Lecture 18: Non-Markovian Diffusion Equations

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This lecture concerns the various continuum limits of continuous-time random walks (CTRW), which include, in addition to the usual case of normal diffusion, rather different mathematical descriptions for cases of anomalous diffusion.

1 Normal Diffusion

We begin with cases of CTRW exhibiting normal diffusion,

1.1 Exponential Decay of Fourier Modes

As a point of reference, we first analyze some basic properties of the diffusion equation,

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2}, \tag{1}$$

which we know describes the continuum (long-time, long wavelength) limit of simple random walks when the Central Limit Theorem holds. Taking the Fourier transform gives

$$\frac{\partial \hat{p}}{\partial t} = -Dk^2\hat{p},$$

from which we find the solution

$$\hat{p}\,(k,t) = \hat{p}\,(k,0)\,e^{-Dk^2 t}.$$

Defining the exponential decay time constant

$$\tau\,(k) = 1/Dk^2,$$

we see that the Fourier modes decay exponentially, and that the modes with small k—or large wavelength—last longest. We can also take a Laplace transform, which yields

$$s\tilde{\hat{P}}\,(k,s) - \hat{P}\,(k,0) = -Dk^2\tilde{\hat{P}}\,(k,s)\,,$$

from which we obtain

$$\tilde{\hat{P}}\,(k,s) = \frac{\hat{P}\,(k,0)}{s+Dk^2}.$$

1.2 The Markovian Diffusion Equation

Now we consider the continuum limit of the continuous time random walk with normal diffusive scaling. The walker is assumed to have a finite mean waiting time, so the waiting-time distribution satisfies

$$\psi(t) = o\left(t^{-2}\right),$$

and thus its Laplace transform will have a small s-expansion governed by

$$\tilde{\psi}(s) \sim 1 - \langle t \rangle s, \; s \to 0,$$

where we assume that $\sigma^2_{\Delta x} < \infty$, $\langle \Delta x \rangle = 0$, and

$$\hat{p}(k) \sim 1 - \frac{\sigma^2 k^2}{2}, \; k \to 0.$$

The Montroll-Weiss equation

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

has for $k \to 0$, $s \to 0$ the long-time limit

$$\tilde{\hat{p}}(k,s) \approx \frac{\langle \tau \rangle s}{s}\left(\frac{1}{\langle \tau \rangle s + \frac{\sigma^2 k^2}{2} + \cdots}\right) \approx \frac{1}{s + Dk^2},$$

where

$$D = \frac{\sigma^2}{2\langle \tau \rangle}.$$

As a result, comparing with the results above, we see that $p(x,t)$ approaches the solution of the normal diffusion equation, Eq. (1), its Green function,

$$p(x,t) \sim \frac{e^{-x^2/4Dt}}{\sqrt{4\pi Dt}}$$

as $t \to \infty$ and $x = O\left(\sqrt{t}\right)$. (This is again the central limit theorem for CTRW.) Since the equation is linear, the same continuum limit holds for any initial condition of the CTRW.

The diffusion equation (1) (and similarly any partial differential equation) can be viewed as 'Markovian' because it can be solved forward in time from only a knowledge of the current state, without any explicit dependence on the previous history of the solution. We will see that the Markovian property no longer holds for anomalous diffusion.

2 Anomalous Subdiffusion

2.1 Mittag-Leffler Power-Law Decay of Fourier Modes

Consider symmetric ($p(x) = p(-x)$), anomalous subdiffusion with an infinite the mean waiting time ($\langle \tau \rangle = \infty$) for which the waiting-time distribution satisfies

$$\psi(t) \sim \left(\frac{\tau_0}{\tau}\right)^{1+\gamma},$$

where $0 < \gamma < 1$ or equivalently has the following small-s expansion of its Laplace transform ,

$$\tilde{\psi}(s) \sim 1 - (\tau_0 s)^\gamma,\ s \to 0.$$

Thus, when $s \to 0$ and $k \to 0$, we have

$$\tilde{\hat{p}}(k,s) \sim \left(\frac{(\tau_0 s)^\gamma}{s}\right) \frac{1}{(\tau_0 s)^\gamma + \frac{\sigma^2 k^2}{2} + \cdots}. \tag{2}$$

The factor in front of (2) is not a constant, and in fact is a singularity, as $\gamma - 1 < 0$. This crucial term, which is negligible in the case of normal diffusion, represents walks that have not moved yet.

We can rewrite (2) as

$$\tilde{\hat{p}}(k,s) \sim \frac{1}{s}\left(\frac{1}{1+(\tau s)^\gamma}\right), \tag{3}$$

where

$$\tau(k)^{-\gamma} = \tau_0^{-\gamma}\frac{\sigma^2 k^2}{2}.$$

Let us define this new function as $\tilde{F}(s,\tau)$, and attempt to invert the Fourier and Laplace transforms. Before we do that, however, we can still obtain a considerable amount of information about $\tilde{F}(s,t)$ using a Tauberian theorem for Laplace transforms near the origin. Noting that

$$\tilde{F}(s,\tau) \sim s^{\gamma-1}\tau^\gamma,$$

which tells us that

$$F(t,\tau) \sim \left(\frac{\tau(k)}{t}\right)^\gamma$$

in the limit $t/\tau \to 0$. Thus, for the case of anomalous subdiffusion, we have *power-law* decay of the Fourier modes with exponent $-\gamma$ and amplitude

$$\tau(k)^\gamma \sim \frac{\tau\tau_0^\gamma}{\sigma^2 k^2},$$

or

$$\tau(k) \sim k^{-2/\gamma}.$$

When $\gamma = 1$, we obtain $\tau(k) \sim k^{-2}$ as before, although the qualitative behavior of the two systems is very different, as power-law decay is much slower than exponential decay: the initial conditions are observed at longer times, and are not "smoothed" out as much in the process.

The function $F(t,\tau)$ can be defined in terms of the Mittag-Leffler functions $E_\alpha(z)$:

$$F(t,\tau) \equiv E_\gamma\left(-(t/\tau)^\gamma\right),$$

where

$$E_\alpha(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(1+\gamma n)}.$$

Consequently, when $\gamma = 1$, we have

$$E_1(z) = \sum_{n=0}^{\infty} \frac{z^n}{n!} = e^z,$$

and then

$$F_1(t,\tau) = E_1(-t/\tau) = e^{-t/\tau}.$$

Therefore, the Mittag-Leffler decay for $0 < \gamma < 1$ is a natural generalization of exponential decay for $\gamma = 1$. The only other Mittag-Leffler function that can be written in analytical forrm is $\gamma = 1/2$, for which

$$E_{1/2}\left(-(t/\tau)^{1/2}\right) = e^{t/\tau}\mathrm{erfc}\left((t/\tau)^{1/2}\right),$$

where $\mathrm{erfc}(x)$ is the complementary error function.

For the non-exponential cases $0 < \gamma < 1$, the asymptotic expansions of the Mittag-Leffler functions are

$$E_\gamma\left(-(t/\tau)^\gamma\right) \sim \begin{cases} \exp\left(-\frac{(t/\tau)^\gamma}{\Gamma(1+\gamma)}\right), & t \to 0 \\ \frac{1}{\Gamma(1-\gamma)}\left(\frac{\tau}{t}\right)^\gamma, & t \to \infty \end{cases},$$

so we have stretched-exponential decay at short times and power-law decay at long times.

2.2 Anomalous Relaxation Equation

We now want to find a continuum equation to describe the anomalous power-law relaxation of Fourier modes whose solution is $F_\gamma(t,\tau(k)) \equiv E_\gamma\left(-(t/\tau)^\gamma\right)$. The Laplace transform $\tilde{F}$ is defined as

$$\tilde{F} \equiv \frac{1}{s\left(1+(s\tau)^{-\gamma}\right)}. \tag{4}$$

For comparison, the differential relaxation equation for relaxation,

$$\frac{dF}{dt} = -\frac{1}{\tau}F, \tag{5}$$

whose solution for $F(0) = 1$ is $F(t) = \exp(-t/\tau)$, has the Laplace transform,

$$s\tilde{F} - 1 = -\frac{\tilde{F}}{\tau}. \tag{6}$$

Therefore, combining (4) and (6), we have

$$s\tilde{F} - 1 = \frac{1}{1+(st)^{-\gamma}} - 1 = -\frac{(s\tau)^{-\gamma}}{1+(s\tau)^{-\gamma}} = -s^{1-\gamma}\tau^{-\gamma}\tilde{F}(s).$$

This relaxation equation can be nicely interpreted in terms of fractaional derivatives, which generalize the more familiar integer derivatives of calculus. We shall see that fractional derivatives are generally *integral operators.*

2.2.1 Fractional Calculus

One way to define a fractional derivative operator ${}_0\mathcal{D}_t^{-q}$, acting on a function $F(t)$, due to Riemann and Liouville, is via its Laplace transform,

$$\widetilde{\left({}_0\mathcal{D}_t^{-q}F\right)}(s) = s^{-q}\tilde{F}(s).$$

For Re$q > 0$, it can then be shown by inverse transform that this operator is given by the following fractional integration operator (or fractional derivative of negative order),

$$ {}_{t_0}\mathcal{D}_t^{-q} F(t) \equiv \frac{1}{\Gamma(q)} \int_{t_0}^{t} dt' \, \frac{F(t')}{(t-t')^{1-q}}, \tag{7} $$

For comparison, recall that the ordinary integer derivative of an analytic function, $F(z)$, in the complex plane can be written as a very similar contour integral according to the Cauchy derivative formula,

$$ \frac{d^n F(z)}{dz^n} = \frac{n!}{2\pi i} \oint \frac{F(\omega)}{(\omega - z)^{1+n}} \, d\omega. $$

Positive Riemann-Liouville fractional derivatives can be expressed in terms of the fractional integral (7) by applying ordinary integer derivatives,

$$ {}_{t_0}\mathcal{D}_t^{\alpha} = \frac{d^n}{dt^n} \, {}_{t_0}\mathcal{D}_t^{\alpha - n} \tag{8} $$

for Re$\alpha > 0$ where n is a positive integer chosen so that $q = n - \alpha$ satisfies $0 < \mathrm{Re}\, q < 1$ in the definition of the fractional integral, Eq. (7. For example, it is left as an exercise to show that the well known rule for integer derivatives of a power,

$$ \frac{d^n}{dt^n} t^m = \frac{m! \, t^{m-n}}{(m-n)!} $$

has the analogous, more general form,

$$ {}_0\mathcal{D}_t^{\alpha} \, t^{\beta} = \frac{\Gamma(1+\beta) \, t^{\beta - \alpha}}{\Gamma(1+\beta-\alpha)} $$

for the Riemann-Liouville fractional derivative. (Recall that $\Gamma(1+n) = n!$ for $n = 1, 2, 3....$)

Another example of the operator in Eqs. (7)–(8) is the Weyl fractional derivative, ${}_{-\infty}\mathcal{D}_x^{\alpha}$, which can be defined more conveniently through its Fourier transform

$$ \widehat{{}_{-\infty}\mathcal{D}_x^{\alpha} F}(k) = (ik)^{\alpha} \hat{F}(k) $$

More generally, the Riesz fractional derivative (or gradient operator), ∇^{α}, preserves a very similar transformation property in higher dimensions,

$$ \widehat{\nabla^{\alpha} F}(\vec{k}) = -|\vec{k}|^{\alpha} \hat{F}(\vec{k}) $$

Recall that this operator arises in the continuum limit of Lévy flights (for $0 < \alpha < 2$) to account for non-local behavior in space; here we have non-local behavior in time, as we now explain.

2.3 Non-Markovian Diffusion Equations

We have

$$ \begin{aligned} \widetilde{\left({}_0\mathcal{D}_t^{-q} F\right)}(s) &= \frac{1}{\Gamma(\gamma)} \int_0^{\infty} dt \, e^{-st} \int_0^t dt' \, \frac{F(t')}{(t-t')^{1-q}} \\ &= \frac{1}{\Gamma(\gamma)} \int_0^{\infty} dt' \, F(t') \int_{t'}^{\infty} dt \, \frac{e^{-st}}{(t-t')^{1-q}}. \end{aligned} $$

We would like to write this in the form

$$\begin{aligned}
\left(\widetilde{{}_0\mathcal{D}_t^{-q} F}\right)(s) &= \frac{1}{\Gamma(\gamma)} \int_0^\infty dt'\, e^{-st'} F(t') \int_{t'}^\infty dt\, \frac{e^{-s(t-t')}}{(t-t')^{1-q}} \\
&= \frac{1}{\Gamma(\gamma)} \int_0^\infty dt'\, e^{-st'} F(t') \int_0^\infty dx\, e^{-sx} x^{q-1},
\end{aligned}$$

where $x \equiv t - t'$. Then, letting $u = sx$, we have

$$\begin{aligned}
\left(\widetilde{{}_0\mathcal{D}_t^{-q} F}\right)(s) &= \frac{1}{\Gamma(\gamma)} \int_0^\infty dt'\, e^{-st'} F(t') \int_0^\infty du\, s^{-q} e^{-u} u^{q-1} \\
&= \Gamma(q)\, s^{-q} \tilde{F}(s).
\end{aligned}$$

Therefore,

$$s\tilde{F} - 1 = -\tau^{-\gamma} \left(\widetilde{{}_0\mathcal{D}_t^{1-\gamma} F}\right)(s),$$

and thus, taking the inverse Laplace transform, we obtain

$$\frac{dF}{dt} = -\tau^{-\gamma} \left({}_0\mathcal{D}_t^{1-\gamma} F(t)\right),$$

where $F(0) = 1$, as the continuum relaxation equation whose solution is the Mittag-Leffler function, which generalizes Eq. (5) for simple exponential relaxation.

The space-time continuum equation we want to solve then is

$$\frac{\partial \hat{p}}{\partial t} = -\tau^{-\gamma} \left({}_0\mathcal{D}_t^{1-\gamma} \hat{p}(k,t)\right) = -\tau_0^{-\gamma} \frac{\sigma^2 k^2}{2} \left({}_0\mathcal{D}_t^{1-\gamma} \hat{p}\right),$$

which we can write as a fractional partial differential equation:

$$\frac{\partial p}{\partial t} = D_\gamma \left({}_0\mathcal{D}_t^{1-\gamma}\right) \frac{\partial^2 p}{\partial x^2}, \tag{9}$$

where we define a generalized diffusion constant $D_\gamma = \sigma^2 / 2\tau_0^\gamma$. Note that this is actually an *integro-differential equation*, as it can be written in the form

$$\frac{\partial p}{\partial t} = \frac{\sigma^2}{2\tau_0^\gamma \Gamma(\gamma)} \int_0^t dt' \left(\frac{1}{(t-t')^{1-\gamma}} \frac{\partial^2 p(x,t)}{\partial x^2}\right).$$

The net implication of all of this is that the system is non-Markovian and has non-negligible 'memory' of its past states.

Without going through the details, we note the obvious generalization to higher dimensions,

$$\frac{\partial p}{\partial t} = D_\gamma \left({}_0\mathcal{D}_t^{1-\gamma}\right) \nabla^2 p. \tag{10}$$

2.4 Time-delayed Flux

The non-Markovian nature of subdiffusion can also be understood by writing the fractional diffusion equation (10) as a conservation law, in terms of a flux J:

$$\frac{\partial p}{\partial t} = -\vec{\nabla} \cdot \vec{J},$$

where

$$\vec{J}(x,t) = -\frac{d}{dt}\int_0^t dt' \, \frac{D_\gamma}{(t-t')^{1-\gamma}} \, \vec{\nabla} p\left(x,t'\right).$$

Therefore, the probability flux for subdiffusion involves an integral of the usual gradient-driven flux for all previous times, weighted by a kernel with long-range power-law decay. (Note that Fick's Law,

$$\vec{J}(x,t) = -D_1 \vec{\nabla} p(x,t) \tag{11}$$

is recovered in the limit of normal diffusion, $\gamma = 1$.)

Physically, this is a result of the infinite mean waiting time: In order to know how many walkers are entering a given region now, we need to know how many walkers were nearby within stepping range for essentially all past times, since some of them are likely to have waited an extremely long time before taking a step into the region. In this way, the 'instantaneous' flux of normal Markovian diffusion must be replaced by a time-convolved 'delayed' flux for anomalous subdiffusion.