**Introduction to Polymer Physics**
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**Lecture-47**
**Zimm Model – II**

Welcome in the last lecture we have been discussing the Zimm model that accounts for the hydrodynamic interactions present between beads on a polymer chain. We define those interactions as coming from the fact that the force acting on any particular bead basically results in a flow field around it and that flow field in turn also affects the other particle in the system and we have used the language of mobility matrix to relate the effect of forces acting on different beads on the velocity of a given particle.

So, we have been doing the derivation of Zimm model not really going into all their steps but looking at the main ingredients because as I mentioned that the actual the derivation is quite tedious in the books but the main steps I am trying to illustrate and then I hope to come to the main conclusions in this lecture and try to demonstrate what exactly we can get by doing the Zimm model.

So, just a quickly recap what we have been able to do so far is that we have developed the equation of motion or the Langevin equation under certain approximations and is given by-

$$\frac{\partial \vec{r}}{\partial t} = \sum_m h(n-m)\left(k\frac{\partial^2}{\partial m^2}\vec{r}_m + \vec{f}_m\right)$$

So, now just like what we did in the case of Rouse model we wrote the equation in terms of the equations for the Rouse modes. So, I will use a similar linear transformation transformation because the boundary conditions remain same of course since the PDE is different the final answers will be different. So, we will use the linear transformation that is we defined the variable $X_p(t)$ as-

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

In fact we can also do the same inverse transformation from $X_p$ to r once we get the answer in terms of $X_p$. And if I use that, what we get one solution is the expression in terms of $X_p$ we can call them the Zimm modes now if you prefer, and this is-

$$\frac{\partial}{\partial t}\vec{X}_p(t) = \sum_q h_{pq}\left(-k_q\vec{X}_q + \vec{f}_q\right)$$

In fact what we had is very similar to what we had in the Rouse case except that now we have a summation up appearing on the right hand side. So, just to recall what we had in the case of a Rouse model is-

$$\zeta_p\frac{\partial}{\partial t}\vec{X}_p = -k_p\vec{X}_p + \vec{f}_p$$

There the motion of the bead was affected only by the forces acting on that particular bead. Now since the bead motion is affected by other beads as well therefore on the right hand side we have an additional summation happening and instead of a 1 by $\zeta_p$ we now have matrix $h_{pq}$, so we actually solve for $h_{pq}$ and $h_{pq}$ can be written in terms of the function h that we have got earlier something like this-

$$h_{pq} = \frac{1}{N^2}\int_0^N dn \int_0^N dn \cos\left(\frac{p\pi n}{N}\right)\cos\left(\frac{q\pi m}{N}\right)h(n-m)$$

If I now solve this what I do get is-

$$h_{pq} = \frac{\sqrt{N}}{\left(3\pi^3 p\right)^{\frac{1}{2}}\eta_s b}\frac{1}{2N}\delta_{pq}$$

We get something like this which is a diagonal matrix because of the presence of the term $\delta_{pq}$

so $h_{pq}$ its diagonal matrix. And the term $\frac{\sqrt{N}}{\left(3\pi^3 p\right)^{\frac{1}{2}}\eta_s b}\frac{1}{2N}$ except the $\delta_{pq}$ I can write like some

$h_{pp}$ because it is a function of p alone not q. So, then going back to the equation I had earlier and the relation for $h_{pq}$ we have derived what we do get is-

$$\frac{\partial}{\partial t}\vec{X}_p = \sum_q h_{pp}\delta_{pq}\left(-k_q\vec{X}_q + \vec{f}_q\right)$$

Which in turn gives me something that is similar to what we had for the Rouse model of course there are certain approximations in the actual derivation but the final answer looks same as the Rouse model-

$$\zeta_p\frac{\partial\vec{X}_p}{\partial t} = -k_p\vec{X}_p + \vec{f}_p \; where \; \zeta_p = \frac{1}{h_{pp}}$$

So, just like we what we had in the Rouse model we also have to do the p = 0 case separately and for p = 0 case it turns out that-

$$\zeta_0 = \frac{3}{8}\left(6\pi^3\right)^{\frac{1}{2}}\eta_s b\sqrt{N}$$

So, after doing the full solution within the approximations that we have made so we have first made the Stokes approximation then we got Oseen tensor as the expression for the mobility matrix then we made the pre averaging approximations and some other approximation and finally what we have been able to is to write the equation in terms of a mathematical form that is very similar to what we had for the Rouse model because we only had diagonal terms appearing in the expression of $h_{pq}$ because of presence of the Kronecker Delta, $\delta_{pq}$ that is only after all those approximations, if we would have not made the approximations of course this would not really look similar to what we have got. Nonetheless the key scaling results would still hold true even if we relax some of the assumptions that we have made they are simply made for mathematical simplicity.

So, now if we talk about the center of mass diffusion we have the relation that was same as for the center of mass diffusion of the Rouse model except the ζ value is different in this case. So, we have-

$$D=\frac{k_B T}{\zeta_0} \propto \frac{1}{\sqrt{N}}$$

That tells me that the diffusion still decreases by N but with an exponent 1 by 2 with an exponent that we have for $R_g$ in θ solvent i.e.

$$R_g \quad N^{\frac{1}{2}} \text{ for } \theta \text{ solvent}$$

So, that is how we have established that the static scaling that we get for $R_g$ is the exponent of that scaling is same as the scaling a dynamical scaling we get for the diffusion coefficient.

We can also define the relaxation times just like we did for the Rouse model which in this case would give-

$$\tau_p=\frac{\zeta_p}{k_p}=\tau_1 p^{\frac{-3}{2}} \text{ here } \tau_1=\frac{\eta_s}{\sqrt{3\pi}}\frac{\left(b\sqrt{N}\right)^3}{k_B T}$$

Since this is what we have got for Zimm model in a theta solvent case. If I want to do a Zimm model in a good solvent case then we also have to incorporate the effect of excluded volume that we have ignored so far.

So if I am doing the Zimm model in the good solvent case what we have is in addition to the spring energy we also have excluded volume that we include by adding an additional force which we have discussed when we have been discussing excluded volume earlier in the course-

$$U_1=\frac{1}{2} v k_B T \sum_{n,m} \delta\left(\vec{r}_n-\vec{r}_m\right)$$

And then again we will solve an equation that we have got in the θ solvent case except that again the $\zeta_p$ values will be different for the good solvent case. So, on solution we will get something like this-

$$\zeta_p \frac{\partial \vec{X}_p}{\partial t} = -k_p \vec{X}_p + \vec{f}_p(t)$$

Here now –

$$\zeta_0^{-1} = \frac{1}{\eta_s N^{\nu} b}$$

And

$$\zeta_p^{-1} = \frac{1}{\eta_s N^{\nu} b} p^{\nu - 1}$$

Using this relation which implies D proportional to 1 by $N^{\nu}$ where ν is like whatever we have got for the static scaling and then-

$$\tau_p = \frac{\tau_1}{p^{3\nu}} \; where \; \tau_1 = \frac{\eta_s N^{3\nu} b^3}{k_B T}$$

So, the key point was not really to go through all the derivation of Zimm model we have skipped many steps in derivation but the key point was to demonstrate a couple of things. The first thing is starting from the Rouse description we have a formal procedure to relax assumptions that basically we have made in the Rouse model so we could incorporate dynamic interactions by solving somewhat extended version of Langevin equation.

We have used a similar linear transformation that we use in the Rouse model of course the math is more complicated but the basic solution procedure remains somewhat similar of course we have to make other approximations related to the flow field and so on that was not present in the Rouse model so that is the reason why Rouse model even if it is wrong serves as a good fundamental basis on a good starting point to start thinking about the Brownian motion of polymer chains. These complicated models like Zimm model can be developed using the ideas that we have in the Rouse model by making some or more relaxation to the assumptions that we have made in their house model.

So both of them give you qualitatively same results that the diffusion coefficient will decrease by increasing the number of repeating units on the polymer chain or the number of beads in a polymer model. But only the Zimm model is able to give the correct scaling that is found in the experiments and it turns out that the scaling that we get from here that is what I refer to as a dynamical scaling comes out to be same as what we have got in the case of $R_g$ or the end-to-end distance of a polymer chain that we referred to as a static scaling and therefore the scaling relations even though we did not really describe in detail in the course serve a very important role in the whole description of polymer physics the approach we have followed did not really go into details of how we get the different scaling relations but a whole theory of polymer physics can only be built can also be built just by looking at the scaling descriptions that are present and try to build theories out of it and this is the approach that de Gennes followed in his book and we have refrained from that kind of a discussion in this course.

We have tried to be somewhat rigorous so as to speak but in the end the scaling laws contain at least equal physics if not more than compared to what we have been doing ok and this happens to be true for not only polymer physics but many other phenomena in condensed matter physics and therefore often there are alternate descriptions based on the scaling ideas that of course does not include the mathematical details as much as we have been doing right here but it is basically based on more physical intuition because to get the correct scaling exponent you have to make the correct scaling model and that of course is by no means an easy job.

So, if you are interested in learning about the static and dynamical scaling behavior I refer you to the book by de Gennes Scaling Concepts in Polymer Physics and you will find that many of the results that we have obtained in our in this particular course and even many other results can also be obtained purely by scaling arguments and which are it tells you about the powerfulness of the arguments. It turns out even after doing all sorts of rigorous mathematics we cannot get the correct scaling relation only to find that the scaling laws based on the correct physical intuition give us the same scaling the correct scaling law without going deeply into all the mathematics and this is what is beautifully illustrated by the example of Rouse and Zimm model. The Rouse model is already complicated Zimm model is even more complicated. But if I start from the

scaling idea we can think of getting similar expressions without going into all the detailed math okay.

So, with that I want to conclude here and in the next lecture we will start talking about the flow and deformation behavior when we depart from equilibrium and in a more macroscopic sense or a microscopic sense then what we have so far been doing we have so far been looking be looking at the motion at the level of a molecule or motion at a level of say a bead or a segment within the molecule but if I look at the deformation at a macroscopic or a microscopic level it requires a very different kind of a math that we know by the name of continuum mechanics and that is what we will start in the next lecture.

So, with that I stop here, thank you.