Simple Concepts Related to Single Macromolecule Prof. Abhijit P Deshpande Department of Chemical Engineering Indian Institute of Technology - Madras

Lecture - 14 Size, Mobility and Flexibility

Hello and welcome to this lecture on polymers, we are looking at single macro molecule in the second week of the course, single macro molecule, its size, its shape, its flexibility or rigidity has an extremely important role in terms of describing properties of these polymers. So, that is why in this particular lecture, we will look at aspects of size and shape of these macromolecules how does a macro molecule move around? If it is there in a solution state or if it is there in a molten state can also be inferred based on a single macromolecular behavior and of course, how does stretching of material when we deform a rubber and it comes back how is that explained also based on single macromolecular behavior.

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So, all these aspects, we will focus in this particular lecture by first defining few models. So, we will look at some simple models which are used in terms of defining a single macromolecule ideal chain is the simplest model; think of what is meant by ideal in this context? And so, if I just give you a hint that ideal gas is something that you already know. So, you can see why that ideal concept is useful in this case. We look at a few different models, which are used for polymers, macro molecular behavior, and we will get a, some idea about size and shapes of these macromolecules and also the rigidity or flexibility associated with a macromolecule.

So, statistical properties as we discussed in the last lecture are important because this polymer is a random chain object and conformational changes keep on happening. Mind you, these conformational changes are only possible in rubbery state, molten state or when there is in the solution state. If it is an amorphous frozen state or crystalline state, then these are not as relevant, but even to obtain amorphous or crystalline state quite often we may be having the polymer in a liquid form and eventually going to the solid form.

So, what happens to conformations in the liquid state has a bearing on what is the kind of solid state we get in the end. So, therefore, conformational changes and single macromolecular behavior is very important even for deciding what solid state we get. So, to define this quantitatively for we define an ideal chain; where each and every link and bond that we talked about in the last lecture is free to rotate any which way. So, the way I had drawn also last time, if you remember for polyethylene, I had said that this could be the one or so, these 3 are the possibilities.

So, basically what we have is there is a conical section in which the conformation is possible, but an ideal chain the way we think of is the one link is like this, the second link can be any which way and so, therefore, the third link and now, I use a slightly different color to draw it, so, these can also be anything. So, therefore, this is completely freely jointed chain. So, ideal chain is also referred to as a freely jointed chain. Clearly you can see that this is the simplest possible model if you have to consider a real macromolecule then the fact that there is always this 109 degree angle between 2 subsequent C-C bonds is not incorporated in a freely jointed chain.

So, that will be an additional input to get another model. So, in case of ideal chain, the end to end distance can be shown to be the number of links and the length of the link square. If you look at it in terms of distance, this is mean square distance but the distance or it is also called root mean square distance. So, this is something you might have also seen in current in electricity or any other random variable, where mean is going to be 0, root mean square is a useful measure.

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\langle R^2 \rangle = R_o^2 = N_s |a_i^2| = N_s a_s^2
$$

$$
\rho(R) = \left(\frac{3}{2\pi \langle R^2 \rangle}\right)^{3/2} \exp\left(-\frac{3R^2}{2\langle R^2 \rangle}\right)
$$

So, you can think of how this end to end vector the way I described it in the last lecture a useful statistical property to describe it is not mean itself, but root mean square. So, in case of an ideal chain R_0 is proportional to square root of the number of links or in other words, ideal chain, the end to end distance is proportional to square root of molar mass. So, if I increase the molar mass by 100 times the contour length increases by 100 times, but end to end distance only increases 10 times. So, you can see the coil like nature of this macromolecule object. I increase the length of the chain 100 times, but the end to end distance only increases 10 times. And the distribution of how one end with respect to the other end changes is a Gaussian distribution for an ideal chain. And I am sure a lot of you can recognize the Gaussian distribution, if you are not familiar, just read about normal and Gaussian distributions and the random walk theory that I talked about can be used to show that an ideal chain where there is 1 step and then the second step, and then the third step, fourth step, fifth step and so, any steps which are taken and one step can also overlap on the other. So, therefore, that will lead to a random walk or of N_s steps in 3 dimensions and you can show the distribution will be a Gaussian distribution. So, therefore, ideal chain is also called a Gaussian chain.

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Now, as I mentioned already instead of the free 2 links being completely free to take any rotational and positional state, we know that 2 subsequent bonds are have to have an angle theta with respect to them and there is only a conical geometry in which the 3 different conformations can be there. So, I just draw these 3 different conformations again the way I had drawn them in the last lecture.

And so, these 3 conformational states all of them have to have this tetrahedral angle of 109 in case of polyethylene, but depending on the polymer this angle can change. Now, you can also think in terms of you know, instead of hydrogens which are there on polyethylene what if they are fluorines? For example, teflon is all fluorines or what happens if one of the hydrogen gets replaced by benzyl, phenyl group in case of polystyrene.

So, you can see that how conformational changes become different when you start substituting atoms with another set of groups. And therefore, again single macro molecular behavior becomes very good description of what the overall bulk behavior of polymer is, because with the presence and absence of different types of groups and how they interact with each other, we can find out how easy or difficult the conformational change is, therefore, we can find out the statistical properties of a single macromolecule. And once we know that, we can also say many things about the bulk response of the polymer.

So, the description once we have the polymer chain rather than being freely jointed, it is freely rotating then that angle of rotation comes into the overall description and for polyethylene, the cos θ is around -1/3 and therefore, the end to end distance for a polymeric

chain of polyethylene is given by this. You can see here this question, recent question from an exam. So, it is a polyethylene chain with a given molar mass. Once molar mass is given, I hope you can recognize that we immediately know what is N_s ? And in this problem of course, as is also given. So, we have the knowledge of both N_s and as.

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\left\langle R^2 \right\rangle = N_s a_s^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)
$$

So, therefore, we should be able to calculate the end to end distance as is being asked and again the root mean square. So, you can attempt this, I will give the answer at the end of the lecture. Because of a bulkier group, quite often, we will have steric factors and again rotations which are possible may become more difficult and so, hindrance because of steric factors is also there. And so, for many common polymers we have a steric factor of 2 and therefore, end to end distance is again higher, you can see that ideal chain model shows N_s into a_s². As soon as you bring in the fact that C-C bond, there is 109 tetrahedral angle, the end to end distance increases by twice then if you add steric hindrances, because of bulkier groups, then end to end distance becomes even higher. So, end to end distance therefore, can be described based on many of these models and depending on the situation one or the other model may be more appropriate.

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\langle R^2 \rangle = \sigma_{steric} N_s a_s^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)
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At this point, you may ask the question as to is ideal chain model really useful at all because it says no interaction between different parts of polymeric chain. While you are answering this question, you should also consider and ask the following question is ideal gas model useful at all to describe gas behavior? And if you can find answers to the question, why is ideal gas model model useful? You will be able to also find answer to the question why is ideal chain model useful?

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So, single macromolecule understanding is useful, because it has consequences for polymer response in the solution state, in the melt state as well as motion of macromolecules. So, some of the quantitative features that we will describe later on is related to in a polymer solution, we will define an overlap concentration. Now, this polymer is a coil like object and if we put few polymer molecules, they will be separate and away from each other, but we start adding more and more polymer, then there is a chance of them overlapping.

So, we can define a solution to be dilute or non dilute depending on what is the overlap concentration. Then once we add the polymer into the solvent, there is going to be a viscosity modification. So, we will define something called the intrinsic viscosity of a polymer solution. This is a very important concept which describes how polymer and solvents interact with each other. And how addition of a polymer influences the behavior of the solution? Of course, polymer solutions are very important from applications in variety of viscosity modifications. So, this is an important area from conceptual as well as application point of view also, the behavior of single macromolecules is very useful from the point of view of measurement.

So, if we take a polymer solution and measure the light scattering, because I have described these polymer chain molecules as coil like objects, what happens is scattering of light due to these macromolecules in solution depends on what is the size and shape of this macromolecular coil. And so, light scattering is in fact used to determine the size and molar mass of macromolecules. Similarly, diffusion coefficient of polymer will also depend on how big or small and what shape this macromolecule takes. Another important feature of this size and shape and of macromolecules is useful when we are thinking of how do macromolecules move in case of lots of biological characterization techniques?

We separate or we analyze bio macromolecules using permeation through gel and so, permeation of these macromolecules through gel depend on size and shape and interactions that this macro molecule has with the surrounding media. And in fact, we also use gel permeation chromatography to characterize the molar mass because molar mass determines the size and shape of the macromolecule and then, based on the size and shape the permeation rate is determined. So, if we allow a macromolecular sample to permeate through a gel depending on the size and shape, we can do a chromatography, which means separation based on a certain property. In this case the property will be the size and shape which is nothing but related to molar mass.

The other idea that we have already seen is related to ease of conformational changes or flexibility of macromolecules. So, if it is a, macromolecule is rigid conformational changes will not be as often if we are at a higher temperature then conformational changes will be easy. So, therefore, properties mechanical properties, properties of how much can a polymer crosslink polymer swell hydro gel can swell? And how dynamics of polymer chains influences the damping behavior or the viscous dissipative behavior in a polymer or in short visco elasticity of polymers all of these are extremely important features that can be answered by just looking at single macromolecules models that we have described so far.

So, let us continue quantifying the size and shape by looking at now, another quantity called radius of gyration. So, general answer that we are seeking is how much volume does a macromolecule span? Or the other way to look at it is, what is the extent of macromolecule from its centre of mass? So, since we have macromolecular chain and the mass is everywhere we can calculate the centre of mass of this polymer and then say you know what is the distance of different parts of macromolecule compared to this and what is the average distance? And that idea is encapsulated in radius of gyration.

So, if we look at a polymer molecule and we can draw this volume, in which it is pretty much encased and since conformational keep on changing from one instance to the other on an average, the macromolecule is encompassed in this volume defined by radius of gyration and it is defined based on the position of each and every atom that is described. So, earlier remember we had described the bonds using a_i . So, first bond was a_1 second bond was a_2 and third bond was a3. Now, we can describe each and every position here by opposition vector. So, if we have origin somewhere then this is r_1 and this is r_2 and so, on. So, we can define the radius of gyration as again an ensemble average of how the position of each and every first, second, third, fourth atom with respect to the centre of mass and r_c is the centre of mass and for an ideal chain radius of gyration and end to end distance are related to each other and this is conceptually intuitive, because, end to end distance also keeps on changing when conformation keeps on changing radius of gyration also is keeps on changing when conformational changes happen, but R_0 and R_g are average measures.

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R_g^2 = \frac{1}{N_s} \sum_i \left(|r_i - r_c|^2 \right)
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r_c = \frac{1}{N_s} \sum_i r_i
$$

So, at a given condition R_0 and R_g described on an average what is the volume spanned by the macromolecule? And since R_0 is proportional to square root of molar mass, radius of gyration also is proportional to square root of molar mass.

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And what happens to the size and shape of macromolecules when we apply shear. So, for example, when there is no flow the molecule is almost spherical volume. But, if we apply shear, then what happens is part of the macromolecule has to be moving faster compared to the other part, if we increase the shear rate and we will discuss this during polymer processing and rheology that when we increase the shear rate now, this macromolecule has a tendency to get stretched.

So, you can see that, in this single macromolecule behavior, we have 2 very important ideas associated with polymer processing and rheology. That if I take a macromolecule, under no flow condition it pretty much occupies a spherical shape. But as soon as I start shearing, when I start shearing 1 part of macromolecules has to be forced to move faster than the other. What is happening now is polymer is becoming elongated. I said there are 2 very important concepts in this related to rheology and polymer viscoelasticity.

The first one is that macromolecule is getting stretched. And therefore, it is also going to get oriented. So, stretching and orientation is one set of idea. The other is recovery or the elasticity, because as soon as we stop flow, what will happen is this macromolecule would want to come back and so, there is an elasticity or recovery of polymer melt or a polymer solution. So, let us see how powerful the concept behind a single macromolecular response is. So, this macromolecule can be visualized as if it is a spring kind of an object.

What happens when you put it under flow? One part of the spring has to move faster than the other parts just spring starts getting stretched, it starts getting oriented. As soon as you leave the flow, then again, spring wants to come back. And so, stretching orientation of a single macromolecule is the key to understanding viscoelasticity of polymeric materials. Similar thing can also happen if we change the physic-chemical condition of the polymer.

If we have a macromolecule, which has charges on it, but we change the pH in such a way that it is neutral, then we have basically being encompassed in spherical volume. But as soon as we make it charged by changing pH, what happens is now there is dissociation of ions and now all along polymer chain, there are negative ions, and then these negative-negative will repel and the polymer chain which wanted to come closer to each other in the coil state cannot come any more closer and on an average polymer becomes more extended.

So, you can see that size and shape of macromolecule and a single macromolecule can give a lot more clues about how the response of the overall bulk response is. In case of a charged macromolecule, what do you think will be the viscosity in this condition as opposed to viscosity in this condition? In one case, when we are shearing the molecule, it is a sphere like molecule which is getting moving and in other case, it is already much more elongated object which has to move around. And if I now add more and more polymers in neutral case or more and more polymer in charge case, I would expect that the viscosity buildup may be different in the 2 cases, because in 1 case, I am adding just spherical objects in 1 case I am adding rod like objects.

So, therefore, the single macromolecular response is very useful for determining bulk behavior of polymeric systems. And if you recall in lecture earlier, we had looked at diffusion behavior of proteins, when we looked at biopolymers and their classification, we looked at diffusion behavior of proteins and also when we looked at define molar mass, we had looked at the diffusion behavior of protein in lecture 5 and diffusion coefficient of a polymer molecule or any other particle is dependent on its size and simple relation to describe that is Stokes-Einstein relationship. And based on this now, you can see the diffusion coefficient of a polymer will be related to molar mass because radius of gyration is dependent. Just you can go back to 1 or 2 slides before 5 minutes before and then answer the following question. How does a diffusion coefficient of an ideal chain vary with molar mass of macromolecules?

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Since ideal chain 2 parts of chain can overlap and that is therefore, is a model which is suitable for only certain kinds of situations. We have models associated with expanded chain or also it is called excluded volume interactions. The fact that 2 polymer chains cannot overlap and therefore, there is some volume which is excluded, because 1 part of the chain is there now, this other part of the chain cannot occupy the same volume, by the way it is very similar to Vander Waals equation where we say volume instead of V it is $V - b$ where b signifies the volume occupied by the molecules themselves. And so, theory to describe these kinds of chains are, random walks self avoiding random walks and distribution in this case is different compared to Gaussian.

So, as an exercise you could plot the Gaussian distribution and this distribution and see how much is the difference? And why is this gene called expanded gene? What you will see is on average, the end to end distance is much higher in case of expanded chain also notice in case of ideal chain, the end to end distance was proportional to square root 0.5 now is proportional to 0.6. So, therefore, end to end distance is also higher, because we are now including excluded volume interactions. So, in that lecture, we had described the diffusion coefficient as a function of molar mass using 2 different theories were molar mass minus 0.5 and molar mass to the power minus 0.6. Now, you know, what is the background behind? Why we use those theoretical curves to try to compare the diffusion coefficient of protein with molar mass.

Now, a very powerful message from that graph will be that look such simple models as ideal chain and expanded chain come so close to describing real protein molecules macromolecules

with all kinds of interactions and complications and shapes and sizes that are there. So, that is the first powerful message that and therefore, these models though seem very simple are extremely useful. Of course, to get exact quantitative match more modifications to each and every system may be required. One other aspect that we need to keep in mind is when would ideal chain model be useful and when would expanded chain model be useful and for a given polymer solvent system, we will later on define a theta condition we will define when interactions between solvent and polymers are such that, that polymer-polymer chain interactions are absent.

So, the polymer chain becomes ideal. And this can be done by changing either a polymer in a solvent system or for a given polymer solvent system when we change the temperature we can manipulate the interactions. So, therefore, we can have theta solvent or a good solvent. And this can be achieved by changing temperature or looking at different polymer solvent systems. And so, in a future lecture, we will take a closer look at some of these ideas.

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Now, to finish this lecture, we have looked at macromolecular confirmations, leading to size and shape of the macromolecules its mobility in terms of diffusion coefficient, one very crucial aspect, which is related to the bulk response is the flexibility or rigidity of macromolecules. So, macromolecules as a spring, we have already seen this. So, this should be familiar, the fact that the macromolecules get extended immediately there is an elastic recovery because macromolecules would want to come back and so, this can be used to describe flexibility, rigidity of macromolecules.

So, when we have an ideal chain and we stretch it, what happens? So, let us say if I have a macromolecule like this, and it is end to end distance is given by this, now, if I stretch this macromolecule, so, I take the macromolecule and I stretch it, what will happen is now on an average the macro molecule gets stretched out and therefore, in case in terms of the end to end distance would increase. Also the conformational changes become less to understand why am I saying conformational changes become less, you can think of the extreme scenario, what if I take a macromolecule and keep on stretching, if I stretch it all the way such that the macromolecule just becomes like this, basically no conformational changes can happen, because I have completely extended and stretched the molecule. But if I bring the 2 ends closer and closer, then macromolecule can take lots of conformations.

So, therefore, whenever I am changing the stretching of macromolecule I am changing the confor number of states that the polymer macromolecule can adopt. And so, this therefore, can be understood in terms of what happens to the entropy of macromolecular system when stretching is done. And again, we can use ideal chain model to look at this. So we can use statistical mechanics to look at Gaussian distribution, and what happens to Gaussian distribution when we keep on searching the macromolecule we can also think of this as the probability distribution being affected by an interaction energy, we already talked about how we can think of polymer chain as 2 beads which are connected by spring. And so the spring is basically feeling some interaction, and the more the interaction, the chain, the length will be different. And so this potential energy of interaction is describing how the distance is between the 2 ends of macromolecules.

And of course, when we have a potential, then the derivative of the potential so if you remember, whenever we have a potential, it is derivative with respect to position gives us the force. So, therefore, force which is experienced by this macromolecule object, who is stretched whose stretching is directly proportional to the distance between them and is very similar to a spring constant in case of a Hookean spring force proportional to the extension of this spring. And so, the spring constant is 3RT by the mean square end to end distance.

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\rho(R) = \left(\frac{3}{2\pi \langle R^2 \rangle}\right)^{3/2} \exp\left(-\frac{3R^2}{2\langle R^2 \rangle}\right) \to \frac{v_c}{RT} = \frac{3R^2}{2\langle R^2 \rangle}
$$

$$
\frac{F_c}{RT} = \frac{3R}{\langle R^2 \rangle}
$$

This is very important, because what it says is the spring constant increases with temperature, in case of a macromolecule. And again, just to emphasize, whatever I have been saying, that such model, which is only at a single macro, single macromolecule level, can immediately lead us to very important understanding of the bulk behavior. For example, rubber modulus as a function of temperature, in fact, modulus increases with temperature for rubber, because most often, you might think that materials modulus will decrease with temperature, but for rubbers, where the elasticity is due to these macromolecules, adopting different conformations, the modulus is proportional to temperature.

And that can be explained based on the idea that entropy changes when we stretch a macro molecule or the 2 ends of macromolecules feel a interaction size see as we return here, and therefore, there is a force of interaction. So, with this, we have looked at stretching of macromolecules also, one other aspect of macromolecules, which is useful, and I have alluded to it, when I talked about peak and polystyrene and many of these polymers, where there are either steric hindrances or conformational changes are not possible, then in such cases, the bending of the macromolecules will also be different. And so the persistence length that we talked about in terms of flexibility of macromolecules can be used to look at the bending rigidity of macromolecule, and this concept, is also useful in describing solution and melt response of macromolecules.

So in a nutshell, by looking at single macro molecular response, by looking at its statistical properties, by looking at the size and shape that it acquires, we have be able to explain the mobility of macromolecules and we will be able to explain the viscoelasticity of polymeric systems.

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So, with this, we will close this lecture in terms of answering the question related to polyethylene. I hope all of you have got the answer based on the model where the polyethylene chain is constrained by the tetrahedral angle associated with the C-C bond. Thank you.