Introduction to Polymer Physics

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Lecture – 23
Entangled Polymer Dynamics

Hello everyone in the previous lecture we started our discussion of polymer dynamics and we specifically focused on dynamics of polymer chains which are unentangled. We looked at two different model one which was applicable for unentangled polymer melts and that was a Rouse model. And the other one which better described the behavior of chain dine polymer chain dynamics in dilute solutions and that is the Zimm model

In today's lectures, what we will do is focus on the Dynamics of Entangled Polymers. So, entangled polymeric chains are basically long much longer in nature. So, if the polymer chains are long then typically they will tend to entangle with each other and the dynamics of such entangled polymer chains is quite different from that of unentangled polymer chains.

In today's lecture will primarily focus on dynamics of entangled polymer chains in melt like state. So, we will introduce concept of entanglements in melts; we will specifically focus on a concept where which is proposed by Sir Sam Edwards, that is a tube concept. And we will discuss how this the system of an entangled polymer chains can be described using this tube concept and we will also talk about the related parameters.

And thereafter we will see how this tube concept can be used or was used by design to propose a model for the dynamics of entangled polymer chains and this model is referred to as reptation around. So, we will focus on reptation around.

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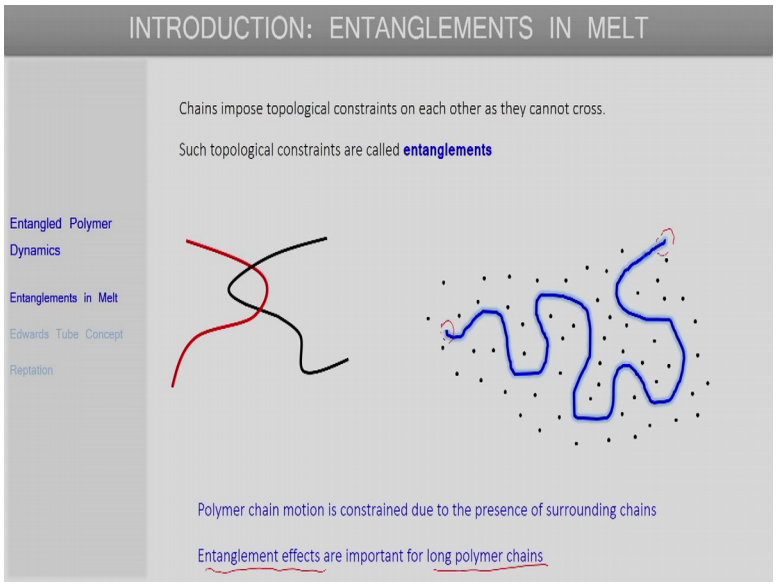

If we talk about entanglements; so, entanglements can be thought of as what is called topological restrictions that the presence of other chains imposes on a given chain because the chains cannot cross each other.

So, since the chains are formed by covalent linkage of monomeric units; if two chains get it is entangled in a way then they cannot cross each other. And that restriction or constraint imposed by the presence of surrounding chains on a given chain that can be thought of as representing entanglements. These entanglements as we discuss topological constraints it probably is much easier to visualize this using some simple cartoons.

So, we can think of a; consider that two chains that are shown here; one in red and the other in black. And if we consider the motion of the black chain here and let us say the black chain is moving to the right; then a point will come when this portion of this black chain will be restricted from motion because of this portion of the red chain; since the black chain cannot cross the red chain that constraint will be imposed on the motion of this black chain by the presence of this red chain.

So, this is a very simple kind of pictorial representation of what an entanglement effect might be. And here we have just two chains now imagine if the case is more complex where we have the presence of large number of chains and all of them entangled with each other which might be the case for a melt of long linear polymer chains.

So, if we have such a complex case where their multiple entanglements present then what one can do is again in a simplified manner represent the presence of entanglements as constraints imposed by the surrounding chains on a given chain. If we again consider let us say chain that is highlighted in this diagram. And if we consider all the dots that are around this chain to represent the constraints that are imposed by the surrounding chains on its motion ok.

So, if that is the case then what we can say is that this polymer chain is not free to move about a diffuse in any which way that it likes; its motion is constrained by the presence of all these dots which represent the effect of the chains surrounding this highlighted polymer chain. So, all are these constraints restrict the motion of the diffusion of this polymer chain.

And due to this restriction this polymer chain that we have that can only move in a way which avoids all these obstacles that are present. And one way to accomplish that could be that if we consider this as a tail end of how the polymer chain; then the motion might be thought of as starting where the tail retracts in a way. So, this part of the tail retracts in a way; so, that some kind of loop or kink is formed still respecting the constraints imposed by the surrounding chains. And this kink or loop is then moved or this kink moves along the contour of the entire given chain all the way towards the head of the chain which may be here.

And while moving it is respecting all the constraints that are imposed by the surrounding chains. So, this is a very simplistic picture because as the any motion that takes place within the given polymer chain; the surrounding chains will also be moving during that time. So, the nature of the constraint imposes itself might be a bit dynamic, but for simplicity if we assume that we have these fixed obstacles. And polymer chain motion takes place through let us say a kink or a loop developing at one end and then getting transported along the contour to the other end; then after some time the chain conformation might look something like this where part of the tail has retracted up to this point and the head has extended here.

As we discussed the polymer chains in an entanglement; entangled polymers the polymer chains are constrained by the presence of surrounding chains and the effects of entanglement is especially important for long polymer chains. So, if the polymer chains

are short the entanglement effect site either will be not present or will be small. So, if on the other hand the polymer chains are quite long; then a single chain might be entangled in many different places. And the effect of entanglement on the dynamics of polymer chain will be highly pronounced as we will see.

Next we will what we will do is try to discuss a concept which is called the Edwards tube model or the Edwards tube concept which simplifies the description of a motion of a polymer chain in the presence of all these surrounding constraints.

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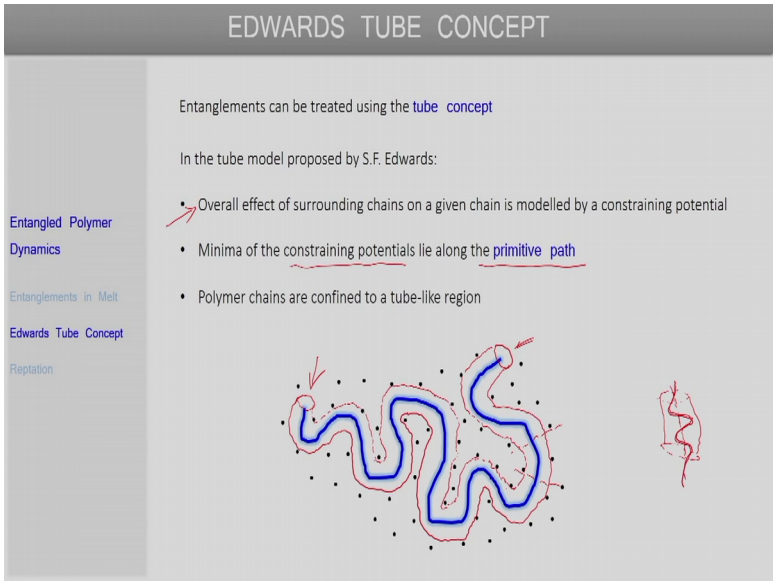

The concept; the concept of entanglement was treated by proposing the tube concept by a Sam Edwards in the 1960s and in this model the key points of this model are that we have a given chain and it is surrounded by a bunch of other chains. So, that the motion of the given chain is restricted and the path that it can take is also restricted by the presence of the other obstacles around it. The presence of the surrounding chains is modeled as a constraint on our given chain ok.

All that let us say monomeric units in a given chain they are acted upon by some kind of constraining mathematical potential which represents the constraints imposed by the surrounding chains. If we consider since these are mathematical functions and initially a quadratic kind of constraining force potential was considered.

If we consider the regions in which this constraining potential has the potentials on each of the monomers exhibits minima, then that path is what is defined as the primitive path. If the minima of the constraining potentials they lie along what is called a primitive path. So, this primitive path is the region of space which corresponds the minima of this; constraining potentials representing the surrounding constraints.

And due to the presence of surrounding constraints what is assumed is that the polymer chain itself is constrained in a tube like region ok. And this primitive path kind of represents the center of this tube like region and the polymer chain itself is bounded by this tube like region defined by the presence of the surrounding chain around this is a given polymer chain.

So, again if we go back to the cartoon that we had drawn earlier for representing entanglements and constraints and if we consider our highlighted polymer chain here; then we can think at this particular instant when this snapshot is can say we can consider the polymer chain to be confined to some kind of a tube like region that is defined by the presence of other constraints all around this polymer chain.

So, roughly if we considered this kind of a tube we can say that the motion of our polymer chain is constrained to happen in a some kind of a tube like region as I am roughly drawing here and so, this is one end of the tube this is the other end. And what this Edwards tube concept states is that the given polymer chain is confined to a kind of a tube like region and the central the let a path denoting the center of this tube like region will correspond to the primitive path where the constraining potential will have their minima.

It should not be it is not the case that the length of the tube like region corresponds to the contour length of our polymer chain. So, within if we consider let us say small section of this tube like region here. So, let us say if we consider this section here portion of the tube like region the polymer chain in here itself can adopt different confirmations ok. So, all the primitive path might be somewhere along the center; the polymer chain itself can have a different confirmations inside. The contour length of a polymer chain usually will be much larger than the length of the tube that we had confining tube that we have; so, that is the Edwards tube concept.

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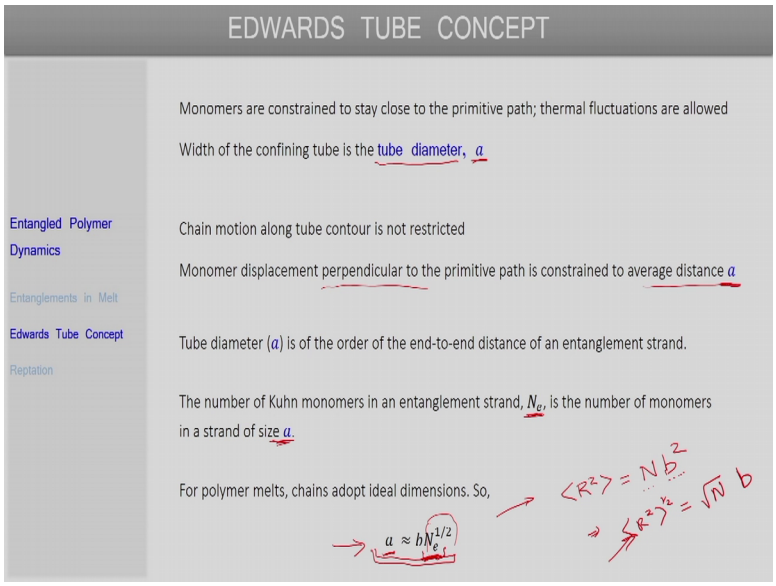

And in this model that is proposed by Edwards; the monomers on the given polymer chain they are constrained to stay close to the primitive path that defines as the center of the tube. But if they are not completely bound to the centers; so, they can of course, fluctuate around the central primitive path due to the thermal effects.

So, thermal fluctuations are allowed although monomers the potential tries to constrain them along the primitive path or close to primitive path. But since they will be thermally fluctuating, so they will adopt confirmations that will be centered around the primitive path, but will not necessarily coincide with the primitive path. If we consider the tube the confining tube, then what we can say is that we can quantify its width of the tube by a quantity known as a tube diameter and it is typically represented by a.

What this tube models proposes is that along the tube if the chain motion is happening along that you, then it is not restricted at all. Because along the tube entanglement effects are not that the tube is defined by the sounding constraints of within the tube the chain is free to move. However, perpendicular to the primitive path which marks kind of the center of tube the motion perpendicular to this primitive path that is constrained.

And monomers motion perpendicular primitive path is constrained to happen on an average up to a size characterized by this tube diameter a. So, the monomer displacement that is perpendicular to this primitive path that is constraint to an average distance a; it can say happen by a distance more than a, but on an average that displacement will be.

Next if we consider this tube diameter that we have. So, since tube diameter is a quantity which characterizes an entanglement effects the what one can say is that number of monomers that is present in a given entanglement strand that will also be equal to the number of monomers that will be present in a polymer strand of length equal to the tube diameter. So, in other words the tube diameters the size a corresponds to the or is of the same order of the as the length of an entanglement strand of the polymer. So, when we say an entangled strand of the polymer; it is an average measure of the size of the portion of the polymer chain between two entanglement points ok.

So, polymer chain given for long polymer chains in general will be entangled at different many different points along its backbone let us say. So, on an average the length of the polymers a portion of the polymer chain between two entanglement points that is the size of the entanglement strand and the entanglement strand itself is the portion of the chain between any two entanglement points.

So, what we are saying is that the tube diameter size this a is of the same order as the size of an entanglement strand of the polymer chain. So, that again itself suggests that number of monomers or the let us say number of Kuhn monomers that are present in a given entangled strand entanglement strand, that will be equal to the number of Kuhn monomers that will be present in a polymer chain having or portion of the polymer chain having length a.

So, if we make that observation then from there we; another observation is that since we are talking about the melt state. So, in the melt state we have already discussed previously that the polymer chain assumes ideal chain dimensions because the excluded volume effectively screened in the dense melt state. So, the chain dimensions correspond to the ideal dimensions; the relation the fact that on any polymers strand of size a which is a tube diameter will contain any number of Kuhn monomers.

And the fact that the ideal chain dimensions shall be adopted by the polymer; these two can be combined to relate the quantity a with the quantity N e. And that we can do simply by writing this expression a will be of the order of b times N e to the power half. So, this comes directly from what we have studied earlier about statistics of or the size of ideal polymer chains.

So, we study that if you have any ideal polymer chain that can be represented as an equivalent freely jointed chain. And there the mean square end to end distance that can be represented as N b square, where N is the number of Kuhn monomers in our polymer chain and b is the Kuhn length. What this suggests is that the root mean square end to end distance which will be the characteristic size of the polymer that will be square root of N times b.

So, that is exactly what we have written here this N e to the power half is square root of N e and N e is the number of Kuhn monomers present in within our entangled strand. And we say that the entanglement strand has an average length which corresponds to the tube diameter a. So this same relation has been reformulated for the case of our entanglement strand and tube diameter.

So, we see that this tube diameter a is of the order of b which is a Kuhn length times square root of the number of Kuhn monomers present in a given entanglement strand. So, again it should be emphasized at N e is the number of monomers or monomer units present Kuhn monomer units; present in a entanglement strand and not on the full polymer chain. A given polymer chain will be composed of many entangled strands and N e this number corresponds to just a Kuhn monomers single entanglement strand.

So, now that we have this expression we can think of our confining tube. So, the tube that is confining our polymer chain we can think of it as being composed of n over any different sections. So, the tube confines the entire polymer; so, it corresponds to a total let us say N number of monomer units. So, this N corresponds to the number of monomers are present in the entire polymer chain, N e is the number of monomers in a given monomers in a given entanglement strand.

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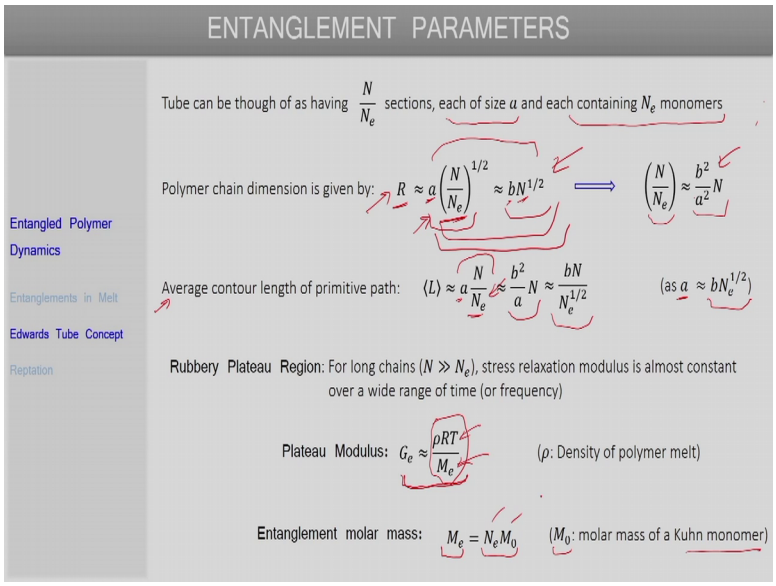

And since the size of an entangled strand is of the order of the tube diameter, we can say that each of these sections has a size a and each contains N e monomers.

So, if we have if we consider our confining tube because it might be might have a much different shape than this, but just as an example; we can consider an entire confining tube as being composed of different sections, if each of these sections has length a; which is equivalent to the tube diameter itself, then we will have N over N e such sections. The reason for it that is since then this length is a this will have approximately N e number of Kuhn monomer units in here.

And since the total chain contains n Kuhn monomers; the number of such sections will be given by N over N e and each section contains N e monomers. What we can say is that the entire polymer chain its dimension can be represented using our equivalent freely jointed chain consisting of N Kuhn monomers and having Kuhn at b. Or equivalently we can also write its dimension to correspond to the fact that it consist of N over N e different entanglement strands and each and each entanglement strand has a length a.

We can also think of our entire polymer chain as being a random walk or a freely jointed chain consisting of segments having length a total of N over N e such entanglements strands present along the polymer chain. If you use both these cases or considerations; then the polymer chain dimension let us say R that can be represented in two different ways either by this or by this.

So, the second one is just representation where we are considering the polymer to be an equivalent freely jointed chain having a Kuhn length b and number of Kuhn monomers N. In the first case here we are considering the polymer to be again kind of freely jointed chain or a random walk, where the size of a given segment corresponds to that of an entanglement strand a and we have the total of N over N e such entanglement strands. And all these entangle strands together constitute a kind of random walk which leads to our entire polymer chain.

So, since both these are equivalent we can say that the polymer chain dimension can be represented by either of these relations. And what we can infer from these two is that this ratio N over N e will be of the order of b square over a squared times N. And that can be done simply by rearranging their terms here and squaring this N over N e to the one half. That is what we obtain for the chain dimension we can represent it in two different ways by considering a chain to be a random walk either of the Kuhn monomers or of the entangled strands themselves.

Now average control lengths of the primitive path; so, we have a primitive path defined. So, it the contour length of this primitive path that we can represent simply as a times N over N e; so, we have consider tube to be divided into n over any different sections and each section has a length a. So, the total the contour length of the primitive path will be simply the product which is a times N over N e.

Now, this N over N e that we have here that we already see is of the order of this ratio. So, if you substitute that then we get this term; so, we are substituting N over N e by b square over a square times N; so, we get this term. And then finally, from here we can simplify to this term because we already know that a which is the tube diameter and which is also the length scale of an entanglement strand or dimension of an entangled strand that is just b times N e to the power square root N e to the power half. So, that gives us the dimensions of the primitive path and we already have the polymer chain dimensions here.

Next let us consider another concept that is important here and that is referred to as the rubbery Plateau region ok. So, if for long linear polymer chains where the number of Kuhn monomers N is much larger than the number of Kuhn monomers present in a given entangled strand; so, if the entanglement effects are strong what is observed is that if the

stress relaxation modulus is obtained as a function of time or as a function of frequency equivalently; then what seen is that there is a wide region or wide range of time scales or frequency scale over which this stress relaxation modulus actually shows an almost nearly constant value.

So, this region where the stress relaxation modulus is nearly constant is called the rubbery plateau region. The value of the modulus at in this rubbery plateau region is referred to as a Plateau modulus. This Plateau modulus can be represented we will not go into the details of this, but it can be represented to be of the order of this ratio; where rho is the density of the polymer melt R of course is a gas constant, T is the absolute temperature, M e is the molar mass of an entanglement strand.

So, it is called the entanglement molar mass, M is called entangling molar mass and it can be represented as N e times M naught, where M naught is a molar mass of a Kuhn monomer. So, a single entangled strand has N e number of Kuhn monomers and N a subscript e number of Kuhn monomers and each Kuhn monomer has a molar mass M naught. So, entanglement molar mass will be the simply the product of these two.

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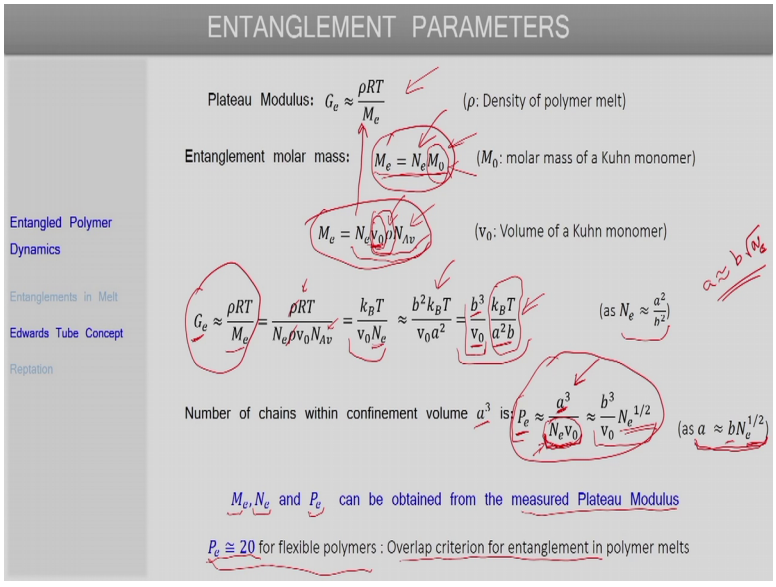

So, now if we consider the Plateau modulus as defined previously and the entanglement molar mass; this entanglement molar mass the expression we can simplify further. So, here what we have done is in the Kuhn monomer molar mass that we have represented as a product of these 3 terms.

So, here v naught is the volume of a given Kuhn monomer, rho is the overall density of a polymer melt and N is a Avogadro number that has to be present because we are talking about a molar mass that is the mass of 1 mole of Kuhn monomers. So, this v naught is a volume of a single Kuhn monomer and rho is the density. So, this product will give the rho times v naught will give the mass of a single Kuhn monomer. and if you want the mass of one mole of Kuhn monomer we need to multiply by the Avogadro number. So, if we substitute this expression for N e which is N e times v naught times rho times N Avogadro.

If you substitute this here then the expression for the Plateau modulus can be simplified and we have this where the rho will cancel and this R divided by the Avogadro number that is simply the Boltzmann constant. So, if we make these simplifications; we get this expression for our Plateau modulus and which can again be further simplified. Because this N e; N e is this ratio a square by b square; so, the way we had defined let us say a as being b times square root of N e previously.

So, this a was defined to be on of the order of v times square root of N e; then from here if he a square root of N e is a by b and then taking square on both sides and N e will just be a square by b square that is we had what we have substituted here. And here in this last step we have just multiplied and divided by b to get these two. So, this term is just b cube by the volume of a Kuhn monomer and b cube is the cube of the length of the Kuhn monomer and this second term is just k B T divided by a square b.

So the Plateau modulus in a simplified form can be written as shown here. Next one last concept or parameter related to the entanglement is what is called the number of chains within a given confinement volume. So, since our tube diameter which is the confining tube the tube diameter is represented by a. So, the confining volume we represent by cube of this; so, the confinement volume will be a cube and we are trying to find out the number of polymer chains present within this confinement volume and that number is represented as P e; so, it is a number of polymer chains in the given confinement volume.

So, the volume that way we are looking at is a cube and the volume of a single entanglement strand that is N e times v naught. So, v naught is the volume of a Kuhn monomer and N e is the number of Kuhn monomers in an entanglement strand. So, this product this will give us the volume of a occupied by a given entanglement strand. So,

this ratio gives us this quantity P that quantifies a number of entanglement strands present within given confined volume a cube.

Now again previously we have just discussed that a is given by this b square root of N e. So, if we substitute that the instead of a cube we will get b cube N e to the power 3 by 2. And since we have N e in the denominator here that will cancel and we get b q or v naught N e to the power half; so, that is the expression for p that we get.

So, finally, what we need to understand here is that the Plateau modulus g is something that is exponentially measurable. And if we have the value of Plateau modulus and other parameters related to entanglements such as M e; the entanglement molar mass N e which is a number of Kuhn monomers in a given entangled strand. And P which is the number of that same tangle strands present in a given confined volume a cube.

These can be obtained directly because the g which is a Plateau modulus can be measured. And once g is measured M e we can obtain from this expression and once M e is known then N e we can obtain from this expression or this expression either one, then this will give us N e. And once N e is also known then from these expressions we can get P e so, all of them can be obtained.

And if such a calculation of measurements of Plateau modulus and from there calculation of P e is done for a different linear flexible polymers in melt state; then what is found is P e is found for most cases to be close to 20. So, P e is found to be close to 20 for flexible polymer. So, this condition P e being close to 20 that defines what is called the overlap criterion for entanglement in polymer chains. So, now, that we have discussed a tube concept and the entanglement; where an associated entanglement parameters, let us now move on and see how the dynamics of polymer chains within the confining tube like region can be studied.

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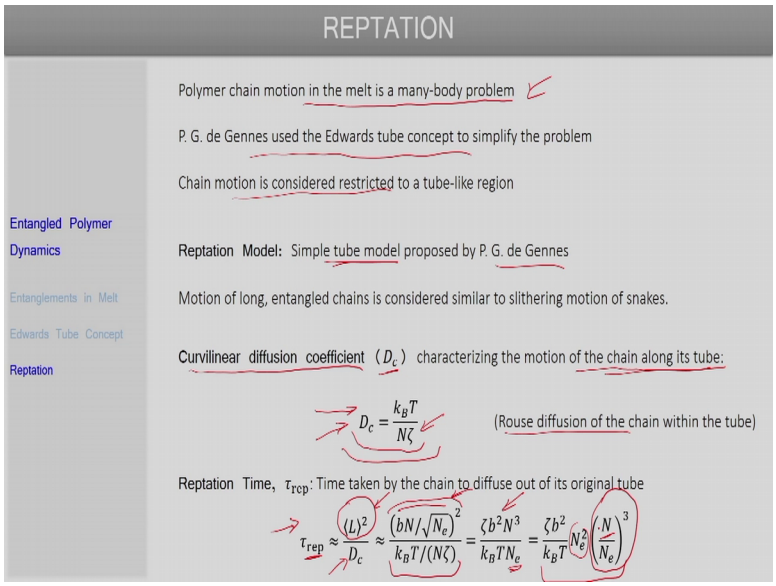

Polymer chain motion in a melt that is a many body problem at the first glance; the reason for this is a given polymer chain if it is moving its motion depends on the presence and the corresponding motion of many other polymer chains surrounding it. And since we have it is a dense system and the polymer chains are long if we try to study the dynamics directly as a many body problem, it will be a very complex problem to study and it might not actually be amenable to solution as well.

One elegant approach that was proposed to study the polymer dynamics of polymers chains entanglement for entangled polymer chains was that by P.G de Genne. And this approach makes use of the adversative tube concept the concept that we have already discussed. And here the main point is that for any given polymer chains the surround chains are around it; again impose constraints and the constraints are imposed such that the motion of the given polymer chain is restricted to in a confining tube and as a chain moves of course, the confining tube also moves along with the chain.

De Genne who actually won a Nobel Prize for his contribution two important contributions to polymer physics now if use the Edwards tube concept to simplify this many body problem and proposed that the chain motion can be considered to be restricted to the tube like region. Any model of polymer entangle polymer dynamics which uses the steep concept is comes under the category of tube model. So, the model

proposed by de Genne initially is the simplest tube model science called a reptation model.

And it is simple trip tube model proposed by de Genne and here what is assumed is that if you have a long linear polymer chains present in a melt state and highly entangled; then their motion takes place in a manner that can be thought of us and allow us to the motion of a sneak that is just slithering around various obstacles. So, if we consider let us say a large number of snakes in a given pit.

So, the way the snakes; so, of course, if the lot of snakes are present in a small volume one can think of as a snakes as being kind of entangled with each other. So, the motion of the snake will be a slithering kind of motion where it traverses making sure that the obstacles present by the other snakes is are avoided. So, it takes the slithering kind of motion and that motion is what inspired this term reptation the origin of this some reptation is reptile. So, it is a reptilian slithering kind of motion that is what one can visualize as a reptation model to be like.

And now getting to the mathematical aspects the motion of polymer chain within this tube; so, if we are considering the confining tube as proposed by Edwards and if I can see the motion of polymer chain within this tube. So, within this tube the motion is actually not constrained the constraints are such that they restrict they are kind of restricting the motion to within this tube, but the motion within this tube is actually unconstrained. So, the curvilinear kind of motion within this tube can be characterized by a curvy linear diffusion coefficient D c. D c can be found out easily because within the tube the motion is unconstrained there is the entanglement effects are not there. So, one can describe the motion simply as a kind of a Rouse motion of the polymer chain if you are looking only at the motion along the tube.

So, for Rouse motion we already discussed in the previous lecture that the diffusion coefficient simply is given by k B T over n times zeta when N is again the number of Kuhn monomers present and zeta is the friction coefficient corresponding to each monomeric unit. So, we within the or along the tube the chain motion is actually not affected by entanglements. And we can say that the Rouse diffusion kind of model describes this motion and the diffusion coefficient that we can obtain from that model.

Next if we consider the time scale. So, in the reptation model the reptation time is defined as the time required for a given polymer chain to come completely out of its original tube. So, at any instant if the polymer chain is present inside a certain confining tube and if we consider now this tube to be fixed in the polymer chain slowly diffusing out of it. So, the time required for the entire polymer chain to diffuse out of the original tube that it was present inside that corresponds to reptation time. And of course, if the polymer chain moves out it will create its own new confining tube around it because of the presence of the obstacles presented by the other chains.

But the overall time it takes for a given polymer chain to come out of its original tube that corresponds to the repetition time. And that we can order of this reptation time can be obtained simply as the ratio of the square of the primitive path length of the primitive path length corresponds to the let us say contour length of our tube and. So, ratio of the square of the primitive path length and the curvilinear diffusion coefficient which corresponds the diffusion coefficient of the polymer chain within the tube so, the square of the length scale traversed by the poly machine divided by the corresponding diffusion coefficient for that motion.

So, if we again simplify this if initially in this lecture we had discussed that the primitive path length which will just be a times N over N e that can be written in this format and D c of course, we have already written like this. So, if we substitute them and take the ratio; we get this expression for the reptation time. And again we can just multiply and divide by N e square; so, we get this expression where we have this kind of a cube dependence of this reptation time on the number of Kuhn monomers present in our polymer chain.

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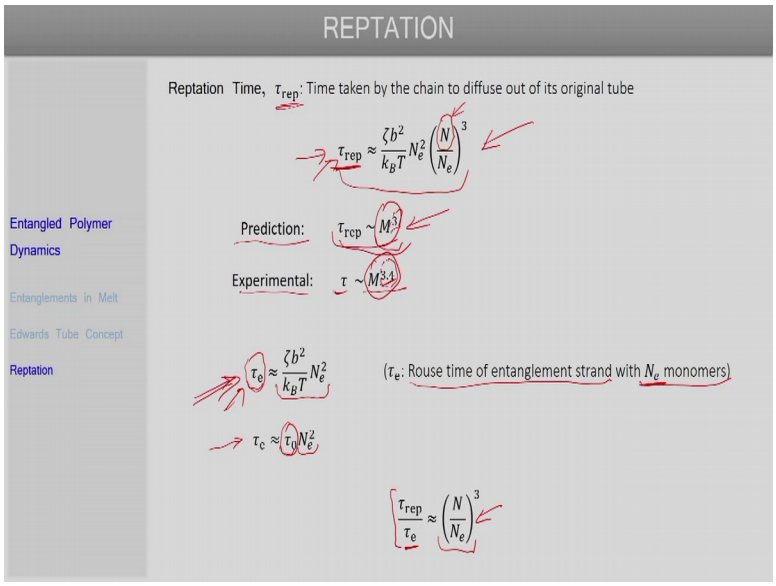

So, now if we again this is the same expression rewritten here the reptation time expression that we just discussed. What one can see from this expression is that and this is a as predicted by the reptation model of design; what we see is that reptation time actually scales as cube of the molar mass of the polymer chain.

And the reason for this is that the number of Kuhn monomers present in a polymer chain that will be directly proportional to the molar mass of the polymer chain. So, since the reptation time scales has cube of the number of Kuhn monomers in the polymer chain; it will also scale as cube of the molar mass of the polymer chain. So, that is the prediction of this reptation theory or reptation model.

Experimentally it is been observed that this kind of a relaxation time to which the reptation time corresponds to that scales as M to the power 3.4. So, if we go back to the previous lecture last lecture there we discussed that for the Rouse kind of motion; the characteristic time actually scales as just N. So, here in the case of reptation the reptation model predicts the time to scale as M cube whereas, experimental prediction m as an to your 3.4. So, we see that the exponents are not that different one is 3, one is 3.4, but quantitatively of course, if we try to obtain quantitative data that will be different because of the almost 10 percent or 15 percent difference in exponents.

So, the patient model captures the behavior to some extent, but we will discuss later there are some deficiencies in the simple reptation model because of which this exponent is

not accurately captured ok. Now we can if we consider the entanglement strand; so, we can define characteristic relaxation time for the entanglement strands of the polymer chain as well. And that we can define as represented as tau e which will be given by this expression.

And we can use this expression here because an entanglement strand is the region of polymer chains between two entanglement points. So, the characteristic relaxation time of this entangled strand can be described using the Rouse model. Because the entangle strand itself is a portion of the chain that has a size smaller than the length scale of our presence of entanglements.

So, this Rouse time of our entanglement strand with which contains any monomers and from the Rouse model that can we can write simply like this. And this tau e this time can be thought of as representing a time characteristic time beyond which a polymer actually becomes aware of the presence of other constraining polymer chains in its neighborhood.

So, if you are observing the polymer chain motion at a time scale below this tau e which is the Rouse time for the entangled strand; then the polymers chain actually will not at this time scale be aware of the presence of constraints around it. But above this that time tau e if we are making observation at a time scale larger than tau e then of course, the effect of entanglements will be present. Now if we consider so, this tau e again from previous lecture we can simply now write us tau naught times N e square the tau naught is an Kuhn monomer relaxation time.

Now, we can consider the ratio of the reptation time and this Rouse time for an entanglement strand. And if we take the ratio of this and this and if we simplify we will see that it is of the order of N over N e cube. Now this N over N e this just represents a number of entanglements present along a given chain right the chain contains n number of Kuhn monomers a given entangled strand contains N e number of Kuhn monomers.

So, N over N e will be the overall number of entanglements present along a given chain. So, we see that the reptation time over the; this tau e that scale says cube of this number of entanglement present along the polymer chain.

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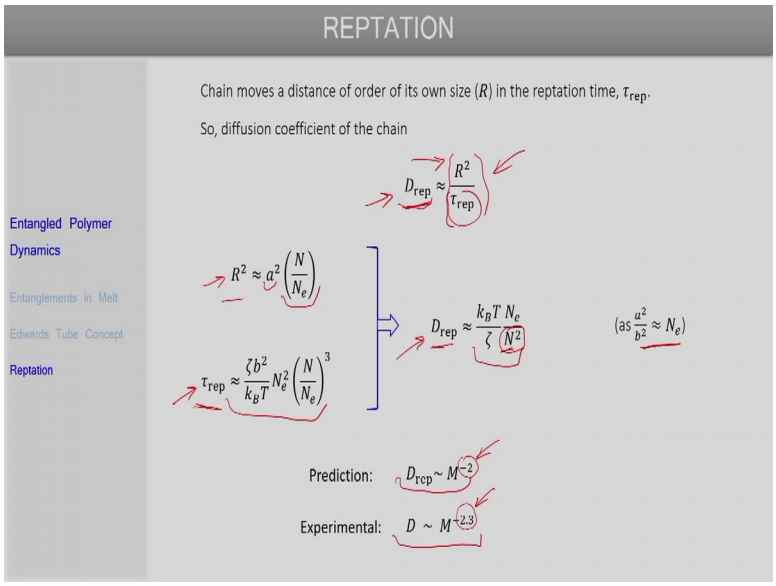

So, now let us consider the motion of the polymer chain again. So, the timescale that is defined by the reptation time; we discussed that this timescale corresponds to the time over which the polymer chain moves a distance equivalent to its own size ok. So, it is the characteristic relaxation time for the entire polymer chain in this reptation model because this is a time scale over which the polymer chain is moving by a distance that is equivalent to its size. The for the entire polymer chain the diffusion coefficient we can simply write as some square of some length scale divided by this reptation time.

And that square the length scale is basically the length scale that traversed by the polymer in this reptation time and that as we discussed is the size of the polymer chain. So, we can the diffusion coefficient we for repetition we can get as just R square over tau reputation that is what we have written here. So, the diffusion coefficient of the chain in this reptation model is just the square of the some characteristic polymer size which can be the end to end distance divided by the reputation time. So, this is the order of the diffusion coefficient of the chain. And this diffusion coefficient corresponds to the diffusion in the entire entangled polymer melt and not inside just the confining tube.

So, previously we had also use that curvilinear diffusion coefficient that corresponded to the diffusion of the chain just within the confining tube. But if you are looking at the overall picture then the polymer chain as it diffuses through the entangled melt; that

diffusion coefficient of the polymer chains in that system that will be given by this expression.

This polymer if we consider the size of our polymer chains, we can see that it is a square times N over N e. And this is again something that we have already discussed in a slightly different form to form previously in this lecture. So, and this tau reptation and the expression repression also we have discussed in a couple of slides back. So, we take these two expression one for R square and one for the reptation time and we substitute both of those expressions here; then the expression for the diffusion coefficient in this repetition model reduces to just this.

Where apart from taking the ratio we have also made use of the fact that a square by b square is equal to simply N e. So, the diffusion coefficient of reptation we see it scales as reciprocal of N square or equivalently it will scale as reciprocal of M square, where M is a molar mass of the polymer because the N which is number of Kuhn monomers and M which is a molar mass they are directly related.

So, what we can say is that in this reptation model the diffusion coefficient scales as reciproprocal of M square or M to the power minus 2; so, that is the prediction of this model. Experimentally, it has been observed that the scaling is again a bit stronger; so, the exponent is minus 2.3 experimentally observed one; whereas, the predictor is minus 2. So, we still again see some discrepancy although it is able to capture the dependence to some extent, but there is some discrepancy in the value of the exponents between prediction of reptation model and experimental findings.

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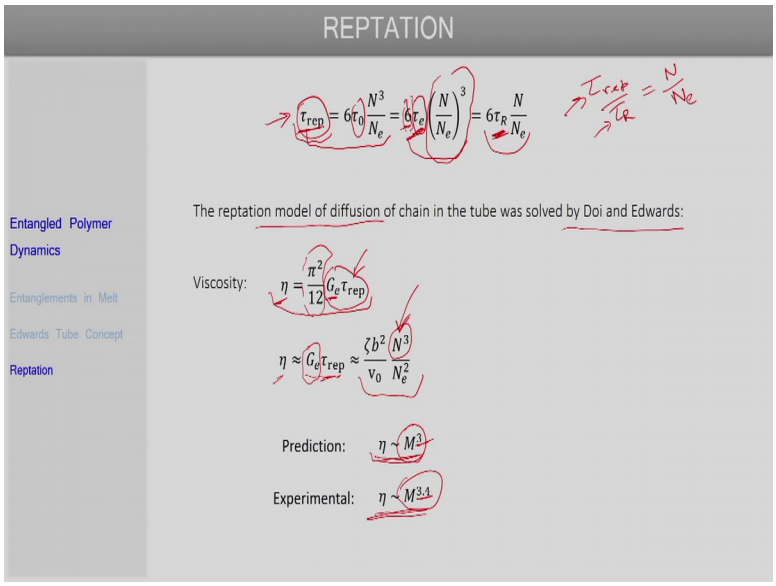

So, now if we look at the different time scales that are involved in this reptation model; this tau reptation if we try to compare them in this reptation time tau rep that corresponds to the relaxation time of the entire polymer chain in the reptation model. And it is related to tau naught which is the smallest relaxation time that we have that is the relaxation day of the single Kuhn monomer.

So, relationship is something like this these things of course, can be obtained using the different expressions earlier written for the reptation time and tau e and others. It is the reptation time is related to the Rouse time for an entanglement strand tau e by this expression. So, earlier the fact this factor 6 was not there, but we already have discussed that tau rep by tau that is after order of this.

So, this factor 6 is something that that makes that is a constant pre factor, but the dependence is over N over N e to the power 3. And finally, if we consider just the Rouse time of the entire chain; so, this tau is the Rouse time of a single entanglement strand which is a portion of the chain. The Rouse time the entire chain tau R is considered, then that is related to the reptation time using this expression. So, again what we can say is that the reptation time by the Rouse time of the entire chain is just given by this ratio N over N e and N over N e is again just a number of entanglements present along a given polymer chain.

So, this Rouse time will correspond to a characteristic relaxation time a polymer chain if no entanglements will be well present ok. And the reptation is from time is a relaxation time of the entire polymer chain; when an entangled entanglements are present. So, we see that due to the presence of entanglements; the reptation time actually increases it is higher than the Rouse time in the characteristic relaxation time the polymer chain becomes longer than if entanglement effects were not present.

Now, this reptation model was mathematically in rigorously solved by Doi and Edwards in 1970s. And we will not go through the any detailed mathematic mathematics of that, but we will just identify a couple of results that come out of the solution and discuss that particularly fine from the point of view of viscosity. So, now from the solution of this reptation model of diffusion by a Doi Edwards the expression of viscosity that is obtained is this where G e as we discussed earlier is a Plateau modulus and tau rep is a reptation time.

So, from here what we can say is that this viscosity is of the order of G times tau rep this is just a constant tree factor. So, if we are considering just what is the order of this viscosity of our melt; then that will be and the product these two. And G e; this we have already discussed earlier is given by certain expression tau rep expression we have also discussed.

So, if we combine both those expressions and simplify then the expression for the viscosity obtained is this. And again we see that the dependence of viscosity on number of Kuhn monomers or equivalently on the polymer molar mass is of the power 3 type. So, if we again compare that with experiments; then the prediction of this model is that the viscosity scales has molar mass to the power 3 because again molar mass and number of Kuhn monomers they are directly related; so, we can write this and experimentally viscosity is observed scalars and to your 3.4.

So, again there is a small, but non negligible discrepancy between the exponents. So, from these results what we see is that the repetition model is a good model for a good simple model for describing effects of entanglement in polymer melts. And it does predict some results which match reasonably with experimental findings; especially in terms of how it is a viscosity or diffusion coefficient scale with the molar mass.

But if the exact scaling is not captured by this model and a couple of reasons why that happens is that one of the reasons is that in an actual case the confining tube length also can fluctuate ok. So, the contour length of the confining tube that can change and that part is not captured in the simple reptation model of design. So, that is one factor which leads to a discrepancy.

And the other factor is that if we are talking about the given polymer chain constrained by many other polymer chains surrounding it. So, the other polymer chains surrounding it are also mobile they are also moving around. So, at after some at a given time if a polymer surrounded by a certain number of chains; after some time some of the those chains would have moved out of a region near it and some new chain might have come in.

So, the; so this kind of phenomenon is referred to as constraint release and this also is a factor which affects the polymer dynamics. So, these couple of things one is the fluctuation in contour to length and there is constraint release; these are not capturing the simple reputation models of design. And that is why the results that we obtain from this model are slightly off compared to experimental results, but still the reptation model is a very good description of entanglement entangled dynamics of long linear polymer chains in a melt. And it is a simple model and its reasonably well captures a lot of qualitative phenomenon; so, it is a good map model in that sense.

So, here we will conclude our discussion of polymer dynamics where in the previous lecture we talked over the dynamics of unentangled polymer chains whether it is a polymer short polymer chains in the melt state or polymer chains in dilute solution and today we discussed the dynamics of entangled polymer chains. So, we described different models which are applicable to different cases we discussed the Rouse models, Zimm model as well as a reputation model today. And we also discussed the different kinds of characteristic times which are associated with the different relaxation of different parts of the polymer chain.

So, the longest relaxation time will correspond to the relaxation of the entire polymer chain, but relaxation of small segments or different segments of different lengths of the polymer chain; they will also have their own character characteristic relaxation times. So, with that let us conclude our discussion of polymer dynamics and it must be

mentioned that what we have discussed is very preliminary. And it is just the surface of this entire subject and if someone is more interested they are referred to a very excellent text a book by Doi and Edwards which is name theory of polymer dynamics.

Thank you.