Introduction to Polymer Physics

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Lecture-54
Models for Entangled Polymeric Systems- I

Welcome. In the last lecture we have discussed the Rouse model of polymer chain using that model for determining the constitutive law for a polymer solution. So, we have discussed the Rouse model earlier in the length in the class as well when we were looking at the diffusion coefficient of a polymer chain. The new application of Rouse model is when we are in a situation of flow and deformation. So, we were halfway through the derivations we complete that in today's lecture and then we also talked about what do we miss in the Rouse model in the context of the flow and deformation of polymer solutions and how can we possibly correct that in improved models.

So, just to quickly recap, we are looking at a polymer chain represented using the bead spring model and if the polymer chain passes through a plane containing the material point P this exerts a stress on the plane containing material point P and this stress I can write in terms of the stress contributions from the Rouse modes and then if I add those contributions over all rouse modes I get the total stress because of this polymer chain on the plane containing material point P this is the idea that we have been developing. So for the contribution to the pth Rouse mode S_{pxy} in the case of a shear flow what we have obtained is the expression right here-

$$v_x = \acute{\gamma}\, y$$

$$\frac{d}{dt} S_{pxy} + \frac{2}{\tau_p} S_{pxy} = \frac{r\, k_B T}{k_p}$$

This is of course a linear ordinary differential equation so if I solve this using the methods of type that we have used in this course a lot we will get something like-

$$S^t_{pxy} = \int_{-\infty}^{t} dt' \frac{k_B T}{k_p} \exp\left[-2\frac{(t-t')}{\tau_p}\right] \acute{\gamma}(t')$$

And so if I want to get the stress tensor in this case only the xy component is interesting everything else is 0 this is something like this-

$$k_p S_{pxy} = ¿ \int_{-\infty}^{t} dt' G(t-t') \gamma(t)$$

$$\sigma_{xy} = \frac{C}{N} \sum_p ¿$$

Here, G (t) as the elastic modulus which is in this case is-

$$G(t) = \frac{c}{N} k_B T \sum_{p=1}^{\infty} \exp\left(\frac{-2t}{\tau_p}\right) where\, \tau_p = \frac{\tau_1}{p^2}$$

Therefore,

$$G(t) = \frac{c}{N} k_B T \sum_{p=1}^{\infty} \exp\left(\frac{-2tp^2}{\tau_1}\right)$$

So this pretty much governs the response of the material the polymer solution in this case to the applied shear rate $\acute{\gamma}$. In other words it tells you about the amount of shear rate that you will obtain if you if you apply the stress σ_{xy}. This is the key constitutive relation that we are interested in the subject of Rheology we talked about the experimental details later but this is very central to the idea of experimental Rheology as we understand it, the main objective is always to find this elastic modulus or the relaxation modulus relaxation would be a better word for this as it covers both liquid and solid and solid states and the response of material due to the applied stress or due to the applied shear is given by this relaxation modulus that we obtain and as we have obtained in this particular case is the expression of the relaxation modulus for the case of a Rouse model.

So, now if I want to get the viscosity from here we will show that there is something called the steady state viscosity and it is-

$$\eta = \int_0^{\infty} dt\, G(t)$$

$$¿\frac{c\zeta N b^2}{36}$$

ζ is the drag coefficient that we discussed in the Brownian motion of polymer chain.

The key idea is my viscosity is proportional to the number of repeat units or equivalently we can say the viscosity is proportional to the molecular weight of the polymer chain. So, this is what we get from Rouse model the only problem with this result is it is wrong and the reason why it is wrong is because we are missing in one important ingredient that is known as entanglement. This result will only be valid if the system is not entangled and as we have been talking when we talked about concentrations of polymer solutions we said that the entanglements begin at rather small concentrations as soon as we are in a semi dilute regime the polymer solution is highly entangled and the threshold to get to the semi dilute regime turns out to be very small in fact it goes like 1 over the number of repeat units and therefore the validity of Rouse model to get the viscosity of the polymer chain would be very limited to very either very small applied shear rates or applied shear stress or in the limit when the concentrations are extremely low that is very dilute solution regime as soon as we go to relatively higher or practical concentrations we start to have entanglement effects and in that case the Rouse model will not give you the correct result for the viscosity.

Now this issue was less serious when we looked at equilibrium behavior because we have used the bead spring model to get the equilibrium behavior. It was not even that serious when we looked at say the diffusivity of polymer chains because even in that limit the Rouse model is applicable for I would say relatively larger number of systems. So, as long as we are interested in the equilibrium properties the effects of entanglements are not so serious or can be neglected in many cases. But the entanglements will start to affect dramatically as soon as we are interested in the dynamic behavior such as flow and deformation.

So, one way to understand the idea of entanglement is to think of like the Maggie noodle. If I want to take say one strand of the Maggie noodle out from the cup of noodle it is going to be very difficult and it is not going to follow a straight path because the noodle has to pass through many, many of the other noodles in the system and this is where the idea of entanglements become clear and that's what we will apply in the case of polymer models that incorporate the effect of entanglements.

So let us say we have a polymer chain or a noodle strand that is instead of being alone it is present in a system that is containing many other polymer chains. Now you can imagine that if I want to move this chain or the noodle it is not going to be very trivial because I cannot simply translate it in the direction I want. For example if I simply pull it in this direction I hope to get something of the like this sort the same chain here but that will never happen because this would require crossing of many, many polymer chains and in fact crossing of the two chains is essentially impossible.

So, earlier I have said in random walk models that the overlaps are possible because there is no, it is not equivalent to say two nuclei sitting on each other but what we are talking about is a very different idea. If I try to pull this like it dynamically you have to really pass a molecule through the other molecule that is impossible within the molecule it can fold there is a possibility of overlap between two segments depending on how we define it but it is impossible to cross a chain.

So, let us say if we have a carbon chain so this essentially would have been like a chain of carbons and if for example there is another carbon chain right here then this cannot simply cross that carbon chain right. So, now in; when we look at the same thing and say in 3 dimensions that this is not always happening because they can be moving in a different plane but if you imagine that it is an entangled system containing many of those chains, any large movement of any polymer chain will always involve crossing off the other crossing with other polymer chains so this is not the way the polymer chains can move. So, now if I want to move the system the way to follow if you think carefully would be not to pull it in any direction but to pull it along the contour of the polymer chain that is I can hold one end or the other end and I start pulling in the direction along the contour, so, some part of the polymer chain from the other end is lost and some part of the polymer chain is created so this is lost and this is created.

You can imagine the same thing happening if you have say an entangled system of wires so nowadays if you have say many of the gadgets plugged in the charge that you will have say an iPod a mobile phone or many mobile phones and you will have say an entangled system of wires and if you try to pull any of the wires it is going to be difficult if it is entangled. So, you have to find a way to carefully locate its end and then pull it in a way that does not disturb the other wires. The same ideas at play here when the polymer chain is being pulled, we pull in a way that does not disturb or causes minimal disturbance to other chains in the system. If we try to drastically pull it that would be not allowed or that would require a very high force.

So, essentially what it means is if I am causing any deformation of the polymer chain that deformation would be more difficult when it is entangled that is one, that means the viscosity is going to be very high viscosity of course is going to be much higher than what we have gotten from the Rouse model because the Rouse model does not account for entanglements. So, since the degree of freedom of the polymer chain is restricted the motion is also restricted or it will be more difficult to cause the motion. So, it turns out that because of entanglements the viscosity of the polymer chain varies with the molecular weight with not the power of M as given by the Rouse model but a power of 3.4 has been experimentally predicted and that really tells you how severe the effect of entanglements are in the case of the dynamic properties.

Now we have not really considered the entanglements when we have been doing the random walk models because at that time I was interested in the equilibrium behavior of the polymer chains we looked at the equilibrium behavior also in a concentrated solution but in all those cases the entanglements does not play such a role because the polymer chain is not really moving a whole lot its motions are essentially small fluctuations around the equilibrium position. In this case we are actually trying to deform a material containing a polymer chain this will mean drastic motions of polymer segments if I compare that to the equilibrium fluctuations. So, entanglements therefore have at least less effect if no effect in equilibrium properties but they have more drastic effects if I am interested in the dynamic properties particularly those that give rise to flow and deformation. So, this is where we have to think of a new class of models beyond what we have discussed in the random walk context that can account for the effect of entanglements.

So, one of the ways we can at least start thinking of the entanglement effect is to assume that these polymer which are entangled is essentially forming like a polymer network. The only difference from something like a rubber is that the junctions that we form are not really permanen, ultimately the polymer chain can move along its contour for example so it is not that whatever junctions we are forming with other chains are permanent but it is the junctions that provides some constraint to the flow of the polymer chain. So, these junctions are a temporary cross links and they provide constraint or resistance to flow, and this model is what is known as a pseudo network or temporary junction model.

The advantage of doing that is now I can start using the ideas we have developed in the case of a rubber the polymer network to analyze the behavior of these entangled system with only one additional thing that is the cross links in this case is not permanent as opposed to what we have assumed in the case of rubber those were chemical cross-linking these are some sort of a physical cross linking that can change or the polymer chains can really slip through the junctions so as to speak.

So, as the polymer chain then moves some junctions are created and some junctions are lost when the polymer chain undergoes a movement. So, if for example this polymer chain somehow manages to move and form the new polymer chain. So, now in the new chains we will have some new junctions and some old junctions will be gone. There will be some new Junction that is created and some old junctions which are lost in movement. So, in general the junctions or temporary cross links are being created destroyed with time.

The key idea here is like of course this is not the only one chain moving there are also other chains are also moving. So, if I look at the whole polymer system under deformation then with time actually at a very rapid rate the junctions are being created and destroyed so instead of looking at the system as individual polymer chains I would think of it as a network where the junctions or cross links have some rate of creation some rate of destruction and some lifetime and then we can write some sort of a balance equation for those junctions and start thinking about the stress relations stress-strain relations for such a system.

I am not going to all the math but I am trying to just illustrate some key ideas or key physics that is at work when we are looking at entangled systems. There is one more way to think about it and that is instead of assuming them to be junctions we assume that to be a kind of as link or a slip link right. So, think of like some sort of a ring that is formed at each junction.

Now instead of calling the intersections as junctions I will say that it is some sort of a ring formed at every such intersection. So, now instead of saying that the junctions are being created or destroyed when I move the chain the chain essentially forms some new slip links and some old slip links are destroyed. So, you can basically slip through these rings that pretty much think of like the ring containing your keys and assume that there are many polymers chains passing through that and then essentially it slips through this when it is passing. So, it is not really no movement it is essentially a kind of a restricted movement. So, if there are like two polymer chains and they can only move in a particular way the chains cannot really break apart the ring. So, they have to move under a restricted kind of a zone and that is why the motion will be restricted as opposed to thinking of like motion in any possible direction the way we think in the case of diffusion. This model is called the slip link model so polymer chain moves through slip link or links.

So, we can imagine that the polymer chain one of them it is essentially consisting of many of these rings which represents its intersection with other polymer chains in the system and when it moves you can see when it is moving through the slip links or the rings it essentially is moving along the contour so what the slip link is doing is it ensures that the movement occurs along the contour that is what essentially it is doing. So, if I think of a new position let me use a different color, so some of the slip links remain and some are lost and of course some new slip links will be formed in the system. So, now the slip links are I would say not created or destroyed in the meaning of a junction but you can think of that it forms like new slip links with other chains and it passes through the old slip links.

So, now once that chain passes through the old slip links there may still be say other chains in that slip link or in ring they remain there only one chain managed to pass through there right. At any given time you will have many of these slip links in the system and they may contain one chain two chain whatever number of chain and the motion is through those links, the new ones can be created if the new intersection takes place and then we have to keep track of how many slip links we have, what are their positions, what is the effective distance between slip links, how much time it takes for a polymer chain to pass through the strip links and so on.

There is an alternative way to think about the same problem and that is actually the most famous of all these models we have discussed and that is called the tube model. So, now what we say is instead of having a junction or a slip link we assume that if I have a polymer chain the polymer chain is contained in essentially a tube enclosing it and again the motion of the polymer chain is along the contour. So, if the chain moves here some part of the chain is destroyed at the end and the new position of the chain is formed. So, now we can say that the tube is being created or destroyed.

So, whether we are doing a pseudo Network model or we are doing a slip link model or we are doing a tube model all of them I would say to some extent are similar representations and the key idea of all of this is that the polymer chains move by reptation motion this is the key idea that we have and by reptation what we mean is the movement along the contour.

So, the next class we will elaborate on some of these models and then try to have some mathematical understanding, of how exactly we can understand the stress-strain behavior for the system of polymers containing entanglements or I would say realistic systems of polymers because as I said most polymer systems will be or polymer solutions will be in the entangled state.

So, with that I conclude here, thank you.