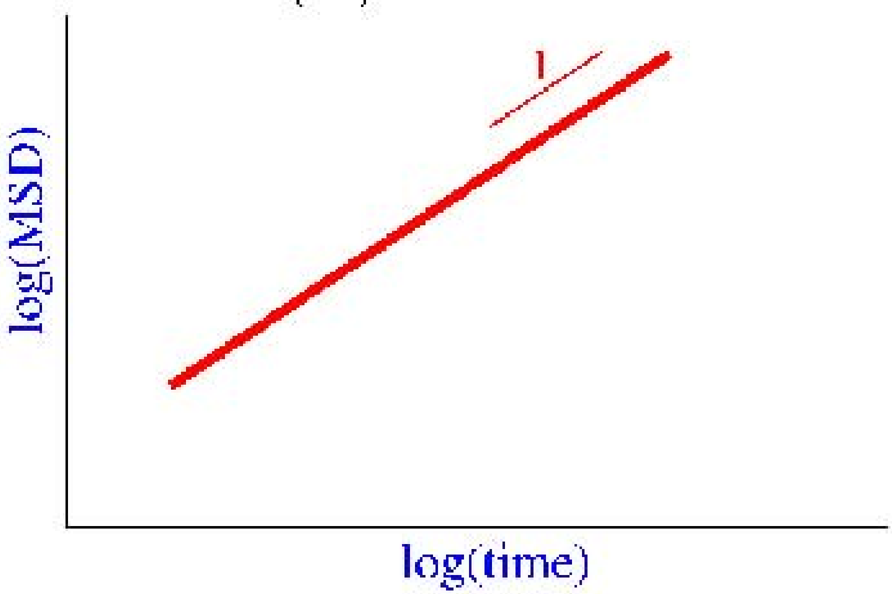
Particle diffusion

In a simple liquid, e.g., water: Brownian motion

$x(t)$ is the particle displacement along the x axis at time t.

Mean-square displacement (MSD) is linear in t:

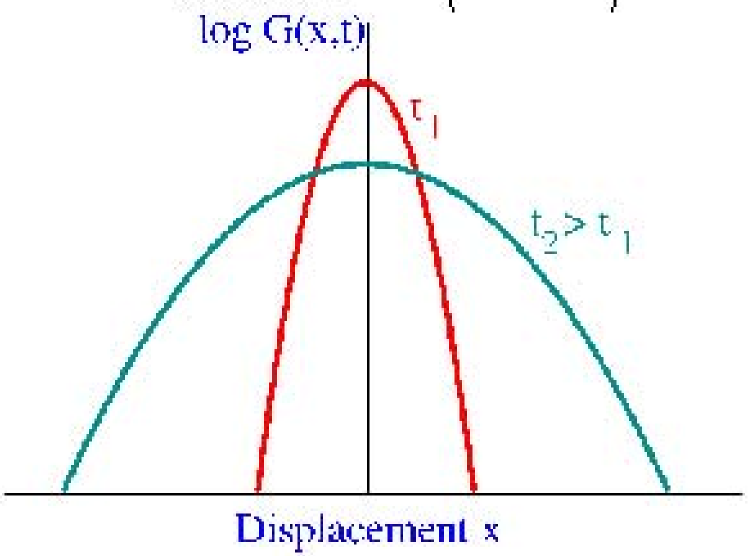
$$\langle x^2 \rangle = 2\,Dt$$



Normal diffusion

The displacement distribution (DisD) is Gaussian:

$$G(x,t) = \frac{1}{2\sqrt{\pi\,Dt}} \exp\left(-\frac{x^2}{4\,Dt}\right)$$



In a complex fluid, this can be different. Most attention has been paid to MSD, in particular, sublinear MSD (**anomalous diffusion, subdiffusion**).

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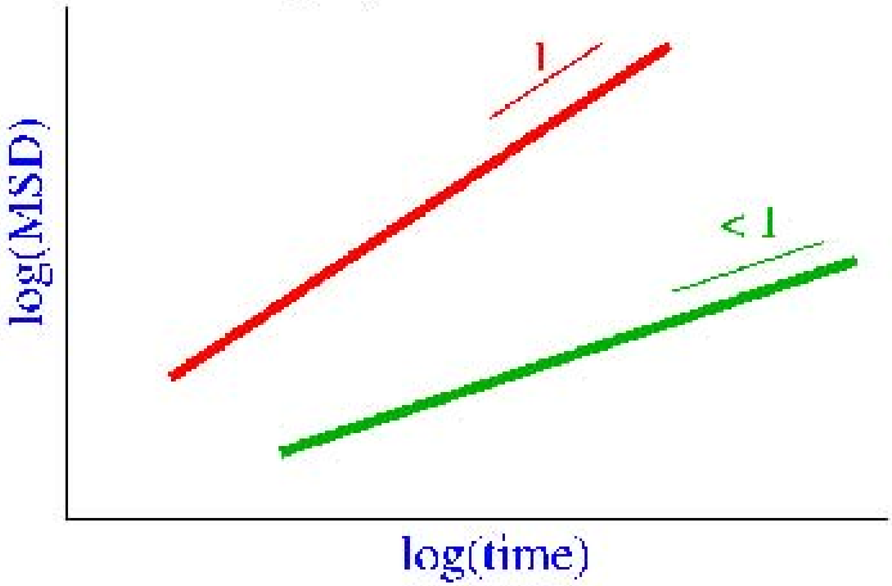

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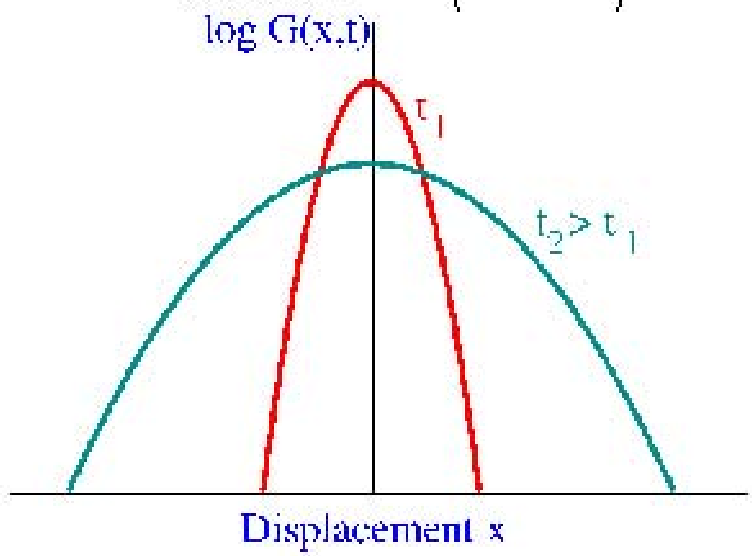

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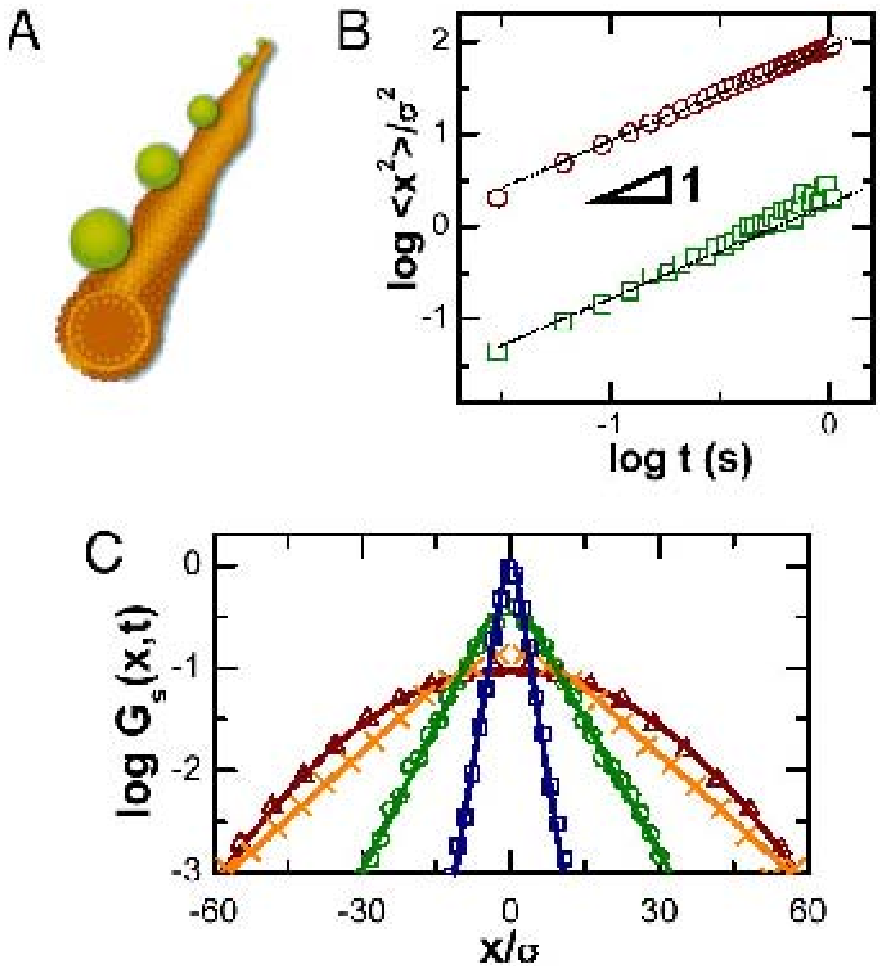
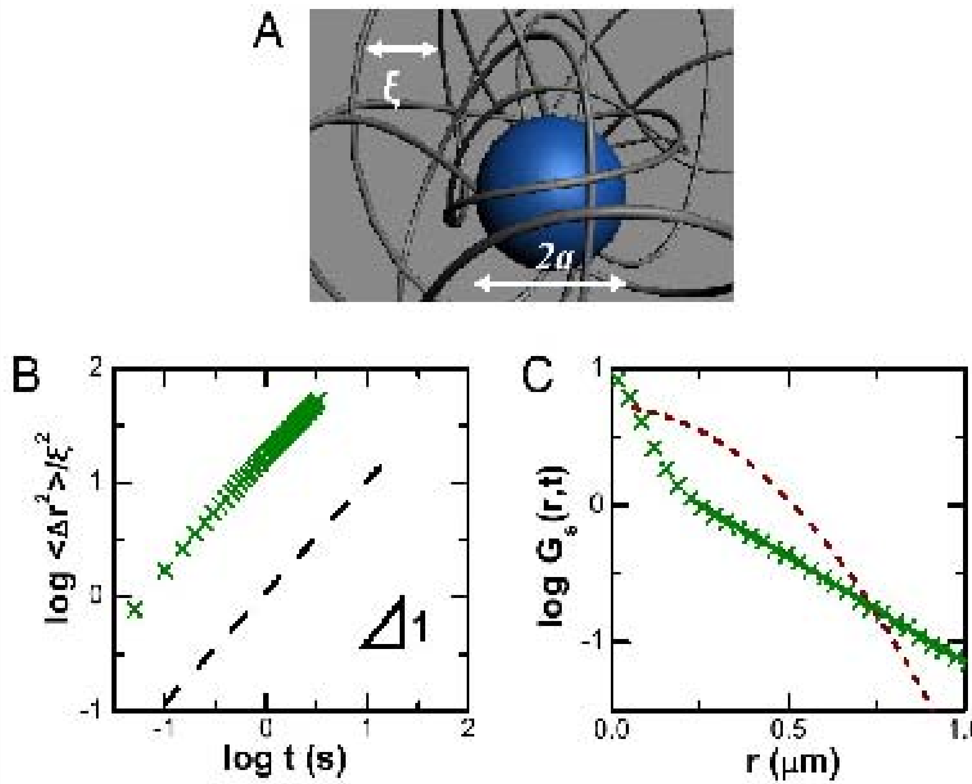
“Anomalous yet Brownian” diffusion

S. Granick's group [B. Wang et al., PNAS 106 (2009) 15160].

1. Beads on lipid bilayer tubes (1D)



2. Nanospheres in entangled actin filaments (3D)



Non-Gaussian distribution of displacements, at least at short times, with exponential tails; yet the MSD is linear in time.

When is the MSD linear?

1D for simplicity. Consider a random walk. Assume $\langle \Delta x_n \rangle = 0$

Then the MSD after N steps is

$$\langle x_N^2 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \Delta x_i \Delta x_j \rangle = \sum_{i=1}^{N} \langle \Delta x_i^2 \rangle + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle \Delta x_i \Delta x_j \rangle$$

The first term is linear in N, if $\langle \Delta x_i^2 \rangle$ does not depend on i (stationary).

The second term is zero when all correlators $\langle \Delta x_i \Delta x_j \rangle$ $(i \neq j)$ are zero.

Not the same as independent! "Uncorrelated but not independent"

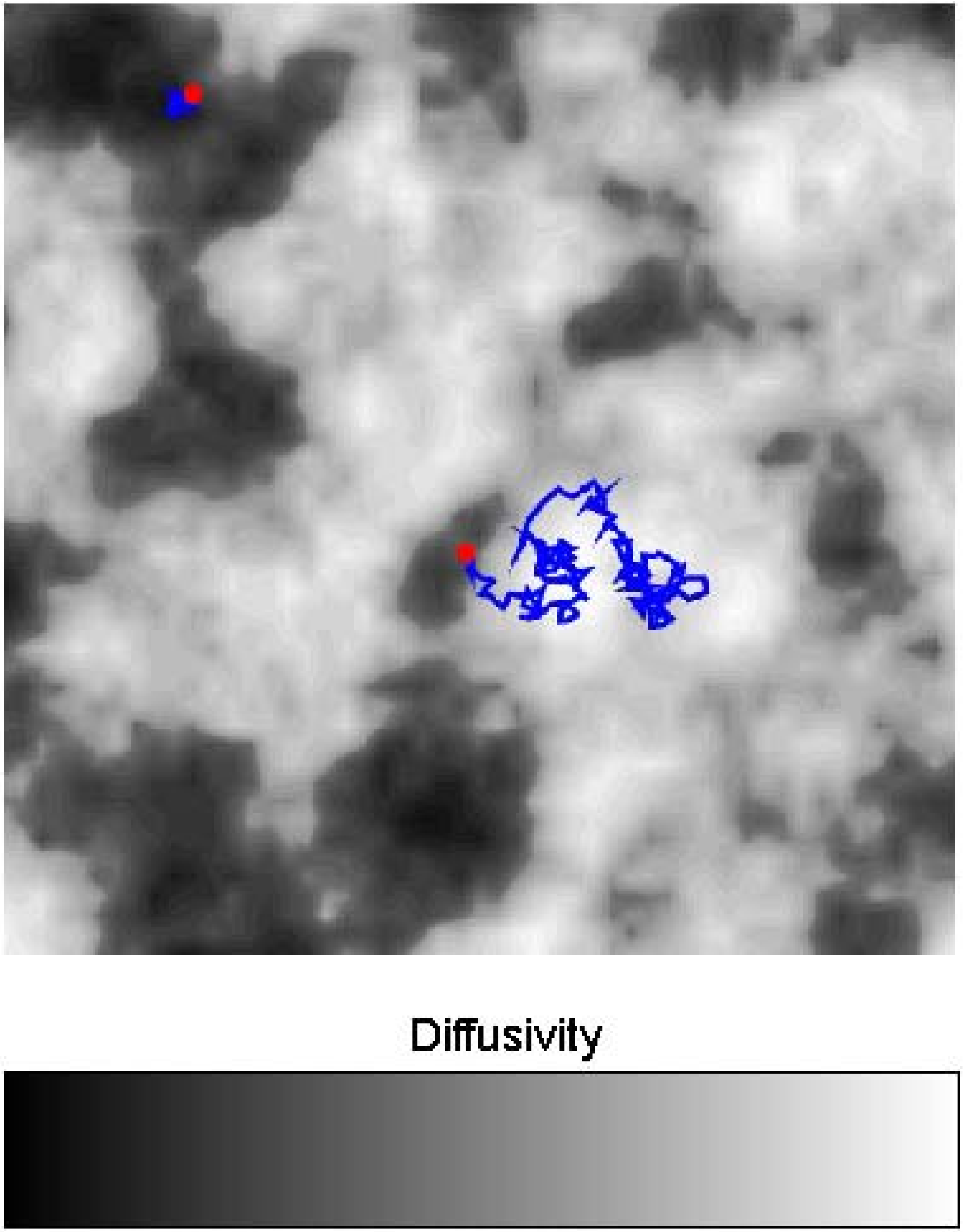
Suppose step **directions** are independent, but step **magnitudes** are correlated:

$$\langle \Delta x_i \Delta x_j \rangle = 0 \qquad \langle \Delta x_i^2 \Delta x_j^2 \rangle \neq \langle \Delta x_i^2 \rangle \langle \Delta x_j^2 \rangle$$

Memory of step magnitudes

This will make the displacement distribution non-Gaussian, even if the individual jumps are Gaussian-distributed.

Coarse-grained picture of a disordered medium



Regions of low and high diffusivity

On shorter time scales, particles diffuse normally, but at different rates

But for any given particle, the diffusion rate changes gradually, both because of the particle moving between different environments and because the environment itself changes

Memory of step magnitudes, as large jumps are more likely to occur during periods of higher diffusivity and be followed by other large jumps until diffusivity changes

A 1D toy model

Particles move independently of each other, each with its own diffusivity.

At step i, the probability of displacement Δx_i is

$$P(\Delta x_i) = \frac{1}{\sqrt{4\pi D_i}} \exp\left(-\frac{\Delta x_i^2}{4 D_i}\right)$$

This looks like normal diffusion, but the typical step size (or the diffusivity D_i) itself changes from step to step:

$$D_{i+1} = D_i + \Delta D_i$$

The diffusivity change ΔD_i should be small and random, thus D_i undergoes a (possibly biased) random walk, i.e., “diffuses”, hence

Diffusing diffusivity model

Exception: diffusivity is confined to interval [0,1]. Whenever moves out, reflect back into the interval.

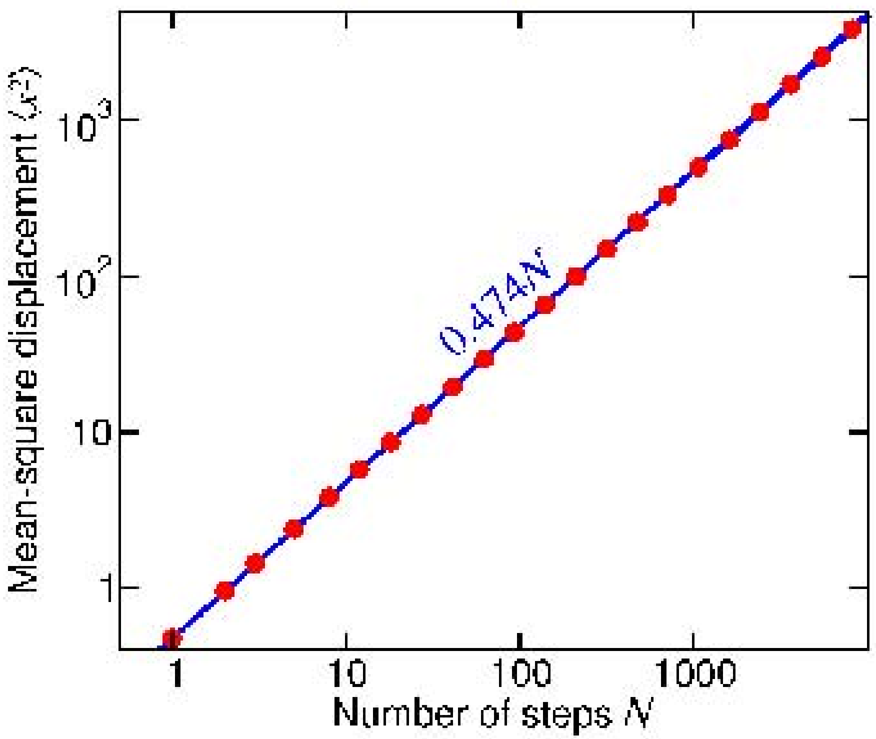
The initial distribution of diffusivities is chosen equal to the stationary one.

$D_{i+1} = D_i + \Delta D_i$ Simplest model:

$$P(\Delta D_i) = \frac{1}{\sqrt{4\pi\delta}} \exp\left(-\frac{(\Delta D_i + s)^2}{4\delta}\right)$$

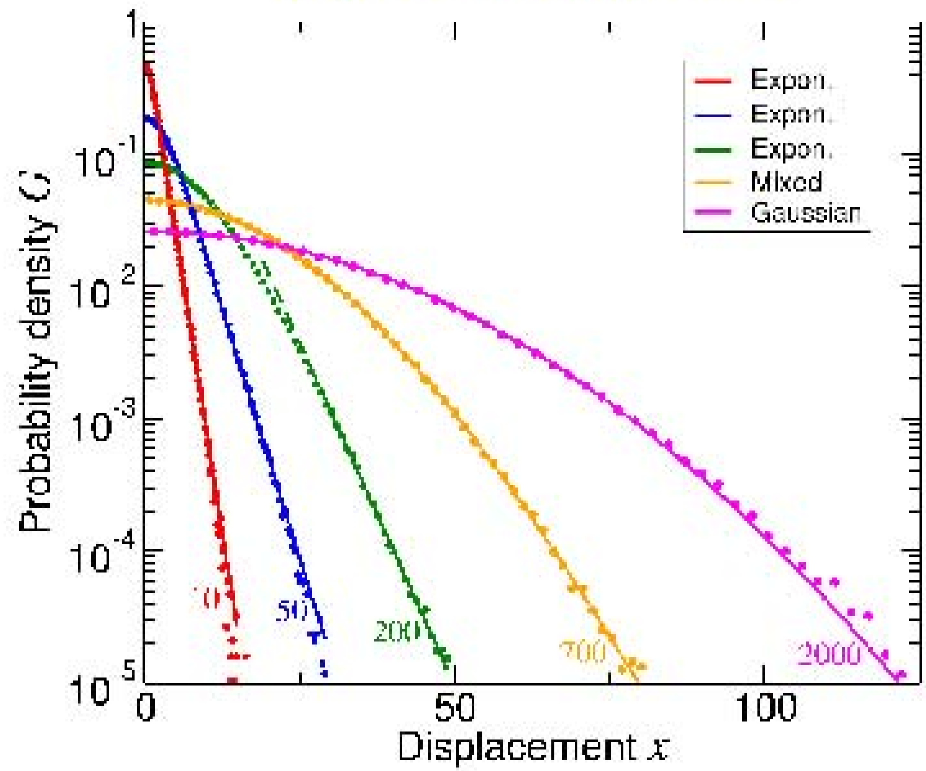
Bias s necessary to make lower diffusivities more probable

Mean-square displacement



Perfectly linear

Displacement distribution



Exponential fits for small N

Gaussian fit for largest N

"Mixed" fit for intermediate N – interpolate between an exponential at small x and a Gaussian at large x

$$G(x) = A \exp\left(-B\sqrt{1 + (x/x_0)^2}\right)$$

A similar behaviour when instead of bias, ΔD is coupled to particle displacement.

At short times, the displacement distribution (DisD) depends only on the distribution of diffusivities (DifD).

When the DifD is exactly exponential, the DisD is likewise exactly exponential, but the exponential remains a good fit to the DisD for a variety of DifDs. E.g., in the two cases we have considered, the DifDs are ~ exponential and ~power-law, respectively.

The model can be modified to produce subdiffusion.

Summary

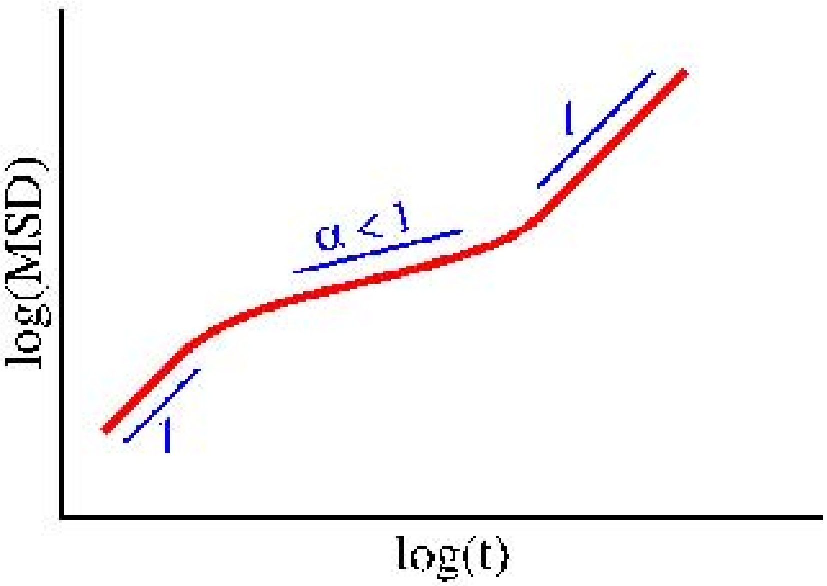
1. “Anomalous yet Brownian” diffusion is expected when a random walker has “diffusivity memory”, but no “direction memory”.

2. We have considered a model with these properties, where particles undergo diffusion with a variable rate that itself undergoes a random walk (“diffusing diffusivity”).

Particle diffusion

Can be different in complex fluids containing colloidal particles, macromolecules, filaments, etc. “Crowded environment.”

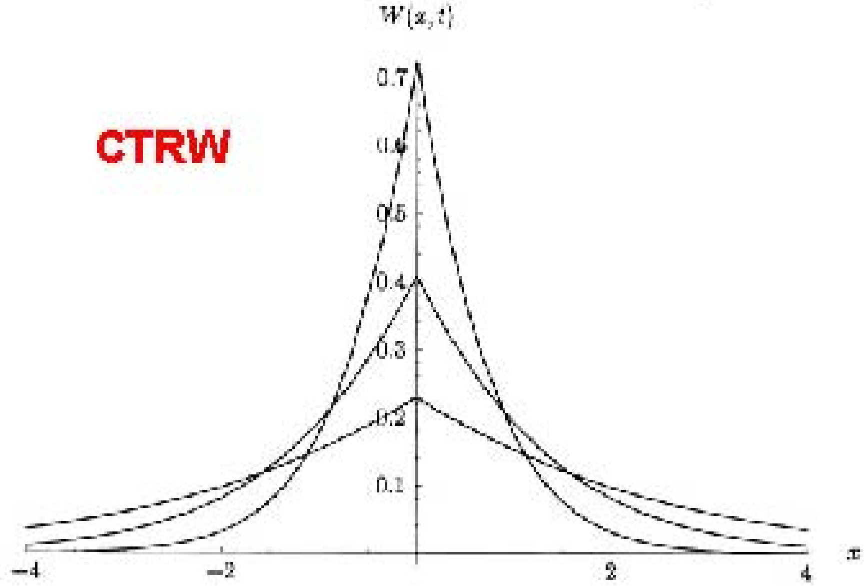
Anomalous diffusion (subdiffusion)



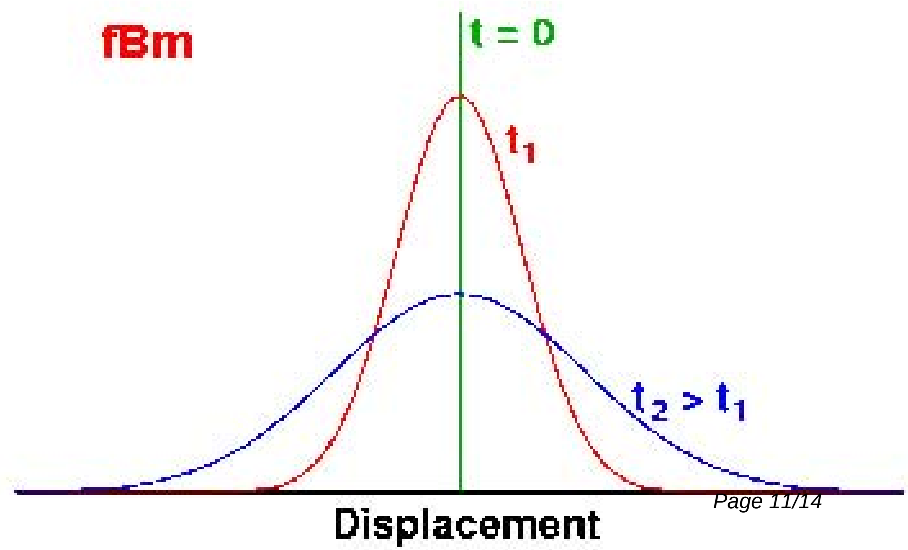
A correlated random walk (some memory).

Nonlinear MSD can coexist with Gaussian DisD. **Is the opposite situation possible?**

Displacement distributions are model-dependent:



R. Metzler, J. Klafter, Phys. Rep. 339 (2000) 1.



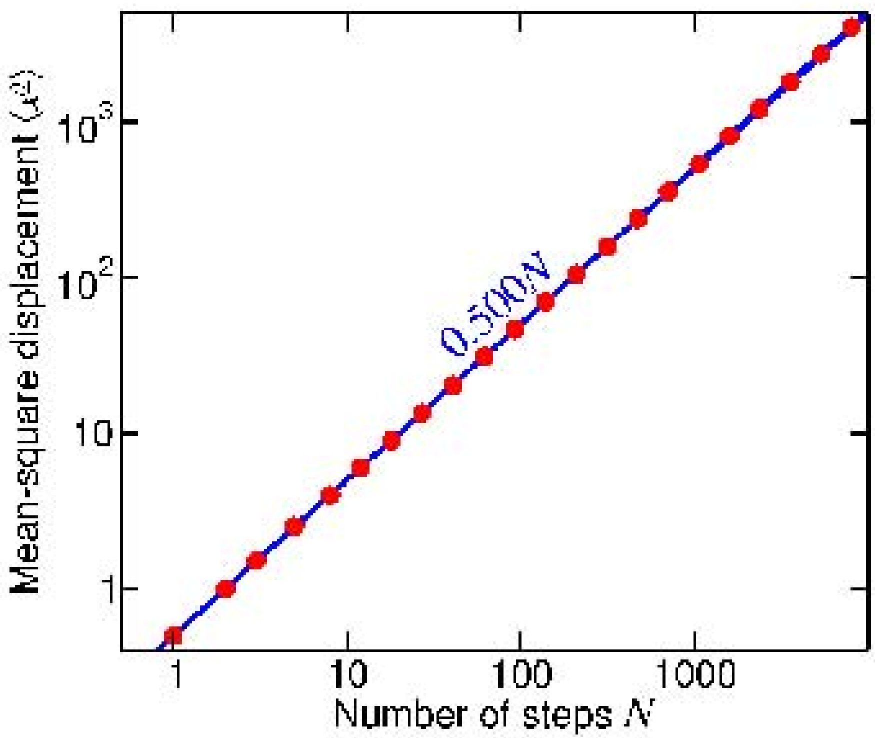
More physically motivated approach

Coupling diffusivity changes to particle displacement

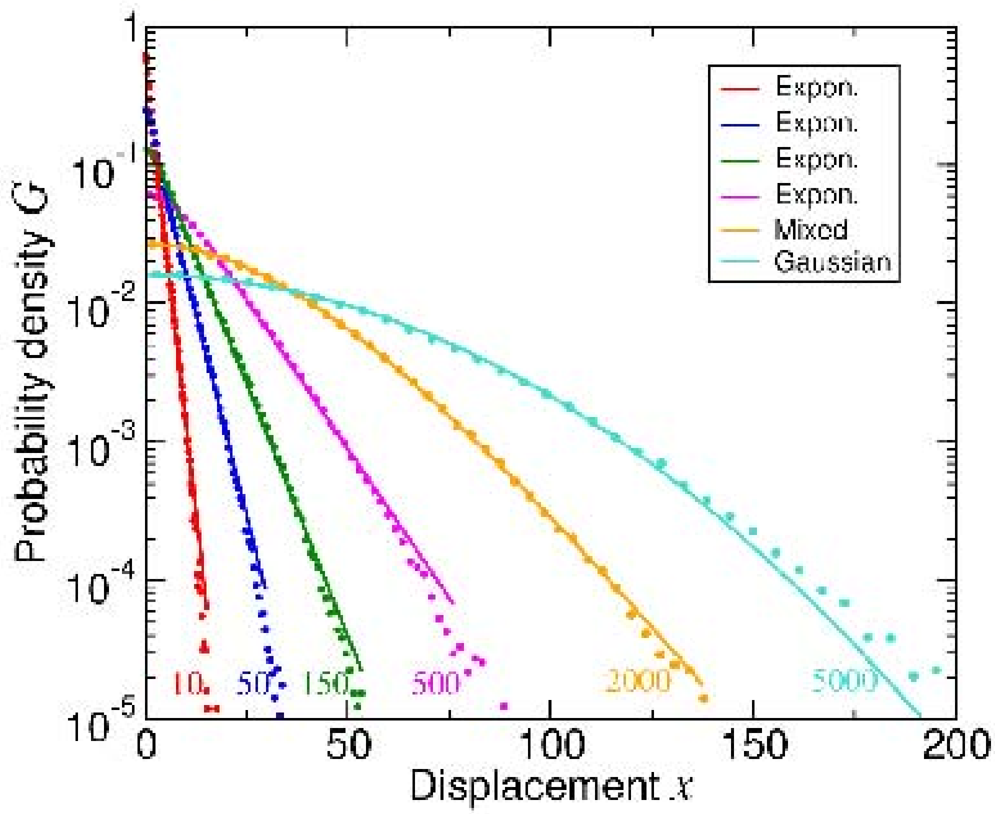
The more the particle moves, the larger the diffusivity change.

$$D_{i+1} = D_i + \Delta D_i \qquad P(\Delta D_i) = \frac{1}{\sqrt{4\pi\delta}} \exp\left(-\frac{\Delta D_i^2}{4\delta}\right) \qquad \delta = \delta_0 + f(\Delta x_i)^2$$

Mean-square displacement



Displacement distribution

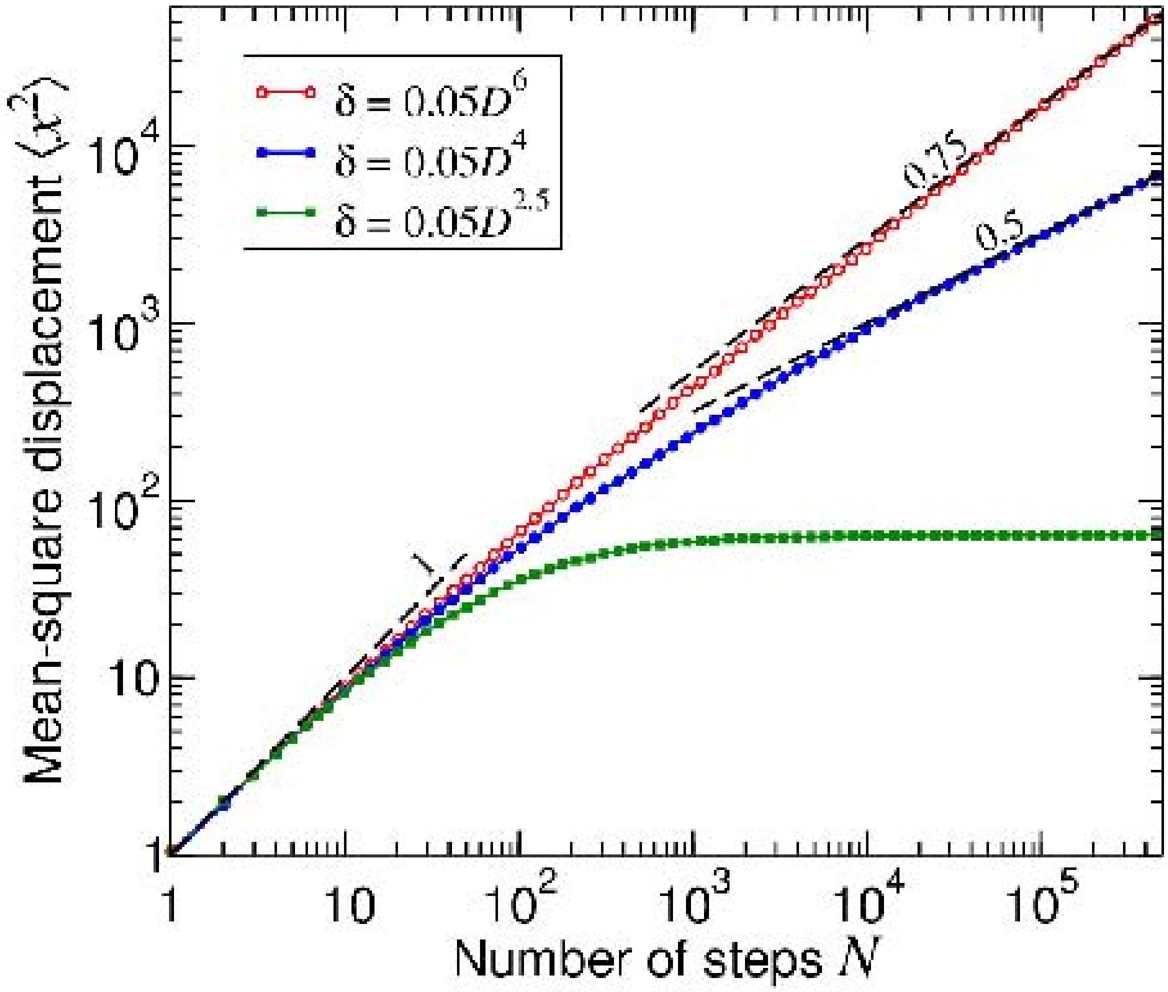


Still good exponential fits at small N

Subdiffusion

$$D_{i+1} = D_i + \Delta D_i \qquad P(\Delta D_i) = \frac{1}{\sqrt{4\pi\delta}} \exp\left(-\frac{\Delta D_i^2}{4\delta}\right)$$

$$\delta = \delta(D) = CD^b,\ b > 3$$



$$\langle D(N)\rangle \propto N^{-c} \Rightarrow \langle x^2(N)\rangle \sim N^{1-c}$$

$$c = \frac{1}{b-2}.$$

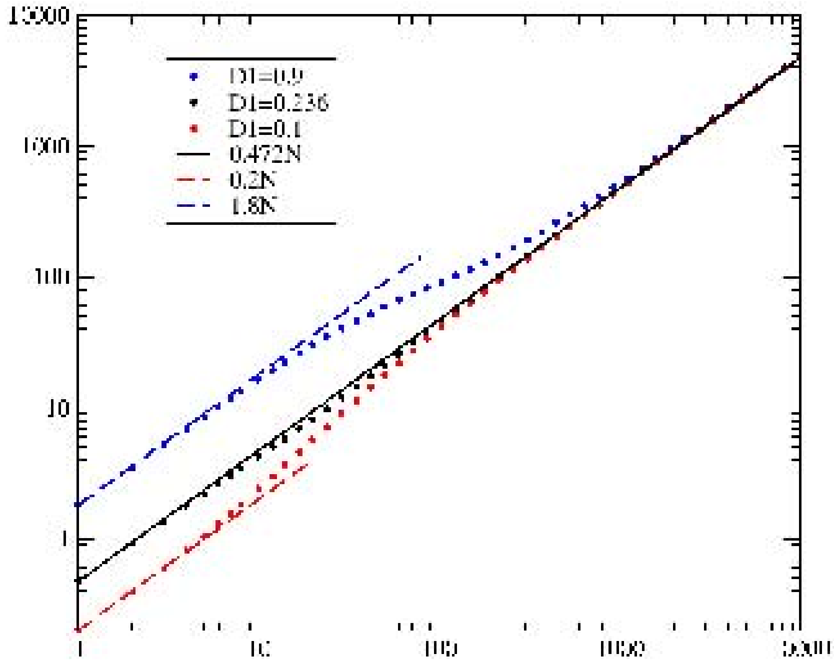
$$\nu = 1 - c = \frac{b-3}{b-2}.$$

A possible alternative to CTRW and fBm models.

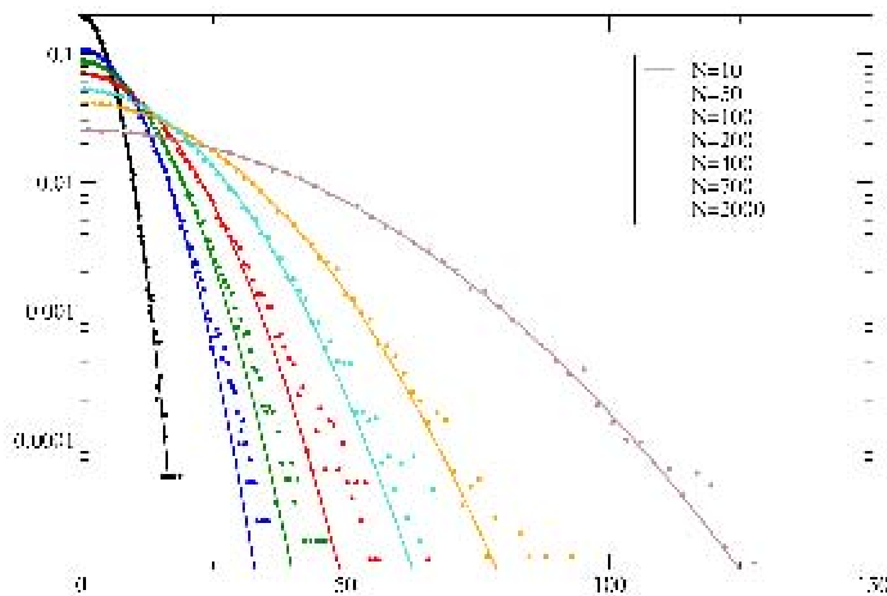
So far, we have assumed that we start with the equilibrium $p(D)$. Important for linearity of MSD.

Suppose all particles start at a particular value of *D* instead (e.g., all of them start close in space instead of being randomly distributed).

MSD



Displacement distribution



Initial $D = 0.9$

MSD is nonlinear; displacement distribution is quite close to Gaussian.