- Random walks
- Diffusion equation

- The atomic hypothesis: matter is composed of small individual particles in perpetual motion that interact with one another, attracting one another when distant, repelling one another when close (R. Feynman)
- The state of perpetual motion at the atomic scale is perceived at a macroscopic scale as temperature, and the average kinetic energy per atomic degree of freedom is $kT/2$, $k = 1.38 \times 10^{-23}$ J/K. An atom with mass m and average velocity $\bar{v}$ has kinetic energy at temperature T

$$\frac{m\,\bar{v}^2}{2} = 3\,\frac{kT}{2}$$

- The average microscopic velocities of various atoms, molecules can be found as

$$\bar{v}^2 = \frac{3\,kT}{m}$$

- Consider a particle that can take position $x \in \mathbb{Z}$
- Let $p(m,n)$ denote probability that particle starting from $x=0$ is at position m after n steps
- Denote by r,l number of steps to the right $(+)$ and left $(-)$

$$m = r - l, n = r + l \Rightarrow r = \frac{1}{2}(m+n), l = \frac{1}{2}(n-m)$$

- Toss a coin n times, there are 2^n possible results of which the number of reverse side up is

$$C(n,r) = \frac{n!}{r!\,(n-r)!}$$

- Probability of being at position m is $p(m,n) = C(n,r)/2^n$

- The discrete 1D random walk with n unit steps has probability

$$p(m,n) = C(n,r)/2^n = \frac{n!}{r!\,(n-r)!} \cdot \frac{1}{2^n}, r = \frac{1}{2}(m+n)$$

for a particle starting at 0 to be at position $m \in \{-n, -n+1, \ldots, n\}$

- Intuitively, the mean position $\bar{m} = 0$. Verify, the mean is the first moment

$$\bar{m} = \sum_{m=-n}^{n} p(m,n)\, m, \sum_{m=-n}^{n} p(m,n) = 1$$

- Combinations satisfy $C(n,r) = C(n,n-r)$, hence

$$2^n p(-m,n) = C\left(n, \frac{1}{2}(-m+n)\right) = C\left(n, \frac{1}{2}(m+n)\right) = 2^n p(m,n) \Rightarrow \bar{m} = 0$$

- The variance is the centered second moment

$$\mathrm{Var}(m) = \overline{(m - \bar{m})^2} = \sum_{m=-n}^{n} p(m,n)\, m^2$$

- $r = \frac{1}{2}(m+n)$ has binomial distribution with $\bar{r} = n/2$, $\mathrm{Var}(r) = n/4$

$$\mathrm{Var}(m) = \overline{m^2} - \overline{2m\,\bar{m}} + \overline{\bar{m}^2} = \overline{m^2} - \overline{\bar{m}^2} = \overline{m^2}$$

$$\mathrm{Var}(m) = \overline{(2r-n)^2} = 4\,\overline{\left(r - \frac{n}{2}\right)^2} = 4\,\frac{n}{4} = n$$

- Stirling's formula $n! \cong \sqrt{2\pi n}\; n^n\, e^{-n}$ is useful in evaluating $C(m,n)$.

$$\ln n! \cong n \ln n - n + \frac{1}{2}(\ln 2\pi + \ln n) \cong n \ln n - n$$

- Consider space, time step sizes $\Delta x, \Delta t, m = x/\Delta x$, $n = t/\Delta t$

$$\bar{x^2} = \frac{\Delta x^2}{\Delta t} t = 2Dt, D = \frac{\Delta x^2}{2\Delta t}$$

- The Gaussian (normal) distribution with probability density function

$$u(x;\mu,\sigma) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right]$$

has mean, variance, with D the diffusivity (diffusion coefficient)

$$\bar{u} = \mu, \mathrm{Var}(u) = \sigma^2 = 2Dt$$

- For $\mu = 0$, obtain $u(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) = \mathcal{N}(0, 2Dt)$

- Consider small domain $A\Delta x$, define number of particles at cross section at x as $N(x)$
- Net movement of particles: $-\frac{1}{2}[N(x+\Delta x)-N(x)]$
- Particle flux is number of particles crossing interface per unit time, unit area

$$J_x=-\frac{1}{2A\Delta t}[N(x+\Delta x)-N(x)]$$

- Concentration is number of particles in unit volume $c(x)=N(x)/(A\mathrm{d}x)$

$$J_x=-\frac{\Delta x^2}{2\Delta t}\cdot\frac{c(x+\Delta x)-c(x)}{\Delta x}$$

- Make $\Delta x, \Delta t\rightarrow 0$ to obtain Fick's law $J_x=-D\,\frac{\partial c}{\partial x}$

- Change in number of particles in volume

$$-\frac{\partial}{\partial t}(cA\Delta x) = [J_x(x+\Delta x, t) - J_x(x, t)]A$$

- In the limit, obtain the diffusion equation

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}$$