The Diffusion Equation

- So far, we've considered the random walk of a single particle. At each time step, the particle scattered in a random direction and move a distance L. The RMS displacement was found to be:

$$\sqrt{\langle S_N^2 \rangle} = L\sqrt{N}$$

- This quantity, $\sqrt{\langle S_N^2 \rangle}$, is statistical in nature and <u>NOT</u> absolute for each given particle. You can think of it as a statistical bound when we consider many random walk cases. We'll treat this idea more carefully soon.

- However, when we consider many particles all undergoing a random walk, we find that the system is well behaved; that is, a simple behavior emerges that is <u>deterministic</u>, even though we've considered an ensemble of independent <u>random</u> walks.

- Our goal is to describe the time and space evolution of the density $\rho(x,t)$ of a cloud of particles undergoing random walks.

- We start by taking the continuum limit of the ensemble of random walks.

- At each time step Δt, the particle's position x changes by a step ℓ:

$$\vec{x}(t+\Delta t) = \vec{x}(t) + \vec{\ell}(t)$$

Observation about Random Walks

① Random Walks are <u>scale invariant</u>

- <u>scale invariance</u> - if the length, energy, or other variables of the system are multiplied by a common factor, the base features of the system remain the same.

- The jaggedness of the random walk looks the same at any scale as long as N is large.

② Random Walks exhibit <u>UNIVERSALITY</u>

- <u>Universality</u> - In the limit when a large number of particles (Interacting components) come together, the properties of the system are independent of the dynamical details of the system

- The angles over which a given particle moved is inconsequential to the RMS displacement.

Can we write the probability distribution of possible x outcomes at each step?

① For the 1D random walk, we can write the distribution as

$$\mathbb{P}_{1D}(l) = \frac{1}{2}\,\delta(l+1) + \frac{1}{2}\,\delta(l-1)$$

the Delta function picks out whether we move +1 or -1

② For the 2D walk, the distribution at each step is

$$\mathbb{P}_{2D}(\vec{l}) = \frac{\delta(|\vec{l}| - L)}{2\pi L}$$

The delta function picks out a vector of length L and random direction θ.

Quiz: is this normalized?

Now,

- the goal is to calculate the probability distribution $\rho(x, t+\Delta t)$ at the next step, given the probability distribution at the current step, $\rho(x;t)$.

  Note that if the particles are non-interacting, the probability distribution of one particle describes the density of all particles.

- For the particle to move from $\vec{x}'$ at time t to $\vec{x}$ at time $t+\Delta t$, the step $\vec{l}(t)$ must be $\vec{x}-\vec{x}'$. The probability of finding the particle at x is then

$$\mathbb{P}(x-x')\cdot\rho(x';t)$$

That is, the probability of initially being located at x', times the probability of moving from x' to x

- We need to consider all possible starting points x' that can get us to x... so we integrate!

$$\rho(x, t+\Delta t) = \int_{-\infty}^{\infty} \rho(x', t)\, \mathbb{p}(x-x')\, dx'$$

Changing variables,

$$z = x - x'$$

$$\rho(x, t+\Delta t) = \int_{-\infty}^{\infty} \rho(x-z, t)\, \mathbb{p}(z)\, dz$$

Now we make a few assumptions:

1. No Drift: The distribution has a mean of zero. Drift occurs when the center of mass of all particles moves.

2. The distribution has standard deviation a.

3. The step sizes are very small compared to the length scale over which ρ varies. ρ can then be Taylor expanded around $x=0$ (or $x=x_0$)

$$\rho(x-z, t) \simeq \rho(x-z, t)\Big|_0 - z\frac{\partial \rho}{\partial x} + \frac{z^2}{2}\frac{\partial^2 \rho}{\partial x^2} + \ldots$$

from this we get

$$\rho(x, t+\Delta t) \simeq \int \left[\rho(x,t) - z\frac{\partial \rho}{\partial x} + \frac{z^2}{2}\frac{\partial^2 \rho}{\partial x^2}\right] \mathbb{p}(z)\, dz$$

Finally,

$$\boxed{\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}} \quad \text{with } D = \frac{a^2}{2\Delta t} \quad \Rightarrow \quad a = \sqrt{2D\Delta t}$$

1D Diffusion equation

i.e. the width of the distribution increases w/ $\sqrt{\Delta t}$

Diffusion!

Drift Diffusion

Now, we ask what happens if we relax our first assumption of no drift, and hence a constant mean of zero.

Let's consider what happens when we add an external force F and allow for drift.

Similar to the diffusion case,

$$x(t+\Delta t) = x(t) + \ell(t) + \underbrace{F\gamma\Delta t}_{\text{External force term}}$$

γ: mobility $\Rightarrow$ units? $\frac{\ell}{Fs} = \frac{\cancel{m}}{\left(\frac{kg\,\cancel{m}}{s^{\cancel{2}}}\right)\cdot\cancel{s}} = \frac{s}{kg}$

Let's derive an expression for γ