Introduction to Polymer Physics

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Lecture-14

Radius of Gyration for an Ideal Chain, Concept of Ideality

In the last class we have discussed about a measure of the size of a polymer chain different from the end to end distance and the measure was the radius of gyration. So, in the today's class I will take it further and first derive the expression for the (R_g) gyration radius for an ideal chain that we have discussed and then we will talk briefly about the idea of excluded volume in that I will elaborate the following lectures.

So, let us first do a recap of like what we had covered earlier, so I said that if we have like a polymer chain the end to end distance does not reflect the fact that the polymer occupies how much volume in space. So, a better measure is something of this sort where what is said is that we look at an equivalent sphere that has the same volume as that occupied by the polymer chain and then we looked at different formulas for this quantity R_g, R_g^2 to be more specific again we are interested in the mean square average this was what we derived was something of this type-

$$\langle R_g^2 \rangle = \frac{1}{M^2} \sum_{i=1}^{M} \sum_{j=1}^{M} \langle \vec{r}_i - \vec{r}_{cm} \rangle^2$$

$$\vec{r}_{cm} = \frac{1}{M} \sum_{j=1}^{M} \vec{r}_j$$

Here the centre of mass location r_{cm} is defined as the summing over the positions of individual segments or beads or the actual point locations inside the polymer chain.

We can defined R_g^2 for any polymer model depending on how I am defining my units the i's will change, let us say for a bead spring model the i's can represent the position of the beads, for the freely jointed chain model it can be the mean positions of segments since the number of segments are large or the number of beads are large how exactly we are defining those particular points is not very important. In reality, in experimental case we should think of it as every point on the polymer chain and we should do an average and we get the R_g^2 and if it not really matter so much on what model we are doing, how many segments we are modelling provided the number of segments are large.

Now I want to look at how the above expression will change for an ideal chain, so of course the expression we have derived remain the same but we can do further simplifications if it assume an ideal chain. So, let us assume an idea chain, an ideal chain is the one that follows the Gaussian statistics in the models of the chains.

When we go from a discrete to a continuous representation of a chain and the idea was let us say you have a felt say freely jointed chain model and the chain and it has large number of segments as a continuous chain. So, of course if the number of segments are small there will be larger error. But if the number of segments are large the approximations becomes I would say more just and in any case the polymer chain in reality is always in continuation, it is not like a discrete kind of a thing. And so what we said is then we can talk about a contour variable, in place of talking about M segments, I can say we have a contour variable s that runs from say s=0 to s=M and for that particular assumption of a contour what we can then do is we can replace the summations over the indices i and j by integrals over the contour variable.

$$\sum_{i=1}^{M} \rightarrow \int_{0}^{M} ds$$

$$\sum_{j=1}^{M} \rightarrow \int_{i}^{M} ds'$$

If I now use these 2 relations in the earlier formula that we have derived what I will get is-

$$\langle R_g^2 \rangle = \frac{1}{M^2} \int_{0}^{s} \int_{s}^{M} \langle \vec{r}(s) - \vec{r}(s') \rangle ds' ds$$

For the ideal chain and that we have already discussed earlier we know that R_e^2 the end to end distance square is proportional to the number of segments and so if I cut my chain in here. Let us say if I look at the section of the polymer chain between s and s prime that itself is also Gaussian. So we can write as-

$$\langle \vec{r}(s)-\vec{r}(s')\rangle=(s-s')b^2, where\, b \rightarrow 0$$

Because between s to s prime the number of segments has to proportional to s-s prime multiplied by a factor that we anyway assume to be small because we are going from a discrete to a continuous presentation. Now we can write the whole equation as:

$$\langle R_g^2\rangle=\frac{b^2}{M^2}\int_0^M\int_s^M (s-s')\,ds'\,ds$$

So, now there is small detail here that depending on how I am defining s and s' If s is higher than s' then we have to look at the quantity s- s' because that is a positive number, if s' is however higher than s we have to look at s'- s we are essentially looking at this particular quantity and since we are doing s' from s to M. The s' is assume to be higher than s because for the s variable I am going from 0 to M and for the s' variable I am going from s to M. okay, so in that case this is really s'-s.

So, now to do the integration I will define a new variable let us call this s'' this is equal to s'-s and then if I do a ds'' = ds'. We get finally-

$$\langle R_g^2\rangle=\frac{b^2}{M^2}\int_0^M\int_0^{M-S} s''\,ds''\,ds=\frac{b^2}{2M^2}\int_0^M (M-s)^2\,ds$$

I can apply the same idea again I can think of a new dummy variable that is let us say s'''

$$s'''=M-s\wedge ds'''=-ds$$

So, now we have

$$¿-\frac{b^2}{2M^2}\int_M^0 s'''^2\,ds'''=\frac{b^2}{2M^2}\int_0^M s'''^2\,ds'''=\frac{b^2}{2M^2}\cdot\frac{M^3}{3}=\frac{Mb^2}{6}=\frac{\langle R_e^2\rangle}{6}$$

So what we have derived is for an ideal chain is-

$$\langle R_g^2 \rangle = \frac{\langle R_e^2 \rangle}{6} = \frac{M b^2}{6}$$

So, now there may be a bit of a confusion here because we said that I want to define a new kind of an average and the new average will look at the volume occupied by the chain in place of the end to end distance. Then what we figured out is actually what we get is the mean square of this quantity is anyway is mean square of the end to end distance divided by 6. So, both are essentially related but this may not be possible if I think of other kind of chain models and that is where this quantity become useful that is one thing to make here.

The other thing to make out from here is we are not saying that the end to end distance of the chain in a particular configuration. So, in a given configuration this can be R_e and R_g can be very much different but if I take an ensemble average over them over the squared value of both of them then they are related. So, there can be cases where end to end distance is small for a particular configuration for other configuration of confirmation it can be very different. But if I take a mean square averaged then the number I will get is related to the mean square average of the R_g as well So, they are related only in the sense of the ensemble average they are not related in the sense of a particular configuration. So, volume occupied by a configuration is given by the R_g and that will be different then the R_e in most cases.

So, now I want to take another demonstration, what happens if the chain is not ideal? So, let me take an example of a polymer that is like a rod that is very stiff polymer that is like pretty much like a rod. So it is not an ideal chain it is very stiff actually this model really applies to things like DNA which is really very stiff molecule and in that case if I look at many confirmations there will be slight differences but by and enlarge the chain looks pretty straight.

So, if I have a rod like polymer again I can use the idea of defining a contour variable s running from 0 to M. But now it is very easy to identify where my centre of mass is it is right at the centre and we know the location of it that is M/2. So, if I now include the b variable we know for the fact that r_{cm} has to be M/2 multiplied by b, so in this case we do not have to go to calculate r_{cm} in detail we know it is a straight rod, so we know the centre of mass.

$$\vec{r}_{cm}=\frac{M}{2}b$$

So now,

$$R_g^2=\frac{1}{M}\sum_{i=1}^{M}\left(\vec{r}_i-\vec{r}_{cm}\right)^2$$

In this case I am not even looking at the ensemble average because there is only one confirmation of the chain and that is like a rod and there are no other confirmations. So, you can look at actual the R_g values and this idea really extends to objects of any shape actually that's where it is coming from at we can define radius of gyration of objects of different shape. We are applying to polymer physics and then we get different results but that idea itself is general. So, now with the same kind of a discrete to continuous representation we get-

$$R_g^2=\frac{1}{M}\sum_{i=1}^{M}\left(\vec{r}_i-\vec{r}_{cm}\right)^2$$

$$\cong\frac{b^2}{M}\int_0^M\left(s-\frac{M}{2}\right)^2 ds$$

$$s-\frac{M}{2}=s^{'}\wedge ds=d\,s^{'}$$

$$R_g^2=\frac{b^2}{M}\left[\frac{s^{'3}}{3}\right]_{\frac{-M}{2}}^{\frac{M}{2}}=\frac{b^2}{M}\cdot 2\cdot\frac{M^3}{24}$$

So, now of course instead of the R_g^2 going like M, now it is going like M^2 that is the kind of behaviour we expect in the rod like chain essentially what it means is now I can also define the length of the rod as l

$$R_g^2=\frac{b^2M^2}{12}=\frac{L^2}{12}$$

The purpose of this was simply to demonstrate how do we go ahead and calculate the radius of gyration for different kind of shape, you can try the examples for disc cylinders and so on and that will give you and understanding of how the volume occupied by objects change for as a function the geometric variable that you have.

So, now very briefly I want to discuss an idea that will left earlier for the want of a better word what we are talking about is something like the chains the segments of a chain which are far of along the contour. They can also come together and interact and that is not being covered in the ideal chain models we have discussed. So, of course we say that if we have a polymer chain then for short range or short distance along the contour. The correlations are present but as along the correlations decay with the distance along the contour the chain is ideal. So, if I take two particular points s and s' now these two points may appear to be physically close but they are a very far of an along the contour. If I have to find the contour distance between them I have to essentially compute the distance between the two points.

When I look at say my s-s' that represents the distance along contour and what we said is if correlations between segments decay rapidly with distance along contour. Here s-s' is the chain is that is ideal and we have by scaling R_e^2 proportional to M. In fact as we just we derived R_e^2also goes like it.

Now what do we mean by this correlations. So, if we remember from the in the very beginning I said that if I look at the actually at a molecular level. They come from the fact that the adjacent carbons share a covalent bond and that is the reason why this bond distance is very less flexible. For example, if I look at say particular angle theta between three carbons then it is no longer as stiff like a bond but a still we have an overlap of electron clouds here. The overlap electron clouds here the electron clouds represent the covalent bond and these two electron clouds have some interactions between them and so, theta is flexible then but still not so flexible.

However if I look four carbons then we can define what is known as torsion angle or a rectangular angle. Now they are relatively more flexible we can have rotations around the carbon bond and that is how we get different confirmations. So, the main idea was that if I go along the carbon chain at short distances we have a strong bonded interactions and at long distance is the bonded interactions decay because between two adjacent carbons we have covalent bond sharing between three. We have overlap of two clouds of electrons that is between the two carbons - carbon bonds that we had and then between say four carbon atoms in a series. We have a torsion that is relatively more flexible we can have rotations around it and if I think of say five carbon let say between a carbon a and say a+1, a+2, a+3 a+4, a+5. Now between a and a+5 it is even less correlations what it is means is the position of these two are less correlated or they can be varied relatively more easily or they can actually if I really extend the idea to say 20 or 30 carbons. We can a start to see that there is almost no correlation in what case I will I can pretty much choose the position of carbon distant along the chain independent of where my carbon is far of along the chain.

Now what we missed here is something that is known as non-bonded interactions so, of course electron clouds grading gives rise to bonded interactions overlap of clouds give rise to say an angle interaction and so on. But that is not the only interactions the present in the system for example you can have a situation where you have negative charge here and positive charge here now these two guys even if they are distant along the contour since they are physically close. And they have a positive charges there will be large attractions between them which is not being considered in the ideal chain model. Now coulomb interactions is not all the interaction again you can have other interaction which can be relatively less strong than coulomb but they appear can most cases one of them is known as the Van der wall interactions which is relatively weaker than coulomb. But it is not something that it is weak enough to be ignored.

So, in that case we also have to account for this so as when we discuss the ideal chain models what we essentially saying is the non-bonded interactions are not included and unlike the bonded interaction that vary with the distance along the contour so, the bonded interactions vary with the distance along the contour. The non-bonded interactions vary with physical distance. This can be more precisely that physical distance will be the difference in the positions of segment s and s-s' and the distance along the contour is absolute value of s-s' okay. So, this is where we will define the idea of excluded volume and see like what implications it has on the behaviour of the polymer chain.

So, I will close with this and then we continue with discussion in the next lecture.