Diffusion in a half space : from Lord Kelvin to Path Integrals

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Overview

Random walk in 1D lattice

Let us consider a random with the lattice frame as the X-axis with a scale of unit length. A walker starting at origin can move towards right with say probability 'p' and towards left with 'q'. (As the walker can move only in either right wards or left, p+q will be 1) The position of the walker(K units to the right of the origin) after N steps is given by

$$P(k, N) = \binom{N}{k} \cdot p^k q^{N-k}$$

The distance travelled by the walker

$$x = kl - (N - k)l = (2k - N)l$$
$$= (2k - N)$$

By introducing the Gaussian approximation,
Position x after N jumps can be expressed as the sum of individual jumps xi $\in (-l, l)$

$$x = \sum_{i=1}^{N} x_i$$

The Mean Value of all possible random walks is $< x >$

$$< x >= \sum_{i=1}^{N} < x_i >= N < x_i >$$

$$< x >= N[pl - (1-p)l]$$

$$gives < x >= Nl(2p-1)$$

The variance V is given by $\sigma^2 =< x^2 > - < x >^2$

$$\sigma^2 = 4Nl^2 p(1-p)$$

From central Limit theorem, the probability distribution is given by

$$G(r,N) = \frac{1}{\sqrt{2\Pi\sigma^2}} \exp(-\frac{(x- < x >)^2}{2\sigma^2})$$

In diffusion a general case involves a molecule having equal probability to either move in left direction or right. So, p=q=1/2.By considering these the probability distribution is given by

$$G(r,N) = \frac{1}{\sqrt{2\Pi N}} \exp(-\frac{x^2}{2N})$$

Generalizing it to 3 dimensions we obtain

$$G(r,N) = G(x,N)G(y,N)G(z,N)$$

Diffusion equation

The probability distribution function of a 3D lattice is given by

$$G(r,N) = \frac{1}{\sqrt{(2\Pi N)^3}} \exp(-\frac{r^2}{2N})$$

The G(r,N) also satisfies a differential equation

$$(\frac{\partial}{\partial N} - \frac{\nabla^2}{2})G(r,N) = 0$$

G(r,N)is the probabilty density for the walk to end at r starting with initial position r_0(*say origin*) *within a N steps of randomwalk* (*free diffusion*)

Boundary conditions

- Absorbing Boundary:
  This is the case when a walker sticks to the boundary upon reaching the boundary and gets absorbed. So the probability of finding the walker at the absorbing boundary is zero
  G(r,N)at r$\in dR = 0$
- Reflecting Boundary:
  The random walker is allowed to touch the boundary and then step back with probability of one. Thus the flux across the boundary vanishes.
  $\nabla G(r, N).n \ at \ r \in dR = 0$

A small surface is denoted by dR at the boundary and the unit vector perpendicular to the surface is n.

Half space diffusion

Consider a random walk starting at
$r_0 = \bar{z}a$ *away from the plane* $z = 0$ *and confined to the* $z > 0$ *half* $-$ *space.*
The probability distribution must satisfy the diffusion equation

$$(\frac{\partial}{\partial N} - \frac{\nabla^2}{2})G(r, N) = 0$$

with initial conditions G(z=0)=0 and G(r,0)=$\delta(r - a\bar{z})$
The solution of the differential equation is

$$G(r, N; a) = \frac{1}{(2\Pi N)^{\frac{3}{2}}}[\exp(\frac{(r - a\bar{z})^2}{2N}) - \exp(\frac{(r + a\bar{z})^2}{2N})]$$

By Taylor expansion of e and assuming

$$a << \sqrt{N}$$

$$G(r,N) = \frac{1}{(2\Pi N)^{\frac{3}{2}}} \exp(\frac{-r^2}{2N})[\exp(\frac{az}{N}) - \exp(\frac{-az}{N})]$$

$$G(r,N) = \frac{1}{(2\Pi N)^{\frac{3}{2}}}[(1 + \frac{az}{N}) - (1 - \frac{az}{N})]$$

$$G(r,N;a) = (\frac{2az}{N})\frac{\exp(\frac{-r^2}{2N})}{(2\Pi N)^{\frac{3}{2}}}$$

There exist a z dependent as well as z independent term involved in it.The degrees of freedom involving parallel to the boundary are not affected.

- Self avoiding walk :
  A random walk is said to be a self avoiding when no point in space is visited more than once.
  The polymers in which the self avoidance condition is removed are called as Phantoms/ Gaussian Chains
  The number of different orientations W of a polymer are denoted by

$$W\alpha(\varepsilon)^N N^(\gamma - 1)$$

- ε is effective coordination number which depends on microscopic details.
- $(\varepsilon)^N$ is number of an unconstrained N step random walk with ε options available at each step.
- $N^(\gamma - 1)$ is number of constraints such as self-avoidance and obstacles being present.

Configurations of Polymer (W)

If the distribution function G(r,N) is knownthen the exponent γ can be obtained by simply integrating G(r,N) over the whole space. The Phantom polymer will have $\gamma = 1$

The number of configurations of the polymer is

$$W\alpha \int_{-\infty}^{\infty} dxdy \int_{0}^{\infty} dz \frac{az}{N^{\frac{5}{2}}} \exp(\frac{-r^2}{2N})$$

$$W\alpha \int_{-\infty}^{\infty} \exp(\frac{-x^2-y^2}{2N}) dxdy \int_{0}^{\infty} dz \frac{az}{N^{\frac{5}{2}}} \exp(\frac{-z^2}{2N})$$

By substituting $\frac{z^2}{2N} = t$ and integrating

$$W\alpha(4N).(\frac{N}{2}).\frac{1}{N^{\frac{5}{2}}}$$

$$W\alpha N^{\frac{-1}{2}} so, \gamma = \frac{1}{2}$$

Thus the presence of the reflecting plane reduses the number of acessible configurations compared to the unconstrained case.

Counting Walks on Lattice

Consider a one-dimensional random walker on a lattice (a discrete z-axis) with an absorbing boundary at z=0. Suppose that the walk starts some distance n from the origin; our task is to calculate the number of paths leading from n to some other point m, without touching the boundary.It is easier to calculate the number of paths that touch the boundary and then subtract them from the total number of paths leading from n to m.
The reflection principle states that the number of N step paths originating at n, ending at m, and touching or crossing the boundary z=0 is equal to the number of N step paths that originate at -n and end at m. The number of paths not touching the boundary are

$$W = \binom{N}{\frac{N+m-n}{2}} - \binom{N}{\frac{N+m+n}{2}}$$

Using Path Integrals

A flexible chain is described by a path function c(τ) where τ is the measures the position along the chain.The energy of a self-avoiding chain in external potential is given by

$$H[c] = \frac{1}{2}\int_0^N c'^2(\tau)d\tau + \int_0^N U(c)d\tau - \frac{v}{2}\int_0^N \int_0^N \delta[c(\tau) - c(\tau')]d\tau d\tau'$$

First two terms are harmonic potential between neighbouring segments of the chain and the external potential respectively. The last term indicates each time the chain self interacts a v is reduced.
The partition function for such chain is sum over all possible paths c(τ) given by a path integral.

$$z(N) = \int D[c(\tau)] \exp(-H[c])$$

If the external potential is set zero, Z(N) counts the number of configurations of a Gaussian chain of length N.

We allow the polymer to cross the boundary and introduce a strong repulsive interaction between the plane at z=0 and the chain. Each time the polymer crosses or touches the plane, it is reduced by a large amount of energy. The modified Hamiltonian is then

H=H$_0$ + H_1

$$H_0 = \int_0^N \frac{1}{2} c'^2 d\tau$$

$$H1 = g \int_0^N \delta[c_z(\tau) - c_z[0]] d\tau$$

The partition function is

$$z(g, N) = \int D[c(\tau)] \exp(-H_0[c] - H_1[g, c])$$

By using $\exp(-x) = 1 - \frac{x}{1} + \frac{x^2}{2!} - \frac{x^3}{3!}$..... The general term in Z(g,N) will be

$$Z(g,N) = \int D[c(\tau)] \exp(-H_0[c]) \frac{(-g)^n}{n!} \prod_{l=1}^{n} \int \delta[c_z(\tau) - c_z[0]] d\tau$$

By using Fourier transform

$$\delta[x - X] = \int_{-\infty}^{\infty} \frac{1}{2\Pi} \exp(-iK(x - X)) dK$$

We get

$$Z(g,N) = (\frac{-g}{2\Pi})^n \int D[c(\tau)] \exp(-H_0(c)) \int_0^N d\tau_n \int_0^{\tau_n} d\tau_n - 1..... \int_0^{\tau_2} d\tau_1$$

$$\prod_{l=1}^{n} \int_{-\infty}^{\infty} dK_l \exp(-iK_l[c_z(\tau_l) - c_z(0)])$$