Introduction to Polymer Physics

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Lecture-55
Models for Entangled Polymeric Systems- II

Welcome all of you. In the last lecture we have been discussing about entanglement and the models to study entanglement so today I will take it further and talk in some more details about the tube model that we discussed towards the end and how do we characterize the effect of entanglement for the purpose of looking at the behavior under flow of an entangled polymer solution.

So, just to quickly recap of what we did in the last lecture so we said that a polymer chain under even slightly reasonable concentrations not very high concentrations as well, even for rather small it is reasonable concentrations is in a entangled state just like I would you can think in terms of a Maggie noodle so the noodle will be like a polymer chain that is highly entangled other noodles and so the motion of that polymer chain would not be like by simple translation for example it has to be following its contour that is what we called a reptation and that is where we discussed various models to look at reptation starting from the student work model where we assume that the entanglement points form like junctions or cross links which are temporary in nature then we said that we can also think of the junctions as like slip links and finally we said that we can assume that polymer is confined at tube and it is a tube that is then being created and destroyed as the polymer is moving.

Let us say we have polymer chain that moves in the solution of other polymer chains, we could have called each of these junctions like these ones as a slip link or junction that is temporary in nature but what we can also assume is that this polymer chain is in a tube that follows its contour when the tube is of course not of a very regular shape because the polymer contour is again not quite regular and the polymer sort of moves within that tube.

So, we will somewhat take this idea further and we are saying is we have tube where the polymer is confined and the motion leads to creation of new tube segments at the expense of the destruction of some tube segments and of course the polymer has moved such that some polymer has come came and then some part of the polymer was destroyed here because the polymer moved along the contour.

So, now if I want to look at the motion of the polymer chain then depends on what time scale what we are looking at and we will see different kinds of movements so for very short time scale the tube will remain as it is but the polymer chain will sort of wiggle inside the tube that is to say that. Let us say this is my tube and the polymer chain is confined here then the polymer chain can for example move within the tube change the conformation but it still remains, so the boundaries of the tube are dictated by the other polymer chains around it so as long as the small changes in conformation do not affect the position of other polymer chains in the system those small changes are allowed so as long as they are like wiggling within the tube the other polymer chains are not being affected and that sort of wriggling is of course allowed however if we wait for long enough the kind of motion we will see is that of motion out of the tube at the expense of depletion from some part so the new tubes.

So, for short timescale we will see a wiggling or change in conformation within the tube and at long time scale we are going to see the creation and destruction of either the parts of the tube or the full tube depending on how much is the time scale we are looking at. If I say look at very long time differences we will see a very different tube from what is present initially, if we look at somewhat intermediate time we will see that some part of the tube has been created and some part has been destroyed as we move from here to there okay. So, tube essentially is a very hypothetical concept that just tells you that this is the region within which the polymer chain can undergo movements new regions can form as the polymer chain moves by reptation and old regions may go away as the chain moves by the same process because ultimately the chain follows its contour to move within the system and this is what happened when we try to flow or deform an entangled solution.

So, if I am interested in long timescales then we can define what is known as a primitive path and using the idea of primitive paths we can go ahead and start characterizing the motion within the model of a tube. So, the way I will define the primitive path is the shortest distance within two ends of tube. If there is a tube then if I connect the two ends with the shortest possible path this will be my primitive path so for short timescales when the polymer chain is wiggling then primitive path anyway is a poor approximation because ultimately what we want to see is the change in the confirmations within the tube and of course the primitive path does not provide a way to differentiate between these different confirmations but if I want to look at a larger timescale then in that case the primitive path is undergoing a change and I can represent the motion in terms of the primitive path so this is let us say my primitive path so after some time you will have the motion of this and you will form a new primitive path again this is the part which is destroyed and this is the part which is created.

Now we can go further if we make certain assumptions here, and the first assumption we are going to make is the contour length of primitive path let me use the word L is constant, we will talk later about the fluctuations in the contour length in a slightly more detailed model and then we also assume that the primitive chain or the primitive path can move back and forth only along itself that is along its contour length with certain diffusivity and finally what we can also assume is that this primitive path for a primitive chain is ideal in nature that shows Gaussian characteristics that which of course is an approximation and if I assume that then in terms of continuous contours we can define the tangent at different locations if 's' is my contour variable and we can assume that the correlation function for $\langle \vec{u}(s)\vec{u}(s') \rangle$ decays with increasing s - s' .

So, let us say if this is my chain any position here is 'r' that is a function of s and of course time and I can write between two points s and s' along the contour the r of s - r of s prime squared is and this has to be ensemble averaged is equal to some constant multiplied by absolute value of s - s' as long as the distance between the two points is higher than a.

$$\left\langle \left| \vec{r}(s,t) - \vec{r}(s',t) \right|^2 \right\rangle = a \vee s - s' \vee ¿$$

So, then this a is somewhat similar to the Kuhn's length that we discussed in the random walk model the only difference is that now we are not talking about the actual polymer chain but the representation of the polymer chain in terms of primitive path that only is good when we are looking at the motion at longer length scales when the small wiggling within the tube can be neglected in comparison to the overall motion of the tube itself. okay, so, then if I look at the squared of the end-to-end distance of the tube that will be equal to something like contour length multiplied by the value of a that we have defined and this has to be equal to the contour length of actual polymer chain that it represents that is the actual polymer chain may have had some other conformation at this particular time but that conformation will also have the same end-to-end distance as that of a primitive chain because we take the primitive chain length as equal to the length of the contour length of the tube and since the polymer is confined in the tube the end-to-end distance of the polymer chain also has to be the R_e. So, this is equal to the actual contour length of the polymer chain multiplied by the actual Kuhn's length that we can we can talk about in the polymer chain multiplied by the b and therefore we can get-

$$R_e^2 = La = (Nb)b$$

$$so, L = \frac{Nb^2}{a}$$

This provides us a way to find the parameter a.

So, if I now go back to thinking in terms of the freely jointed chain model of the primitive path that would also look like something like this where this becomes the effective Kuhn length so as to speak of the primitive path and so the number of steps in primitive paths can be approximated provided the number of steps are large that is 'a' is smaller in comparison to the L. It can be approximated as something like-

$$Z = \frac{L}{a} = \frac{Nb^2}{a^2}$$

Using these ideas we can get the time scale for relaxation of the polymer chain within the entangled system the ratio of that with the time scale the relaxation time we get for the rouse model and we can get certain relations. So, let us say τ_d is the relaxation time for entangled system and let us say τ_r is what we get from the Rouse model we can get some relation that is a function of Z and I am only giving one example of one of the relations we get within certain approximations. There is more to it but we are not going in whole detail but at least this provides some sort of a framework to characterize the polymer chain by its primitive path and then characterize the number of steps in that primitive path and then using that we can talk about the diffusivity the relaxation time and so on. As I have said earlier the diffusivity is an equilibrium property and therefore it is not much affected by the presence of entanglement but the relaxation because of the flow and deformation would be more easily affected by entanglement actually that must be accounted for in the model.

So, there is one more way to look at it instead of talking about the Z as L by a, I can also say Z as the ratio of the molecular weight of the polymer chain with some effective molecular weight corresponding to one Kuhn step or effective Kuhn step within the system where I am approximating the primitive path by a chain this will be called entanglement molecular weight and again it is a similar parameter like a.

$$Z = \frac{M}{M_e}$$

So, I can talk of a, as like a length along the chain or a molecular weight at which entanglement start to appear in the system.

In reality what happens is this L is also not constant because this L is not really a parameter coming from the maximum possible length of the carbon chain. L is a primitive path that is already determined from the end to end distance and therefore it can fluctuate with time and we should have some mechanism to account for the fluctuations and it is typically done by assuming that we have some equilibrium length Leq and we look at fluctuations as the difference between L and Leq.

So, what we say is that the free energy of polymer chain of contour length L is given as something like this-

$$U(L)=\frac{3k_BT}{2Nb^2}L^2-F_{eq}L$$

Here, F_{eq} is an equilibrium tensile force acting on the chain and it turns out that I can write F equilibrium as something like this-

$$F_{eq}=\frac{3k_BT}{Nb^2}L_{eq}$$

And using this idea we can get the magnitude of the fluctuations as something like this-

$$\left\langle \left(L-L_{eq}\right)^2 \right\rangle=\frac{Nb^2}{3}$$

And using that I can characterize the effect of fluctuations within the system.

So, now if I have say a branching happening in the chain. So, let us say if this was the linear chain I have been discussing and if there is a branch that is coming out of it and if it is now present again with other branched polymer chains in the system. If I now draw a tube then of course the tube will not be just one tube it will be like two tubes corresponding to the two arms - one is this tube and one is along the arm and now you can see that it really cannot move by reptation as in what we had for the linear chain because now if I say move along the contour of one of the arms and let us say if I want to come here then that would mean that this arm will also has to come by translation and come here and as I said the translation of tube is not what is intended all the tubes must be moved by reptation and there is no way we can move both these tubes by reptation because they have different contours and in this particular case what happens is we will not look at the creation and destruction of the tube alone what we can also look at is the deformation of the tube. So, tubes will somehow deform to cause the motions.

So, this is like a whole subject working with the idea of a tube model that is used to discuss the flow and deformation behavior of polymers and if you have noticed I have been very short in my description of polymer dynamics. I just try to give you some basic feel of like what kind of

things can happen but this is a subject of another course on polymer dynamics and I can give you some references in the in the course where you can read more about these models.

But the idea so far has been to give you some initial ideas about how to approach the problem of flow and deformation in general and then how does it apply for the case of polymer solutions what kind of new theories we will need and of course you have to read more details if you are interested in pursuing any of this is the kind of mathematical treatment that we have done is simply to outline the key steps of the models that we have discussed and not to go into the deep details because that will require another course on polymer dynamics.

So, with that I conclude my discussion of polymer dynamics. I would say the theoretical part of it and in the next week of lectures I will talk about the polymer Rheology more from the experimental point of view and how do we connect those experimental ideas to the theoretical models that we have discussed now and before in the course.

So, with that I conclude here, thank you.