Introduction to Polymer Physics
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Lecture-45
Problem in Rouse Model, Hydrodynamic Interactions

Welcome in the last few lectures we have been discussing the Rouse model that discusses the diffusion or the Brownian motion of a polymer chain and so far we have went through a long derivation and essentially what we have been trying to do is try to replace the positions of beads on the polymer chain by some sort of Rouse modes as variables in the equation and by doing that what we were able to do is we reduced a partial differential equation that we had into a series of ordinary differential equations which are easier to solve. But more importantly these Rouse modes have certain physical significance in them and that is where we ended our discussion in the last class trying to look at the significance of Rouse modes.

So, I will continue the discussion today and then I will talk about briefly what are the problems, in the rouse model has I already have hinted it earlier. But we look in more details the problems of rouse model and then I will discuss briefly what is known as Jim model that corrects for those problems and give us the correct scaling behaviors for diffusion coefficient of polymer chain.

So, just to just to recall what we have been doing is we are looking at the continuous analogue of a bead spring model where we have a contour variable running from n = 0 to n = N that is the number of segments in there I have the variable r that is now a function of n and t that tells me the position of the beads and segments along the chain and for that r we started with the partial differential equation like this-

$$\frac{\partial \vec{r}}{\partial t} = \frac{k}{\zeta}\frac{\partial^2 r}{\partial n^2} + \frac{\vec{F}_r(t)}{\zeta}$$

Which had the boundary conditions $\frac{\partial \vec{r}}{\partial n} = 0$ for the free ends at n = 0 and n =N and what we did we did what I refer to as a linear transformation using what I call the Rouse modes defined by this particular equation-

$$\vec{X}_p(t) = \frac{1}{N} \int_0^N \cos\left(\frac{p\pi n}{N}\right) \vec{r}(n,t)\, dn$$

So, earlier we wrote in terms of a basis function and then using the boundary conditions in the PDE we got the expression for the basis function that is 1 by N cos p□□n by N integral over r dn and using that I then have equations of this sort this was a PDE and this is now a set of ODE's we have-

$$\zeta_p \frac{d\vec{X}}{dt} = -k_p \vec{X}_p + \vec{f}_p$$

Where p = 0,1,2…… and so on.

And then finally we said of course we defined that present for k_P, ζ_p and so on. And then we said if I am interested in the center of mass of a polymer chain that characterized the position of the overall polymer chain space. The center of mass is given by the first or 0th Rouse mode that basically characterizes the center of mass and therefore characterizes what I referred to as the diffusivity of center of mass or the net overall diffusion of the polymer chain. And then finally we derived that X_1 or the first Rouse mode then characterize the time correlation of the end to end distance R_e (t).

The higher Rouse modes have a very clear meaning and the meaning is the following that if I have a polymer chain in a space if I divide the chain into 2 halves along the contour that is at n = N/2 then if I look at the segment as one half which may have certain end to end distance and the other half have certain end to end distance and if I look at the motion of these individual halves then basically it is characterized by the second Rouse mode just like X_1 characterized the time correlation of the end to end distance that is for the entire polymer chain. If I divide the chain 2 halves then this individual chains do have a local motion and the local motion is of the 2 halves is given by X_2 (t) the second Rouse mode.

Similarly if I now divide the chain into 3 parts then we will have divisions at N at N/3 and 2N/3 and so on. So, we now have 3 polymer chains or 3 segments and then for these 3 parts the local motion of 3 one thirds are given by X_3 (t). So, if I extend this kind of logic then X_p (t) characterizes the local motion of a chain of N by p segments. So, there would be piece of chains in a given chain or bead such segments be such chains containing N by p segments each within the polymer chain and the local motions of those sub chains are given by the Rouse modes X_p (t).

Using this idea if you can see that as I go to higher and higher Rouse mode or as I am increasing the value of p, I am essentially looking at a more localized motion within the polymer chain very high values of p characterizes very local motions. Let us say between 2 beads or 3 beads and the lower values of Rouse mode lower values of p correspond to the motion of relatively larger chains and in fact X_0 characterize the center of mass of the overall chain. So, therefore not only the idea of rouse modes basically is helpful to reduce the partial differential equation in two differential equation what is more important is that they actually characterize the motion of polymer chain at different levels.

So, this is not really a one to one transformation, we do not work directly right r and t as some kind of a one to one mapping to some X (t) variables this is not the case on the other hand what we are doing is we represent these different Rouse modes as a linear transformation over R given by the particular function and it then characterizes the motion at different length scales that we would see would see in a polymer chain.

So, that is where this whole idea become very important and in experimental literature you will find descriptions of the sort the motion at second Rouse mode third Rouse mode depend depending on what kind of experimental resolution do I have I would be able to see motion at different length scales and if I am really zooming in I am basically looking at higher X_p value, X_p for larger p if I am zooming out I am looking at lower X_p or lower values of p in the thing and in that sense the X_p completely characterize the chain motion at all sorts of length scale.

So, there is a couple of problems in the Rouse models and the most important problem is if I look at the net diffusivity within the rouse model we find that it scales like 1 by N that is if I increase the number of segments the diffusivity decreases this is although correct at a qualitative level this is what does happen in a system the larger polymer chains will have lower overall diffusivity they may have a high degree of local motion but the overall diffusion or the overall motion of center of mass would be lesser the chain has a larger value of n. But it turns out that the scaling is not quite correct the scaling experimentally is found to be something like $\frac{1}{N^{\nu}}$ where ν happens to be the same scaling coefficient that we had got for the R_e or the R_g as we were doing in the very beginning of the class of the course that we obtain certain scaling for R_e and R_g using random walk models and they were of course different in a good solvent and a bad solvent in the theta solvent regimes those scaling laws do appear again in diffusivity and this is what is referred to as a dynamical scaling and what we had earlier is referred as static scaling.

This particular result comes out to be somewhat surprising to begin with because on one hand R_g is a quantifier of a length and D is a quantifier of some kind of a motion of a polymer chain. So, the reason the thing that we get the same scaling law for both of them is somewhat surprising. However keep in mind that both of them represents the equilibrium behavior nowhere in here we have so we have assumed that we have departed from equilibrium this is like referring to the Brownian motion that is taking place at equilibrium. So, since both of them refer to equilibrium properties it turns out that the scaling behavior is identical to what we get in the in the case of the end to end distance and so on.

Now thing is that we do not get the correct scaling law if I am doing the Rouse model it is at qualitative level it is correct but it is not giving us that the correct value of scaling exponent. So, the reason why it fails is because we have made an assumption in what we have done so far and the assumption is that we have the bead as a free particle that is only experiencing an external force because of the presence of other beads in the system but it is not affected by for example other polymer chains in the system and the spring force is the only external force that is acting on the system. What really happens is that the force acting on a bead also in turn affects the force acting on the other beads and this is what is referred to as hydrodynamic interactions okay and if I include those interactions in the model this is what is called a Zimm model.

So, we will first discuss what we mean by hydrodynamic interactions and then we go on to discuss the Zimm model of a polymer solution. So, before I get there I must tell you that even though the Rouse model is nowhere in derivation we have assumed that it is a polymer solution or a melt we were looking at a single polymer chain. It turns out the Rouse model do work for the case of a polymer melt for the reason I am not going to detail but it gives you correct scaling for the polymer melt systems. It does not work for dilute polymer solutions or even what is known as a semi dilute polymer solution.

So, let us now try to set the ground for the Zimm model by discussing what is known as hydrodynamic interactions and before I do this for a polymer chain I am just doing it for a system containing more than one Brownian particle what we have earlier discussed was a Brownian motion of a free particle that is just one particle in the solution and now we want to do for more than one particle we see like what does happen in that case and then we extend the idea to a polymer solution.

So, let us see that now in a system we do not have just one particle we have more than one particle so this can be for example a case of a suspension that contains more than one particle if they are connected they would form a polymer chain but let us not get into that at a moment, then if for example take a particular bead. Let us call it the bead N we apply a force F_n or the force is applied due to some external field present in the system as we will soon do for a spring force in the case of a polymer chain let's say a force is applied there due to whatever reason then this force will basically lead to the movement of this particular bead.

Now once the bead moves in a solvent it does affect the flow field around it. So, all the other beads in the system would see a flow field that is created by the movement of this particular bead. Think an analogy- think of like fishes in water if say one fish starts moving in water the water around the fish will develop a flow field and other fishes will also see the same flow field okay. So the motions of one fish do cause a change in the flow in the flow field and those change must be then affecting the motion of other phases of course this is a very distant example but it serves the idea.

Similarly all the other beads let us say the bead m here, this bead also is moving due to the external force or whatever force acting on it that bead is also giving rise to a flow field and then bead n here the black one the bold the field one also is affected by the flow field created by m. So, in totality all the beads in the system are experiencing different forces or every same force but all the beads are contributing to the flow field that is present in the system it is not that the flow field is given and all the beads are simply responding to that flow field all the beads are themselves responsible for the flow field that is present in the system and therefore the velocity or the motions of each of the beads are coupled with the other beads. This is what is referred as a hydrodynamic interaction.

It is more pronounced if the size of the bead is larger, it is less pronounced when the size is smaller in a limit when we have a dilute solution and sizes are smaller we can ignore this effect but it turns out that that limit is seldom reached. In most systems the effect of hydrodynamic interactions are quite significant and they must be included for a proper description of the system.

So, now in general if I am looking at the velocity of the n^{th} bead it must be related to the velocity of the m^{th} bead and in fact it must be related to all possible values of m that is we must sum over all the m values going from all beads and the coefficient of that relation is what is known as a mobility tensor. So, it must be a tensor because tensor dotted with a vector would give you a vector.

$$\vec{V}_n = \sum_{m = all beads} \acute{H}_{nm} \cdot \vec{F}_m$$

Here $\acute{H}_{nm}$ is called a mobility matrix. The forces are what is giving this rise to the velocities so velocity of any particular bead in the solution is affected by the forces acting on different beads of course the velocities also have to be related but that will come from this relation. We are essentially relating the velocity to the forces acting on different beads. So, a very dilute solution it turns out that I can write the mobility matrix as something like identity tenser-

$$\acute{H}_{nm}=\frac{\acute{I}\delta_{nm}}{\zeta}$$

Where ζ is the drag coefficient that we have discussed earlier or friction coefficient. This is a matrix that has once 1s diagonal and 0's everywhere. What that means is if I look at the α β component of this mobility matrix that would be $\delta_{\alpha\beta}$. The chronicle δ will represent the identity tensor because for α = β we have diagonal terms which are 1 and α ≠ β, we have off diagonal terms which are 0 multiplied by δ_{nm} by ζ and therefore we can write as-

$$V_{n\alpha}=\sum_m H_{nm,\alpha\beta}F_{m\beta}=\sum_m \frac{\delta_{\alpha\beta}\delta_{nm}}{\zeta}F_{m\beta}$$

It give rise to it is only true for only nonzero for and n = m that is one thing and it is only nonzero for α = β so what do we get is essentially simply-

$$V_{n\alpha}=\frac{F_{n\alpha}}{\zeta}$$

It is similar to the expression that we have used to discuss the Brownian motion of a free particle okay. Here we have not explicitly put a random force term but the idea remains there that if I really go to a very dilute limit then the velocity of a bead is only affected by the force is acting on the bead the bead will not see other beads of course they will have a flow field around it but that flow field will not affect it.

Assume that there are only say 2 fishes in a very large pond and if the fishes are far away they are of course swimming there they have certain flow field wherever they are swimming but that flow field is not affecting the flow field of a fish here the fish is moving here because of the force is acting on this the fish is moving there because of force acting on this only when the two fishes come close enough their force fields their flow fields will affect each other and then we can say that whatever force I apply on this fish will also affect the velocity of that fish that we have.

So, only in a very some but less dilute solution when the beads are relatively close together we can have start having this hydrodynamic interaction. And it turns out that we do not really need to very dilute we do not need to go to a concentrated case it already starts appearing for relatively more dilute cases that we have in physical circumstances.

So, with this idea now the objective we have is how I get that flow field. So, we want to know that how the flow field is created in the solution because force is present on the beads. So, we have to solve for the velocities and we know from fluid mechanics that to solve for velocities we have to go to Navier stokes equation. It turns out that since we are interested in motion close to equilibrium or motion at equilibrium we do not really need to go to a large Reynolds number because of course turbulent flow is far from equilibrium we actually can go to a very low Reynolds number and there we have what is known as Stokes equation and that is what can be used to get the flow field that we are interested in.

So, we will start from this point in the next lecture and try to derive the expression for this velocity. And using that we will derive what is known as the Zimm model of polymer solutions.

With that I conclude here, thank you.