Introduction to Polymer Physics

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Lecture-07
Models of Semi flexible Chains (Kratky Porod Model)
Part I

In the last lecture, we discussed random walk models for polymer chains and the main assumption that we made was the interactions along the contour, or the correlations along the contour decay with the distance along the contour. Based on that, we discussed a variety of models starting from the freely jointed chain, where the segments were moving in an uncorrelated way, and then we discussed one dimensional random walk also referred as the drunkard walk, then we discussed the random walk on a lattice that was like a 2D lattice to begin with and then we generalised to the case when it can be any lattice where the number of possible paths are like z.

We also studied the case where these models do allow for the chains to folding back to itself, in that case if we allow for the folding back and that we studied for the case of z dimensional random walk and we found that we still get the same scaling law i.e. The mean square end to end distance is going like the number of repeat units or the mean square end to end distance going like the number of steps or segments in random walk.

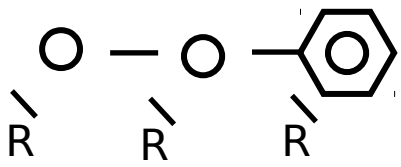
Finally we studied the constants in the equations which are associated by something known as the Kuhn length (b) and number of Kuhn segments (M). If we decrease the b or increase the M what essentially we have a chain that is more flexible and opposite of that is if we have the higher value of the Kuhn length and lesser value of the number of segments, this is less flexible or we can say this one to be more stiff and the other one to be less stiff. This is an idea typically applied to flexible polymers with variable stiffness. There is a better model for the chains that are

not really flexible. There are a class of models for semi flexible polymers, which are not really as flexible as they have certain stiffness, known as the wormlike chain (Kratky-Porod model).

Let's look at what kind of chemistries will give rise to stiffness in polymers. So, far we have not really alluded to any kind of chemistry, what we said was many polymer chains show a generic or universal behaviour that can be given by the model that we referred as an ideal chain. But the idea behind it was that if we look at the backbone of polymer chain then it consist of carbons which have a bond between them, 3 carbons adjacent will have an angle between them. But, then there are rotations around the carbon-carbon bond, which give rise to some kind of a torsion like movement and that give rise to many confirmations of polymer chains.

So, chains which are stiff have certain chemistries, which prevent the rotations to happen between them with an ease that we are discussing in all through. It can happen for example in 3 or 4 cases, the first one is when there is some kind of a delocalisation of valance electrons, let us discuss what happens in that case.

So, let us say if we have a polymer chain that contains benzene rings in place of usual carbon backbone and let us say we can have also possibility of having some functional groups on the benzene ring. Then as you can expect from the chemistry of benzene that the electrons or the valance electrons here are delocalised, which is also referred as the conjugation of pi electron, and in that case it turns out that the chains are relatively stiffer.



This can also happen if there is hydrogen bonding between chain segments, for example- DNA which is not a polymer but it does contain certain repeating units, so what really happens in this case is we have some sort of hydrogen bonding between the 2 strands that give rise to what we

known as the double helix structure, and these strands are now locked in place due to hydrogen bonding.

There is one more case when this can happen, that is, if you have a strongly charged polyelectrolyte, for example, the polystyrene sulfonate- in that case what happens is we have like a polymer chain which have many charged groups present along the chain and they do have some kind of coulomb repulsion, and if you have segments of chain which have like Coulomb repulsion between them they tend to more streched, or they tend to have higher correlation then compared to what we discussed for flexible polymer chain.

There is one other case when that happens i.e. when you have a bulky side group present on the polymer chain. For example if we have something like a large side group C_6H_{13} present as a side group then because of that we do not have easy rotations around the backbone.

So, in these kinds of chemistries (discussed above) and may be some other chemistries, we have to think beyond the flexible chain model. We have some inherent stiffness at least for certain distances along the contour. So, for these kind of scenarios will develop what is known as a worm like chain or Kratky-Porod model.

The worm like chain or the Kratky-Porod model builds on an earlier model that we have described as the freely rotating chain with one small change. So, in the freely rotating chain the 2 conjugative segments are at an angle theta with each other. The next segment will again be has certain angle theta and so on , so now you think of like what really happens when theta becomes very small. In that case our chain will look something like this which is stiffer then compare to the case when theta was large. So, if I take a limit of the freely rotating chain model for the case of a small theta what do us get is a worm like chain model which means:

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

In this equation we will take the limit theta going to 0, and as we can see θ is going 0 which means the cos θ is going to 1 and unlike the case when theta was a larger number in that case the cos θ is much smaller than 1 and so we have a decaying correlation as |n-m| increases, in this case the correlation decay less rapidly with increase in |n-m|.

So, we will discuss one other idea, the idea is that we can represent the chain like a line as we have been doing in many cases and we take the distance along the contour known as the contour length. So, we can discuss the chain in terms of a contour variable as that is going from 0 to sum value L_c where L_c is my contour length, so we gave the analogy with the rope and a rope is like in a folded state. Then as we move along the contour of the rope and the distance we measure is the contour length. The other way to think about it is if we stretch the rope the length that we see is my contour length. If we stretch this we will have is the straight line of a length L_c.

If we look at the polymer chain then we don't really have a segments as in the case of the freely jointed chain. If we set for example b going to 0, then what we will have is something that really follows the contour of the polymer chain. As we look at b going to 0, as in the earlier cases if we use a representation like that for a freely jointed chain then we have a bond vectors b1, b2 and so on and we set that the length of this vector is 0 then we can see the tangents will give you the bond vector. So, when b is going to 0 the bond vector is the tangent. the other way to say that is we can represent the chain where we have variable s going from 0 to $s=L_c$, at any position on the chain r is a vector as and if we draw a tangent there then u of s that will be the limiting value of the bond vector when b is going to 0. So, we can write as:

$$\vec{u}(s)=\frac{d\vec{r}(s)}{ds}=\vec{b}(s)=b=0$$

This is the idea will use in the case of a Kratky –porod model. So, now let us look at this in more details. Earlier we had something like this:

$$\langle \vec{b}_n \cdot \vec{b}_m \rangle = b^2 (cos\theta)^{|n-m|}$$

And now we are representing the polymer chain as a line going from contour variable s=0 to s=Lc. Then we can think of the 2 points along the contour n and m and the contour length between these 2 points become my L and so I can write:

$$|n-m| = \frac{l}{b}$$

$$\langle \vec{b}_n \cdot \vec{b}_m \rangle = b^2 (cos\theta)^{\frac{l}{b}}$$

Now we since θ is going to 0 we can think of this function cos theta in terms of it is Taylor series. So, now we will write the Taylor series. Here it is:

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2} f''(x) + \ldots$$

X=0 , h= θ

$$cos\theta = \cos 0 + \theta(-\sin 0) + \frac{\theta^2}{2}(-\cos 0) + \ldots \approx 1 - \frac{\theta^2}{2}$$

So, keep in mind that we can only do this when θ is a small, when it's larger then we cannot do a tailor expansion as this will only work when the theta value is small.

So now, we will use one other formula that works for the case when b is going to 0 and that is the limit of p we can write this as-

$$\langle \vec{b}_n \cdot \vec{b}_m \rangle \approx b^2 \left[\lim_{\frac{1}{b} \to \infty} \left(1 - \frac{\frac{\theta^2}{2b}}{\frac{1}{b}} \right)^{\frac{1}{b}} \right]^l \approx b^2 \exp\left(\frac{-l\theta^2}{2b} \right)$$

So now we can write the 2b/theta square to be some quantity that I will define as l_p which is called as persistent length. Now if we look at it b is very small θ but l_p happens to be finite as we are dividing 2 numbers which very small. So, this is a finite quantity is the persistent length and it is like half of the Kuhn length. So, now I can write the equation we have derived in terms of the persistent length.

$$\frac{2b}{\theta^2} = l_p = persistent\, length$$

$$\langle \vec{b}_n \cdot \vec{b}_m \rangle = b^2 \exp\left(\frac{-l}{L_p} \right)$$

Now since we represent the bond vector by the tangent in the limit of b going to 0 what essentially it implies is we can divide this by b square here and these becomes my tangents at those points at n and m. So, the tangents here will be given by bn/b, bm/b both for the limiting cases of b going to 0. It can be written as:

$$\left\langle \frac{\vec{b}_n}{b} \cdot \frac{\vec{b}_m}{b} \right\rangle = \exp\left(\frac{-l}{L_p} \right)$$

Finally we can write this expression as:

$$\langle \vec{u}(s)\cdot\vec{u}(s')\rangle = \exp\left(\frac{-|s-s'|}{L_p}\right)$$

Here l is the distance along the contour and the variable s is to define the contour. So, s is going from 0 to Lc, so between n and m if I find the s values take it is difference we will get smaller than l.

So, this is a relation that now we can use to find the end to end distance of the polymer chain in the terms of R_e.

$$\vec{R}_e = \vec{r}(L_c) - \vec{r}(0)$$

$$\int_{s=0}^{L_c} \frac{d\vec{r}(s)}{ds} ds = \int_{s=0}^{L_c} \vec{u}(s)\, ds$$

So now when we do the Re^2 averaged we will have something of this sort-

$$\langle R_e^2\rangle = \left\langle \int_{s=0}^{L_c} \vec{u}(s)ds \cdot \int_{s'=0}^{L_c} \vec{u}(s')ds' \right\rangle = \int_{s=0}^{L_c} ds \int_{s'=0}^{L_c} ds'$$

We have used different variables s and s' just to recall from the previous discussion as we used different indices for the 2 terms and the reason was to include the cross terms is here we want to include the cross term.

Now we will find the mean square displacement from the above equation:

$$\langle R_e^2\rangle = \int_{s=0}^{L_c} ds \int_{s'=0}^{L_c} ds' \langle \vec{u}(s)\vec{u}(s')\rangle$$

$$¿ \int_{s=0}^{L_c} ds \int_{s'=0}^{L_c} ds' \exp\left(\frac{-|s-s'|}{L_p}\right)$$

So, now I have, so this integral we can do in 2 parts. So, for s less than s' this is going to be

$$\int_{s=0}^{L_c} ds \int_{s'=0}^{L_c} ds' \exp\left(\frac{|s'-s|}{L_p}\right) + \int_{s=0}^{L_c} ds \int_{s'=0}^{s} ds' \exp\left(\frac{-s-s'}{L_p}\right)$$

$$¿ 2 \int_{s=0}^{L_c} d_s \int_{s'=0}^{s} ds' \exp\left(\frac{-s-s'}{L_p}\right)$$

For s higher than s' we are going to have-

$$\left\langle R_e^2 \right\rangle = 2 \int_0^{L_c} ds\, e^{\frac{-s}{L_p}} \int_0^{s} ds'\, e^{\frac{s'}{L_p}} \left[\frac{e^{\frac{s'}{L_p}}}{\frac{1}{L_p}}\right]$$

$$¿ 2 L_p \int_0^{L_c} ds\, e^{\frac{-s}{L_p}} \left[e^{\frac{s}{L_p}} - 1\right]$$

$$¿ 2 L_p \int_0^{L_c} ds \left[1 - e^{\frac{-s}{L_p}}\right]$$

$$¿ 2 L_p \left[L_c - \frac{e^{\frac{-s}{L_p}}}{\frac{-1}{L_p}}\Bigg|_0^{L_c}\right]$$

$$¿ 2L_p\left[L_c + L_p\left(e^{\frac{-L_c}{L_p}} - 1\right)\right]$$

$$\left\langle R_e^2 \right\rangle = 2L_p^2\left[\frac{L_c}{L_p} + e^{\frac{-L_c}{L_p}} - 1\right]$$

There are 2 variables in this problem L_c = contour length and L_p = persistence length,
Using this expression in the next class we will describe how we can look at the limits of a stiff chain and show that in one limit it becomes rod like chain, in other limit we have got flexible chain.

So thank you.