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

Lecture-04
Random Walk Models of Single Chain I: End to End Distance of a Polymer Chain, Freely Jointed Chain, "Drunkard walk"

In this lecture we will talk about one of the most common toy models used in polymer physics that is called the freely jointed chain and then we will build different types of random walk models.

As we have discussed in the introduction classes that one of the problems we are interested in is the end to end distance of polymer chain. Here we referred this as the R_e and as we know that we don't typically look at a particular confirmation because as we have studied that a polymer chain can take different types of many confirmation. So, we will not look at the R_e of a particular configuration but average R_e of many possible confirmations and try to find out is the mean end to end distance. The mean end to end distance in these models from 0 (we will discuss how) so, we will consider squared mean of the mean end to end distance.

Now there are two ways to find this average. First one is known as the ensemble average- ensemble meaning that it corresponds too many confirmations. So, we take a look at all possible confirmation in principle compute R_e for those confirmations and then take an average of this. In this way we look at the average property. We can find this in a two ways- one way look at one polymer chain in the system with as a function of time. So, this polymer chain will keep on changing it is confirmation. We compute the R_e of the polymer chain as a function of time and then do time average.

The other way to look at the same thing is let say we have a beaker composed of many polymer chains and we will compute the R_e of all the chains in the system and then do what is known as in spatial average.

Therefore, this ensemble average can be do done in two ways time average or an spatial average and one of the principles of thermodynamics or statistical mechanics that becomes very handy here is if we look at very large systems then the time average become equal to spatial average which again becomes equal to the ensemble average. Systems which show this behaviour unknown as ergodic systems and this particular principle is known as ergodicity principle.

Okay, so we will use this idea it will make certain difference in some cases where ergodicity does not apply but in most cases that we care about we don't differentiate between the time average and spatial average we referred to the ensemble average of the any property.

So, going back to the representation of the polymer chain as a random walk let me briefly illustrate of what exactly why exactly the random walk represents model of a polymer chain.

Let us consider a polymer chain which we know is a chain of carbon which are made up of C---C covalent bond so all these covalent bonds are really very strong. So, this carbon-carbon bond distance cannot really change by much between any three of these carbons as we have something known as the bond angle which happens because of the covalent bond. Covalent bond is form by overlapping of electron clouds**.** So the interaction between the electrons clouds on the two bonds that give rise to certain bond angle, this is of course weaker than the bond but it is the still quite strong. So, the bond angle also does not change by a lot. if we look at say the four at adjacent carbon. Then what we have here is what is known as torsion angle between say 1, 2, 3 and 4 and the torsion angle can be relatively weaker then compared to the bond distance or the bond angle and so on. So, if we go further along the chain the interactions will be weaker and weaker and so on. It really means is if we look at this kind of a polymer chain beyond certain number of carbons the position of the carbons distant along the chain becomes somewhat uncorrelated. For example the position of c1 and c2 are very much correlated c2 cannot just be anywhere the position of c2 depends on c1. c1 and c3 has a bond angle so, c3 also cannot be real anywhere it

has to be somewhat correlated to c1. C4 is relatively freer to be anywhere but again it has to be correlated with c1, but if we go alike distant along the chain what will happen is the carbon and carbon far off in the polymer can become highly uncorrelated. It means the interaction between the carbons going along the contour are becoming weaker. After certain distance on the chain these interactions will almost die off and then we can say that these carbons are uncorrelated. In this case we will take the entire distance and referred that as a segments of my model such that we will build the polymer model composed of this kind of segments where each of these segments can really move in an uncorrelated related fashion because this will correspond to certain number of carbons. But beyond after certain distance the carbons have become somewhat uncorrelated and for this reason we can say this as a model of polymer chain known as freely jointed chain model. In this model segments are uncorrelated which means they are connected in the middle like a hinge but then carbons can be pretty much anywhere in the chain.

Let's assume this is a model of freely jointed chain these vectors as some bond vectors. So, let say if the first one I will refer to it like a b1 second one is let say b2 third one is let say b3 and so on. And the last one becomes like bm then bi is what I referred to as a bond vector or segment vector. This by the way is not a carbon- carbon bond. This bond vector represents sequence of carbons after which the positions become uncorrelated.

$$\vec{R}_e = \sum_{n=1}^{m} \vec{b}_n$$

$$\langle \vec{R}_e \rangle = \left\langle \sum_{n=1}^{m} \vec{b}_n \right\rangle = \sum_{n=1}^{m} \langle \vec{b}_n \rangle = \vec{0}$$

And if we follow this then end to end distance between carbons along the carbon chain will become bond vectors. If we look at any particular bond vector and adjacent bond vector and some nth bond vector the next bond vector is free to be in any direction. It can even like folding back onto the previous segment. Now we will see the movement and what does the folding back mean and so on. So, bn+1 is uncorrelated with respect to bn this really means that the bn+l can be at any angle with respect to bn. As we look at the end to end distance vector this is some over.

So, now let us say we have capital M total segments. Then one segment is referred as M. As we can also talk in terms of nodes this is my 1, 2, 3and so on. So, we will come to the m+1 and we have M segments then Re is sum over all these bond vectors simply by the standard vector addition rule. We can sum from and equal to 1, 2 and M bi which will be same as the end to end distance vector.

$$\left\langle R_e^2 \right\rangle = \left\langle \vec{R}_e \cdot \vec{R}_e \right\rangle$$

$$¿ \left\langle \sum_{l=1}^{M} \vec{b}_l \cdot \sum_{m=1}^{M} \vec{b}_m \right\rangle$$

$$¿ \sum_{l=1}^{M} \sum_{m=1}^{M} \vec{b}_l \cdot \vec{b}_m$$

$$¿¿$$

$$¿ \sum_{l=1}^{M} \sum_{m=1}^{M} \left\langle \vec{b}_l \cdot \vec{b}_m \right\rangle = \sum_{l=1}^{M} b^2 = M\, b^2$$

Therefore,

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

Here we have found ensemble average. As we are summing an averaging same as summing over we can write this as the bond vectors. As we look at different- different confirmations we will find that bi has equal probability of being in this direction then being in the opposite direction and that is true for all possible directions. It means that if we take average of these bond vectors then we will get is 0 because the polymer chain can really take any number of confirmation. it is equally probable to have this confirmation. Then the opposite of this where we have the end to end distance vector as like –Re. So, there is no real difference between this confirmation and that confirmation so, if I average over the bond vectors I must get a 0 vector. The R_e^2 will correspond to the dot product of the Re by the same formula.

So, now I am using two different indices the reason why this is important is because if I really take these two sums. We do have like cross terms for example think of like multiplying the sum with itself, of course I will have terms like b0 square b1 square and so on. But I will also have cross terms like b0. b1+bo . b2 and so on. okay. So, to include the cross terms we must be using this particular formula where I am using different indices for that two Re vectors. Okay.

So, now if I do that this becomes by simply rearranging the location of sums and I can do that because the second summation is independent of l bl. So, I can really move the summation, this summation to there. Okay so, again just I said earlier I can move summation outside and do the averaging inside. Okay, and now we have something interesting here that if I look at this bl and bm.I am summing over all possible values of l and m what you will see is if l is not equal to m then of course the bl and bm are uncorrelated so, for any given value of bl bm can be in any direction. For any value of bl bm can be any direction so, what it really means it is equally probable to be along this direction and its opposite equally probable to be along this direction and it is opposite and so on. What this really amounts is if I average over this product this will be equal to

0. On the other hand, if l is equal to m then of course bl and bm are the same vector so, I am multiplying the same vector. So, bl. bm become equal to something like a b square provided we assume all the segments are of a constant length b. So, then we can replace this particular sum by something like b square which is equal to m b square. But it really means is Re square is proportional to m and now since we said that I am replacing certain number of carbons by a segment. If the number of carbons increases the number of segments also increases so, at really it means is just like I can say the mean **r** Re square proportional to m. But it also means is mean Re square is proportional to n where n is the number of repeat units since n/m is some constant.

Here we do not really care how many repeat units are present in a segment, the key measure is the mean squared displacements on the average of unit square displacement is proportional to the number of segments and since we are representing many repeat units by one segment the mean is squared displacement squared averaged so, the also proportional to n which is the ideal chain behaviour.

Now we will discuss something interesting which is like model where we began from the actual chain of carbons and then try to make a physical assumption that beyond certain number of carbons the positions of the carbons become uncorrelated or the segments become uncorrelated and therefore we can represent them as some kind of freely jointed chain.

Let us consider a simpler model which gives you the same final answer. As going back to our discussion of toy models- one way to do a toy model is start from a carbon chain representation try to build toy representation and then find the answer. The other way to look at it is look at like what do you want and try to build toy models which give you the same answer.

We will now focus on the One Dimensional Random walk model which is also referred as the drunkard walk. The idea behind this is very simple, you think of a man who is highly drunk and he has lost his senses and he starts from bar and he is on the way to home. So, let say it if he starts here this is really start from he doesn't know where is home is so, he makes like one step to his left or to it is his right and then after going there he again forgets his previous step. So, again he makes one step to the left or to the right at every given time his steps are either to the left or to the right with almost equal probability provided that he has lost all his senses. He will not remember in what direction he walked in the last step. In that case he perform a walk something again to this provided that his only walking left and right. He makes certain steps to the left then certain to the right and so on. If his home is somewhere far off he may or may not reach his home.

This model has nothing to do with the polymer chain except keeping the main idea that two adjacent steps of the drunkard walk are completely uncorrelated just like what we did in the freely jointed chain. If we want to represent the segment vectors or his step vector then that vector is either to the left or to the right. So, either it is something like +b along the x direction that is my unit vector in x direction or it is say –b in the x direction when he is going to the right and one is going to the left and both of them have equal probability to occurred.

So, now again if he is making capital m steps then the end to end distance that he has travelled is the sum over all these as steps.

if we take average over this and calculate the ensemble average of any particular step it will again be 0. As he can go to the left or to the right with equal to probability so, this must be equal to 0 and so, again the average of the end to end distance vector must be equal to null vector.

if we do a Re squared average then again we can see that if l is not equal to m, bl and bm represent two different segment vectors or step vectors which are completely uncorrelated. So, provided he moved to the left in step number2 in a step number3 or step number5 he could make a move both to the left or to the right with equal probability.

There is no dependence between how he moved in a step with how he will move in any other step right. So, again we can say that this will be 0 again you can say that but the same logic as earlier when l will be equal to m then we are multiplying two vectors which are the same. So, this must be equal to b squared and so, we again have the same result where m now is the number of the steps that he makes in the drunkard walks and again we do see the same relation I had earlier and now this has to do nothing to do with the polymer chain. But now if I somehow associate each of the drunkard step with certain number of carbons for example again we can see that we have the relation Re square proportional to the number of repeat units.

Here we discussed two different kinds of model i.e. one is a freely jointed chain and another one dimensional random walk or a drunkard walk and both gives you the same result that the mean squared end to end distance is proportional to the number of steps and that is what referred as an ideal chain model.

Okay. So, what I will now show you is a this idea is actually more general and this will apply to even models which are more elaborate then what we have discussed so for, for example I can go to two dimensional random walk and then also I will have the same result I can go to more detailed chain models certain to try to model the polymer chain in a better way an again I will get the same result. The key message is for this lecture is that there is universality we can build a class of models that all will give you the same result the same kind of a scaling behaviour the same kind of proportionality relation.

And there will be a class of polymer chains which do so, this behaviour in this has been proved experimentally many chains do so, this kind of an ideal behaviour and this is what I will discuss in the next class.

Okay so, thank you.