Introduction to Polymer Physics
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Lecture-06
Random Walk Models of Single Chain III: Freely Rotating Chain, Definition Persistence Length

In the last couple of classes we have been discussing the random walk models to get the mean squared end to end distance of a polymer chain. So, in the first step of models we discuss the freely jointed chain and the one dimensional random walk or a drunkard walk. then in the last class we looked at slightly more detailed models like two dimensional random walk, where a more general z dimensional random walk and so on, and then finally we looked at the case where we disallow the folding back of a chain onto itself. And then in all the cases so, for we saw that the relationship we get for the mean square end to end distance is physically proportional to the number of repeat units.

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

This relation seems to quite universal in nature as we have done a various types of models. So, now we will extend the idea and try to put the more details into the model and try to make it more realistic, and then come back and established it does not really matter.

The whole idea why the toy models do work in polymer physics because the results, the scaling laws are so simple and it applies for such a variety of cases that many different models give you the same results. The reason why they work is also because it does not really matter how are they building the model what really matters is what assumptions are going to be made in the model. The first we assume that the segments where uncorrelated and then we said that the segments are somewhat correlated in the sense that the chains cannot fold back onto itself i.e. adjacent segments cannot be folding back to itself. We have noticed in the model the correlations of this particular type where q characterises the distance along the contour. Then this particular correlation always decays rapidly as q increases. So, in the first two models the freely jointed chain and one dimensional random walk except for q equal to 0, this particular correlation was equal to 0. even in the other two cases- the first one was the two dimensional random walk again q was equal to 0. Then in that case we had b square after that it was 0. Then for the case when we do not allow for the folding back into the chain then in that case it decayed something like this. So, as z for z higher than 2 this particular expression will always decay. So, now when z = 2 a special case because if we do have one dimensional random walk and if we disallow folding back then we see it becomes like a straight chain.

So, for z= 2 case if we disallow folding back then there is only one confirmation of the chain that goes again as the idea that the chain can take many confirmations. However, this does not happen for z = 3 or a higher whether equal to 4 or higher because in that case even if for a 2d walk when we fold back we can explore in the other direction, and again fold back in the other direction and so on. Therefore it will not be a straight line. So, for z = 2 there is a problem and for z = 4 or 6 and so on, we do not encounter this kind of a difficulty. This really works and now we will try to build a more elaborate model on this particular assumption and try to establish that this is the central idea to the all these models. And that is the reason why do we get these kind of scaling law. This is referred as short range correlation along the contour. Which means when we go along the contour then the distance along contour cannot be like a chain folding back it would self. So, by no means the models we have developed prevent folding back after longer distances. For example let say the two points are meeting at a certain point. The two point which are meeting are very distant along the contour. So, from one point to other we go all the way to come back to the same point the distance along the contour is high and there is like a cross over of polymer chains or segments that is not being considered in all with all these models that is allowed even if we allow for the case where the folding back is not allowed. Let us elaborate on this idea more and then we can talk about like what can happen in the case of a polymer chains.

So, we will develop a more elaborate model or at least seemingly realistic model referred as freely rotating chain. Now we will prevent the next segment to fold back into the previous segment. We also assume that the next segment has to be at angle θ with respect to the previous segment. So, let us say this is my b_{m+1} and this is my b_m then this has to be at an angle θ.

It will form a cone like structure which means it can really rotate around a cone while maintaining this same ϴ. It can many possible values as long as the angle between the two remains the same. now we will try to average over all possible values of b_{m+1} for a given value of b_m, Here we have two component- let say x and y, the movement although this will keep on changing after every segment. So, x and y components will basically cancel because it is equally probable to have bond vector in any direction. The y components cancel in this case but let say if a bond vector is here it is equally probable to have bond vector there. If we look at these two vectors the y components are cancelling but the x components added. What you can see here is:

$$\langle \vec{b}_{m+1} \rangle_{\vec{b}_m} = \vec{b}\cos\theta$$

So, now if we look at again the Re^2 again as we have been doing for all the models. We have something like this happening now this is now again correlated even for the value l not equal to m. And the correlation again will be something like this. So, we can write:

$$\langle R_e^2 \rangle = \sum_{l=1}^{M} \sum_{m=1}^{M} \langle \vec{b}_l \vec{b}_m \rangle$$

Here l > m

$$¿\langle \langle \vec{b}_l \rangle_{\vec{b}_1,\vec{b}_2\dots\vec{b}_{l-1}} \cdot \vec{b}_m \rangle$$

$$¿\langle \langle \vec{b}_l \rangle_{\vec{b}_1,\vec{b}_2\dots\vec{b}_{l-1}} \cos\theta\, \vec{b}_m \rangle$$

$$¿\langle \langle \vec{b}_l \rangle_{\vec{b}_1,\vec{b}_2\dots\vec{b}_{l-1}} \cos\theta^2\, \vec{b}_m \rangle$$

And we can continue doing it until this becomes equal to b_m or we can continue until something like (l-q) = m and at that point we will stop because $b_m.b_m = b_m^2$.

In general what you will have is relation that goes like this something of this sort:

$$\langle \vec{b}_l \cdot \vec{b}_m \rangle = b^2 \cos\theta^{|l-m|}$$

Now as long as the cos θ is not equal to 1 (as for cos θ = 1 we will have like a straight chain) then in that case there is no other confirmation but as we go to like higher powers of cos θ we will have progressively smaller values which means as (l-m) absolute value increase basically $b_l.b_m$ decays.

Now we can do the math again, again we will have some short of infinite series again we make similar assumptions that we have earlier case of the two other of the walk on a lattice without folding back. And then we can again recover relation that will basically be having one extra factor apart from $M_b{}^2$. So, let us try to do that:

$$\langle R_e^2 \rangle = \sum_{l=1}^{M} \sum_{m=1}^{M} \langle \vec{b}_l \vec{b}_m \rangle$$

$$¿ \sum_{l=1}^{M} \sum_{q=1-l}^{M-l} b^2 \cos\theta^{|q|}$$

We can replace this particular sum by q from infinity. And we will have something like:

$$\langle R_e^2 \rangle = \sum_{l=1}^{M} \sum_{q=-\infty}^{\infty} b^2 (\cos\theta)^{|q|□}$$

$$¿ b^2 \sum_{l=1}^{M} \left[1 + 2 \sum_{q=1}^{\infty} \cos\theta^q \right]$$

θ
θ
$1-\cos¿$
¿
$1+\cos¿/(¿¿)$
¿
$¿Mb^2¿$

Let us like try to sum up all these cases that we have discuss. what we have seen is Re^2 first of all is always proportional to M that really means Re^2 proportional to the number of repeat units provided that every segment or a step correspond to certain number of repeat units. The other thing we have seen if we look at the actual relation. We can write in this particular way because keep in mind what exactly was b, b was the parameter of the model. We did not take b from any kind of a polymer property so for right b is like a model dependent parameter. So, how much difference it make if I replace for example this entire quantity by some kind of a b effective square right. It is any way like a model parameter that is a model parameter for a toy model we are developing. So, then this will actually be the relation that we have got for all the models:

One dimensional model, two dimensional model, free jointed chain model and 2-D random walk model. We have:

$$\langle R_e^2 \rangle = M b^2$$

For freely rotating chain model we have:

θ
θ
$1-\cos¿$
¿
$1+\cos¿/¿$
¿
$\langle R_e^2 \rangle = Mb\sqrt{¿}$

And for 2-D random walk with folding we have:

$$\langle R_e^2 \rangle = Mb\sqrt{\frac{z}{z-2}}$$

Now let us try to see like what exactly b and M means, of course it is an effective parameter. Ultimately the number of segments we are choosing to represent the polymer chain is something that is property of the toy model as this is not a property of the polymer chain. So, let us start looking at what does b and m represent and how can we use that to represent different kinds of polymeric systems. So, let us try to look at the significance of this is small b and capital M.

This small b is often referred as the Kuhn length. If I take a small b as the Kuhn length then M is something like the number of Kuhn segments. The Kuhn length is by the way theoretical construct. It is by scientist name Kuhn.

We can associate certain kind of meaning to it by comparing 2 cases where I represent a polymer chain by fewer Kuhn segments and another case may present a polymer chains with more Kuhn segments. So, let us say if we have a polymer chain and in one case we take the Kuhn length to be rather high, in another case we take the Kuhn length to be somewhat smaller. In the first case-1 we use fewer segments to represent the polymer chains and in the second case-2 we use more segments to represent polymer chains. If you remember as we increase the number of segments we will have more possible confirmations so, case 1 will give rise to lesser number of confirmation than case-2. The number of confirmation basically is will get to the entropy of the polymer chain and in turn it is related to flexibility. So, what this means is this will be less flexible, so case 1 is lesser flexible than 2.

So, now what does not mean, so let us say if we have 2 polymer chains one of them is stiffer compared to the other, you can think about an extreme when we use only one segment to model the polymer chains in the case where the Kuhn length is taken equal to the contour length where contour length is the entire length of the polymer chain this is my contour length. So, if we take like very large value what I get is like a rod. On the other hand if we think of another extreme where Kuhn length to be like extremely small, Then the polymer chain will be having many

Kuhn segments. The reason why we are saying that this will have more flexibility is also because every Kuhn segments is uncorrelated. So, if I have more segments then the next segment is uncorrelated and so on. So, we have the correlation at sorted distances along the chain and that is why we are saying that it will much more flexible.

There is something called the persistence length which happens to be like half of the Kuhn length. In certain polymer theories like the freely jointed case we have discussed and this is an often use parameter to characterise the stiffness of the polymer chain. So, if molecule has a higher stiffness it will have a higher value of persistence length we also refer to as $l_{p.}$ If it is has a lesser persistence length that means the polymer chain is more flexible.

So, for same toy model we can associate different kinds of polymer flexibility by simply tweaking 2 model parameter this M and b i.e the number of Kuhn segments and the Kuhn length and by this way we can study polymers of different flexibility.

So, now just to complete the exercise if I want to look at the whole length of my fully stressed chain, if the chain become like fully stressed which is a very less likely confirmation. But it is indeed possible because the chain can take many confirmation, there can be case where the chain is fully stressed. So, in that case the length of the polymer chain become equal to M multiplied by b and this is what we refer to as a contour length. So, think of a small row that is like this and then you think of like stretching like this, so this forms the case when it is fully stretched that length is what is contour length. Other way to think about it if I measure the distance along the row that will give rise to the contour length of polymer chain.

I will stop with this thank you.