8.08 Statistical Physics II — Spring 2019
Recitation Note 12

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Contents

1 Lattice Random Walk

1.1 One Dimension

Consider the random walk on an one-dimensional lattice. At each time step, the particle jumps to the right with probability q and left with probability $1 - q$. The distance of each jump is l. In the context of kinetics, l is the mean free path.

Denote x_n as the movement at n-th step. By definition, x_n is a Bernoulli random variable $x_n \sim \mathrm{Ber}(p)$. Different x_n, $n \in \mathbb{N}$ are independent. The position of the particle after N steps is $x_N = \sum_{i=1}^{N} x_i$. By the linearity of the expectation:

$$\mu_N \equiv \langle x_N \rangle = \sum_{i=1}^{N} \langle x_i \rangle = N\langle x_1 \rangle = N\left[ql - (1-q)l\right] = Nl(2q-1). \tag{1}$$

For a symmetric random walk $q = 1/2$, $\mu_N = 0$ due to the symmetry.

To compute the variance of x_N,

$$\langle x_N^2 \rangle = \left\langle \left(\sum_{i=1}^{N} x_i\right)\left(\sum_{j=1}^{N} x_j\right)\right\rangle = \sum_{i,j=1}^{N} \langle x_i x_j \rangle \tag{2}$$

$$= \sum_{i=1}^{N} \langle x_i^2 \rangle + 2 \sum_{1 \le i < j \le N} \langle x_i \rangle \langle x_j \rangle \tag{3}$$

$$= Nl^2 + N(N-1)l^2(2q-1)^2. \tag{4}$$

It follows

$$\sigma_N^2 \equiv \langle x_N^2 \rangle - \langle x_N \rangle^2 = 4Nl^2 q(1-q), \tag{5}$$

which is maximized when $q = 1/2$ and is zero when $q = 0$ or 1. Note that $\sigma_N^2 \sim N$ instead of N^2.

One can also compute the probability mass function of x_N. The probability that the particle jumps right k times among the first N steps is

$$p(k, N) = \binom{N}{k} p^k (1-p)^k, \tag{6}$$

and x is related to k as

$$x = kl - (N-k)l = (2k - N)l. \tag{7}$$

Essentially, this is the probability mass function of a binomial random variable, which is the independent sum of identical Bernoulli random variables.

Perhaps it is more illuminating to consider the $N \to \infty$ limit. According to the central limit theorem, x_N tends to distributed normally $x_N \sim \mathcal{N}(\mu_N, \sigma_N^2)$:

$$p(x, N) = \frac{1}{\sqrt{2\pi}\sigma_N} e^{-\frac{(x-\mu_N)^2}{2\sigma_N^2}}. \tag{8}$$

This is a Gaussian wave packet, whose center drifts with velocity $\mu_N/N = l(2q-1)$, and whose size spreads out with time.

We now restrict ourselves to the symmetric/unbiased random walk $q = 1/2$. The probability that the particle returns to the origin after $2n$ steps is:

$$P(x_{2n} = 0) = \frac{1}{2^{2n}} \binom{2n}{n} \sim \frac{1}{\sqrt{\pi n}}, \tag{9}$$

where we have used Stirling's approximation:

$$n! \sim \sqrt{2\pi n} \left(\frac{n}{e}\right)^n. \tag{10}$$

Define the indicator random variable $X_n = 1$ if $x_n = 0$. $X = \sum_{i=1}^{\infty} X_i$ counts the total number of returns. Then

$$\langle X\rangle = \sum_{i=1}^{\infty}\langle X_i\rangle = \sum_{i=1}^{\infty} P(x_{2i}=0) \sim \frac{1}{\sqrt{\pi}}\sum_{i=1}^{\infty}\frac{1}{\sqrt{i}} = \infty, \tag{11}$$

which diverges.

The expected number of returns $\langle X\rangle$ is related to the probability of return. Denote ρ as the probability that the particle ever returns to the origin, and ρ_k as the probability that the particle returns to the origin exactly k times. Obviously

$$\rho_k = \rho^k(1-\rho), \tag{12}$$

by treating the whole random walk as $k+1$ independent random walks. In this way,

$$\langle X\rangle = \sum_{i=1}^{\infty} i\rho_i = (1-\rho)\sum_{i=1}^{\infty} i\rho^i = \frac{\rho}{1-\rho}. \tag{13}$$

Therefore,

$$\langle X\rangle = \infty \Leftrightarrow \rho = 1,$$
$$\langle X\rangle < \infty \Leftrightarrow \rho < 1.$$

The return probability of one-dimensional symmetric random walk is one $\rho_{\mathrm{1D}} = 1$.

1.2 Higher Dimensions

Random walks in higher dimensions can be treated similarly to the one-dimensional case. In the following, will only focus on the return probability ρ for symmetric random walks.

In two dimensions, the probability the particle returns to the origin after $2n$ steps is

$$P(\mathbf{x}_{2n}=0) = \frac{1}{4^{2n}}\sum_{k=0}^{n}\binom{2n}{k}\binom{2n-k}{k}\binom{2n-2k}{n-k} \tag{14}$$

$$= \frac{1}{4^{2n}}\sum_{k=0}^{n}\frac{(2n)!}{(k!)^2\left((n-k)!\right)^2} \tag{15}$$

$$= \frac{1}{4^{2n}}\sum_{k=0}^{n}\binom{2n}{n}\binom{n}{k}^2 \tag{16}$$

$$= \frac{1}{4^{2n}}\binom{2n}{n}\sum_{k=0}^{n}\binom{n}{k}\binom{n}{n-k} \tag{17}$$

$$= \frac{1}{4^{2n}}\binom{2n}{n}^2, \tag{18}$$

where the particle goes up and down k times and left and right $n-k$ times. In the last line, we use the fact that choosing n from $2n$ items can be achieved by dividing $2n$ items into two piles of n items, then pick k items from the first pile and $n-k$ from the second.

Notice $P(\mathbf{x}_{2n}=0)$ is exactly the square of its one-dimensional counterpart. Now, the expected number of returns is

$$\langle X\rangle = \sum_{i=1}^{\infty} P(\mathbf{x}_{2n}=0) \sim \frac{1}{\pi}\sum_{i=1}^{\infty}\frac{1}{i} = \infty. \tag{19}$$

Therefore, the return probability of two-dimensional symmetric random walk is also $\rho_{\mathrm{2D}} = 1$.

In three dimensions, the computation is more complicated. At the end of the day, $\langle X \rangle$ is related to $C\sum_{i=1} 1/i^{3/2} < \infty$. Therefore, $\rho_{\rm 3D} < 1$. This result was first proved by Pólya in 1921. In fact, $\rho_{\rm 3D} \approx 0.34$, and the probability decreases with increasing the dimensions[1]. Random walks with $\rho = 1$ are called "recurrent", and those with $\rho < 1$ are called "transient". There is a famous quote by Shizuo Kakutani:

A drunk man will find his way home, but a drunk bird may get lost forever.

2 Continuous Random Walk and Diffusion

2.1 Fokker-Planck Equation

$p(x, N)$ can be derived recursively instead of directly. It is not hard to see

$$p(x, N+1) = qp(x-l, N) + (1-q)p(x+l, N). \tag{20}$$

This is the master equation. The initial condition is $p(x, 0) = \delta(x)$. In the limit of small jumps and small time steps, the master equation reduces to

$$p(x, t+\Delta t) = qp(x-\Delta x, t) + (1-q)p(x+\Delta x, t). \tag{21}$$

By Taylor expanding $p(x,t)$ to second order:

$$\frac{\partial p}{\partial t} = -v\frac{\partial p}{\partial x} + D\frac{\partial^2 p}{\partial x^2}, \tag{22}$$

where

$$v \equiv (2q-1)\frac{\Delta x}{\Delta t}, \quad D \equiv \frac{\Delta x^2}{2\Delta t}, \tag{23}$$

are the drift velocity and the diffusion constant respectively. This is Fokker-Planck equation. In general, both v and D can be position-dependent, and the Fokker-Planck equation becomes

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial}{\partial x}v(x)p(x,t) + \frac{\partial^2}{\partial x^2}D(x)p(x,t). \tag{24}$$

Since probability is conserved, Fokker-Planck equation can be rewritten into the continuity equation

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}, \tag{25}$$

where the probability current

$$J(x,t) \equiv v(x)p(x,t) - \frac{\partial}{\partial x}D(x)p(x,t). \tag{26}$$

Fokker-Planck equation is equivalent to Fick's law of diffusion. In this way, we have derived the Fick's law from the microscopic random walk model. The phenomenological parameter v and D relates to the microscopic parameter according to Eq. (24).

2.2 Einstein Relation

At equilibrium, there is no probability flow $J(x,t) = 0$ and the probability distribution is given by

$$p(x) \propto \frac{1}{D(x)}\exp\left(\int_{-\infty}^{x} dy \frac{v(y)}{D(y)}\right). \tag{27}$$

[1] See `http://mathworld.wolfram.com/PolyasRandomWalkConstants.html`.

Consider a particle moving in a fluid. According to Newton's second law:

$$m\frac{d^2x}{dt^2} = -\lambda v(x) - \frac{\partial U(x)}{\partial x} + F_r, \tag{28}$$

where λ is the drag coefficient and F_r is the random Brownian force. At equilibrium, $d^2x/dt^2 = 0$ and

$$\langle v(x) \rangle = -\frac{1}{\lambda}\frac{\partial U(x)}{\partial x}. \tag{29}$$

Insert into Eq. (27) and let D be a constant,

$$p(x) \propto \exp\left(-\frac{U(x)}{\lambda D}\right). \tag{30}$$

On the other hand, according to Boltzmann distribution:

$$p(x) \propto \exp\left(-\frac{U(x)}{k_B T}\right). \tag{31}$$

Therefore,

$$D = \frac{k_B T}{\lambda}. \tag{32}$$

This is the Einstein relation, which was proposed by Einstein in 1905. Essentially, the relation states that the same random forces that cause the erratic motion of a particle in Brownian motion would also cause drag if the particle were pulled through the fluid. It is an example of the fluctuation–dissipation relation.