

Lecture 25: Large Steps and Long Waiting Times

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scribed: May 10, 2005, proofread: December 28, 2006

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.

Two useful references are [1] and [3] – 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 $|x| \rightarrow \infty$

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

In d dimensions, 1 in the above equation would have to be replaced by d .

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

- **Super-diffusion**, $0 < \alpha < 2$ and $\gamma > 1$. In this case $\sigma_X^2 = \infty$ while $\bar{\tau} < \infty$ so the typical step sizes are large but the time between them is not. This gives a Lévy flight with the scaling

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

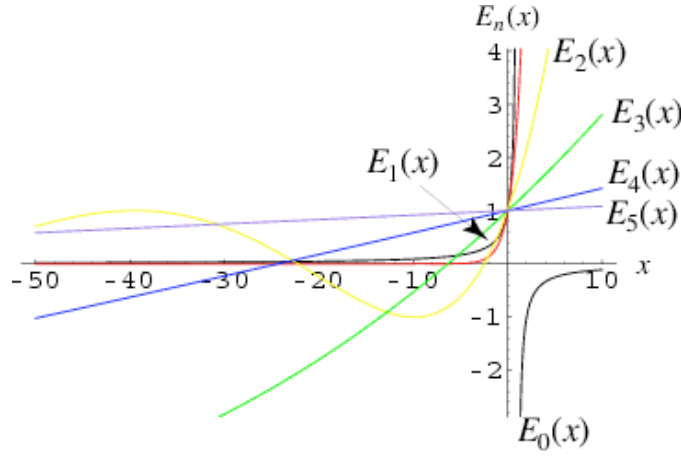


Figure 1: The Mittag-Leffler function.

of the position given by $\bar{X}(t) \propto (\frac{t}{\bar{\tau}})^{\frac{1}{\alpha}} \gg \sqrt{\frac{t}{\bar{\tau}}}$. 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 $\bar{X}(t) = \sqrt{|X^2|} < \infty$ and $\bar{X}(t) \propto t^{\frac{\gamma}{2}} \ll \sqrt{t}$. 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.

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

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

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

Inverting the Laplace transform yields a Mittag-Leffler function, which recall can be thought of as a “generalized” exponential function² and is shown in figure 1. 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, $u = ak(t/\tau_0)^{\gamma/\alpha}$ so that $k = u/a(t/\tau_0)^{\gamma/\alpha}$ and $dk = du/a(t/\tau_0)^{\gamma/\alpha}$ and rescale the position variable $Z = X/a(t/\tau_0)^{\gamma/\alpha}$. Defining the probability density function of Z to be $f(z)$ this is related to the PDF of x via $p(x, t) = f(x/a(t/\tau_0)^{\gamma/\alpha})/a(t/\tau_0)^{\gamma/\alpha}$

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

Thus we can define $\bar{X}(t) = a(t/\tau_0)^{\gamma/\alpha}$ as the scaling of X and we have superdiffusion if and only if $v = \gamma/\alpha > 1/2$ i.e. $\alpha < 2\gamma$ and subdiffusion if and only if $\alpha > 2\gamma$. The complete phase-space of diffusion behavior is shown in figure 2. Note that the borderline cases are subtle and it is possible to derive examples such as Gaussian distributions but with anomalous scaling.

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. We shall model the polymer as a Brownian random walk near a wall. The random walks starts off at a distance a from the surface, every time it hits the surface it restarts at a distance a . This gives us a renewal process. We shall first compute the time-independent probability distribution of the N_s ’th polymer adsorption site on the plane. Then, we shall find the probability distribution of the polymer length subject to the polymer adsorbing to some place \vec{r}_s on the plane. Define the following notation:

- Let N be the length of the polymer, which can be written as time t/τ_0 , and define $\tau_0 = 1$.
- N_s be the number of visits to the surface.

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>

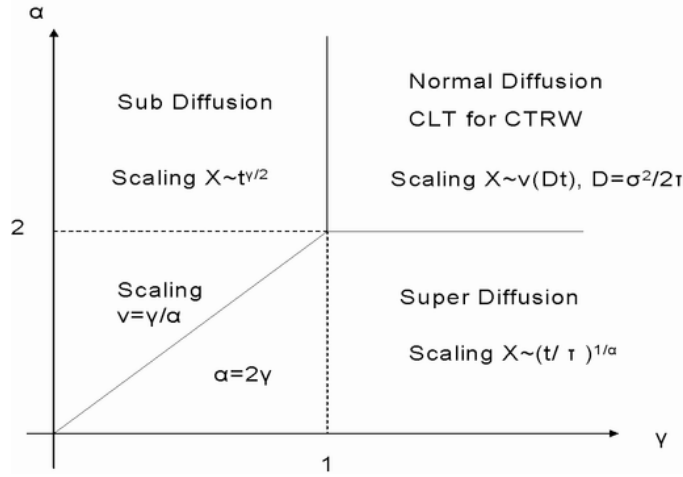


Figure 2: Phase space of diffusion behavior.

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 $\sigma = a(1 + \rho)/(1 - \rho)$.

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 by Redner [2]. 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

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

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:

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

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 $rdrd\theta$ and the mean also diverges

(borderline logarithmic case). This density is actually the two-dimensional generalization of the Cauchy distribution, a special case of the multidimensional Lévy-stable distribution. Its Fourier transform takes a simple form:

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

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:

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

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 D . The waiting time distribution is the Smirnov-density:

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

The Laplace transform is given by

$$\tilde{\psi}(s) = e^{-\sqrt{\tau_1 s}}$$

where $\tau_1 = a^2/D$. 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.

References

- [1] R. Metzler and J. Klafter, *The random walks guide to anomalous diffusion. a fractional dynamics approach*, Physics Reports **339** (2000), 1–77.
- [2] S. Redner, *A guide to first-passage processes*, Cambridge University Press, 2001.
- [3] B. J. West, M. Bologna, and P. Ergolini, *Physics of fractal operators*, Springer, 2003.