Introduction to Polymer Physics
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Lecture - 03
Ideal and Real Chains

In today's lecture will be discussing Ideal as well as Real Chains. So, in the previous lecture we discussed the ideal chain confirmations in detail and the property that defined in ideal chain was that distant regions of that same chain do not interact with each other. So, we will see that will carry on the discussion on ideal chain a bit further today and then we will also briefly talk about the behavior of real chains where in fact, the distant regions of the same chain actually can interact with each other and due to that the confirmation and the behavior of real chains are seen to be slightly different from that of ideal chains. So, these are the areas that we will be covering in the lecture today.

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So, before we begin we will just go through the over an overview of the content of today's lecture. So, we will be just summarizing the different models that we covered in the last lecture of ideal chains and then we will be talking the distribution of the end to end distance. So, in the last lecture, we discussed the fact that polymer chains can have many different confirmations and the end-to-end distance actually is not a fixed quantity,

but it can take many values depending on the different confirmations that the polymer chain is adopting.

So, we discussed this aspect in from a qualitative point of view. Today, we will look at the mathematical function that can be used to describe this distribution of end-to-end distance in a more quantitative way. So, after that we will briefly look at the topic of radius of gyration of poly machines and this quantity radius of gyration actually is another measure of a size of poly machine and it is actually in many cases a better measure than the end-to-end distance because it is a, it can be defined for all the different kinds of polymer chain architectures that are available.

So, after discussing radius of gyration, we will also look at next behavior of real chains and in particular we will be discussing real chains from the point of view of excluded volume interactions and the final topic that we will be covering is that of behavior of qualitatively covering, is the behavior of this polymer chains in solution and in particular the concept of theta condition and theta solvent. So, to summarize in the last lecture we covered 4 models of ideal polymer chains.

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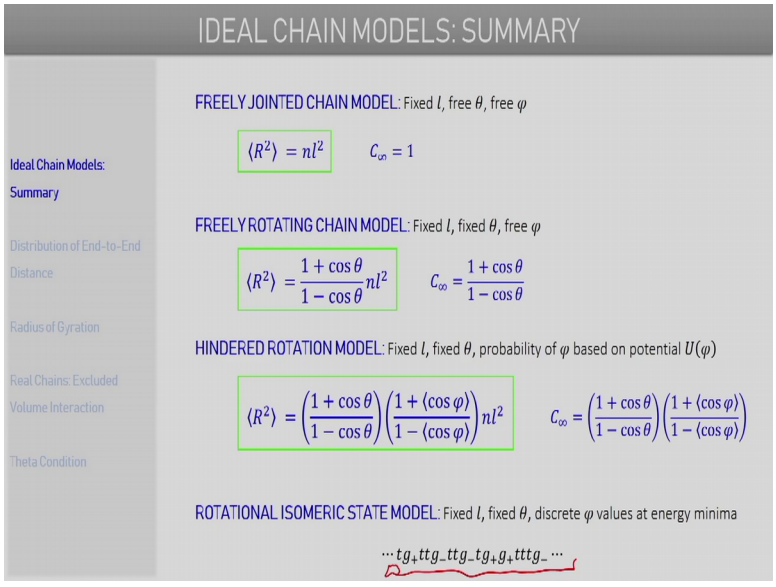

So, the simplest model was the freely jointed chain model where the bond length was fixed, but the bond angle and the torsion angle these were allowed to have any free value. So, this was the most flexible model among the different models that we studied the simplest one as well, but of course, the least realistic one the ah. We also studied the

freely rotating model where the bond length as well as a bond angles are fixed. So, in most of the real polymers the bond angle also have fixed values. So, this is more realistic model, but here again the bond the torsion angles were allowed to have any value. So, in that sense from that point of view this model is also highly flexible, because the torsion angle could adopt any values and we, we know that it is the different torsion angle values that provides polymer chains or the polymer backbone its flexibility.

We also covered the Hindered rotation model in the last lecture where the bond length and bond angles were fixed, but the bond the torsion angle was not fixed free in this case, the torsion angle was allowed to take values based on a certain potential. So, the probability of a, the occurrence of a certain torsion angle was proportional to a Boltzmann factor, which was an exponential function based on a certain kind of potential energy related to the torsion angles.

So, essentially the rotation in this model is Hindered due to the presence of a certain potential and only torsion angles, where this potential energy is favorable torsion angles which correspond to a low energy confirmations those are the ones which are more favored in this model. And we also finally, discussed very briefly the rotational isomeric state model, which is the most sophisticated models amongst ones that we discussed and which is widely used for predicting confirmations of polymer chains. So, in this model, the bond length bond angles again are fixed, the torsion angles cannot take any values any free value, the torsion angle can only adopt discrete certain discrete values in this case for this model.

So, as an example for polymer, like polyethylene they are typically three torsion angles which correspond to minimum energy confirmations, and usually they are referred to as trans and gauche plus gauche minus as discussed in the previous lecture. So, this rotational isomeric state model for such a polymer will basically allow only these torsional states and the entire polymer chain backbone or the conformation of polymer chain back one that can be represented simply as a sequence of these different torsional states. So, one such representative sequence is shown here where we see that torsional states such as trans gauche plus and gauche minus occur with different probabilities along the chain backbone and this basically defines the conformation of the polymer chain.

So, we also discussed about the different mean square end-to-end distances that we obtain by the; for these different models. So, for the freely jointed model the mean square end-to-end distance was basically nl square and n was a number of points and l was the length of a bond and correspondingly the characteristic ratio was infinity in this case is just 1.

Similarly, for the freely rotating chain model again the R square this mean square n to n distance that is still proportional to nl square, but we have a proportionality constant here, which is a function of the fixed bond angle theta and in this case the characteristic ratio is defined as 1 plus cos theta by 1 minus cos theta and this value will be greater than 1. So, one thing again to emphasize is that theta is not strictly speaking the bond angle, but it is the angle between the bond vectors or angle between the adjacent bond vectors.

So, for the Hindered rotation model again the mean square into n distance depends on n l square, its proportional to nl square, but the proportionality constant actually has 2 terms, one dependent on the fixed bond angle theta and another term, which depends on the an average of the cosine of the torsion angle. So, for this case again one can obtain a value for a characteristic ratio as C infinity. So, that basically summarizes our discussion of the different ideal chain models in the previous lecture and today we will just move ahead and discuss how the chain ends are basically distributed and how the distribution of chain ends or the end-to-end distance, how the distribution of that end distance can be represented mathematically for these simple ideal chain models.

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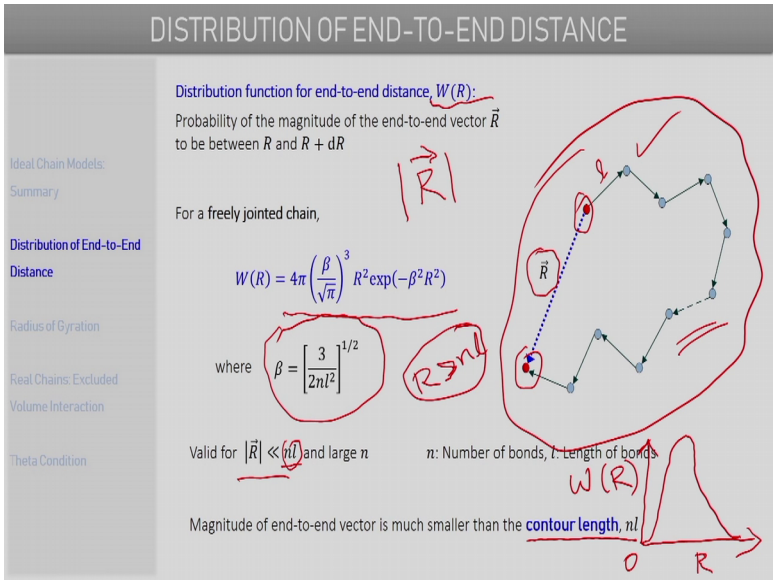

So, again if we consider a schematic of a polymer chain as shown here then the 2 red circles basically let us say these two represent the 2 chain ends and we have a polymer chain where the bonds are reprinted by these vectors here and this dashed vector basically represents that this polymer chain is quite long and we are only showing a few bond vectors at the beginning and at the end. So, for such a representation the end-to-end vector we are representing by this capital R, this vector capital R. So, now, our aim is to study the distribution of this end-to-end distance. So, the magnitude of the end-to-end vector that is what the end-to-end distance is and we wish to study how this end-to-end distance is distributed for different confirmations of the polymer chain.

The distribution function for this end-to-end distance let us say that we represent that this distribution function by W R. So, this function is W and itself a function of the end-to-end distance R. So, we are calling it W R and this distribution function is basically gives the probability of the magnitude of the end-to-end vector lying between R and R plus delta R. So, essentially if we have an end-to-end vector R then its magnitude will be given by let us say this vector R with mod sign so, let us this is the magnitude. So, this decision function basically is gives a probability that this magnitude will lie between a distance R and R plus delta R.

So, essentially its magnitude is close to this value R. So, next if we consider freely jointed chain it can be shown that this function has the form that is shown here. So, the function W R actually has a Gaussian form where this parameter beta is given by the

expression here. So, this, this function or this Gaussian function basically gives us a distribution of the end-to-end distance.

So, if we were to plot this W R with as a function of R ok, so if we let us say plot this function W R as a function of the end-to-end distance R then it will actually go through a maximum and then again decay at longer hours, the distribution of end-to-end distances has a maximum, shows a maximum and of course, for very large values of R the probability that two ends are so separated by that large distance that that small. So, basically this probability function decays down as the distance R becomes large.

This distribution now that we have this distribution we must consider this limitations. So, the mathematical function that we have shown here it is not valid for all cases, it is only valid when the number of chain segments or the number of bond vectors if that is that number is large so one condition is that that n small n should be very large for this kind of distribution to be valid and the other is that the end-to-end distance is that we are considering that should be significantly lower than the maximum stretched length of this polymer the polymer chain.

So, if we consider again the polymer chain that that shown here; then the maximum length that this polymer chain if this is a freely jointed polymer chain then the maximum length again will correspond to this number nl, which is n number of bond vectors times l the length of a single bond vector. So, the end-to-end distance should be smaller than this the maximum dimension that this polymer chain can adopt. So, only for such conditions this distribution function is valid. Now as we just discussed this small n is the number of bonds in small l is the length of bond. This quantity small nl this quantities actually has a name and this quantity is referred to as contour length of a polymer chain.

So, the contour length of any polymer chain is basically its length as measured by moving along the backbone of that polymer chain. So, if one moves along the backbone of the polymer chain then the length that is measured will come out to be n times l and that is referred as a contour length. So, basically the condition for validity of the end-to-end distribution function is that the end-to-end distances that are being described should be significantly lower than the contour length of the polymer chain. The reason for this limitation is that the Gaussian function that we have considered here if we take a close look at it even for values of R even for values of this end-to-end distance R greater than

nl even for these such values the distribution function actually does not decay to 0, it has a very small, but a finite value, but physically speaking this any end-to-end distance greater than nl is physically not possible, it is an unphysical scenario.

So, but the mathematical function that we have it gives a nonzero probability for the occurrence of such end-to-end distances as well are greater than nl. So, so that is why this function, functions form is basically valid only for R, R into n distance is smaller than the maximum stretch length of your polymer chain, for values of R equal to greater than nl, this does not describe the correct behavior because it will predict nonzero probability for occurrence of such end-to-end distances as well which is completely unphysical.

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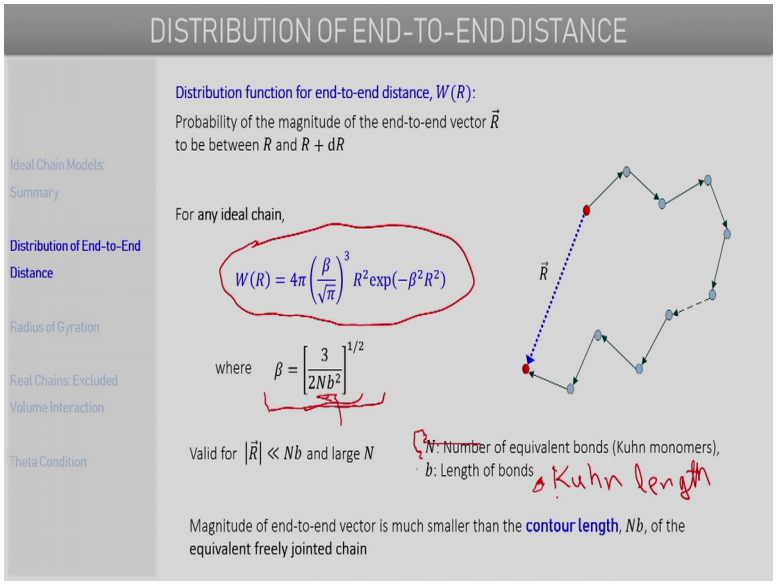

So, this is the discussion that that applies to a freely jointed chain, now let us consider the case of for not just not a freely jointed chain, but any ideal chain. So, for any ideal it can be any chain which where the interaction between distant regions of the same chain are not present that is the definition of ideal chain. So, for any such ideal chain, which is not necessarily freely jointed, it can be freely rotating, it might be something that is, that is described by the rotation isomeric state model.

So, for any such ideal chain one can actually rewrite the same distribution function for the end-to-end distance WR. So, that same equation or expression is valid, the only thing is that the parameter beta that we had described earlier the definition of beta changes. So,

if we look at this expression for beta here instead of the small n we have a capital N here and instead of l square be a have b square here.

So, if you remember from the previous lecture, we had defined these quantities capital N and the small b as the number of segments, a number of bonds and the bond length for equivalent freely jointed chain. So, any ideal chain can be represented or can be mapped using an equivalent freely jointed chain. So, that this equivalent chain that we have mapped onto it that behaves like a freely jointed chain; so, this capital N and b basically are the number of bonds and the bond length for the equivalent freely jointed chain for our ideal chain here.

So, again the validity in this case also applies only when the end-to-end distance that we are considering is much smaller than capital N times b, which is again the contour length for this equivalent freely jointed chain corresponding to any ideal chain that we have and also the number of such bonds should be quite large. So, as we discussed the capital N is the number of equivalent bonds are also differ Kuhn monomers and this we discussed in last lecture and b is the length of this equivalent bond and it is also can be written as or it is also known as the Kuhn length and this is also something that we discussed in the previous class when talking on the equivalent freely jointed chain. So, again as discussed the magnitude of the end-to-end vector should be much smaller than the contour length of our (Refer Time: 18:26) ideal chain that we have.

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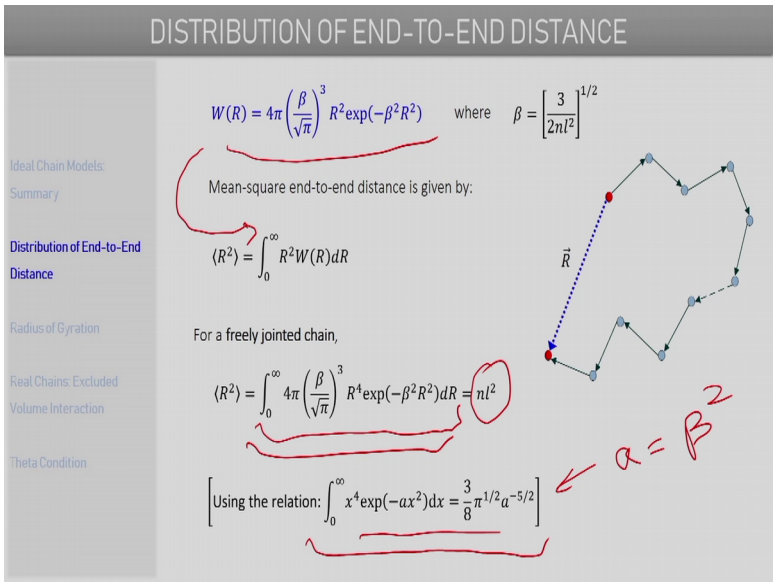

So, if we consider this distribution function if we want to find out the mean square end-to-end distance using this distribution function that that is possible and that can be done by simply integrating R square multiplied by this distribution function WR times d R and integrating from 0 to infinity. So, this basically is what is called the second moment of this distribution function, this second moment of this distribution function gives us the mean square displacement.

So, for an ideal chain or freely joined chain let us say if we substitute the expression for WR here which is given here. So, if we substitute this expression here in this equation then for a freely jointed chain the mean square end-to-end distance that is given by this integral and upon integration it can be shown that this integral comes out to be just nl square, which is a result for a freely jointed chain that we, that we discussed in the previous lecture.

So, to basically carry out this integration one can use the standard mathematical. integration formula x to the power 4 e exponential of minus x square dx integration of 0 to infinity that is 3 by 8 square root of pi a to the power minus 5 by 2. So, if you use this relation and in here if we use this parameter a as beta square then we can use this relation to integrate this expression here and prove that the mean square end-to-end distance is equal to nl square in this case as well.

So, the this distribution function that we have discussed as it is applicable to any ideal chain provided that we are using the Kuhn length and the number of Kuhn monomers and for a regular freely jointed chain of course, its applicable as well. So, next let us discuss another important quantity for describing or characterizing the size of a polymer chain and that quantity is referred to as the radius of gyration.

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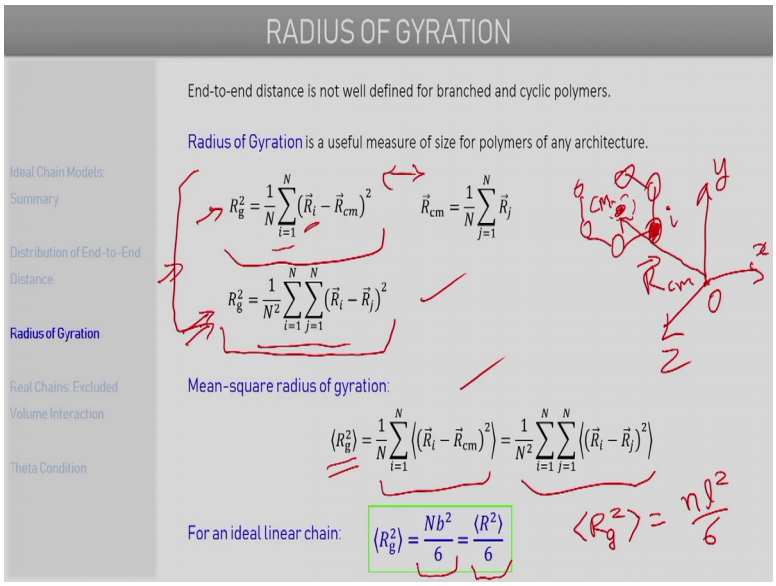

So, this radius of gyration this quantity actually is quite useful because it is something which can be defined for any kind of polymer architecture. So, if we consider the mean square end-to-end distance the measure of size that we have been using till now. So, that mean square end-to-end distance actually is using it is problematic for certain polymer chain architects just like a cyclic order ring polymer. So, for a cyclic polymer, there are no chain ends. So, the mean square into n distance basically is 0 for that case. So, again that is a problem in that case the mean square end-to-end distance does not give us any information about the size of a cyclic polymer.

Similarly, if you have a branched polymer, so for a branched polymer again there are many chain ends, there not just 2 change, there are multiple chain ends in a branched polymer. So, again there if we can try to calculate the mean square end-to-end displacement that the quantity itself is not well defined because we have many chains and it is a not just 2 chain ends. So, what we notice is that mean square end-to-end distance is a good measure of size of linear polymer chains, but when we consider other kind of polymer chain architectures like branch polymers or cyclic polymers then the mean square end-to-end distance itself fails to describe the size of such polymers, polymer chain architectures.

So, radius of gyration as we will see is actually use useful measure of the size of polymers of any architecture and the reason for this is the radius of gyration basically is

defined in a way such that it is possible to define it for any kind of polymer chain architecture. So, the equation defined the radius or the square of the radius of gyration is shown here and the square of the radius of gyration is defined as 1 over N and summation over all the; let us say monomer units present in your polymer chain. So, summation over all of that and the summation is carried on the quantity R i minus R cm square. So, this R i and R cm are basically what is called position vectors ok.

And the R cm here is the position vector of the center of mass of your polymer chain and R i is the position vector of the individual monomer units on the polymer chain. So, the R cm or the center of mass position right to the center of mass can simply be represented as an average of the all the position vectors of all the monomer units present in the polymer chain. So, let us say if we again draw a simple schematic of a polymer chain like this and let us say our coordinate system is such that the origin is located somewhere here we have our it is x, y and z axis like this. So, let us say that this monomeric unit let us denote it as monomer unit number i. So, if we draw vector from the origin to this monomeric unit that is what this position vector R i represents.

So, the R i in this formula here is the position vector of any ith monomer unit on your polymer chain from the origin of the coordinate system that we have chosen ah. So, this in this summation here i runs from 1 to n. So, in this so, basically we will be considering the position vector of each monomer unit in the polymer chain. Now the R cm are the position vector of our center of mass of the polymer chain. So, if we let us say let us say that this is a point which represents a center of mass cm or the cm stands for center of mass the cm or center of mass of this polymer changes at a certain point located here. So, now, the position vector or the vector connecting the origin to this point the center of mass that is what this vector R cm is.

So, this R cm is the position vector of the center of mass and as we discussed if we know the positions of all the monomer units present then just the average the average of those vectors are just summing taking the vectors sum of all the position vectors of the monomer units and dividing that by the number N that will give the position vector of the center of mass. So, if we combine these two, if we combine these two relations, if you combine these two relations and of course, to do carry out some mathematical steps then what can be shown is that the radius of gyration square can be represented using the formula here.

So, in this formula we see that there is a double summation over both i and j. So, for any two monomer units that is i and j this R i minus R j basically represents the vector between these two monomer units and the square of that and again double summation of that if it did perform that step and then divide by N square that is that will also give you R g square that is what this formula tells us. So, if we let say have a polymer chain and the monomer the location all the monomer units are known then instead of separately carrying out a calculation the center of mass and using this first formula here instead of doing that we can directly use this second formula here since we already have the positions of all the monomer units known in the polymer chain.

So, next let us talk about the mean square radius of gyration. So, as we discussed in the last lecture the polymer chain ends basically other distance learning polymer chain inch is not fixed it keeps on changing and the reason for that is the polymer can adopt many different confirmations it because of its backbone flexibility. So, depending on the vast number of different conformation that are possible one can have a vast number of end-to-end distance as possible and that is why we chose a mean square end-to-end distance to represent the polymer size. So, same is true for the radius of gyration as well.

So, the equation, these equations that we have defined here, these are valid only when we are considering a single polymer chain conformation, but as we as we know the polymers have flexible backbones and they can adopt a huge number of confirmations. So, again the radius of gyration also cannot be uniquely defined because for each other different conformation the radius gyration actually will be different.

So, different confirmations will correspond to different positions of the monomer units, which will lead to different values of radius of gyration. So, for these reasons instead of using a unique radius of gyration value mean square radius of gyration values also employed. So, the mean square radius of gyration again represented by the angle brackets which as we have discussed before represents the ensemble average. So, this mean square radius of gyration that again is simply can be defined in using either of these 2 relations.

So, in both these cases the angle brackets represent the ensemble average of these quantities, which means the average over all the different polymer chain confirmations that are possible. So, next for an ideal linear chain ok, so the equations that we have

discussed till now for a radius of gyration or the mean square radius of gyration those equations are valid for any kind of polymer chain.

So, for any kind of chain molecule those equations are mathematical equation definitions of the radius gyration and they are strictly valid. The only assumption in the all those equations is that the all the monomer units have the same mass, if the monomer units are of different masses then the individual mass of the monomer units also has to be accounted for the equations that we have here these equations actually will not be directly applicable one will have to modify them to include the different monomer masses.

But if we have a linear any linear polymer chain and if all the monomer units are of the same type, which means they will have the same molar mass. So, in that case those equations are valid. Now if consider the special case when the polymer chains are ideal polymer chains, so in that case one can actually show will not go through the derivation of the proof here a proof here, but it can be shown that for an ideal linear polymer chain the mean square radius of gyration is basically given by N b square by 6, which is also again equal to the mean square end-to-end distance by 6.

So, again here the capital N and the small b represent the number of bonds and the bond length of the equivalent freely jointed chain. So, capital N is basically number of Kuhn monomers and small b is the Kuhn length of the equivalent freely jointed chain corresponding to any ideal chain that we are considering. So, if we consider of just a simple freely jointed chain. So, in that mean square and radius of gyration can simply be written as nl square by 6. So, we see that the radius of gyration for ideal polymer chains that in magnitude its smaller than the mean square end-to-end distance.

So, later on will also again encounter radius gyration when we talk about measurement of poly and molar mass and we will see that this is a property that can be measured experimentally. So, that is another advantage of using radius of gyration to describe polymer chain dimensions because apart from the fact that it can be defined for any chain architecture, it is also something that is experimentally measurable. So, till now we have been talking about ideal chains and the different models of ideal chains and so on.

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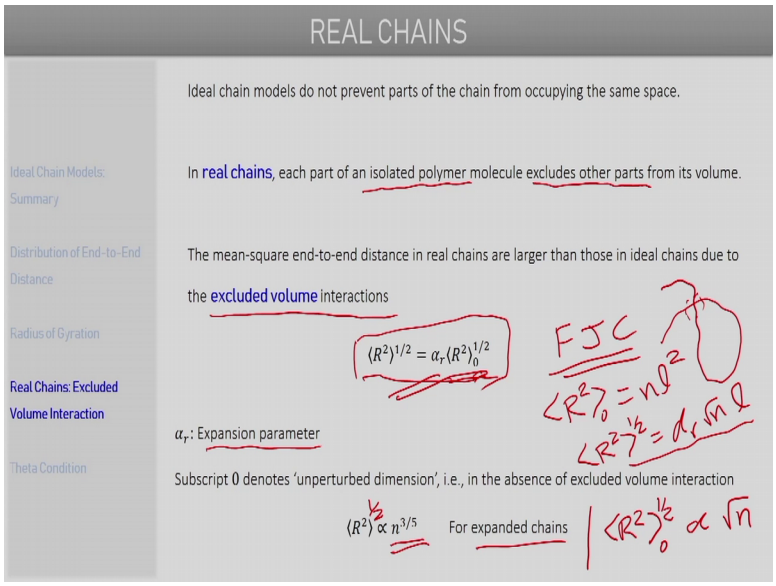

Next let us spend a little bit of time on the unreal chains. So, we know that ideal chains are chains and basically idealized concept where the polymer chain is such that even the distant parts of a polymer chain does not, it distant parts of the polymer chain do not interact with each other ok. So, if the two, there are two monomers which are located far apart along the polymer chain then they can come very close in space and then still they are not interacting that certain ideal chain model implies. So, if let us say if we have a polymer chain like this, one of the confirmations can be like this.

If we can consider an ideal chain then basically a conformation where part of the polymer chain basically intercepts with another part that is allowed ok. So, physically speaking that is something that will not happen to the same physical region of space cannot be occupied by 2 different monomers on the same polymer chain.

So, physically that is not a very realistic kind of model, but that is what now that is what the fundamental assumption in for an ideal chain model is. So, in a real chain real chain basically such interactions are allowed. So, a real chain is of course a chain where a polymers segments are poly monomeric units on the polymer chain those we even those which are separated by long distances along the polymer backbone, if they are close enough to each other in space then they will interact and they different parts of a polymer chain cannot overlap with each other. So, basically what the for real chains what happens is that if you are considering till now all the models in everything that we ever discussed

is for isolated polymer chains so, for the signal, if we have a single isolated polymer chain how does it behave.

So, for an isolated polymer chain in real chains any and each part of the isolated polymer chain molecule can actually interact with other parts of the same molecule because each part actually excludes other parts of the same chains from the volume that it is occupying. So, if a certain part of a certain monomeric unit in each real chain is occupying a certain physical volume of space then if we are considering some other monomeric unit in the same chain, which is some distance away along the polymer backbone then that other monomeric unit cannot occupy the same physical region of space as being occupied by this monomer.

Parts of the polymer chain basically exclude the other parts from the volume that they are occupying and that is something that physically reasonable as well. So, what happens because of this fact that in real chains parts of chains exclude other parts from the volume that they are occupying the mean square end-to-end distance in a real chain basically it turns out to be larger than those in ideal chains and this is because of what is called the excluded volume interactions.

So, as we discuss excluded volume interactions are interactions which result from the fact that a certain part of a given polymer chain excludes other parts of the same chains from the volume that it is occupying. So, such interactions are called excluded volume interactions and in an ideal polymer chain such interactions are not present, so distant parts of the polymer chains can overlap and such confirmations are allowed.

In a real chain if different part distant parts of a polymer chain of the same polymer chain are overlapping with each other and then such confirmations will not be allowed and due to excluded volume repulsion basically the dimension that a real polymer chain adopts that those dimensions are tend to be higher or larger than the size that ideal polymer chain adopts. So, the real polymer chains because of these excluded volume interactions are larger than the corresponding ideal chain.

So, the relation between these the dimensions of this real polymer chains and the ideal polymer chains that relation is shown here and in this relation the parameter alpha R where alpha R is referred to as a expansion parameter and this basically is a measure of how much larger the real polymer chain is compared to the ideal polymer chain size. So,

the subscript 0 here, this subscript 0 here that basically denotes what is called unperturbed dimension are the dimensions in the absence of excluded volume interactions.

So, these unperturbed dimensions are basically dimensions of an ideal polymer chain and if we apply this expansion factor alpha R to the dimensions are ideal polymer chain then we will get the dimension of a real polymer chain. So, let us say if we consider a freely jointed FJC or a Freely Jointed Chain model we consider an example of that then in such a model this the unperturbed dimension or R square naught is just nl square, so this is just the ideal chain dimension.

So, in this case, what is called the dimension of the real chain that will correspond to alpha R square root of n times l because we are in this relation the R not square root of R not is considered here in the definition of alpha R. So, basically if we have an idea about the dimension of an ideal chain and if we know what the expansion parameter is of you can relate the expansion parameter to some things which are known. So, if we have the in these information then based on this the dimension of the real polymer chain can be predicted directly using the relation that is shown here.

So, we know that for ideal polymer chains this mean square end-to-end distance basically square scales has n or the number of bond vectors present in the polymer chain. So, for a real polymer chain there should be a half here actually. So, for real polymer chain the square root of this mean square end-to-end distance or square root of this R square that actually is proportional to n to the power 3 by 5 or n to the power point 6 for if the chain is expanded due to excluded volume repulsions. So, in that case this the end-to-end distance basically scales as n to the power 0.6 or 3 by 5. If we consider ideal polymer chains then this scaling for that is a ideal polymer chains this scaling is this proportionality is to square root of n which is n to the 0.5.

So, we see that as a number of monomer units or segments in the chain increase then the rate at which the size or the end-to-end distance of a polymer chain increase that rate is higher for a real polymer chain compared to the ideal polymer chain, because in ideal polymer chain it scales as n to the power 0.5 whereas for a real polymer chain the square root of the mean square end-to-end distance that scales end-to-end to the power 0.6 or n to the power 3 by 5.

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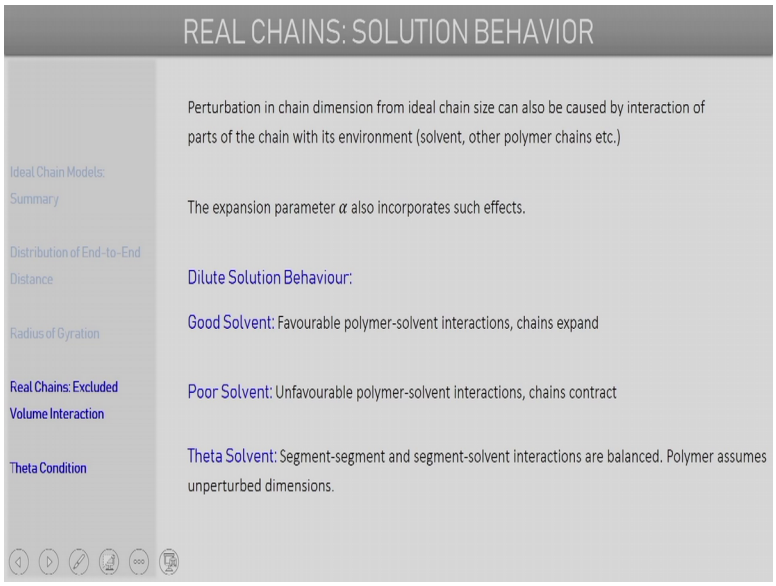

Finally let us talk a little bit about before conclude let us start to talk a little bit about the behavior of real chains in the presence of other substances like if the polymer changes that is in a solution. So, it will be surrounded by solvent molecules or if the polymer chain is not isolated, but in if it is in the presence of or if it is surrounded by other polymer chains of its own kind like in the case of an amorphous polymer sample or a polymer melts so, in such cases how the behavior will be.

So, specifically for now will focus on the behavior of real chains in solution, as we have just discussed the real chains have a larger dimension than ideal chains and this perturbation from ideal chain dimensions result from excluded volume interactions. So, basically different parts of the polymer segment cannot overlap and they if they come close to each other this excluded volume repulsion and that is why overall the size of the real polymer chain is expanded or larger compared to the size of an ideal polymer chain which is the unperturbed dimension.

So, we discussed in the previous slide that we there is an expansion parameter alpha which can be used to relate the real polymer chain dimension to the ideal polymer chain dimension and this expansion parameter actually in the last slide we discussed the case of an isolated polymer chain, but even if a polymer chain is present in a solution where its surrounded by other solvent molecules even in such cases the this expansion

parameter takes care of the effect of the surrounding molecular environment. So, that such details are actually incorporated in this expansion parameter.

So, let us consider the behavior of dilute solutions. we were focusing specifically in dilute solutions, for now because in a dilute solution the polymer chains themselves will not interact with each other, different polymer chains will not interact with each other the polymer solution is dilute the chains will basically remain isolated from each other and each chain will be separately surrounded by solvent molecules.

So, in such dilute polymer solutions where the chains are not overlapping different chains are not overlapping with each other or not getting entangled with each other and where the chains have essentially isolated from each other. There the primary interactions that are of interest are the excluded volume interactions that are internal to individual isolated chains and the interaction between the solvent molecules and the monomeric units or the segments of the polymer. So, what will happen is that if we have a polymer chain present in such a dilute solution then excluded volume interactions will want to expand the polymer chain dimension from its ideal dimension.

So, the segment repulsion will want the polymer chain to swell. Now if the polymer, but because the solvent is also present around it depending on the nature of the interaction of this polymer chain with the solvent the actual behavior of the polymer chain will be dictated by both these interactions. So, the interactions internal interactions between segment due to excluded volume interactions and the segment solvent interactions both of these will govern how the polymer chain basically what kind of dimensions they adopt in solution.

So, if we have a good solution. So, we have really doing a very qualitative discussion here. So, if we consider a good solution a good solution is where the polymer segments basically have favorable interaction in the solvent molecules. So, what said is that the polymer segments like the segment solvent molecules and in that case internally the segment repulsion due to excluded volume interactions that will try to expand the polymer chain and since the polymer is having favorable interaction with the solvent molecules it does not have much problems with expanding. So, polymer will adopt an expanded conformation with alpha or the expansion parameter value larger than 1.

So, for in the presence of a good solvent the polymer will swell and it will adopt an expanded conformation where the size will be larger significantly larger depending on how good the solvent is it will be larger than the unperturbed or the ideal chain chained dimension. Next if we consider the other extreme where the solvent is poor and where the polymer segments basically are not interacting favorably with the solvent molecules.

So, if the polymer segment and the interaction with the solvent is poor or unfavorable in that case what will happen is that the internally again the segment repulsion will be such that the polymer will try to adopt an expanded conformation, but because the polymer chains themselves are interacting poorly or unfavorably the surrounding solvent molecules that other effect basically will try shrink the size of the polymer chain.

So, essentially in a poor solvent where the solvent segment interactions are unfavorable, the polymer chain will not adopt any expanded conformation it will adopt contracted or a strong kind of conformation and in fact, if the solvent quality is very poor, so that the interaction is very unfavorable between the polymer and the solvent then in such case of the solvent it essentially becomes a non solvent such that the polymer chains basically precipitate out of that solution. So, in the case of a poor solvent if we have condition where the segment repulsion due to excluded volume interaction of the polymer chain if that repulsion is counteracted in counterbalanced by the solvent segment unfavorable the interactions, if these 2 effects are exactly balancing each other then basically we have a situation where the polymer chain adopts nearly ideal conformation, ideal chain conformation, or ideal chain dimensions.

So, such a situation or such a condition is referred to as a theta condition and the solvent for which such condition arises such solvents are called theta solvent. So, in the theta solvent what we have is that the internal polymer segment repulsion due to excluded volume, they are balanced by the solvent segment repulsion.

So, these two interactions which are working in opposite direction balance each other in such a way that the size of this; these are real polymer chains, but because of the balance of these two interactions the size of these real polymer chains basically correspond to a dimension of ideal polymer chains. So, for theta solvents or theta condition the real polymer chains are also known to adopt ideal chain dimensions and there is something

that has been observed explained it is not just some theoretical argument it is observed experimentally as well.

So, what we see is that if the certain conditions are met which is true for a theta solvent then the polymer real polymer chains can also assume unperturbed dimensions and this concept of theta solvent is something that we have introduced here in a very qualitative way, but in the next few lectures when we will talk about polymer thermodynamics we will be discussing this concept of theta solvent in a bit more detail. So, with regards to the confirmations of ideal polymer chains and the behavior of real chains qualitative behavior of real chains this is where we will conclude our discussion.

So, what we have learnt is that the ideal polymer chains can be described by different kinds of models of different complexity and basically if we have a real polymer chain then in that case the dimensions typically are expanded compared to an ideal polymer chain because of excluded volume interactions, but when we can have certain conditions where real chains also adopt ideal chain dimensions one such condition is where the solvent is of such a type that the segment internal repulsion of a real chain is counterbalanced by the solvent segment repulsion and such a solvent is called theta solvent.

So, that is one example another example is where basically is the case of amorphous polymer chain, polymer samples are polymer melts, where from the perspective of polymer chain again the polymer chain will want to expand due to the internal segment repulsions, again due to (Refer Time: 48:48) volume interactions, but because it is surrounded by other chains as well the segments of the a given chain will also interact with the segments of the surrounding chains and those segments segment repulsions will again counteract the internal excluded volume interactions.

And again in such cases where we have a very concentrated a collection of polymers multiple polymer chains the internal repulsion volume repulsions within the chain are counterbalanced by the external repulsions between different chains and again in such cases also its been observed that ideal polymer chains dimensions are assumed. So, that basically concludes our discussion of polymer chain confirmations ideal polymer chain models and qualitative behavior of real chains. In the next lectures for we will be focusing on the thermodynamics of polymer solutions in more detail.