More supplemental notes on the random walk

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Some more notes

Betwen my lectures I was asked questions on topics on which I had not prepared to talk. Almost all the questions were excellent, and I regret that I was not able to answer them in the course of my three lectures. Two in particular seemed worth going to the trouble of preparing written responses. In both cases the notes should be regarded as preliminary and incomplete. However, they should serve as indications of how one might go about constructing complete solutions to the problems posed by the questioners, and how one can address more elaborate versions of the problems posed to me.

First passage times

I was asked to talk about first passage times. Here are some elementary notes on the problem. The question is, given a random walker, or a diffusing particle, at what time does it pass by a point in space? I will consider the simplest version of that question, in which the object of interest walks in one dimension and starts a distance d from the point in question. We will consider a "cloud" of the objects, that start out at the position $x = d$. The density of these diffusers will be $c(x,t)$ and their current density is $j(x,t)$, where Fick's law tells us that

$$j(x,t) = -D_0 c(x,t) \tag{B-1}$$

The diffusion equation is

$$\begin{aligned} \frac{\partial c(x,t)}{\partial t} &= -\frac{\partial j(x,t)}{\partial x} \\ &= D_0 \frac{\partial^2 c(x,t)}{\partial x^2} \end{aligned} \tag{B-2}$$

To keep track of first passage times, we will assume an absorbing wall at $x = 0$, while the starting point of the diffusing particles is $x = d$. What this does is eliminate all walkers that pass by the point of interest. We can solve the diffusion equation with this particular boundary condition by making use of sine functions. The appropriate combination of those functions that yield a delta function at $x = d$ when $t = 0$ and that produces a density satisfying the diffusion equation (B-2) is

$$c(x,t) = \frac{2}{\pi}\int_0^\infty \sin qx \sin qd \; e^{-D_0 q^2 t} dq \tag{B-3}$$

It can be verified that the integral on the right hand side of (B-3) yields the delta function $\delta(x-d)$ when $t = 0$.

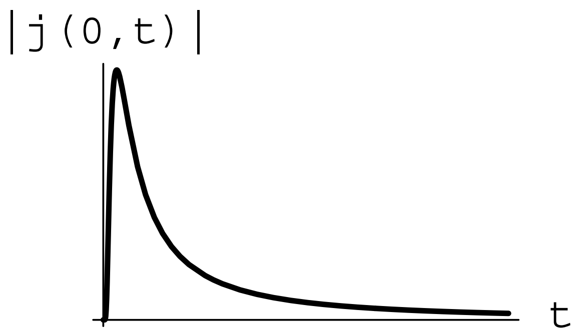

Figure 1: The absolute value of the current density past the origin as a function of time, t for a particular choice of the distance of the starting point from there.

The diffusion current, $j(x,t)$ is given by

$$\begin{aligned} j(x,t) &= -D_0 \frac{\partial c(x,t)}{\partial x} \\ &= -\frac{2D_0}{\pi}\frac{\partial}{\partial x}\int_0^\infty \sin qx \sin qd \; e^{-D_0 q^2 t} dq \\ &= -\frac{2D_0}{\pi}\int_0^\infty q \cos qx \; \sin qd \; e^{-D_0 q^2 t} dq \end{aligned} \tag{B-4}$$

We are interested in the current density at $x = 0$, corresponding to the flux of diffusers past the point at which we monitor the first passage time.

Now, we set $x = 0$ and evaluate the integral on the last line of (B-4). This leaves us with

$$
\begin{aligned}
j(0,t) &= -\frac{2D_0}{\pi}\int_0^\infty q\sin qd e^{-D_0q^2t}dq \\
&= \frac{2D_0}{\pi}\frac{d}{dd}\int_0^\infty \cos qd e^{-D_0q^2t}dq \\
&= \frac{D_0}{\pi}\frac{d}{dd}\int_{-\infty}^\infty e^{iqd}e^{-D_0q^2t}dq \\
&= -\frac{d}{2\sqrt{\pi D_0}}t^{-3/2}e^{-d^2/4D_0t} \qquad \text{(B-5)}
\end{aligned}
$$

A straightforward integration over t verifies that the integrated current density is equal to one, the overall normalization of the diffusion cloud described by our original density. The absolute values of the last line of (B-5) is the rate at which diffusers first pass by the point $x = 0$. The reason for the minus sign is that walkers are moving from the right to the left as they pass by that point. Figure 1 shows what this current looks like as a function of time. One key feature of this current density is that there is a tail in it going as $t^{-3/2}$. This means that the first moment of the distribution, which we would normally evaluate to determine the mean first passage time, is infinite.

How long will a walker avoid a particular region if the walker is confined to a closed volume?

Another question I was asked is how long a walker will avoid the neighborhood of a particular point in space if the walker is forced to remain in a certain volume. I will show you how to solve the problem in the case that the excluded volume is spherical and the volume to which the walker is restricted is a larger spherical volume, the excluded volume sitting in the exact center of the confining volume. See Fig. 2. The boundary conditions that apply at the outer boundary are reflecting, in that walkers that impinge on that boundary are forced to stay in the region and are not eliminated. On the other hand, walkers that attempt to enter the region inside the inner sphere disappear from the distribution. This gives rises to a depletion of the ensemble of walkers in the case of that we start with a collection of them;

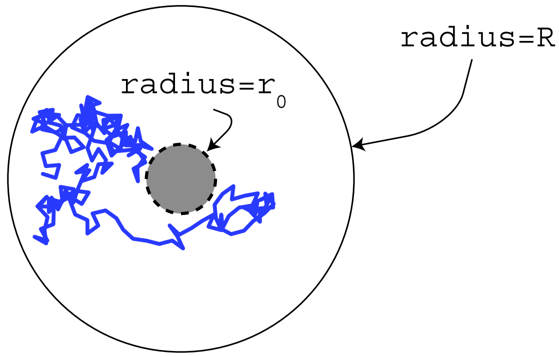

Figure 2: The walker is confined to the region inside a sphere of radius R and outside a region of radius r_0.

if we focus on the statistics of one walkers, then the absorbing boundary conditions at r_0 give rise to a reduction in the total number of walks that the object can execute.

To solve this problem, we will imagine starting with a collection of walkers confined to a spherical shell a distance l from the center of the enclosing sphere, where $l > r_0$. We will work in the continuum limit and take the governing equation to be the diffusion equation. Because we have built rotational symmetry into the system, there will be no dependence on the spherical angles θ and ϕ. The version of the diffusion equation that we need to solve is

$$\frac{\partial c(r,t)}{\partial t} = D_0 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r,t)}{\partial r} \right) \tag{B-6}$$

Here, r is the distance from the center of the spheres. As a prelude to the solution of the problem of interest to us, let's see what we get when there is no excluded volume.

Statistics in the absence of an excluded volume

We look for solutions to (B-6) of the form $c(r,t) = c(r)e^{-\lambda t}$. Then, the equation that we need to solve is

$$-\lambda c(r) = D_0 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r,t)}{\partial r} \right) \tag{B-7}$$

The solutions to this equation that are regular throughout the interior of the sphere of radius R are

$$c_k(r) = \frac{\sin kr}{r} \tag{B-8}$$

for which

$$\lambda = D_0 k^2 \tag{B-9}$$

The current density associated with such a solution is

$$\begin{aligned} j_k(r) &= -D_0 \vec{\nabla} c_k(r) \\ &= D_0 \left(-k \frac{\cos kr}{r} + \frac{\sin kr}{r^2} \right) \end{aligned} \tag{B-10}$$

Reflecting boundary conditions at the boundary $r = R$ translate into the following requirement:

$$\begin{aligned} j_k(R) &= D_0 \left(-k \frac{\cos kR}{R} + \frac{\sin kR}{R^2} \right) \\ &= 0 \end{aligned} \tag{B-11}$$

or

$$kR = \tan kR \tag{B-12}$$

The graphical solution of this equation is indicated in Fig. 3. The boundary

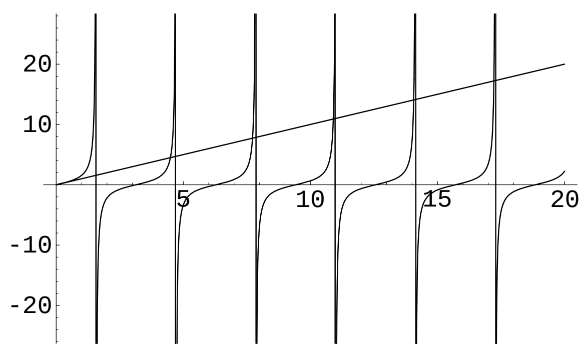

Figure 3: The graphical solution of Eq. (B-12). The horizontal axis is kR.

conditions also allow the constant solution $c_0(r) =$ a constant. This is important, as this represents the density to which the solution to the diffusion equation tends. Let the solutions to (B-12) be k_n, with n going from 1 to ∞. The general solution to the diffusion equation will then be

$$c(r,t) = a_0 + \sum_{n=1}^{\infty} a_n \frac{\sin k_n r}{r} e^{-D_0 k_n^2 t} \tag{B-13}$$

If we start with a set of walkers localized to an infinitesimal spherical shell a distance l from the origin, then

$$a_n \propto \frac{\sin k_n l}{l} \tag{B-14}$$

It can be verified by straightforward analysis (and I leave this as an exercise for you) that the volume integral of the solutions that are not constant is equal to zero. That is

$$\int_0^R \frac{\sin k_n r}{r} r^2 \, dr = 0 \tag{B-15}$$

This means that the total integrated number of walkers is given by the volume integral of the first term on the right hand side of (B-15), which is conserved. Furthermore, all other terms decay exponentially. For the record, the slowest rate of decay is associated with the $n = 1$ term in the sum on the right hand side of (B-15), for which

$$k_1 = \frac{4.49341}{R} \tag{B-16}$$

This means that the asymptotic decay to a constant density is exponential, and the rate of decay is proportional to the inverse square of the size of the region to which the walker or walkers are confined.

There is an excluded volume

The equation that we solve is again of the form (B-7). Now, however, we enforce the boundary condition that the solution is zero at $r = r_0$. The relevant solutions will be of the form

$$\begin{aligned} c(r) &\equiv d_k(r) \\ &= \frac{\sin k(r - r_0)}{r} \end{aligned} \tag{B-17}$$

The reflecting boundary condition at the outer wall is

$$\frac{k \cos k(R - r_0)}{R} - \frac{\sin k(R - r_0)}{R^2} = 0 \tag{B-18}$$

No constant solution for $d_k(r)$ is allowed. The net solution to this equation is

$$c(r,t) = \sum_{n=1}^{\infty} a_n \frac{\sin k_n(r - r_0)}{r} e^{-D_0 k_n^2 t} \tag{B-19}$$

where the k_n's are now the solutions to (B-18). Here, the distribution of walkers decays exponentially to zero, and the rate of decay is asymptotically controlled by the first term in the sum on the right hand side of (B-19). The rate of decay goes as R^{-2}, but is also modified by the ratio r_0/R.