Introduction to Polymer Physics
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Lecture-20
Size, Shape and Structure: Gyration Tensor and Measures of Asphericity

So far in this course we have been focusing about the size of a polymer chain and we discussed two different measures- the end-to-end distance and gyration radius, and we did for various cases accounting for the interactions between the segments first we looked at the ideal chain where there were no interactions then we did the case for a self-avoiding walk when there were repulsive interactions or repulsion between segments and then finally we did for the bad solvent case when there was attractive interaction between segments, but we have focused only on end to end distance or gyration radius or the distribution of same quantity as a function of the number of segments.

So now I want to talk about something different that we care about in a polymer chain and that is the shape of a polymer Chain and structure of the polymer chain. In general the size tells you about how large or long something is let's say sphere can be small or larger even larger this is what is captured by the size, the shape tells you what does it look like. So objects that are having the same size, may have different shapes for example as a circle, a triangle and a square and may have similar characteristic dimensions but they still have different shapes in the group and then finally comes the point of structure which is tells you how ordered or disorders the system.

Let us first talk about shape and why it hasn't come into discussion so far and how can we include that, so far we have not differentiated between the different directions they are assumed to be identical. For example if I am computing the R_g^2. Of course I compute the 3 components R_{gx}^2, R_{gy}^2 and R_{gz}^2 we have done that at least for the lattice case just to demonstrate that I decompose walk in three dimensions in to three one dimensional random walks and I can get the R_{gx}, R_{gy} and R_{gz} for each of them but if I take an ensemble average of all of them squared of them

they have to be equal and in fact should be equal to the $R_g^2/3$ because we know that R_g^2 is $R_{gx}^2 + R_{gy}^2 + R_{gz}^2$.

This particular assumption assumes the chain to be somewhat isotropic that is there is no difference in the different dimensions or does not matter how I look at the chain in every direction it will look out to be identical. If I do it in ensemble levels of course in a particular confirmation R_{gx} can be higher than R_{gy}, R_{gy} can be higher than R_{gz}, but if I take ensemble average for many conformation then the squared average in ensemble sense will be the same in all the three directions. That need not be the case always, for example if we have a rod that can be an approximation for example a stiff chain that in that case is clearly more elongated in one direction compared to others and this must be taken care of when we are doing the analysis.

However if you look at from this from this fixed reference frame let's say if I fix my reference frame and I look at the polymer chain that is stiff or like a rod, there of course the chain can be taking different orientations and again if I think in terms of the average values they have to be the same because it is equally likely that the chain is elongated along the X direction and the chain is the longest along the Y direction and along Z direction in fact at any angle in the three dimensional plane the probability to have a chain axis is identical.. So if I look at from a fixed co-ordinate frame we cannot capture the effect of elongation, so the way of doing this, way of capturing the effect of elongation is we fix our frame of reference to the polymer chain itself. That is to say let's say if there is a polymer chain I will fix my reference frame can set the centre of mass as my origin and then I can set my frame along the chain axis Let's call this 1 2 and 3. And what I also do this to ensure that my R_g along 1 axis 1 is higher than equal to R_g along 2 higher than equal to R_g along 3. If I am doing this in this particular way 1, 2, 3 are referred as the principal axis and then the principal axis and then principal axis are also name as major and minor axis and then this co-ordinate frame will move as the chain takes different orientation. So 1 is always along the most elongated dimension. So in that sense if I take ensemble average is the ensemble average of R_{g1}^2 must be higher than equal to R_{g2}^2 must be higher than equal to ensemble average of R_{g3}^2.

So this is one point that we must fix our frame of reference to the polymer chain, how about there can be other cases where there can be elongation also along the fixed reference frame. For example if you imagine a confined polymer chain. So let us say you have a cylinder through which polymer chain is passing and now since the way we have assume the diameter is either comparable to or lesser than the radius of gyration or it can even be the same order in the effects will start to appear. So if the chain dimensions become comparable to the diameter. In that case the chain has to elongate in other direction because the chain cannot cross the cylinder chain of the cylinder it has to it has to get elongated in other direction because of the confinement.

So in this case when I fix my axis, I will see that along the X the chain will be more elongated and along the Y and Z they have to be less elongated. For a confined polymer chain we can work with fixed reference frame and for stiff chain the reference frame should be fixed to the polymer. Actually also for the confined polymer chain we can fix the reference frame to the polymer that will not make an error but it will not capture the effect of confinement in true sense.

Now let us see how these R_g value along the principal axis relates to the definitions of R_g that we have discussed earlier and it turns out that we can define a general tensor called the gyration tensor which basically captures the anisotropy or the fact that the change can be elongated in one dimension more than other dimension. So one can define a gyration tensor and this can be defined both for the frame of reference fixed to the polymer chain or for the fixed reference frame. So we can define a gyration tensor as

$$\check{S} = S_{\alpha\beta} = \frac{1}{M}\sum_{i=1}^{M}\left(r_{i\alpha} - r_{cm\alpha}\right)\left(r_{i\beta} - r_{cm\beta}\right)$$

$$Here, \alpha, \beta = 1,2,3 \vee X, Y, Z$$

This is in Einstein notation.

Now irrespective of what reference frame I started with if I look at this particular matrix and I compute the Eigen values it always the R_g along the principal axis of the deformation.

$$R_{g1}^2 \geq R_{g2}^2 \geq R_{g3}^2$$

The Eigen values will come by diagonalization of S that is a standard stuff that we do in any Eigen value problem. So essentially the way we do it is we look at determinant of-

$$det\left(\check{S}-\lambda\check{I}\right)=0$$

If I look at Eigen vectors they will give me the principal axis deformation. So this becomes let us say if I start from xyz frame as reference-

$$\begin{matrix} S_{xx}-\lambda & S_{xy} & S_{xz} \\ S_{yx} & S_{yy}-\lambda & S_{yz} \\ S_{zx} & S_{zy} & S_{zz}-\lambda \end{matrix}$$

So we have to solve this particular relation that happens to be a cubic equation in lambda and this gives me the three Eigen values. So now if I want to represent my anisotropy or Asphericity because Eigen values are identical that is what we assume for random walk. We are assuming that this is the shape is akin to the sphere ok, so if we represent my anisotropy or Asphericity in terms of departure from the sphere or isotropic behaviour we can look at the ratio of these Eigen values-

$$\frac{\left\langle R_{g1}^2\right\rangle}{\left\langle R_{g2}^2\right\rangle},\frac{\left\langle R_{g2}^2\right\rangle}{\left\langle R_{g3}^2\right\rangle},\frac{\left\langle R_{g3}^2\right\rangle}{\left\langle R_{g1}^2\right\rangle}$$

It measures the anisotropy or asphericity however there are better measures and I will come to that what we can also see is I can look at different shapes and see like how exactly there R_{g1}, R_{g2}, R_{g3} varies and see like how then we can look at these R_g values and tell about what the shape looks like.

For example for the case of a sphere we have a constant radius we have,

$$\left\langle R_{g1}^2\right\rangle=\left\langle R_{g2}^2\right\rangle=\left\langle R_{g3}^2\right\rangle$$

If it is however ellipsoid now there are actually 3 possibilities,

$$\langle R_{g1}^2 \rangle \approx \langle R_{g2}^2 \rangle > \langle R_{g3}^2 \rangle (called\ oblate\ ellipsoid)$$

$$\langle R_{g1}^2 \rangle > \langle R_{g2}^2 \rangle \approx \langle R_{g3}^2 \rangle (called\ prolate\ ellipsoid)$$

$$\langle R_{g1}^2 \rangle > \langle R_{g2}^2 \rangle > \langle R_{g3}^2 \rangle (called\ general\ ellipsoid)$$

If you have a rod in that case-

$$\langle R_{g1}^2 \rangle \gg 1$$

$$\langle R_{g2}^2 \rangle = \langle R_{g3}^2 \rangle \approx 0$$

As in rod R_{g1}^2 is very high and R_{g2}^2 and R_{g3}^2 have to be very small because they refer to the thickness of the rod that is anyway very small especially compared to the length of the rod.

So what this tells me is these Eigen values contain a measure of the shape and we can characterize the anisotropy using the Eigen value. However the ratio that we have defined as the measures of anisotropy and asphericity are not the best ones out the there, for the simple reason that these ratios take values going from 0 to infinity so it is better to have measures that vary from say 0 to 1, where 0 and 1 refer to two extremes in that sense it will be more convenient than compared to measures we have because this can take a very large value or very small values.

Now we will look at this particular characteristic equation we have derived that is determinant of the gyration tensor $-\lambda I=0$ and based on that apart from the Eigen values $R_{g1}^2\ R_{g2}^2\ R_{g3}^2$ we can also define something known as matrix invariants, what essentially they mean is those invariants will be independent of the rotation or translation of axis. If for example I have defined this variant for a particular reference frame I rotate my axis those quantities will not change and that is what is known invariants and the same thing will be true if I translate my axis somewhere of course the matrix overall will be different but those invariance will remain unchanged.

So in turns out that the characteristic equation that I just showed you contains 3 matrix in variants-

$$3¿ of\ det(\check{S}-\lambda \check{I})=0$$

$$T_r = R_{g1}^2 + R_{g2}^2 + R_{g3}^2$$

$$D = R_{g1}^2 R_{g2}^2 R_{g3}^2$$

$$M = R_{g1}^2 R_{g2}^2 + R_{g2}^2 R_{g3}^2 + R_{g3}^2 R_{g1}^2$$

Using these three invariance actually only two of them, I can define the measure known as a asphericity –

$$\langle A \rangle = \frac{\langle T_r^2 - 3M \rangle}{\langle T_r^2 \rangle}$$

$$T_r^2 - 3M = \left(R_{g1}^2 + R_{g2}^2 + R_{g3}^2\right)^2 - 3\left[R_{g1}^2 R_{g2}^2 + R_{g2}^2 R_{g3}^2 + R_{g3}^2 R_{g1}^2\right]$$

$$¿ R_{g1}^4 + R_{g2}^4 + R_{g3}^4 + 2\left[R_{g1}^2 R_{g2}^2 + R_{g2}^2 R_{g3}^2 + R_{g3}^2 R_{g1}^2\right] - 3\left[R_{g1}^2 R_{g2}^2 + R_{g2}^2 R_{g3}^2 + R_{g3}^2 R_{g1}^2\right]$$

$$¿ R_{g1}^4 + R_{g2}^4 + R_{g3}^4 - \left[R_{g1}^2 R_{g2}^2 + R_{g2}^2 R_{g3}^2 + R_{g3}^2 R_{g1}^2\right]$$

$$\frac{1}{2}\left[2R_{g1}^4 + 2R_{g2}^4 + 2R_{g3}^4 - 2R_{g1}^2 R_{g2}^2 - 2R_{g2}^2 R_{g3}^2 - 2R_{g3}^2 R_{g1}^2\right]$$

$$¿ \frac{1}{2}\left[\left(R_{g1}^4 + R_{g2}^4 - 2R_{g1}^2 R_{g2}^2\right) + \left(R_{g2}^4 + R_{g3}^4 - 2R_{g2}^2 R_{g3}^2\right) + \left(R_{g3}^4 + R_{g1}^4 - 2R_{g3}^2 R_{g1}^2\right)\right]$$

$$¿ \frac{1}{2}\left[\left(R_{g1}^2 - R_{g2}^2\right)^2 + \left(R_{g2}^2 - R_{g3}^2\right)^2 + \left(R_{g3}^2 - R_{g1}^2\right)^2\right]$$

Now we can write as-

$$T_r^2 - 3M = \frac{1}{2}\sum_{i>j}\left(R_{gi}^2 - R_{gj}^2\right)^2$$

Here, $i, j = 1,2,3$

$$T_r^2 = \left(\sum_i R_{gi}^2\right)^2$$

And,

$$\langle A \rangle = \frac{1}{2} \sum_{i>j} \frac{\left\langle \left(R_{gi}^2 - R_{gj}^2 \right)^2 \right\rangle}{\left(\left\langle \sum_i R_{gi}^2 \right\rangle \right)^2}$$

So we can generalize it for a d dimension so essentially I can replace 2 by (d-1) for d dimension now we can see like how exactly it is a good measure, so let's say what happens when we look at a sphere in which case R_g values are identical. So numerator will always be equal to 0 because if I square and take a difference between 0. So A=0 for a perfect sphere on the other hand if I have a rod then R_{g1} of course is equal to the length. But have R_{g2} and R_{g3} are pretty much comparable to 0 and so what I do get from this is A= ½ and on two occasions R_{g1}^2 will appear everything else is 0. So we have 2 R_{g1}^2actually squared of that to R_{g1}^4 and then divided by only one occasion R_{g1} will appear that is squared so this is equal to 1. Keep in mind that we assume in a perfect sphere or a perfect rod ensemble average does not have any meaning here.

The key point here is we are going from 0 to 1 here the higher the value is the more anisotropic or aspherical it is and the maximum possible value is 1. So in this way this particular quantity 'A' characterize the shape of the random walk or all kinds of walk that we have done such as the self-avoiding walk. So we are now covered how to characterize shape of a polymer chain earlier we have looked at the size of the polymer chain. So in the next lecture we start talking about the structure of the polymer chain on polymeric system before we go into it will discuss about what do we mean by the structure talk about order and disorder transitions and we take a detour to talk about the scattering theory and then we will return to the idea of structures of polymer chain or polymeric systems.

So with that I stop here and then thank you.