

Lecture notes on random walks and semiflexible polymers
Part (I) : Statics

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1 Random walks

1.1 Random walk in one-dimension

One-dimensional random walk: Consider a walker on a one dimensional lattice. At every time step the walker tosses an unbiased coin and moves to the left if its a head and to the right if its a tail. Thus for every step there are 2 possibilities and the walker chooses either of them with equal probability. After taking N steps the walker can be anywhere between $-N$ to N and we would like to know: what is the probability $P(n, N)$ that the walker is at some point n ? We note that there are 2^N distinct possible walks, each of which occurs with the same probability. Out of this let us say $T(n, N)$ walks end up at the point n . Then clearly

$$W(n, N) = \frac{T(n, N)}{2^N}. \quad (1)$$

We can find $T(n, N)$ as follows. For any given realization of the walk let n_R be the number of right steps and let n_L be the number of left steps. Then $n_R + n_L = N$ and $n_R - n_L = n$.

Example: One possible realization of a 10-step walk is $LRRLLLRLL$. In this case $N = 10$, $n_R = 4$, $n_L = 6$ and $n = -2$. A different realization of the walk which leads to the same values of N, n_R, n_L, n is $LLLLRRRLL$.

Clearly there are many possible ways of arranging the n_R R 's and n_L L 's and the number of ways would actually give us $T(n, N)$. This is a combinatorial problem and the answer is:

$$T(n, N) = \frac{N!}{n_R!n_L!}. \quad (2)$$

Problem: Check this formula for $N = 4$!!

Now since $n_R = (N + n)/2$ and $n_L = (N - n)/2$ we therefore get, using Eq. (1) and Eq. (2),

$$W(n, N) = \frac{N!}{\frac{N+n}{2}! \frac{N-n}{2}!} \frac{1}{2^N}. \quad (3)$$

Problem: Check normalization: $\sum_{n=-N}^N W(n, N) = 1$. Use the fact that $(1/2 + 1/2)^N = 1$.

Now what we would eventually like to get is a “continuum description”, that is we want to look at length scales much larger than the lattice spacing (say a) and time scales much larger than time taken for each step (say τ). Let us try to get this.

First let us use Stirling's approximation. This states that for large k ,

$$k! = k^k e^{-k} \sqrt{2\pi k}.$$

This formula is infact very good even for k as small as 5; in that case $k! = 120$ while Stirling gives ≈ 118 . Using Stirling's formula in Eq. (3) we get:

$$W(n, N) = \frac{N^N e^{-N} \sqrt{2\pi N}}{\left(\frac{N+n}{2}\right)^{\frac{N+n}{2}} e^{-\frac{N+n}{2}} \sqrt{2\pi \left(\frac{N+n}{2}\right)} \left(\frac{N-n}{2}\right)^{\frac{N-n}{2}} e^{-\frac{N-n}{2}} \sqrt{2\pi \left(\frac{N-n}{2}\right)}} \frac{1}{2^N} \quad (4)$$

After simplification this reduces to:

$$W(n, N) = \frac{(2\pi N)^{1/2}}{\left(1 + \frac{n}{N}\right)^{\frac{N+n}{2}} \left(1 - \frac{n}{N}\right)^{\frac{N-n}{2}} \pi N \left(1 - \frac{n^2}{N^2}\right)^{1/2}} \quad (5)$$

We now consider $n \ll N$ only or more precisely $n \sim O(\sqrt{N})$. In this limit, we get

$$W(n, N) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-\frac{n^2}{2N}}. \quad (6)$$

This is easiest to obtain by taking $\ln W(n, N)$ and expanding. Now let $x = na$ and $t = N\tau$. Then the probability density for the walker to be between x and $x + dx$ is

$$\begin{aligned} P(x, t) &= W(n, N)/(2a) \\ &= \frac{1}{(4\pi(a^2/2\tau)t)^{1/2}} e^{-\frac{x^2}{4(a^2/2\tau)t}}. \end{aligned} \quad (7)$$

The reason we divide by $2a$ and not a is because after N steps the walker can be located either on even sites (if N is even) or on odd sites (N odd). Now defining the diffusion constant $D = a^2/(2\tau)$ we finally get

$$P(x, t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}}. \quad (8)$$

Problem: Check that $\int_{-\infty}^{\infty} dx P(x, t) = 1$. Also verify that $\langle x \rangle = 0$ and $\langle x^2 \rangle = 2Dt$, where $\langle A \rangle = \int_{-\infty}^{\infty} dx A P(x, t)$.

The moments $\langle x \rangle$ and $\langle x^2 \rangle$ can be obtained more directly. The position of the walker x_N after $N = t/\tau$ time steps is

$$x(t) = a \sum_{i=1}^N \xi_i \quad (9)$$

where ξ_i is $+1$ or -1 with equal probability (thus $\langle \xi_i \rangle = 0$) and ξ_i and ξ_j are uncorrelated or independent, which means that $\langle \xi_i \xi_j \rangle = 0$. Therefore

$$\begin{aligned} \langle x(t) \rangle &= a \sum_{i=1}^N \langle \xi_i \rangle = 0 \\ \langle x^2(t) \rangle &= a^2 \sum_{i,j=1}^N \langle \xi_i \xi_j \rangle \\ &= a^2 \left(\sum_{i=1}^N \langle \xi_i^2 \rangle + \sum_{i \neq j} \langle \xi_i \xi_j \rangle \right) \\ &= a^2 N = 2[a^2/(2\tau)](N\tau) = 2Dt \end{aligned} \quad (10)$$

Problem: Write a Monte-carlo program to generate $1 - D$ random walks and verify the law $\langle x^2 \rangle = 2Dt$.

Problem: Let $\xi_i = 1$ with probability p and -1 with probability $q = 1 - p$. Find $\langle x(t) \rangle$ and $\langle x^2(t) \rangle - \langle x(t) \rangle^2$.

Problem: Let $x_i = 2$ with probability $1/2$ and $x_i = -1$ or 0 with probabilities $1/4$ each. Find $\langle x(t) \rangle$ and $\langle x^2(t) \rangle - \langle x(t) \rangle^2$.

1.2 Random walk and the Diffusion equation

An easier method to get Eq. (8) : Since a random walk is like diffusion of particles we expect Eq. (8) to be the solution of the diffusion equation. Let us see how this comes about. As before, $W(n, N)$ is the probability that a particle is at the site n after N steps. It satisfies the following equation

$$W(n, N) = \frac{1}{2}[W(n+1, N-1) + W(n-1, N-1)] \quad (11)$$

Subtract $P(n, N-1)$ from both sides. We then get

$$\begin{aligned} W(n, N) - W(n, N-1) &= \frac{1}{2}[W(n+1, N-1) - 2W(n, N-1) + W(n-1, N-1)] \\ \Rightarrow \frac{P(x, t) - P(x, t-\tau)}{\tau} &= \frac{a^2 [P(x+a, t-\tau) - 2P(x, t-\tau) + P(x-a, t-\tau)]}{2\tau a^2} \\ \Rightarrow \frac{\partial P(x, t)}{\partial t} &= D \frac{\partial^2 P(x, t)}{\partial x^2} \end{aligned} \quad (12)$$

which is just the diffusion equation. Normally in the diffusion equation we have density of particles $\rho(x, t)$ instead of a probability $P(x, t)$. But they are simply related by $\rho(x, t) = \mathcal{N}P(x, t)$ where \mathcal{N} is the total number of diffusing particles.

Now Eq. (12) is a linear equation which can be easily solved by Fourier transforming. Solving means: given an initial distribution of particles $P(x, t=0)$ find the distribution $P(x, t)$ at some later time t . Let us solve for the initial condition $P(x, t=0) = \delta(x)$, that is the case when initially the particle is located at the origin. Taking a Fourier transform:

$$P(x, t) = \int_{-\infty}^{\infty} \tilde{P}(k, t) e^{ikx} dk; \quad \tilde{P}(k, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} P(x, t) e^{-ikx} dx. \quad (13)$$

gives

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{\partial \tilde{P}(k, t)}{\partial t} e^{ikx} dk &= \int_{-\infty}^{\infty} -Dk^2 \tilde{P}(k, t) e^{ikx} dk \\ \Rightarrow \frac{\partial \tilde{P}(k, t)}{\partial t} &= -Dk^2 \tilde{P}(k, t) \\ \Rightarrow \tilde{P}(k, t) &= e^{-Dk^2 t} \tilde{P}(k, 0) = \frac{1}{2\pi} e^{-Dk^2 t} \end{aligned} \quad (14)$$

Taking the inverse Fourier transformation we get:

$$\begin{aligned} P(x, t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dk^2 t} e^{ikx} dk \\ &= \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}} \end{aligned} \quad (15)$$

as before.

Note that the diffusion equation can also be written in the following form:

$$\begin{aligned} \frac{\partial P(x, t)}{\partial t} + \frac{\partial J(x, t)}{\partial x} &= 0 \quad \text{where} \\ J(x, t) &= -D \frac{\partial P(x, t)}{\partial x}. \end{aligned} \quad (16)$$

Higher dimensions: We can consider a random walk on a 2–dimensional, 3–dimensional or in general a d –dimensional lattice and ask the same questions. The combinatorial approach becomes difficult but we get the same diffusion equation which can again be solved quite easily.

To see that we do get the same equation, consider the 2–dimensional case, where a random walker can move up, down, left or right with equal probabilities. Thus if at some time $t = N\tau$ the walker is at the point $\bar{r} = (x, y)$ then, at time $t + \tau$, it can be at either of the 4 points $(x + a, y)$, $(x - a, y)$, $(x, y + a)$, $(x, y - a)$. The probability of it being at any of these 4 points is clearly $1/4$. Let $P(\bar{r}, t)$ be the probability for the walker to be at \bar{r} at time t . Then Eq. (11) gets modified to

$$P(\bar{r}, t) = \frac{1}{4}[P(x + a, y, t - \tau) + P(x - a, y, t - \tau) + P(x, y + a, t - \tau) + P(x, y - a, t - \tau)]. \quad (17)$$

Again subtracting $P(\bar{r}, t - \tau)$ from both sides and defining $D = a^2/(4\tau)$ we get the 2–dimensional diffusion equation

$$\frac{\partial P(\bar{r}, t)}{\partial t} = D\left[\frac{\partial^2 P(\bar{r}, t)}{\partial x^2} + \frac{\partial^2 P(\bar{r}, t)}{\partial y^2}\right]. \quad (18)$$

Similarly in 3–dimensions we get [with $D = a^2/(6\tau)$]

$$\frac{\partial P(\bar{r}, t)}{\partial t} = D\nabla^2 P(\bar{r}, t). \quad (19)$$

To solve this we again Fourier transform:

$$P(\bar{r}, t) = \int_{-\infty}^{\infty} \tilde{P}(\bar{k}, t) e^{i\bar{k}\cdot\bar{r}} d\bar{k}; \quad \tilde{P}(\bar{k}, t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} P(\bar{r}, t) e^{-i\bar{k}\cdot\bar{r}} d\bar{r}. \quad (20)$$

Proceeding exactly as in the 1 – D case we get:

$$\begin{aligned} P(\bar{r}, t) &= \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} d\bar{k} e^{-Dk^2 t} e^{i\bar{k}\cdot\bar{r}} \\ &= P(x, t)P(y, t)P(z, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-\frac{r^2}{4Dt}} \end{aligned} \quad (21)$$

The mean square distance traveled by the walker is $\langle r^2 \rangle = \langle x^2 + y^2 + z^2 \rangle = 6Dt$. We can verify this more directly: Since $\bar{r}(t) = a \sum_{i=1}^N \bar{\xi}_i$, therefore $\langle \bar{r}^2 \rangle = a^2 \sum_{i=1}^N \langle \bar{\xi}_i^2 \rangle = Na^2 = 6Dt$.

Note that the number of walks of length N , from the origin to \bar{r} is $6^N P(\bar{r}, t)$.

1.3 Langevin equations and Brownian motion

The random walk is basically described by the equation

$$x_i = x_{i-1} + \xi_i$$

where ξ_i is uncorrelated noise with zero mean that is

$$\langle \xi_i \rangle = 0; \quad \langle \xi_i \xi_j \rangle = \delta_{ij}.$$

For continuous space and time these equations become:

$$\begin{aligned} \frac{dx(t)}{dt} &= \xi(t) \quad \text{with} \\ \langle \xi(t) \rangle &= 0; \quad \langle \xi(t)\xi(t') \rangle = 2D\delta(t-t'). \end{aligned} \tag{22}$$

This is the Langevin equation describing diffusion. It is the equation of motion for a free Brownian particle (a particle whose velocity is a random function of time) and is the simplest example of a Langevin equation. If we have a large number of such particles then we have seen that their density obeys the diffusion equation which can be written in the form

$$\begin{aligned} \frac{\partial \rho(x, t)}{\partial t} + \frac{\partial J_{diff}(x, t)}{\partial x} &= 0 \quad \text{where} \\ J_{diff}(x, t) &= -D \frac{\partial \rho(x, t)}{\partial x}. \end{aligned} \tag{23}$$

Now consider a different situation where a large number of particles are moving with a deterministic (that is non-random) velocity. The equation of motion of each particle is then

$$\frac{dx(t)}{dt} = f(x). \tag{24}$$

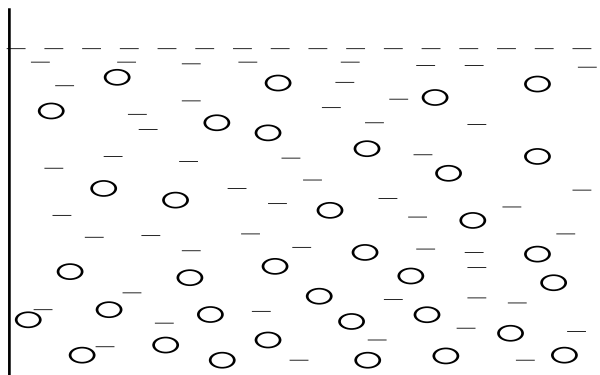
In this case also we can define the density distribution of particles and ask the question: how does the density change with time? This is basically determined from the conservation of particles which is given by the following continuity equation:

$$\begin{aligned} \frac{\partial \rho(x, t)}{\partial t} + \frac{\partial J_{drift}(x, t)}{\partial x} &= 0 \quad \text{where} \\ J_{drift}(x, t) &= \dot{x}\rho(x, t) = f(x, t)\rho(x, t). \end{aligned} \tag{25}$$

Problem: Derive the continuity equation from the condition for conservation of particles which is $\rho(x, t)dx = \rho(x', t')dx'$ where $t' = t + dt$ and $x' = x + dx$. This is infact just the Liouville's equation in classical mechanics.

The Einstein fluctuation-dissipation relation: we will now use the previous results to derive a formula which will enable us to make estimates of the diffusion constant D in real physical systems.

Consider a large number of colloidal particles put inside a fluid.



Each colloidal particle is much larger than the fluid particles which constantly bombard it. The net effect of all the forces imparted on the colloid by the fluid particles can effectively be described very accurately by just two forces:

(i) A *dissipative* part: This is the viscous drag on the particle and is a deterministic force given by

$$F_d = -\gamma\dot{x} = -6\pi\eta av, \quad (26)$$

where $v = \dot{x}$ is the velocity of the particle, a is its radius, η is the fluid viscosity, and $\gamma = 6\pi\eta a$ is Stokes formula.

(ii) A *fluctuating* part: this is a random force with zero average and which is totally uncorrelated in time, that is we take

$$F_f = \xi(t); \quad \langle \xi(t) \rangle = 0 \quad \langle \xi(t)\xi(t') \rangle = 2D\delta(t-t'). \quad (27)$$

What the fluctuation-dissipation theorem (or Einstein relation) tells us is that the two parts above are related to each other. To see how this comes about, consider the state when the colloidal particles have reached a steady state and are in thermal equilibrium at some temperature T . We know that because of gravity there will be a concentration gradient of colloidal particles in the system and their density will vary as:

$$\rho(x) = \rho(x=0)e^{-\frac{mgx}{k_B T}}, \quad (28)$$

where m is mass of each particle. Also there will be two currents set up in the system:

(1) a diffusive current: $J_{diff} = -D\frac{\partial\rho(x)}{\partial x}$.

(2) a drift current: each colloidal particle is acted upon by two deterministic forces, one is the drag force given by $6\pi\eta av$ and the other is gravity given by mg . In the steady state they are equal, which means that the colloid attains a steady speed $v = \frac{mg}{6\pi\eta a}$. This, from Eq. (25), implies a drift current given by $J_{drift} = \frac{mg}{6\pi\eta a}\rho(x)$.

In the equilibrium state there is no net current of particles which means $J_{diff} = J_{drift}$ which gives

$$\frac{\partial\rho(x)}{\partial x} = -\frac{mg}{6\pi\eta a D}\rho(x).$$

But from Eq. (28) we get

$$\frac{\partial\rho(x)}{\partial x} = -\frac{mg}{k_B T}\rho(x).$$

From the two equations above we finally get the Einstein relation:

$$D = \frac{k_B T}{6\pi\eta a}. \quad (29)$$

Note that it relates the fluctuating (D) and dissipative (η) parts of the fluid forces acting on the colloid.

Since everything on the right hand side of Eq. (29) is known we can use it to estimate the value of D .

Problem: Estimate the value of D for a colloid of size $a = 1\mu m$ in water and in air. How far does it travel in a minute? and in an hour?

A more systematic approach

The full equation of motion for a Brownian particle should be

$$\begin{aligned} m\frac{dv}{dt} &= -\gamma v + F(x) + \xi'(t) \quad \text{where} \\ F(x) &= -\frac{dV(x)}{dx} \\ \langle \xi'(t) \rangle &= 0; \quad \langle \xi'(t)\xi'(t') \rangle = 2D'\delta(t-t'), \end{aligned}$$

where $V(x)$ is the external potential acting on the particle. Note that we have denoted the noise by ξ' instead of ξ since, we shall see, that they are slightly different. Now we are working in the high viscosity limit (overdamped, low Reynolds number limit) where it can be shown that it is alright to neglect inertial terms, namely the term on the left hand side of the above equation. In that case we get

$$\begin{aligned} \gamma\frac{dx}{dt} &= F(x) + \xi'(t) \\ \Rightarrow \frac{dx}{dt} &= \frac{F(x)}{\gamma} + \xi(t) \quad \text{where} \\ \xi &= \frac{\xi'}{\gamma} \Rightarrow \langle \xi(t)\xi(t') \rangle = 2D\delta(t-t'); \quad D' = \gamma^2 D. \end{aligned}$$

As we have seen before the current corresponding to the above Langevin equation is:

$$\begin{aligned} J &= J_{diff} + J_{drift} \\ &= \frac{F(x)}{\gamma}\rho(x,t) - D\frac{\partial\rho(x,t)}{\partial x}. \end{aligned}$$

Using the continuity equation $\partial\rho/\partial t + \partial J/\partial x = 0$, this then leads to the following equation for $\rho(x,t)$:

$$\frac{\partial\rho(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{F(x)}{\gamma}\rho(x,t) - D\frac{\partial\rho(x,t)}{\partial x}\right]$$

In the steady state $\partial\rho/\partial t = 0$ (or net current is zero), hence

$$\begin{aligned} D\frac{\partial\rho(x)}{\partial x} &= \frac{F(x)}{\gamma}\rho(x) \\ \Rightarrow \frac{\partial\rho(x)}{\partial x} &= -\frac{\partial V(x)}{\partial x}\frac{1}{D\gamma}\rho(x) \\ \Rightarrow \rho &= \rho_0 e^{-\frac{1}{D\gamma}V(x)} \end{aligned}$$

But we know that the density variation is given by the Boltzmann equation $\rho = \rho_0 e^{-\frac{V(x)}{k_B T}}$. Thus we again get the Einstein relation:

$$D\gamma = k_B T \tag{30}$$

2 Polymers

A polymer is a large chain formed out of some basic repeating units called monomers. A monomer has some fixed chemical composition. For example the monomer $-CH_2-$ gives rise to the polymer polythene. The number of monomers in a single polymer can be as high as 10^6 . We will simply think of the monomers as rigid rods of fixed length. Usually two successive monomers in a polymer chain will not be uncorrelated. But two monomers separated by a large enough distance will be uncorrelated. We define b as the average distance over which monomers become uncorrelated. This will be called the persistence length of the chain.

The simplest model for a polymer is the Freely Jointed Chain model (FJC). We construct the polymer by a series of steps of equal lengths (the persistence length, b). Each step is a vector $\bar{\xi}$ which points in a random direction and is independent of previous steps. Thus for a polymer of N steps with one end at the origin 0 and the other end at \bar{R} [see Fig. below] , we have

$$\bar{R} = \sum_{l=1}^N \bar{\xi}_l \quad \text{where} \quad (31)$$
$$\bar{\xi}_l^2 = b^2; \quad \langle \bar{\xi}_l \cdot \bar{\xi}_m \rangle = 0 \quad l \neq m$$

The FJC looks like the random walk we had defined earlier except that in that case each step could be taken in six directions only, while in the FJC a step can take place in *any* direction. However as we shall find out, many properties of the FJC are exactly like those of the usual random walk.

Right now we would like to know two things about the polymer:

(1) How does its linear size R depend on its total length L ? If it was a rigid object we would expect $R \sim L$, but since its coiled up, we expect $R \sim L^\nu$ with $\nu < 1$.

(2) The elastic properties of the polymer: We want to know how much force it takes to stretch the polymer from its coiled up state to an extended state.

2.1 Properties of the FJC model

The first is easy. From Eq. (31)

$$R^2 = \sum_{l=1}^N \bar{\xi}_l^2 + \sum_{l \neq m} \bar{\xi}_l \cdot \bar{\xi}_m = Nb^2 = Lb,$$

where $L = Nb$ is the length of the polymer chain. Note that the end to end distance $R = \sqrt{Lb}$ depends on the persistence length also. For the extreme case of a rigid rod, $b = L$, and we get $R = L$, as expected.

Computing the elastic properties of the chain: we want to find how much force, f , it takes in order to hold the end-to-end distance at a fixed distance R . Thus we have to find the free energy $F(R, N, T)$. The force is then given by

$$f = \frac{\partial F}{\partial R}. \quad (32)$$

This is really like finding the pressure of a gas from its free energy $F(V, N, T)$ using the formula $P = -\partial F/\partial V$. The free energy, as usual, is given by $F(R, N, T) = -k_B T \ln Z$ where $Z = \sum e^{-\beta H}$ and the sum is over all configurations of the polymer with *fixed* end to end distance R . Now as far as the FJC is concerned all chain configurations have the same energy, which we can set to zero, and hence we get

$$Z = \sum_{\text{all configurations}} 1 = \Omega(R, N) \quad (33)$$

where $\Omega(R, N)$ is the total number of polymer configurations with ends fixed at 0 and \bar{R} . Now, this is just given by

$$\Omega(R, N) = C_N P(R, N), \quad (34)$$

where $P(R, N)$ gives the probability that after N steps the chain ends at \bar{R} and C_N is the total number of configurations [this is similar to Eq. (2) where C_N was 2^N]. The distribution of the end to end vector \bar{R} , that is $P(R, N)$, is infact identical to the usual random walk. We recall that the random walk results are given by Eq. (21). We now want to think of the walk simply as a N -step chain, so we change variables back to $N = t/\tau$ and $D = b^2/(6\tau)$. This then gives

$$\begin{aligned} P(R, N) &= \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3R^2}{2Nb^2}} \\ &= \left(\frac{3}{2\pi L b}\right)^{3/2} e^{-\frac{3R^2}{2Lb}}. \end{aligned} \quad (35)$$

[Note that while we are writing $P(R, N)$ we really mean $P(\bar{R}, N)$ but the notation is alright since there is rotational symmetry.] The proof that $P(R, N)$ for the FJC is also given by Eq. (35) is given in App. (A). *An important point to note is that this formula is accurate only for small extensions $e = R/L \ll 1$.* It is obvious that for $e > 1$ the formula is wrong since we expect $P(R, N)$ to be zero (because we cannot extend a polymer beyond its full length). For many purposes (like if we want to calculate $\langle R^2 \rangle$) this formula is good enough, since the probability for large x becomes so small that its precise value does not really matter. On the other hand, for the force calculation at large extensions, we do really need the exact result since we want to get the exact change in free energy when we make a small change in R . We will see later how this can be done. Right now let us get the results for small extensions.

The free energy is

$$F = -k_B T \ln \Omega(R, N) = -k_B T \ln C_N + \frac{3k_B T R^2}{2bL}. \quad (36)$$

Thus the force is, from Eq. (32)

$$f = \frac{3k_B T}{bL} R = \frac{3k_B T}{b} e. \quad (37)$$

Thus for small relative extensions ($e \ll 1$) we have a linear force-extension law which is like a Hookean spring with spring constant $k = 3k_B T/(bL)$. *Note that though all configurations of a flexible polymer have the same energy, it still requires one to exert a force in order to stretch it. Infact the origin of this force is purely ENTROPIC in nature.*

2.2 Experimental determination of the size of a polymer

Through scattering of light one can measure the pair correlation function, $g(\bar{r})$, given by:

$$g(\bar{r} - \bar{r}') = \frac{1}{N} \langle \rho(\bar{r}) \rho(\bar{r}') \rangle, \quad (38)$$

where $\rho(\bar{r})$ gives the density of monomers at \bar{r} . The average $\langle \dots \rangle$ is over all the degrees of freedom of the polymer, that is, its configurational and also translational degrees of freedom. It is because of the average over translational degrees that $g(\bar{r}, \bar{r}')$ depends only on the separation $\bar{r} - \bar{r}'$. The fourier transform

$$g(\bar{q}) = \int d\bar{r} g(\bar{r}) e^{i\bar{q} \cdot \bar{r}} \quad (39)$$

gives the intensity of the scattered light as a function of the scattering angle [$\bar{q} = \bar{k}_f - \bar{k}_i$ where \bar{k}_i and \bar{k}_f are the directions of the incident and scattered rays. Therefore $q = 4\pi \sin(\theta)/\lambda$].

A scaling derivation of the form of $g(q)$ at large q ($qR \gg 1$).

The pair correlation function $g(r)$ has the following physical interpretation: if we randomly pick up any monomer and fix the origin at its location, then $g(r)$ gives the average density of monomers at a distance r from the origin. If we are looking at distances $r \ll R$ [corresponding to $q \gg 1/R$], then $g(r)$ must depend on the average density of monomers in a sphere of radius r . This is just n/r^d where n is the number of monomers within the sphere of volume r^d [in d dimensions]. Also we know that in general $r \sim n^\nu b$ or $n \sim (r/b)^{1/\nu} \sim (r/b)^{d_f}$, where $d_f = 1/\nu$ is the *fractal dimension of the scatterer*. Thus we get:

$$\begin{aligned} g(r) &= \frac{n}{r^d} = \frac{(r/b)^{d_f}}{r^d} \\ \Rightarrow g(q) &\sim \int g(r) e^{i\bar{q} \cdot r} r^{d-1} dr d\Omega \\ &\sim \int \frac{(r/b)^{d_f}}{r^d} e^{i\bar{q} \cdot r} r^{d-1} dr d\Omega \sim \frac{1}{(qb)^{d_f}}. \end{aligned} \quad (40)$$

Experimentally it is found that for dilute polymers $d_f = 5/3$, which corresponds to $\nu = 3/5$. For a random walk model we would have expected $\nu = 1/2$. The fact that $\nu = 3/5$ means that the polymer is really a more extended or swollen object than the random walk. The random walk gives a more compact object because it does not take into account the important factor of *self-avoidance*. In the random walk model clearly we can have the walk intersecting itself many times. The real polymer obviously does not allow such intersections. Thus the correct way of modelling a flexible polymer should be through the Self-Avoiding-Walk (SAW). This we study in the next section.

It is interesting to note the dependence of the structure factor at large q on the fractal dimension of the scatterer. We note that for a homogeneous distribution of monomers within a sphere corresponds to $d_f = 3$ while for a rod like object $d_f = 1$.

2.3 The Self-avoiding-walk and the Flory theory

In the random walk case, all chain configurations occur with equal probability. In the case of the SAW all chain configurations, *which do not have self-intersections*, can occur with equal probability. As for the random walk, for the SAW too we would like to find- how the size of the polymer varies with number of monomers?, what is the number of possible polymer configurations for fixed end-to-end distance ? etc. The SAW problem is much harder and there are very few exact results. Here we will only discuss an approximate theory due to Flory which gives a very good estimate of the exponent ν .

Flory's argument: the self-avoidance means that it costs energy when two monomers come close together. Thus there is an effective short-ranged repulsive interaction between different monomers. Let us try to make a rough estimate of the contribution of this interaction to the free energy of the polymer. Consider a polymer of size R and consisting of N units. The number of monomers per unit volume is $\rho = N/R^d$. Assume that every monomer interacts with every other so that the interaction free energy per unit volume is $k_B T v \rho^2$, where v is a parameter with the dimensions of volume. The total interaction free energy in the volume R^d is thus

$$F_{int} = k_B T v \left(\frac{N}{R^d}\right)^2 R^d = k_B T v \frac{N^2}{R^d}. \quad (41)$$

We add to this the entropic free energy of the random walk that we obtained earlier, to get the full SAW free energy

$$F = k_B T v \frac{N^2}{R^d} + k_B T \frac{3R^2}{2b^2 N} \quad (42)$$

We minimize this with respect to R to get the most probable configuration:

$$\begin{aligned} \frac{\partial F}{\partial R} &= 0 \\ \Rightarrow R &\sim N^{\frac{3}{d+2}}. \quad \text{Thus} \\ \nu &= \frac{3}{d+2} \end{aligned} \quad (43)$$

In 3-dimensions, we get $\nu = 3/5$, which is the exponent obtained in light scattering experiments. Thus it is seen that the self avoidance condition is important. However there are two experimental situations when the self-avoidance condition becomes unimportant and the polymer behaves *ideally*, that is like an ordinary random walk with $\nu = 1/2$.

(i) At special points in phase space, so-called Θ -point, which may be obtained by changing the temperature and solvent properties.

(ii) In dense polymer solutions (polymer melts).

2.4 The force-extension law for the FJC model

We have seen earlier that for small extensions, the statistical properties of the FJC are the same as the Gaussian random walk. We could compute the corresponding free-energy and obtained a

linear force extension relation which is like a Hookean spring. At large extensions this is no longer true and we will now look at this case.

First let us look at a toy problem, namely the one-dimensional version of the FJC which is just the usual lattice random walk studied in sec. (I). In this case, the exact free energy (without taking the limit $n/N \ll 1$) is given by

$$\begin{aligned}
F(x, L, T) &= -k_B T \ln \Omega(x, L) = -k_B T \ln \left[\frac{N!}{\left(\frac{N+n}{2}\right)! \left(\frac{N-n}{2}\right)!} \right] \\
&= -k_B T \left[c_N - \frac{N}{2} \left(1 + \frac{n}{N}\right) \ln \left(1 + \frac{n}{N}\right) - \frac{N}{2} \left(1 - \frac{n}{N}\right) \ln \left(1 - \frac{n}{N}\right) \right] \\
&= -k_B T \left[c_L - \frac{L}{2b} \left(1 + \frac{x}{L}\right) \ln \left(1 + \frac{x}{L}\right) - \frac{L}{2b} \left(1 - \frac{x}{L}\right) \ln \left(1 - \frac{x}{L}\right) \right], \tag{44}
\end{aligned}$$

where we have made use of Stirling's approximation and c_N (c_L) denotes a part which is independent of n (x). For $x/L \ll 1$ we recover the usual result $F = F_0 + \frac{k_B T x^2}{2Lb}$. For arbitrary extensions, the force is obtained from the free energy in Eq. (44):

$$\begin{aligned}
f &= \frac{\partial F(x, L, T)}{\partial x} = \frac{k_B T}{2b} \ln \frac{\left(1 + \frac{x}{L}\right)}{\left(1 - \frac{x}{L}\right)} \\
\Rightarrow \frac{x}{L} &= \tanh\left(\frac{bf}{k_B T}\right) \tag{45}
\end{aligned}$$

This has the expected behaviours at both small forces when $\frac{x}{L} \approx \frac{bf}{k_B T}$ and large forces for which $x/L \rightarrow 1$. Now we can get this result by working in a *constant force ensemble* instead of a *constant extension ensemble*. Thus let us define the free energy $G = F - fx$. Then

$$\begin{aligned}
dG &= dF - f dx - x df = -s dT - x df \\
\Rightarrow G &= G(f, L, T); \quad x = -\frac{\partial G(f, L, T)}{\partial f}.
\end{aligned}$$

The partition function corresponding to $G(f, L, T)$ is given by

$$Z = \sum e^{-\beta(H-fx)}, \tag{46}$$

where the sum over configurations is now unrestricted, that is we do not fix the end to end distance $x = \sum_{l=1}^N \xi_l$. We will now start using a different notation to describe successive steps $\xi_l = bs_l$, where $s_l = \pm 1$ are like spins. Noting that for the FJC, all configurations have the same energy so that we can set $H = 0$, we get

$$\begin{aligned}
Z &= \sum_{\{s_l\}} e^{\beta fb \sum_{l=1}^N s_l} = [2 \cosh(\beta fb)]^N \\
\Rightarrow G(f, L, T) &= G_0(L, T) - N k_B T \ln \cosh(\beta fb) \\
\Rightarrow x &= -\frac{\partial G}{\partial f} = L \tanh(\beta bf),
\end{aligned}$$

which is the same as we obtained before. But this was much easier!!

Now let us look at the real case, that is, the 3d– FJC model. In this case, unlike the 1–d case, it is too hard to compute $F(R, L, T)$ but finding $G(f, L, T)$ is quite trivial. Since all directions are the same, let us consider that the force f is along the z direction. We will now use the notation $\bar{\xi}_i = b\bar{s}_i$ where \bar{s}_i is a unit 3–dimensional vector. Then proceeding exactly as before we get the following free energy

$$\begin{aligned}
Z &= \sum_{\{\bar{s}_i\}} e^{\beta fb \sum s_i^z} = \sum_{\{\bar{s}_i\}} e^{\beta fb \sum \cos(\theta_i)} & (47) \\
&= \left[\int e^{\beta fb \sum \cos(\theta)} \sin(\theta) d\theta d\phi \right]^N \\
&= (2\pi)^N \left[\frac{(e^{\beta fb} - e^{-\beta fb})}{\beta fb} \right]^N. \\
\Rightarrow G(f, L, T) &= G_0(L, T) - Nk_B T \{ \ln [\sinh(\beta fb)] - \ln(\beta fb) \}.
\end{aligned}$$

This free energy is like that of free spins in a magnetic field (or free dipoles in an electric field). Finally, the extension $z = -\partial G/\partial f$ is obtained as

$$\frac{z}{L} = \coth(\beta fb) - \frac{1}{\beta fb} \quad (48)$$

This is plotted in Fig. (3). We note the following limiting behaviours

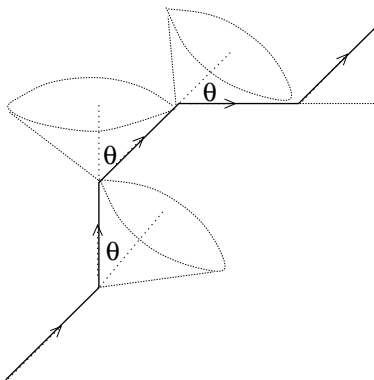
$$\begin{aligned}
\frac{z}{L} &= \frac{bf}{3k_B T} \quad \text{small forces} \\
\frac{z}{L} &= 1 - \frac{k_B T}{bf} \quad \text{large forces.} & (49)
\end{aligned}$$

The small force result is identical to the result we got earlier in the gaussian approximation Eq. (37).

3 The Worm-Like-Chain model

The DNA is a stiff molecule, which means that successive monomers like to point in the same direction. In the FJC model successive steps are independent and the only way the “persistence” of the walk is taken into account is through the effective bond lengths b . The force-extension curves obtained from the FJC model do not explain the experimental data on stretching DNA. We thus need better models to take account of the bending rigidity of DNA. Some such models, which are expected to be equivalent in appropriate limits, are the following:

(1) The Kratky-Porod Freely rotating model: In this model, the angle between successive steps is fixed (say θ). As shown in the figure below a step can occur along any direction on a cone with axis along the previous step and angle θ .



(2) We have earlier described the FJC in terms of noninteracting Heisenberg spins. If we now make nearest-neighbor-spins interact ferromagnetically, then successive spins tend to align and this effectively models persistence.

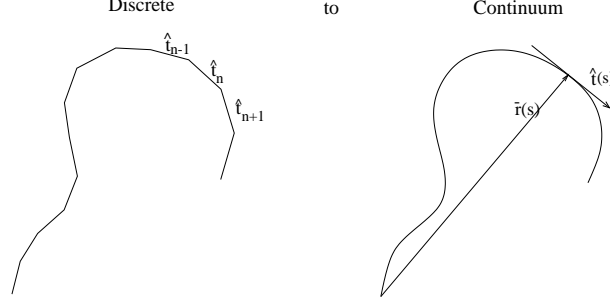
(3) The last two models are discrete models. A continuum description of semiflexible polymers is through the Worm-Like-Chain (WLC) model. In this model one writes an energy for the chain which includes the energy cost of bending or curvature.

For flexible polymers we saw that the free energy had only an entropic part. Here we will see that the free energy has contributions both from entropy and energy.

We will start by describing the WLC model.

3.1 Energy due to curvature

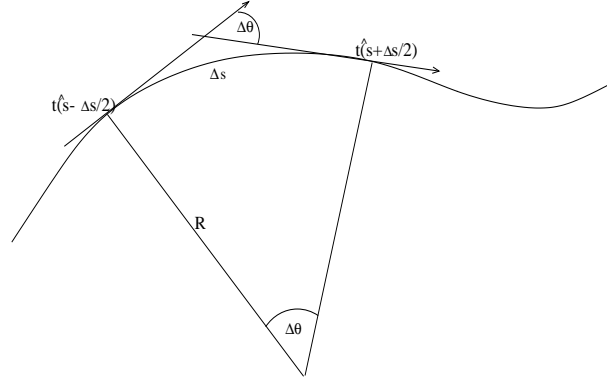
A continuous curve in space can be fully specified by giving the coordinates of every point on the curve. Let s denote the distance of a point from one end of the chain, distance being measured along the polymer’s contour. Then the vector function $\bar{r}(s)$, with s running from 0 to L , completely specifies the curve.



We define the tangent vector at any point s by

$$\hat{t} = \frac{\partial \vec{r}(x)}{\partial s}. \quad (50)$$

Since $d\vec{r}^2 = ds^2$, therefore $\hat{t}^2 = 1$ and so $\hat{t}(s)$ is a unit vector which is tangent to the curve at the point s . Next we define the curvature at any given point.



From figure above we see that curvature $\kappa(s)$ is given by

$$\kappa = \frac{1}{R} = \lim_{\Delta s \rightarrow 0} \frac{\Delta \theta}{\Delta s}. \quad (51)$$

Now

$$\begin{aligned} \cos(\Delta \theta) &= \hat{t}(s - \Delta s/2) \cdot \hat{t}(s + \Delta s/2) \\ &= \left[\hat{t} - \frac{\partial \hat{t}}{\partial s} \frac{\Delta s}{2} + \frac{1}{2} \frac{\partial^2 \hat{t}}{\partial s^2} \left(\frac{\Delta s}{2} \right)^2 \right] \cdot \left[\hat{t} + \frac{\partial \hat{t}}{\partial s} \frac{\Delta s}{2} + \frac{1}{2} \frac{\partial^2 \hat{t}}{\partial s^2} \left(\frac{\Delta s}{2} \right)^2 \right] + O(\Delta s^3) \\ &= 1 - \left(\frac{\partial \hat{t}}{\partial s} \right)^2 \left(\frac{\Delta s}{2} \right)^2 + \left(\hat{t} \cdot \frac{\partial^2 \hat{t}}{\partial s^2} \right) \left(\frac{\Delta s}{2} \right)^2 + O(\Delta s^3). \end{aligned}$$

Now if we differentiate w.r.t s the equation $\hat{t}(s)^2 = 1$, we get $\hat{t} \cdot \partial \hat{t} / \partial s = 0$. Differentiating once more we get $\hat{t} \cdot \partial^2 \hat{t} / \partial s^2 + (\partial \hat{t} / \partial s)^2 = 0$. Using this in the last equation above we get

$$\begin{aligned} 1 - \frac{1}{2} \Delta \theta^2 &= 1 - \frac{1}{2} \left(\frac{\partial \hat{t}}{\partial s} \right)^2 \Delta s^2 \\ \Rightarrow \kappa(s) &= \left| \frac{\Delta \theta}{\Delta s} \right| = \left| \frac{\partial \hat{t}}{\partial s} \right| = \left| \frac{\partial^2 \vec{r}(s)}{\partial s^2} \right|. \end{aligned}$$

The WLC model has a bending energy which is quadratic in the curvature:

$$\begin{aligned} E &= \int_0^L ds \left[\frac{a}{2} \left(\frac{\partial \hat{r}^2(s)}{\partial s^2} \right)^2 \right] - fz(L) \\ &= \int_0^L ds \left[\frac{a}{2} \left(\frac{\partial \hat{t}(s)}{\partial s} \right)^2 - ft_z(s) \right] \end{aligned} \quad (52)$$

The first term is the curvature energy while the second is a Lagrange multiplier which is present since we want to work in a constant force ensemble, instead of one where the end-point $z(L)$ is fixed. The dimension of the rigidity parameter, a , is energy \times length. Note that the energy in Eq. (52) is identical to that of the one-dimensional Heisenberg model in the continuum limit. This connexion is elaborated in App. (A). The free energy we want to compute is the Gibb's free energy $G(f, L, T)$ which corresponds to the following partition function

$$Z = \int D[\hat{t}(s)] e^{-\beta E}, \quad (53)$$

where $D[\hat{t}(s)]$ indicates that we should sum over all possible tangent vector configurations (which is equivalent to summing over all chain configurations with one end fixed). The main problem with evaluating the partition function arises because of the constraint $\hat{t}^2 = 1$. Still it can actually be evaluated exactly, but we shall first compute it in an approximate way in the small and strong force limits.

3.2 Approximate solution in limiting cases

Weak force limit: This case is most easily treated by exploiting the connection with the Heisenberg model. The details are given in Sec. (3.4). The final result is that the response at small forces is identical to the usual gaussian limit Eq. (37) with $b = 2a/(k_B T) = 2A$, where $A = a/(k_B T)$ is the persistence length in the WLC model [see App. (A)].

Strong force limit: In this limit the chain is almost stright so that $t_z \approx 1$ and $t_x, t_y \ll 1$. Hence $t_z = \sqrt{1 - t_x^2 - t_y^2} \approx 1 - (t_x^2 + t_y^2)/2$. Using this to eliminate t_z and keeping terms upto second order in t_x, t_y we get the following simpler energy:

$$E = \int_0^L ds \left\{ \frac{a}{2} \left[\left(\frac{\partial t_x}{\partial s} \right)^2 + \left(\frac{\partial t_y}{\partial s} \right)^2 \right] + \frac{f}{2} [t_x^2 + t_y^2] \right\} - fL. \quad (54)$$

Now t_x, t_y are independent and we shall allow them to vary from $-\infty$ to ∞ (this is ok and consistent since we can verify, at the end, that anyway $\langle t_x^2 \rangle \ll 1$). So now we got to do gaussian integrals only. We first fourier transform the fields

$$\begin{aligned} t_x(s) &= \frac{1}{L} \sum_{n=-\infty}^{\infty} t_x(q) e^{iqs}; \quad t_y(s) = \frac{1}{L} \sum_{n=-\infty}^{\infty} t_y(q) e^{iqs} \\ \text{where } q &= \frac{2\pi n}{L} \end{aligned} \quad (55)$$

so that

$$\begin{aligned} E &= \frac{1}{L} \sum \frac{1}{2} (aq^2 + f) [|t_x(q)|^2 + |t_y(q)|^2] - fL. \\ &= \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{1}{2} (aq^2 + f) [|t_x(q)|^2 + |t_y(q)|^2] - fL. \end{aligned} \quad (56)$$

Since the energy is just like that of a set of independent harmonic oscillators, we get from equipartition of energy

$$\begin{aligned}\frac{1}{2L}(aq^2 + f)\langle |t_x(q)|^2 \rangle &= \frac{k_B T}{2} \\ \Rightarrow \langle |t_x(q)|^2 \rangle &= \langle |t_y(q)|^2 \rangle = \frac{k_B T L}{aq^2 + f}\end{aligned}$$

The extension can now be obtained:

$$\begin{aligned}\langle z \rangle &= \int_0^L ds \langle t_z(s) \rangle = \int_0^L ds \left\{ 1 - \frac{1}{2} [\langle t_x(s)^2 \rangle + \langle t_y(s)^2 \rangle] \right\} \\ &= L - \frac{1}{2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} [\langle |t_x(q)|^2 \rangle + \langle |t_y(q)|^2 \rangle] \\ &= L - \int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{k_B T L}{aq^2 + f} \\ \Rightarrow \frac{\langle z \rangle}{L} &= 1 - \frac{k_B T}{(4fa)^{1/2}} = 1 - \left(\frac{k_B T}{4fA} \right)^{1/2}\end{aligned}\tag{57}$$

Thus in the 2 extreme limits we have:

$$\begin{aligned}\frac{z}{L} &= \frac{2Af}{3k_B T} \quad \text{small forces} \\ \frac{z}{L} &= 1 - \left(\frac{k_B T}{4Af} \right)^{1/2} \quad \text{large forces.}\end{aligned}$$

Compare this with Eq. (49) for the FJC model. A formula which interpolates between the above two extremes is the following:

$$\frac{fA}{k_B T} = \frac{z}{L} + \frac{1}{4(1 - z/L)^2} - \frac{1}{4}.\tag{58}$$

3.3 Exact solution of the WLC model:

We first note that the WLC partition function can be written in the following form:

$$\begin{aligned}Z &= \int D[\hat{t}(s)] e^{-\beta \int_0^L ds \left[\frac{a}{2} \left(\frac{\partial \hat{t}(s)}{\partial s} \right)^2 - f t_z(s) \right]} \\ &= \int d\hat{t}_1 \int d\hat{t}_2 G(\hat{t}_1, s_1 | \hat{t}_2, s_2) \quad \text{where } s_1 = 0, s_2 = L \text{ and} \\ G(\hat{t}_1, s_1 | \hat{t}_2, s_2) &= \int D[\hat{t}(s)] e^{-\int_{(s_1, \hat{t}_1)}^{(s_2, \hat{t}_2)} ds \left[\frac{A}{2} \left(\frac{\partial \hat{t}(s)}{\partial s} \right)^2 - f' t_z(s) \right]}\end{aligned}\tag{59}$$

is the propagator from (s_1, \hat{t}_1) to (s_2, \hat{t}_2) . It can be shown that the propagator $G(\hat{t}, s | \hat{t}', s')$ corresponds to diffusion of a particle on the surface of a unit sphere in the presence of an external potential. Note that s is like time and $\hat{t} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ labels points on the surface of a unit sphere. The diffusion equation satisfied by G is

$$\frac{\partial P(\hat{t}, s)}{\partial s} = \left[\frac{\hat{L}^2}{2A} + f' \cos \theta \right] P(\hat{t}, s) = -\hat{H}P \quad (\text{say})\tag{60}$$

where \hat{L} is the usual angular momentum operator and \hat{H} is the Hamiltonian operator. The initial condition is $P(\hat{t}, s = s') = \delta(\hat{t} - \hat{t}')$. Let $\phi_n(\hat{t})$, ϵ_n denote the eigenfunctions and eigenvalues of \hat{H} , that is $\hat{H}\phi_n(\hat{t}) = \epsilon_n\phi_n(\hat{t})$. Then the solution of Eq. (60) is

$$G(\hat{t}, s | \hat{t}', s') = \sum_n e^{-\epsilon_n(s-s')} \phi_n(\hat{t}) \phi_n^*(\hat{t}') \quad (61)$$

We need to propagate from $s' = 0$ to $s = L$. If L is large then we see that only the ground-state will contribute to the sum in Eq. (61) and denoting $\epsilon_0 = g$ we get

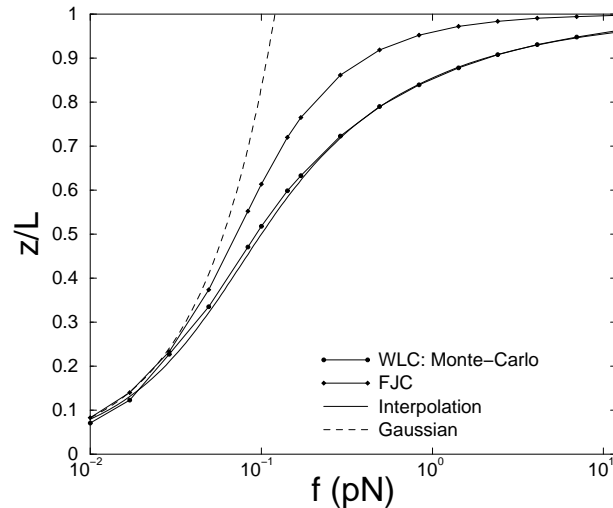
$$\begin{aligned} G(\hat{t}_1, L | \hat{t}_2, 0) &= e^{-gL} \phi_0(\hat{t}_1) \phi_0^*(\hat{t}_2) \\ \Rightarrow Z &= c e^{-gL} \\ G(f, L, T) &= k_B T g L \end{aligned} \quad (62)$$

where c is a factor that is independent of L and so can be dropped off from the free energy in the large L limit. Thus the relative extension of the WLC can be obtained simply from the ground state energy g

$$\frac{z}{L} = -\frac{1}{L} \frac{\partial G(f, L, T)}{\partial f} = -\frac{\partial g(f', T)}{\partial f'} \quad (63)$$

The ground-state $g(f', T)$ cannot be obtained exactly but numerically it can be found very accurately. This then essentially gives us the exact force-extension curve of the WLC model.

In the following figure the force extension curves as given by (i) Gaussian model (ii) FJC model and (iii) WLC chain are shown. For the WLC model we have plotted both the interpolation formula and also the ‘‘exact’’ result, as obtained from Monte-Carlo simulations of the Heisenberg chain. The parameters are $b = 100 \text{ nm}$, $A = 50 \text{ nm}$, $k_B T = 4.0 \text{ pN} \times \text{nm}$.



3.4 Equivalence of the WLC and Heisenberg models

Let us discretize the WLC model by dividing the length L of the chain into N units each of length Δ . Then we get

$$E = \int_0^L ds \left[\frac{a}{2} \left(\frac{\partial \hat{t}(s)}{\partial s} \right)^2 - f t_z(s) \right]$$

$$\begin{aligned}
&= \frac{a}{2} \sum_{l=1}^N \frac{(\hat{t}_l - \hat{t}_{l-1})^2}{\Delta} - f \Delta t_l^z \\
&= \sum_{l=1}^N (-J \hat{t}_l \cdot \hat{t}_{l-1} - f \Delta t_l^z),
\end{aligned}$$

where $J = a/\Delta$ and we have ignored a constant term in the energy. Thus we have now got the Heisenberg model with a nearest neighbor coupling constant J and a constant field, $f\Delta$, in the z direction. The appropriate continuum limit here is $\Delta \rightarrow 0$, $J \rightarrow \infty$ with $J\Delta = a$ finite. We can now obtain various results for the WLC model using the equivalence with the Heisenberg model.

(i) **Persistence length**

Consider the WLC model without any applied force. The correlation, $\langle \hat{t}(s) \cdot \hat{t}(s+r) \rangle$, between tangent vectors at two different points separated by distance r simply becomes the spin-spin correlation of the Heisenberg chain. This is easily obtained:

$$\begin{aligned}
\langle \hat{t}_l \cdot \hat{t}_{l+k} \rangle &= (\cos \theta)^k \\
\text{where } \cos \theta &= \langle \hat{t}_l \cdot \hat{t}_{l+1} \rangle = \coth(\beta J) - \frac{1}{\beta J}
\end{aligned}$$

For large J , successive spins are almost parallel and we get $\cos \theta \approx 1 - \theta^2/2 \approx 1 - \frac{1}{\beta J}$ so that $\theta^2 = \frac{2}{\beta J}$. This then gives

$$\begin{aligned}
\langle \hat{t}(s) \cdot \hat{t}(s+r) \rangle &= e^{-\frac{\theta^2}{2}k} = e^{-\frac{r}{2\Delta/\theta^2}} = e^{-\frac{r}{A}} \quad \text{where} \\
A &= \frac{2\Delta}{\theta^2} = \Delta\beta J = \frac{a}{k_B T}.
\end{aligned} \tag{64}$$

Thus we identify $A = a/(k_B T)$ as the persistence length.

(ii) **Weak force stretching**

For small forces we can find the extension as follows. We note that the extension is simply related to the z -component of the magnetization.

$$\langle z \rangle = \Delta \sum \langle t_l^z \rangle = \Delta \langle M_z \rangle = \Delta \chi(f\Delta), \tag{65}$$

where χ is the zero-field susceptibility given by

$$\chi = \beta(\langle M_z^2 \rangle - \langle M_z \rangle^2) = \frac{\beta}{3} \langle \bar{M}^2 \rangle = \frac{\beta}{3\Delta^2} \langle \bar{R}^2 \rangle \quad \text{since } \langle \bar{M} \rangle = 0.$$

Knowing the spin-spin correlations exactly we can easily find $\langle \bar{M}^2 \rangle$.

$$\begin{aligned}
\langle \bar{M}^2 \rangle &= \langle (\sum_{l=1}^N \hat{t}_l)^2 \rangle = N + 2 \sum_{l < m} \langle \hat{t}_l \cdot \hat{t}_m \rangle \\
&= N + 2 \sum_{l < m} (\cos \theta)^{m-l} = N + 2 \sum_{l=1}^{N-1} (N-l)(\cos \theta)^l \\
&= N \left[\frac{1 + \cos \theta}{1 - \cos \theta} \right] - \frac{2 \cos \theta [1 - (\cos \theta)^N]}{(1 - \cos \theta)^2}.
\end{aligned} \tag{66}$$

For large N , large J we get

$$\begin{aligned}\langle \bar{M}^2 \rangle &= N \left[\frac{1 + \cos \theta}{1 - \cos \theta} \right] \approx N \frac{4}{\theta^2} = 2N\beta J = \frac{2L\beta a}{\Delta^2} \\ \text{so } \chi &= \frac{\beta}{3} \langle \bar{M}^2 \rangle = \frac{2L\beta^2 a}{3\Delta^2}\end{aligned}\tag{67}$$

Thus finally we get

$$\begin{aligned}\langle z \rangle &= \Delta^2 f \chi = \Delta^2 f \frac{2L\beta^2 a}{3\Delta^2} \\ \Rightarrow \frac{\langle z \rangle}{L} &= \frac{2af}{3(k_B T)^2} = \frac{2Af}{3k_B T}.\end{aligned}\tag{68}$$

Problem: Using Eq. (66) show that the size of the WLC is given by

$$\langle \bar{R}^2 \rangle = 2AL - 2A^2[1 - e^{-\frac{L}{A}}]\tag{69}$$

and verify that $\langle \bar{R}^2 \rangle = 2AL$ for $L \gg A$ and $\langle \bar{R}^2 \rangle = L^2$ for $L \ll A$.

A Distribution of end-to-end vector of random walk with steps chosen from any distribution

Let us consider a very general walk where successive steps $\bar{\xi}$ are chosen independently from some probability distribution $p(\bar{\xi})$. After N steps $\bar{R} = \sum_{l=1}^N \bar{\xi}$ and the probability distribution of \bar{R} will be

$$\begin{aligned} P(\bar{R}, N) &= \int d\bar{\xi}_1 d\bar{\xi}_2 \dots d\bar{\xi}_N [p(\bar{\xi}_1) p(\bar{\xi}_2) \dots p(\bar{\xi}_N)] \delta(\bar{R} - \sum_{l=1}^N \bar{\xi}_l) \\ &= \int \prod_{l=1}^N [d\bar{\xi}_l p(\bar{\xi}_l)] \delta(\bar{R} - \sum_{l=1}^N \bar{\xi}_l). \end{aligned} \quad (70)$$

The above formula follows from the fact that the joint probability distribution of any given sequence of steps $(\bar{\xi}_1, \bar{\xi}_2, \dots, \bar{\xi}_N)$ is $\prod_{l=1}^N p(\bar{\xi}_l)$ and we have then summed up over all possible sequences which end up at \bar{R} (the δ -function ensures that). Now using the fact that $\delta(\bar{r}) = \frac{1}{(2\pi)^2} \int d\bar{k} e^{i\bar{k} \cdot \bar{r}}$, we get from Eq. (70)

$$\begin{aligned} P(\bar{R}, N) &= \frac{1}{(2\pi)^3} \int d\bar{k} e^{i\bar{k} \cdot \bar{R}} \int \prod_{l=1}^N d\bar{\xi}_l p(\bar{\xi}_l) e^{-i\bar{k} \cdot \bar{\xi}_l} \\ &= \frac{1}{(2\pi)^3} \int d\bar{k} e^{i\bar{k} \cdot \bar{R}} [\tilde{p}(\bar{k})]^N \quad \text{where} \\ \tilde{p}(\bar{k}) &= \int d\bar{\xi} p(\bar{\xi}) e^{-i\bar{k} \cdot \bar{\xi}} \end{aligned} \quad (71)$$

For the random walk on the cubic lattice we would have $p(\bar{\xi}) = \frac{1}{6}[\delta(\bar{\xi} - b\hat{i}) + \delta(\bar{\xi} + b\hat{i}) + \delta(\bar{\xi} - b\hat{j}) + \delta(\bar{\xi} + b\hat{j}) + \delta(\bar{\xi} - b\hat{k}) + \delta(\bar{\xi} + b\hat{k})]$ so that $\tilde{p}(\bar{k}) = \frac{1}{3}[\cos(k_x) + \cos(k_y) + \cos(k_z)]$. For the FJM, $p(\bar{\xi}) = \frac{1}{4\pi} \delta(\xi - b)$ which leads to $\tilde{p}(\bar{k}) = \frac{\sin(kb)}{kb}$. In both cases we see that $\tilde{p}(\bar{k})$ is maximum at $\bar{k} = 0$ (with $\tilde{p}(\bar{k} = 0) = 1$). For $\bar{k} \neq 0$, $\tilde{p}(\bar{k}) < 1$ and for N very large $[\tilde{p}(\bar{k})]^N$ becomes very small. Thus the only significant contribution to the integral in Eq. (71) comes from very small values of \bar{k} . For small \bar{k} we can expand $\tilde{p}(\bar{k})$ as follows:

$$\begin{aligned} \tilde{p}(\bar{k}) &= \int d\bar{\xi} [1 - i\bar{k} \cdot \bar{\xi} - \frac{1}{2}(\bar{k} \cdot \bar{\xi})^2 + \dots] p(\bar{\xi}) \\ &= 1 - \frac{1}{2} \sum_{l,m} k_l k_m \langle \xi_l \xi_m \rangle + \dots \\ &= 1 - \frac{k^2 b^2}{6} + \dots \quad \text{because } \langle \xi_l \xi_m \rangle = \frac{b^2}{3} \delta_{l,m} \\ &\approx e^{-k^2 b^2 / 6}. \end{aligned} \quad (72)$$

Plugging this back into Eq. (71) we get back Eq. (35). Thus the final distribution of \bar{R} for small $x = R/N$ is independent of the details of the distribution of the elementary steps $\bar{\xi}$.

B structure factor for the Gaussian chain

For the FJM let us assume that the atoms sitting on any link, say $\bar{\xi}_n$, of the chain are localized at \bar{R}_n . Then the density is simply given by $\rho(\bar{r}) = \sum_{l=1}^N \delta(\bar{r} - \bar{R}_l)$ and we get

$$\begin{aligned} g(\bar{q}) &= \frac{1}{N} \sum_{l,m} \langle \delta(\bar{r} - \bar{R}_l) \delta(\bar{r}' - \bar{R}_m) \rangle e^{i\bar{q} \cdot (\bar{r} - \bar{r}')} d(\bar{r} - \bar{r}') \\ &= \frac{1}{N} \sum_{l,m} \langle e^{i\bar{q} \cdot (\bar{R}_l - \bar{R}_m)} \rangle_c, \end{aligned}$$

where $\langle \dots \rangle_c$ indicates average over all polymer configurations with fixed origin. Using the property of a Gaussian distribution $\langle e^{i\bar{q} \cdot \bar{r}} \rangle = e^{-\frac{1}{2} \sum_{\alpha} q_{\alpha}^2 \langle r_{\alpha}^2 \rangle}$ we get

$$g(q) = \frac{1}{N} \sum_{l,m} e^{-\frac{1}{2} \sum_{\alpha} q_{\alpha}^2 \langle (R_l^{\alpha} - R_m^{\alpha})^2 \rangle}. \quad (73)$$

But $\langle (R_l^{\alpha} - R_m^{\alpha})^2 \rangle = |l - m|b^2/3$ (this is just like the result $\langle X^2 \rangle = Nb^2/3$ except that the origin of the walk is shifted to m). Hence we get

$$g(q) = \frac{1}{N} \sum_{l,m} e^{-\frac{1}{6} b^6 q^2 |l-m|}. \quad (74)$$

For large N we can convert this to an integral and get:

$$\begin{aligned} g(q) &= \frac{1}{N} \int_0^N dl \int_0^N dm e^{-\frac{1}{6} b^6 q^2 |l-m|} \\ &= N \int_0^1 dx \int_0^1 dy e^{-\frac{Nb^2 q^2}{6} |x-y|} \\ &= N f\left(\frac{Nb^2 q^2}{6}\right) \quad \text{where} \\ f(x) &= \frac{2}{x^2} (e^{-x} - 1 + x) \end{aligned}$$

For $qR \gg 1$ [same as $q^2 Nb^2 \gg 1$], we get $g(q) \sim \frac{1}{(qb)^2}$ which is the same as what we got from the scaling argument.

Some scales

Consider the DNA of Bacteriophage- λ which is a virus. This has 48502 base pairs.

Length: $L = 48502 \times 0.34 \text{ nm} = 16.6 \text{ }\mu\text{m}$.

Persistence length: $A = 53 \text{ nm}$ [This depends on the ion concentrations in the solvent and the temperature. The value is for a 10 *mM* Na^+ solution at room temperature.]

Root mean square size: $R = (2AL)^{1/2} = 1.3 \text{ }\mu\text{m}$.

Forces: $k_B T = 1/40 \text{ eV} = 4 \times 10^{-21} \text{ J} = 4 \text{ pN} \times \text{nm}$. Therefore

From gaussian model: Force for $0.9L$ extension is $\frac{3k_B T \times 0.9}{2A} = 0.1 \text{ pN}$.

From FJC model, with $b = 2A$: Force for $0.9L$ extension is 0.4 pN .

From WLC model: Force for $0.9L$ extension is 2 pN .

Viscosity of (i) Water: $\eta = 0.01 \text{ gm/cm sec}$, (ii) Air: $\eta = 0.00018 \text{ gm/cm sec}$ and (iii) Glycerine: $\eta = 8.5 \text{ gm/cm sec}$.

Density of (i) Water: $\rho = 1 \text{ gm/cm}^3$, (ii) Air: $\rho = 0.0012 \text{ gm/cm}^3$ and (iii) Glycerine: $\rho = 1.25 \text{ gm/cm}^3$.

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