Introduction to Polymer Physics
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Lecture-13
Definition of Radius of Gyration

In the last couple of weeks we have discussed basically the introduction to the polymer physics and we spent lot of time on the random walk models of polymer physics particularly looking at the distribution of the end to end distance. So, I want to come to one more quantity that characterise the size of a polymer chain which is known as the radius of gyration (R_g).

So, before I come to this let us think of the end to end distance again and see like what it does not characterise, of course at it is a measure of in some senses the elastic energy stored in the spring. We got the relation for the elastic energy in terms of R_e so it is useful quantity but what it does not characterise, so one thing it does not characterise is the actual length of the polymer chain or it is size. For example, Let us consider two chains one of them is very high and the other one is very small but they still have the same value for the end to end distance R_e. The contour length is very different but they have the same end to end distance. It does not tell you also whether the chain is straight or folded. For example the chain could also have been like folded or a straight chain also having the same R_e value. So, although it is the very useful quantity the R_e does not characterise the size of the polymer chain if I really think of like looking through a microscope it will very difficult to find out where are my ends. And even if we are able to find out where the ends are and we measure the end to end distance it does not tell me much about the space occupied by the polymer chain.

So, the quantity we are going to define now is known as the radiation of gyration. It tells something directly about the size of a polymer chain in terms of the volume occupied of the polymer chain and in this sense it is very useful. The way it is defined is if you look at a polymer chain it of course it will occupies certain volume and let say if that volume is v at the volume occupied by the polymer chain in space. Now if I draw a sphere that has the same volume as the

space occupied by the polymer chain. I would call the radius of that is sphere to be the radius of gyration.

So, I want to point out here that this is not quite precise in a sense that there can be a pre -factor between the radius of gyration and the radius of equivalent sphere but it gives the idea in the sense that it captures the a fact of space occupied by the polymer chain in the system.

So, we think about it as I will draw a sphere of a volume v this will be an equivalent sphere. This is a volume of the polymer chain this will be something like-

$$V_{polymerchain} = \frac{4}{3}\pi R_g^3$$

Here, R_g is defined as the radius of equivalent, it is a only equivalent in terms of the volume. We can also defined the R_g values for other kinds of things let us say rods, discs, cylinders and so on and you will discuss that to what is the end. So, but the way the R_g scales with the number of monomers or repeating units in the chain is something that is unique for the polymers.

So, by definition the R_g^2 is defined as

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

Here i= the segments or the beads of the polymer chain depending on how we are representing it. So, within a theoretical model we can think of R_i as the position of segment or a bead and within the experimental situation we can associate for example the position of the carbon atom.

So, the idea itself it is very general but it depends on where I am applying this idea, for a bead spring model the R_i would refer to the position of those beads in space and the centre of mass r_{cm} there is simply the arithmetic mean of those positions, and this particular quantity that we defined we will always look at the R_g^2 value is the radius of gyration.

So, let us now do some arithmetic simplification of this particular quantity it will be like slightly longer but then you will realise basically 2 aspects one what kind of mathematical exercise happens in polymer physics and then we will say also some meaning to the simplified expression that we will derive. Let us start:

$$R_g^2 = \frac{1}{M}\sum_{i=1}^{M}\left(\vec{r}_i - \vec{r_{cm}}\right)^2 = \frac{1}{M}\sum_{i=1}^{M}\left[r_i^2 + r_{cm}^2 - 2\vec{r}_i \cdot \vec{r_{cm}}\right]$$

$$¿\frac{1}{M^2}\sum_{i=1}^{M}\sum_{j=1}^{M}\left[r_i^2 + \vec{r}_i \cdot \vec{r}_j - 2\vec{r}_i \cdot \vec{r}_j\right]$$

Now let us look at like how this happens term by term, so we will first look at the first term then the second and then the third. Let's start with the first term:

$$\frac{1}{M^2}\sum_{i=1}^{M}\sum_{j=1}^{M} r_i^2 = \frac{1}{M}\sum_{i=1}^{M} r_i^2$$

Let's look at the second term:

$$\frac{1}{M^2}\sum_{i=1}^{M}\sum_{j=1}^{M} \vec{r}_i \cdot \vec{r}_j = \frac{1}{M^2}\sum_{i=1}^{M}\vec{r}_i \cdot \sum_{j=1}^{M}\vec{r}_j = \left(\frac{1}{M}\sum_{i=1}^{M}\vec{r}_i\right)\cdot\left(\frac{1}{M}\sum_{j=1}^{M}\vec{r}_i\right) = r_{cm}^2 = \frac{1}{M}\sum_{i=1}^{M} r_{cm}^2$$

Now let us look at the final term which is in this case we have:

$$\frac{1}{M^2}\sum_{i=1}^{M}\sum_{j=1}^{M} -2\vec{r}_i \cdot \vec{r}_j = \frac{1}{M^2}\sum_{i=1}^{M} -2\vec{r}_i \cdot \sum_{j=1}^{M}\vec{r}_j = \frac{1}{M}\sum_{i=1}^{M} -2\vec{r}_i \cdot \vec{r}_{cm}$$

After all the calculations we got we get here is which exactly is what we had earlier.

So let us start with this simplified expression of what we started with and let us see what kind of further manipulations we can do. Our new simplified expression is:

$$R_g^2 = \frac{1}{M^2} \sum_{i=1}^{M} \sum_{j=1}^{M} \left(r_i^2 - \vec{r}_i \cdot \vec{r}_j \right)$$

Here, i and j can be interchanged if I change i with j it does not make any difference. Because I am doing a summation for both i and j from 1 to m okay so, then I can write this thing into two parts which will be looking like something like manipulation. But keep in mind that it is simply arithmetic simplification that we are doing. So, what we are doing is we divide this by 2 then I will write 2 sums this is the first one second one will be simply the same thing with I and j interchanged, so we get:

$$¿ \frac{1}{2M^2} \left[\sum_{i=1}^{M} \sum_{j=1}^{M} \left(r_i^2 - \vec{r}_i \cdot \vec{r}_j \right) + \sum_{i=1}^{M} \sum_{j=1}^{M} \left(r_j^2 - \vec{r}_i \cdot \vec{r}_j \right) \right]$$

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

Now we can do one more simplification. In this case we are summing for all values of i and j but since we are summing since there is no difference in i and j. But we can see here is the summation will be the same for j values higher than I and j values less than i less because I and j can be perfectly interchanged. The probability of i being higher than j is the same of i being a smaller than j okay. So, by this logic instead of summing from I and j both from 1 to m. I can sum i I can sum j from i to m and get this particular relation. We get as:

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

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

So, there is an advantage of using the new expression then compared to the older expression the first one we will see in a moment in the next lecture I will do a whole derivation of this where we can say that the ri –rj square can be thought of in the limit of higher values of m. So, I will get a particular relation that I will use and I will do that just same way we did the discrete to continuous transition earlier. The other advantage is in terms of the practicality, so if I am using the earlier expression then I have to do the calculation in 2 steps. If I know for example the positions of all the segments or beads are monomers as the case in b. Then I have to first find the center of mass using the relation-

$$\{\vec{r}_i\} \rightarrow \vec{r}_{cm} = \frac{1}{M}\sum_{i=1}^{M}\vec{r}_i \rightarrow R_g^2$$

So, $\{\vec{r}_i\} \rightarrow R_g^2$

The advantage now is with new expression is I can start with the R_i values and I can directly get the R_g^2 value without the need of computing the center of mass.

So, if I am thinking of doing onto a computer let's there is a program where I want to find the R_g^2 value of a polymer confirmation at every step both of these calculations computation of r_{cm} or the computation of R_g^2 will involve FOR loops. It is a some sort of arithmetic simplifications that was appearing to be somewhat weird, we are able to find something that has advantage in terms of computation it will be much more efficient and compare to an earlier expression. So, now ultimately we are not interested in again as I was telling you earlier, we are not interested in the R_g^2 of a single confirmation, we are interested in the average R_g^2 for many confirmations.

Now, we are interested in then is this expression-

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

In the next lecture is we can do a discrete to continuous transformation and find a relation between the radius of gyration and end to end displacement for an ideal chain and it turns out to be the both are proportional to each other for the ideal chain. So, but before we go into this I will end the lecture with 1 small detail about how the R_g has to be experimentally evaluated or experimentally measured.

So, if you think of like the way we look at things in a microscope it has a simple camera arrangement we look at things through a lens, one of the best way to think of like how the microscope work is take your smart phone camera and zoom to the maximum zoom you can go to and just think of a microscope as maybe like 10 times more zoom than what you are camera have a 100 times more zoom the camera we are getting better over the time. Now this only works this whole idea is what is behind what is known as an optical microscope which can work if I look at things which are more than a micron. In this case optical microscope can tell you everything about the particular particle I am interested in not everything but a whole lot of detail about the particle.

If the things are less than a micron as the case maybe for a polymer chain or if I want to look at features which are like submicron or less than 1 micron. In that case optical microscope is not enough, in that case what we make use of is what is known as light scattering, where the idea is that if we have any object and let us say in this particular case a polymer chain and if I throw a light of a certain wavelength through this particular sample, the light will be reflected or deflected and I will measure the angle of deflection that is referred as scattering.

Now if I want to look at objects of different sizes I can play with lights of different wavelengths, when for example I am using an x-ray I can see objects which are much smaller than compare to when I use for example a visible light. So, by varying the nature of the light source I can look at

objects in different size range and this is 1 principle that is used in computation of radius of gyration.

So, as we will build further in this week of lectures we will try to associate the definitions we are developing to experimentally measurable quantities and that is where the polymer physics that we have derived start becoming useful. Because so far it was like toy models descriptions that we are giving us similarly qualitative results for ultimately we have to verify those findings where experiments and we are actually building towards it will think of like how can we get experimentally quantifiable measures of the size of a polymer chain and it is structure and then how can I compare that to the theoretical results that we are developing.

So I will stop here, thank you.