Introduction to Polymer Physics
Prof. Dr. Prateek Kumar Jha
Department for Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture-05
Random Walk Models of Single Chain II: General Random Walk on a Lattice

In the last class we discussed 2 types of random walk models- The first one was the freely jointed chain model and the next we discussed was the 1 dimensional walk that is the drunkard walk. In both these case we were able to discover the relation for the mean squared end to end distance is proportional to the number of repeating units, It means square end to end displacement are proportional to the number of segments in the case of a freely jointed chain and the number of steps that drunkard takes the drunkard walk. So, the freely jointed chain in the drunkard walk could move in any direction after every segment, the movement of every segment was uncorrelated with respect to other segments in the system. The models give rise to the same scaling law for the mean square end to end distance displacement.

$$\left\langle R_e^2 \right\rangle \propto N$$

$$\left\langle R_e^2 \right\rangle \propto M$$

So, now we take it further and try to do some more models- first some more lattice models that will elaborate on more realistic things as compared to the 1 dimensional walk model. But what we will observe that it will give same result that we obtained earlier. So, this is where we will establish the universality in somewhat more detail.

Let us talk about what is known as a 2 dimensional random walk which is a simple extension of a 1 dimensional random walk, think of again a drunkard who does not know where the last step was, he could have move to the left or right and now he can move like again left or right but now instead of like only moving in 1 dimension he can also move in 2 dimensions that is like left right, up down or something of that sort.

Now let us discuss 2-D random walk model. In 2-D random walk we have a lattice and the walks are happening on a 2-D lattice. It is an arrangement of points known as a 2-D square lattice. Now in terms of steps which are uncorrelated with each other can be either in the x direction or in the y direction. It really means, in the terms of segment vector that we defined earlier can be in any direction as in the freely jointed case and like +b unit vector in x direction- -b unit vector in x direction as in the 1 dimensional walk case. So, now it can be in any of the available 4 directions where ex and ey are the unit vectors in the x and y and b is again my segment length or a step length.

$$\vec{b_m} = \vec{b_{ex}} = -\vec{b_{ex}} = \vec{b_{ey}} = -\vec{b_{ey}}$$

As the assumption we made here, the probability of each of this to happen was equal, there was 2 possibilities. So, p was like half in each, now in this case p will be one fourth in all these cases.

$$\vec{b_m} = \vec{b_{ex}} = -\vec{b_{ex}} = \vec{b_{ey}} = -\vec{b_{ey}}$$

$$p=1/4 \quad \vec{b_{ex}} = -1/4 \quad \vec{b_{ex}} = 1/4 \quad \vec{b_{ey}} = -1/4 \quad \vec{b_{ey}}$$

In the case as well end to end distance vector will again be the sum over the bond vectors where a sum over or the segments capital M is the number of segments or a steps. And then again I can take the average of this and by the same logic you can see that the ensemble average of the bond vectors will again be 0. Because it can be of course be in the x direction but it can be in the opposite direction equal probability, it can of course be in the y direction or it can also be in the – y direction with same probability. So, there will be like cancellation of the 2, **2** vectors.

$$\vec{R_e} = \sum_{m=1}^{M} \vec{b_m}$$

$$\langle \vec{R_e} \rangle = \sum_{m=1}^{M} \langle b_m \rangle = 0$$

This is known as the expectation in mathematics where we multiply every possible value with this probability and add them together. We multiply each of them by $1/4^{th}$ and add them together which will result in a 0, which means the square of this where the same logic what we had earlier can be something like this and again for l not equal to m, this term has to be equal to 0. And for L=m this term has to be b^2 because then we are multiplying the same vector and what essentially means is you have the same result that mean square end to end distance Mb^2 .

$$R_e^2 = \sum_{l=1}^{M} \square \sum_{m=1}^{M} \langle \vec{b_l} \cdot \vec{b_m} \rangle = b^2 = M b^2$$

This is the case of a 2 dimensional square lattice. Similarly the same idea can be apply for a lattice which has 3 dimensions- actually in any dimension we can talk about general types of lattices. For example a 3D lattice will have points in the 3 dimensions x, y and z think of like moving on a cubic grid and now the possibilities will be like instead of being like 4 in the case of a 2D walk. Now the possibilities are actually 6, it can be b unit vector in x direction, -b the same thing b multiplied by unit vector in y direction- of the same thing similarly in the z direction and you can see that we will have the same result..

So, in general we can talk about a walk in z dimensions that would mean that from any particular point on the lattice there are z positions available it can move in any of them. So, you can think of like all possible kinds of walk in this particular way, so if we have a z dimensional random walk we have many of these possibilities. So, in this case will be like at every point I can go in z possible Directions. So, z = 2 for the 1 dimensional walk, z=4 for 2 dimensional walk and is equal to z for a z dimensional walk. Here z means the coordination number. So as to speak how many directions you have at any particular point.

Now we will try to understand why polymer chains are folding back. For example we take the freely jointed chain there is nothing that stops the next bond vector to be in the same direction as the previous or just like opposite of it, right in a fold back onto itself. We will discuss this in 2 ways- first we will do a case where we allow for the folding back and for the folding back not to occur.

So, let us consider a z dimensional walk or a lattice walk where we do not account for the folding back which means that movement is disallowed and let us see like what happens in this case. Because in this case we put now 1 additional restriction on the next segment in the earlier cases all the segments where uncorrelated now we are disallowing the folding back.

So, now if I have say a bond vector b^m, the next bond vector can take all the directions except the one that folds back onto it. So, if we have say z available directions only z-1 are allowed as we do not allow for the folding back and we will look only at the other directions. Let's see like what happens in this particular case. So, now

ai = available directions including the 1 that folds back onto the previous step.

$$\sum_{i=1}^{z} a_i = 0$$

As we account for all that directions then for every direction opposite direction is equally probable. But now we are disallowing the one that is the – bm, so bm+1 can take all the directions same as what I have written as ai except –bm. So, now I can also represent this sum as sum of all the possible values of the bm+1plus the one that I am disallowing okay. So, sum over all possible values of bm+1 which will have z-1 terms and then the one which is disallowed is – bm because a chain cannot fold back into itself. So, now if I look at this particular sum this must be equal to z-1 times the average of bm+1. Because if I multiply the average by the number of possible values I should get this particular sum. That average now is for a given value of bm, because if the bm is changed then expression will also change. so, from this what I can

$$\vec{b_m} = (z-1)\langle \vec{b}_{m+1} \rangle_{\vec{b}_m} = \langle \vec{b}_{m+1} \rangle_{\vec{b}_m} = \frac{\vec{b}_m}{z-1}$$

So, now again we will have Re^2 and it is ensemble average then we will have

$$\langle R_e^2 \rangle = \sum_{m=1}^{M} \square \sum_{l=1}^{M} \langle \vec{b_m} \cdot \vec{b_l} \rangle$$

Unlike earlier where this value was non 0 only when L=m. Now this value will be non 0 even for other cases this is because let us say if try to find b_m.bm+1, now the bm and bm+1 are no longer uncorrelated. Now the bm+1 can take all possible values but the one that folds back into the bm.

$$\langle \vec{b_m} \cdot \vec{b}_{m+1} \rangle = \left\langle \vec{b}_m \cdot \langle \vec{b}_{m+1} \rangle_{b_m} \right\rangle$$

So, ultimately this is the average of the product, so I can move one of the averages inside and that is what we have done here. So, now this will be from the formula

$$\langle \vec{b}_m \cdot \vec{b}_{m+1} \rangle = \left\langle \vec{b}_m \cdot \frac{\vec{b}_m}{z-1} \right\rangle = \frac{b^2}{z-1}$$

Thus it will be no longer 0.

Similarly if I try to find bm.bm+2 I then we get

$$\langle \vec{b_m} \cdot \vec{b}_{m+2} \rangle = \left\langle \vec{b}_m \cdot \langle \vec{b}_{m+2} \rangle_{b_{m+1}} \right\rangle$$

$$¿ \left\langle \vec{b}_m \cdot \frac{\vec{b}_{m+1}}{z-1} \right\rangle = \frac{b^2}{(z-1)^2}$$

So, now we see some kind of correlation between the bond vectors or segment vectors. It is no longer 0 for the cases except m=L. Now it is non 0 for the other cases. What we see here if z is like higher than 2 that is any rather case then in that cases this correlation is decreasing as the distance along the chain is increasing. So, with the adjacent segments it is b square/z-2 segments which are at a distance to a part this b square/z-1 whole square. So, in general we can write:

$$\langle \vec{b}_m \cdot \vec{b}_{m+q} \rangle = \frac{b^2}{(z-1)^q}$$

Let us go back to the formula for Re^2 and see like how things changes. So, now

$$\frac{b^2}{(z-1)^l}$$

¿

$$\langle b_m \cdot b_l \rangle = ¿ \sum_{m=1}^{M} ❑ \sum_{l=1}^{M} ¿$$

$$\langle R_e^2 \rangle = \sum_{m=1}^{M} ❑ \sum_{l=1}^{M} ¿$$

N

Now there are 2 possibilities- Case 1: L is higher than M then,

$$\langle \vec{b}_m \cdot \vec{b}_l \rangle = \frac{b^2}{(z-1)^{l-m}}$$

Where q=l-m

Case 2: M is higher than L

$$\langle \vec{b}_l \cdot \vec{b}_m \rangle = \langle b_l \cdot b_{l+q} \rangle = \frac{b^2}{(z-1)^{m-l}}$$

If L less than m then we can write this as something like bl.bm or bl.bl+q where q now is m-l. So, what do we see here is something like b square/z-1 on the power m-l okay. So, in general what we see here is the power is always positive.

When l is higher than m, I will use l-m when l is less than m I will use m-l. So, I can write in general this thing as where I replace the power by the absolute values of l-m. let us look at like what that sum is equal to.

$$\sum_{m=1}^{M} \frac{b^2}{(z-1)^{¿q \vee ¿}}$$

$$\langle R_e^2 \rangle = \sum_{l=1}^{M} ¿$$

Here q=m – l

So now if we have series then we will make an assumption and the assumption is that both these indices - l and m or l and q in this case are going to like large values of capital M. since this particular term is decreasing with higher powers it is not much of an approximation as we take this sum from – to + infinity because anywhere the higher powers are going to be 0. So now the equation becomes:

$$\langle R_e^2 \rangle = \sum_{l=1}^{M} \sum_{q=-\infty}^{\infty} \frac{b^2}{(z-1)^{|q|}} = b^2 \sum_{l=1}^{M} \left\{ 1 + 2 \sum_{q=1}^{\infty} \frac{1}{(z-1)^q} \right\}$$

The above equation will corresponds to the case when q is equal to 0 when q is equal to 0 then in that case this is equal to 1, this term and when q is equal to a positive number then we have a series from 1 to infinity. If q is a negative number I will have the same series because anywhere the power is absolute value of q.

So, now we can compute a simple geometric series and this will have a value:

$$\langle R_e^2 \rangle = M b^2 \frac{z}{z-2}$$

So, after doing all this kind of a math what exactly we got, we got like an additional factor of z/z-2 which was anyway a constant. Because if I go from say 2D lattice to 3D lattice or any kind of a lattice, ultimately it is just a number so it will be like something multiplied by this. The scaling law is still going to be unchanged as what we have seen that the scaling law that the mean square end to end distance proportional to the number of the steps or the number of segments. It does not change even if we allow for the case when the folding back is not happening.

Now let's look at the physical reason behind this why is that occurring and the reason is if we look at the 2 adjacent segments then these segments actually correspond to carbon chain which have different confirmations. In a polymer model a segment of certain confirmation will have a segment of some other confirmation. So, when the 2 come together then one confirmation will sits back on the other confirmation. It is not that the chain of same confirmation is sitting on the same confirmation because in that case we can think of the electron clouds and everything start

to overlap which is not what is happening here, what is happening is like a segment of a certain confirmation is overlapping with a segment of a different confirmation. This is the reason why the folding back is not so unphysical which means when the same atom sits on the other atom that is of course not possible and that is of course not happening here all we are saying if the chain of carbon of a certain confirmation is overlapping of the chain of carbon of a certain different confirmation.

The other way to defend our argument is why do we care about like what is happening at the molecular level as long as the final answer is what we intent to get is Re^2 proportional to M. It is being validated by the experiments and it is indeed found that many chains to show this behaviour. Thus, this called the ideal chain model.

So, the next class we will talk about a slightly more detailed model that is called a freely rotating chain model and we will establish the same kind of a result. The whole idea is to show universality and how does this toy models work in our in the case of polymer physics. So, we can built I would say a whole ensemble of a different models and all the models will give you the same result. As it is not that the actual representation of model is affecting the result it actually the assumption that we are making in the models in that affect the results. And this is what we will elaborate in the next class.