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

Lecture-08
Models of Semi flexible Chains (Kratky Porod Model)
Part II

In the last class, we discussed the mean square displacement relations for another stiff chain model, which we called as the worm like chain or the Kratky Porod model. So, we have a polymer chain, and we define a contour variable s that goes from 0 to L_c,, where L_c is contour length and we found the end to end displacement vector R_e, R_e can be written in terms of the position vector R which is a function of s along the contour. So, we can write as:

$$\langle R_e \rangle = \vec{r}(L_c) - \vec{r}(0)$$

If we take a limit b going to 0, then we can talk of segment vectors or bond vectors as the tangent to this particular graph and based on that what we derived was the mean squared end to end distance. We can write this as:

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

Here, L_c = Contour Length and L_p = Persistent length (characterizes the stiffness of the polymer chain).

So, now what we will do we will take 2 extremes, one in which the persistent length L_p is very high and another case when this L_p is very small. So, just to recall briefly the correlation of the tangent vector went like this:

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

So, in this case the magnitude of L_p characterises the amount of correlation that we have in the system.

Now we will take a limit when we have L_p is much higher than L_c which means my persistence length is much higher than the contour length, and in that case L_c/L_p become very small, i.e.,

$$\frac{L_c}{L_p} \ll 1$$

So, we can do a Taylor expansion of the exponential term here, because the argument of the exponential is very small number. Hence we can write:

That is, using Taylor series formula

$$e^{-x} = 1 - x + \frac{x^2}{2} - \frac{x^3}{6} \dots$$

We can write the Taylor expansion as:

$$e^{\frac{-L_c}{L_p}} = 1 - \frac{L_c}{L_p} + \frac{L_c^2}{2L_p^2} - \frac{L_c^3}{6L_p^3}$$

So, if we put this expression in the previous expression (*) what we do get is:

$$\langle R_e^2 \rangle \approx 2L_p^2\left[\frac{L_c}{L_p} - 1 + 1 - \frac{L_c}{L_p} + \frac{L_c^2}{2L_p^2} - \frac{L_c^3}{6L_p^3}\right]$$

After cancellation, we finally get:

$$\langle R_e^2 \rangle \approx L_c^2 \left[1 - \frac{L_c}{3 L_p} + \ldots \right]$$

If L$_c$ by L$_p$ is really very small, that is, when we can say say persistence length is almost like infinity $L_p \to \infty$

then second term also drops down and what we do get is:

$$\langle R_e^2 \rangle \approx L_c^2$$

It essentially means that end to end distance become equal to the contour length and the chain is actually like a rod because only in that case the contour length will be same as the end to end distance. This is referred as the “rod like limit” which is obtained when L$_p$ is much higher than L$_c$.

Now look at the opposite extreme when the L$_p$ is very small and let us see like what happens in that case. So, again we will reproduce the formula (*) here:

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

In the earlier case, we looked at when L$_p$ is much higher than L$_c$, now we look at when L$_p$ is much lesser than L$_c$. So, that means L$_c$/L$_p$ is much higher than 1, so in this case we can really drop the exponential term because the power to the exponential is a negative number and that is very high. So we can write (*) as:

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

Now, try to recall the relationship that we derived for a flexible chain. What we had was:

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

When we take the limit $b \to 0$ we have:

$$L_c = Nb \left(for\ flexible\ chains \right)$$

Comparing we have,

$$b = 2 L_p \vee L_p = \frac{1}{2} b$$

which is something that we discussed earlier that the persistent length must be equal to half of the Kuhn length. So, in this particular limit we can say the chain is flexible.

We have already discussed the couple of cases where the chain has to be stiff: (1) delocalisation of valance electrons , (2) a bulky side group , (3) strong polyelectrolyte where there is coulomb repulsion between the segments of chain, (4) hydrogen bonding between segments like the case of the DNA molecule. But otherwise also, if we look at a particular polymer chemistry and if we look at say small chains containing lesser number of carbons then they have to be stiffer as compare to the chain containing more number of carbons. This is because we will require more segments to represent the chain or the number of confirmations will increase. In the beginning, we have discussed the number of confirmations are equal to 3^m, where m is the number of repeat units. So, using that idea what we can think that smaller chains containing fewer carbons or oligomers will be always more stiff compare to larger chains or the actual polymers.

So, in more systems for the same polymer chemistry if we change the number of repeat units and we look at Re^2, what you will get is in the very beginning (small N), $R_e^2 \sim N^2$. The mean squared end-to-end distance is going like L_c^2 and as L_c is increasing N is also increasing, so my R_e^2 will go like N^2. But after that we recover the behaviour $R_e^2 \sim N$ for longer chains. This has been observed in many polymer chemistries that for smaller values of N, we do see rod like behaviour and then transitions to a flexible behaviour for longer chains and Kratky Porod model is very helpful to look at how the transition takes place.

In an experiment you do some kind of scattering and get the mean size of the chain and from there you want to calculate the end to end distance. The quantity to measure is not the end to end distance but what is known as the radius of gyration, that is one way of doing it, the other way of doing it is we try to do some kind of a simulation that incorporates the detailed chemistry into it. The one thing that is becoming more used in the polymer literature is what is known atomistic simulations, where we can represent the polymer chain not by a toy model but by the complete chemistry that incorporate that means we will represent the polymer chain as composed of all its atoms. The limitation though is that these simulations will not work if the number of carbons become high (realistic polymers), just because the system size become huge. Think of it like as we are not looking the polymer chain in isolation, the polymer chain must be in a solvent and in that case we also need to model the solvents which are present around it, and it turns out that by the current computational resources we can only model like chains of say 20 or 30 or 50 carbons, not beyond it.

So, in the regime where the chain is rod like or going towards flexible behaviour, so in this particular regime when R_e^2 is going like N^2. In that particular regime, we can also do atomistic simulations but it will not work for large N. If we work with like toy models, we are capturing the entire regime but that is still remains to be a toy model. So what we can do is we can validate or find out some of the parameters of Kratky Porod model also by using the simulations, if we are able to get this particular cross over where the chain goes from rod like regime to a flexible regime and this remains we would say a challenge in the polymer simulations but it is now possible for certain polymer chemistries.

The other point here is apart from the polymer chemistry what also is important is the environment of the polymer chain. So, a polymer chain can have different mean square end to end distance if we put the same chain in different solvents. So, the amount of stretching or the amount of a swelling of a polymer chain would depend on what solvent it is present in, whether it is favourable to the polymer, whether the polymer dissolves in that solvent, whether the polymer likes that solvent, whether the polymer hates that solvent, and that is one factor that one has to consider.

The other factor is the effect of temperature. So, the same polymer chain can show different behaviour at different temperatures, so it can be for example more stretched at a certain temperature and if I go to for example higher temperature it can become collapsed or vice versa.

These effects are some things that we have not so far considered in the toy model and for this reason we are limited to the scaling behaviours that are either in the ideal chain limit or in the rod like limit. In later classes, I will tell you when we deviates from this particular scaling laws and how to address that in the models that we have discussed.

So, the other thing I want to remind you is so far we only looked at the short range correlations along the contour but there can also be long range correlations. There is something called an excluded volume interaction that comes into play when 2 segments of polymer chain, irrespective of their distance along the contour come together and it turns out that these interactions depend on the solvent and the temperature, and if we try to include them into the model we will have deviations from ideal chain behaviour. This has been observed experimentally as well for many polymer cases and we will discuss that in the coming lectures.

So, with that, I stop here thank you.