

Lecture 25: Large Steps and Long Waiting Times

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Introduction

This lecture will continue to investigate anomalous diffusion, focusing on the case of simultaneous large steps and long waiting times, thus completing the classification "phase space" of diffusion behavior in terms of the characteristics of the waiting time distribution and the increment distribution. The lecture finishes with an example from polymer surface adsorption¹ in which anomalous diffusion occurs.

Before we begin, we note some references on fractional diffusion from last lecture

R. Metzler, J. Klafter. The random walks guide to anomalous diffusion. A fractional dynamics approach. Physics Reports 339 (2000), pp. 1-77.

B.J. West, M. Bologna, P. Ergolini Physics of Fractal Operators. Springer 2003.

The first is most closely related to the CTRW approach of this class. There is other work in pure math on fractional Wiener processes.

1 "Phase Diagram" for CTRW

The object of this section is to complete the classification of random walks with random waiting time, in terms of the power law exponents of the waiting time and step distributions.

Suppose the waiting time density satisfies, as $t \rightarrow \infty$

$$\psi(t) \sim \frac{A}{t^{1+\gamma}}$$

and the (assumed symmetric for simplicity) step density satisfies, as $|x| \rightarrow \infty$

$$p(x) \sim \frac{A}{x^{1+\alpha}}$$

The parameters α and γ are crucial to the properties of the random walk. The previous lecture investigated the following anomalous cases:

¹See also Problem Set 4 where this question was set as an exercise.

Super-diffusion $0 < \alpha < 2$ and $\gamma > 1$. In this case $\sigma_X^2 = \infty$ while $\bar{\tau} < \infty$ so the steps are large but the time between them is not. This gives a Levy flight with the scaling of the position given by $\bar{X}(t) \propto \left(\frac{t}{\bar{\tau}}\right)^{\frac{1}{\alpha}} \gg \sqrt{\frac{t}{\bar{\tau}}}$. Note that superdiffusion has power law tails - even though it is the sum of a random number of variables with power law tails the power law is still additive.

Subdiffusion, $\alpha > 2$ and $0 < \gamma < 1$. In this case $\sigma_X^2 < \infty$ while $\bar{\tau} = \infty$ so the time between steps is large, but the steps themselves are not. The width of the distribution can be measured by the variance in this case since it is finite, and $\bar{X}(t) = \sqrt{\langle X^2 \rangle} < \infty$ and $\bar{X}(t) \propto t^{\frac{\gamma}{2}} \ll \sqrt{t}$.

Note that the subdiffusion is most straightforwardly characterized in terms of its Fourier transform. The inversion can be performed in terms of Fox functions.

The remaining case to study concerns $0 < \alpha < 2$ and $0 < \gamma < 1$ so that long waits are combined with large steps which produces a tension, and we seek to investigate which effect dominates.

We start with the Montrol-Weiss equation for the Fourier-Laplace transform of the density of random walk, where we Fourier transform over the space coordinate and Laplace transform over the time coordinate.

$$\tilde{\hat{p}}(k, s) = \frac{1 - \tilde{\psi}(s)}{s \left(1 - \tilde{\psi}(s)\hat{p}(k)\right)}$$

The long-time behavior of the random walk is determined by the behavior of the transforms as $s \rightarrow 0$ and $k \rightarrow 0$ and we assume:

$$\begin{aligned} \tilde{\psi}(s) &\sim 1 - (\tau_0 s)^\gamma \text{ as } s \rightarrow 0 \\ \hat{p}(k) &\sim 1 - |ak|^\alpha \text{ as } k \rightarrow 0 \end{aligned}$$

Thus

$$\begin{aligned} \tilde{\hat{p}}(k, s) &\sim \frac{(\tau_0 s)^\gamma}{s((\tau_0 s)^\gamma + |ak|^\alpha)} \text{ in the "central region"} \\ &= \frac{1}{s} \frac{1}{1 + \frac{|ak|^\alpha}{(\tau_0 s)^\gamma}} = \frac{1}{s} \frac{1}{1 + (t_k s)^{-\gamma}} \text{ where } t_k = \frac{\tau_0}{|ak|^{\alpha/\gamma}} \end{aligned}$$

$$\hat{p}(k, t) = E_\gamma(- (t/t_k)^\gamma)$$

Inverting the Laplace transform yields a Mittag-Leffler function, which recall can be thought of a "generalized" exponential function.²

²"The Mittag-Leffler function arises naturally in the solution of fractional integral equations, and especially in the study of the fractional generalization of the kinetic equation, random walks, Lévy flights, and so-called superdiffusive transport. The ordinary and generalized Mittag-Leffler functions interpolate between a purely exponential law and power-like behavior of phenomena governed by ordinary kinetic equations and their fractional counterparts." Source: Eric W. Weisstein. "Mittag-Leffler Function." From MathWorld—A Wolfram Web Resource. <http://mathworld.wolfram.com/Mittag-LefflerFunction.html>

The Mittag-Leffler function. Source: Mathworld.
 See <http://mathworld.wolfram.com/Mittag-LefflerFunction.html>

In particular, special cases occur if $\gamma = 1$ and $E_\gamma(z) = e^z$ or $\gamma = 1/2$ and $E_\gamma(z) = e^{z^2} \operatorname{erfc}(-z)$, which is related to Dawson's integral. In general we have an asymptotic result:

$$t \gg t_k \text{ then } E_\gamma(- (t/t_k)^\gamma) \sim \frac{(t/t_k)^{-\gamma}}{\Gamma(1-\gamma)} \text{ for } 0 < \gamma < 1$$

Inverting the Fourier transform is complicated, but fortunately if we are just interested in determining the scaling we do not need to do so.

$$\begin{aligned} \hat{p}(k, t) &= E_\gamma\left(-\frac{|ak|^\alpha}{\tau_0^\gamma} t^\gamma\right) \\ p(x, t) &= \int_{-\infty}^{\infty} E_\gamma\left(-|ak|^\alpha \left(\frac{t}{\tau_0}\right)^\gamma\right) e^{ikx} \frac{dk}{2\pi} \end{aligned}$$

Change the variable, $u = ak \left(\frac{t}{\tau_0}\right)^{\frac{\gamma}{\alpha}}$ so that $k = \frac{u}{a(t/\tau_0)^{\gamma/\alpha}}$ and $dk = \frac{du}{a(t/\tau_0)^{\gamma/\alpha}}$ and rescale the position variable $Z = \frac{X}{a(t/\tau_0)^{\gamma/\alpha}}$. Defining the pdf of Z to be $f(z)$ this is related to the pdf of x via $p(x, t) = \frac{1}{a(t/\tau_0)^{\gamma/\alpha}} f\left(\frac{x}{a(t/\tau_0)^{\gamma/\alpha}}\right)$

$$f(z) = \int_{-\infty}^{\infty} E_\gamma(-|u|^\alpha) e^{iuz} \frac{du}{2\pi} \text{ or equivalently, } \hat{f}(u) = E_\gamma(-|u|^\alpha)$$

Thus we can define $\bar{X}(t) = a \left(\frac{t}{\tau_0}\right)^{\frac{\gamma}{\alpha}}$ as the scaling of X and we have a superdiffusion if and only if $\nu = \frac{\gamma}{\alpha} > \frac{1}{2}$ i.e. $\alpha < 2\gamma$ and a subdiffusion if and only if $\alpha > 2\gamma$. Thus we can completely characterize the "phase-space" of diffusion behavior:

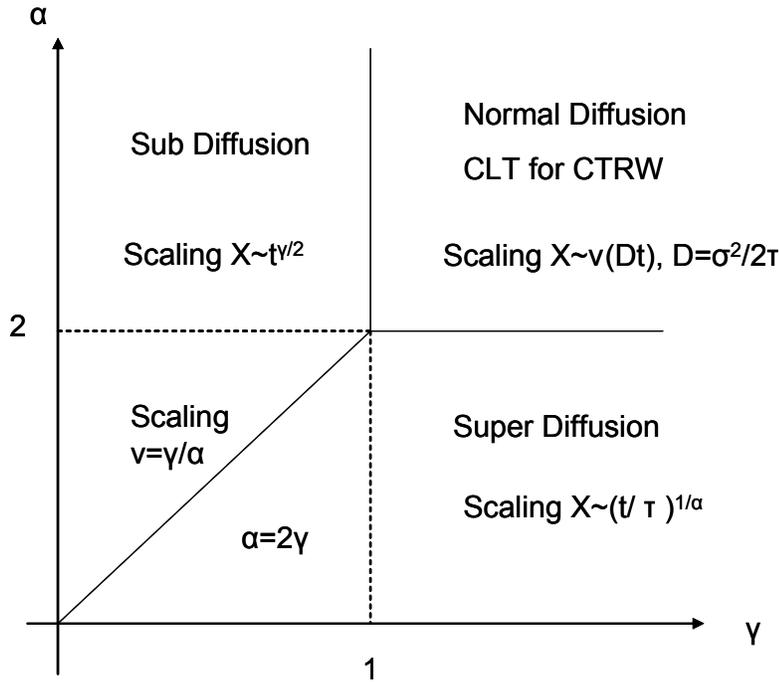


Figure 1: "Phase Diagram for CTRW

Note: The borderline cases are subtle, and it's possible to derive examples such as Gaussian distributions, but with anomalous scaling and other special cases.

2 Example: Polymer Surface Adsorption

The rest of the lecture proceeds to examine an example in which anomalous diffusion behavior arises naturally. Consider the problem of polymer surface adsorption, which we model as a random walk near a wall. Although this is a discrete problem it is most tractably analyzed with continuum methods. We model discreteness by assuming that the polymer chain starts its random walk at a distance a orthogonal to the adsorbing surface and every time it hits the surface it restarts at a distance a . This gives us a renewal process. Define the following notation:

N = length of the polymer (=time t/τ_0 and define $\tau_0 = 1$)

N_S = number of visits to the surface

The random walk takes place in 3 dimensional space and the wall is the xy -plane defined by $z = 0$. The diffusion coefficient is $D = \frac{\sigma^2}{2\tau_0}$ where recall that for independent steps of length a , $\sigma = a$, while for a random walk with persistence the effective step size depends on the correlation coefficient ρ so that $\sigma = \left(\frac{1+\rho}{1-\rho}\right) a$.

The distribution of the location at which the random walk hits the surface is the *eventual hitting probability* as defined in lecture 18, and the calculations are facilitated by utilizing the *electrostatic analogy* outlined there and described in much more detail in Redner's book. In particular calculating the density of the eventual hitting location at a point on the $z = 0$ surface is equivalent to finding the electric field in the normal direction to the surface at that point, where the adsorbing boundary corresponds to a conductor and the electric field is identically zero. We can write

$$p(\vec{r}_s) \propto \text{"electric field"} = -\hat{n} \cdot \nabla \phi = \frac{\partial \phi}{\partial z}$$

where \vec{r}_s is the position vector in the $z = 0$ plane, \hat{n} is the outward normal and ϕ is the electrostatic potential that we will now derive by solving Poisson's equation. Note also that we have omitted a constant of proportionality that can be determined later if necessary since we must end up with a valid probability density function. We derive the electric field by the usual method of images so that the field is zero along the boundary - it is that of a dipole charge at $\vec{r}_0 = (0, 0, a)$ and $-\vec{r}_0 = (0, 0, -a)$. Thus we solve

$$\nabla^2 \phi = q \delta(\vec{r} - \vec{r}_0) \quad \text{where } q = \frac{1}{4\pi D}$$

Thus we can write immediately:

$$\begin{aligned} \phi(\vec{r}) &= \frac{q}{|\vec{r} - \vec{r}_0|} - \frac{q}{|\vec{r} + \vec{r}_0|} \\ p(\vec{r}_s) &= \frac{a}{2\pi} \frac{1}{(r_s^2 + a^2)^{3/2}} \sim \frac{A}{r^3} \text{ as } r \rightarrow \infty \end{aligned}$$

Note: the density for the location of the eventual hitting probability has fat-tails. The variance is infinite - recall that the area element in polar coordinates is $r dr d\theta$ and the mean also diverges (borderline logarithmic case). This density is actually the 2-dimensional generalization of the Cauchy distribution, a special case of the multidimensional Lévy-stable distribution. It's Fourier transform takes a simple form:

$$\hat{p}(\vec{k}_s) = e^{-a|\vec{k}_s|^\alpha}$$

Since we know that the Lévy-stable distributions are stable under addition, we can derive immediately that pdf for the position of the N_s -th position at which the random walk hits the surface:

$$p_{N_s}(\vec{r}_s) = \frac{1}{N_s} l_{1,0} \left(\frac{r_s}{N_s} \right) = \frac{a}{2\pi} \frac{N}{(r_s^2 + N^2 a^2)^{3/2}}$$

We can also find a useful interpretation of the *waiting time* until the random walk hits the wall. This corresponds to the length of the polymer chain in terms of the number of monomers. Since the

waiting time depends only on diffusion in the vertical direction we can derive it from the result for the one dimensional random walk. In particular if the diffusion coefficient for the three dimensional walk is D the vertical components corresponds to an independent one-dimensional random walk with coefficient $3D$. The waiting time distribution is the Smirnov-density:

$$\psi(t) = \frac{a}{\sqrt{4\pi(3D)t^3}} e^{-\frac{3a^2}{4Dt}} \sim \frac{A}{t^{3/2}}$$

The Laplace transform is given by:

$$\tilde{\psi}(s) = e^{-\sqrt{\tau_1 s}} \text{ where } \tau_1 = \frac{a^2}{6D}$$

We will finish considering this example in the next lecture where we derive the full joint distribution in position and time of the polymer-adsorption process, taking into account the fact that step size and waiting time are not independent since they are related through the path of the three dimensional random walk. In particular we will derive the result that the expected number of adsorption sites $\bar{N}_S(N)$ scales like \sqrt{N} even though the limiting distribution is not Gaussian. This is the same scaling as the three-dimensional bulk width of the polymer.