Introduction to Polymer Physics

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Lecture-46
Zimm Model – I

Welcome in the last lecture we started discussing what is known as a hydrodynamic interaction and the motivation for doing this is we had earlier described the Rouse model which qualitatively explains that the diffusivity will decrease as the number of segments increase in a chain but the scaling law was not correct. So, today we will take the discussion further that discussion was on lines like what was missing in the Rouse model and the missing part was this particular interaction I am talking about and then using that we will develop what is known as the Zimm model.

So, until so far what we have discussed in the hydrodynamic interactions is that, if I have a system of particles then the force that is acting on any particle is actually affecting other particles in the solution by the means of the fact that each of the other particle change the flow field around the particle. And then what we had established is the velocity of particle 'n' or bead 'n' must be related to the force acting on other particles in solution by what we refer to as the mobility matrix and as we discussed in a very dilute case we recover what we had for the Brownian motion a free particle but that is really very low concentrations otherwise we have to really solve for the effects of hydro dynamic interactions.

So, the approach we are going to follow as you already hinted is we are using the Stokes approximation or low Reynolds number hydrodynamics that essentially is based on two key ideas.

The first idea is that we assume that the fluid is incompressible and for that we have the continuity equation-

$$\vec{\nabla} \cdot \vec{v} = 0$$

And in Einstein Notation we have-

$$\frac{\partial}{\partial r_\alpha} v_\alpha = 0$$

The second assumption is we assume that the inertial forces are small that is anyway true for low Reynolds number. It turns out that we have a factor of R_e coming in front of the pre factor of one of the equation and we can drop the term if the Reynolds number is small and that term is our inertial term. So, in that case we can write the expression for the force acting in terms of what is known as the stress tensor i.e.

$$\vec{\nabla} \cdot \acute{\sigma} = -\vec{g}$$

Where $\vec{\nabla} \cdot \acute{\sigma}$ is my stress tensor and $\vec{g}$ is my external force. Again we can write this equation in Einstein notation as-

$$\frac{\partial}{\partial r_\beta} \sigma_{\alpha\beta} = -g_\alpha$$

Now for the stress tensor σ we use what is known as a constitutive equation that is true for a class of materials So, if I have say a Newtonian liquid later on in our lectures we will go in details above the continuum mechanics and then I will talk in more details about what the constitutive equations really mean. But at this point you can recall from your transport phenomena class if you had that the stress tensor is given like this for a Newtonian liquid-

$$\sigma_{\alpha\beta} = \eta_s \left(\frac{\partial v_\beta}{\partial r_\alpha} + \frac{\partial v_\alpha}{\partial r_\beta} \right) + P \delta_{\alpha\beta}$$

Here η_s = solvent or solute viscosity.

So, now to approximate the external force we will use the idea that the external force is because of the other beads that are present in the solution and every bead correspond to a force say F_m then the net external force should be-

$$\vec{g}(\vec{r})=\sum_{m} \vec{F}_m \delta(\vec{r}-\vec{r}_m)$$

Where r_m is a position of m^{th} bead and the sum is over all values of all values of m.

Essentially the idea is that that at any location r we will look at how many beads are present and then for those many beads we will simply add up the values of force acting on the bead. So, of course this kind of a treatment makes an assumption that really have a point particle with size 0 because we are using a delta function. But nonetheless it gives us a good approximation of the mobility matrix so we will essentially use that term here. So, if I now use this expression what I then get is the equation of motion as the as the following-

$$\eta_s \nabla^2 \vec{v} + \vec{\nabla} P = -\sum_{m} \vec{F}_m \delta(\vec{r}-\vec{r}_m)$$

So, we can solve this particular equation by a technique of Fourier Transform I will get –

$$\vec{v}(\vec{r})=\sum_{n \neq m} \acute{H}(\vec{r}-\vec{r}_n) \cdot \vec{F}_n$$

This is what we have for m^{th} particle okay where this function H, I want to differentiate that with the mobility matrix by noting that this is a function that we get by making an approximation that is a Stokes approximation. So, this H is referred as the Oseen tensor which is given by the relation-

$$\acute{H}(\vec{r})=\frac{1}{8\pi \eta_{ns}}(\acute{I}+\hat{r}\,\hat{r})$$

Where r cap is a unit vector parallel to r okay of course this is equal to infinity at r = 0 because the denominator has an r in there.

Now this is a flow field that is being generated and of course the particles are moving in the flow field. We will make one more assumption here an assumption is that the motion of the beads at a particular point is same as the flow field that is prevalent at that particular point. So, we are going to assume that the motion of say n^{th} bead is the velocity that exists at the position of the n^{th} bead which then is a-

$$\vec{V}_n = \vec{v}(\vec{r}_n) = \sum_m \acute{H}(\vec{r}_m - \vec{r}_n) \cdot \vec{F}_m$$

Here $\acute{H}(\vec{r}_m - \vec{r}_n)$ is the Oseen tensor and then this Oseen tensor is now the mobility matrix $(\acute{H}_{nm})$ we have defined in the very beginning.

So, there are certain assumptions that we have made here. We have made the Stokes approximation that allows us to solve the flow field expression and for that I have got an expression in terms of what I call the Oseen tensor. Then I make one more approximation that the flow field basically also provides the expression of velocity of the bead that is the beads are also moving by the same velocity as the existing flow field at that point and using these two ideas I have established that the mobility matrix is essentially given by the Oseen tensor.

The only trick here is that at r = 0 this is basically infinity and the reason why this issue happened is because we have treated the particles as being point particles we did not account for the size of those particles okay. So, if I account for the size we can of course derive the expression and in that case we will not have this kind of a problem. But there is an approximate yet workable solution to this and that solution is that for m = n we will assume that the mobility matrix is simply $\check{H}_{nm} = \frac{\check{I}}{\zeta}$ or this can use the diagonal terms of the mobility matrix, of course we have to define a mobility matrix for every pair of n and m.

So, with these ideas I can then write the expression for the Brownian motion or the Langevin equation for interacting Brownian particles just to differentiate from the free particle case. So, now we have the mobility matrix appearing in our equation-

$$\frac{\partial}{\partial t}\vec{r}_n=\sum_m \acute{H}_{nm}\cdot\left(\frac{\partial U}{\partial \vec{r}_m}+\vec{f}_m\right)$$

So, earlier just to recall we had an equation for free particle that was like-

$$\frac{\partial}{\partial t}\vec{r}_n=\frac{-1}{\zeta}\frac{\partial U}{\partial \vec{r}_n}+\frac{\overline{F}_r}{\zeta}$$

Now the equation is modified because we are considering the interactions between various particles or considering the fact that the force acting on any particles affects the motion of all the other particles in the system earlier it was like the force acting only on that particle effects its motion.

So, now if I consider the case of an ideal chain that is no excluded volume which by the way correspond to what we referred as a θ solvent condition. You see like now I am becoming more discreet in our representation we are differentiating between the θ solvent and other solvents and the reason is like this is what will give us the correct scaling laws in addition to accounting for the interactions that we have discussed.

So, then in that case just to recall from our previous discussion, any bead in the system is experiencing the spring force due to the m + 1th bead and m -1th bead, the bead after this or bead before this and if I had this spring constant K then the force acting on that bead or the energy due to these two spring interactions is given as something like that-

$$U=\frac{1}{2}k\left(\vec{r}_{m+1}-\vec{r}_m\right)^2+\frac{1}{2}k\left(\vec{r}_m-\vec{r}_{m-1}\right)^2$$

So we can write this as-

$$\frac{-\partial U}{\partial \vec{r}_m}=-k\left(\vec{r}_m-\vec{r}_{m+1}\right)-k\left(\vec{r}_m-\vec{r}_{m-1}\right)+k\left(\vec{r}_{m+1}+\vec{r}_{m-1}-2\vec{r}_m\right)\approx k\frac{\partial^2\vec{r}}{\partial m^2}$$

And that is how we take it to the continuous space the r_m now become r as a function of m and time.

So, use the same idea here and then we have the expression that is-

$$\frac{\partial}{\partial t}\vec{r}_n=\sum_m \acute{H}_{nm}\cdot\left(k\frac{\partial^2}{\partial n^2}\vec{r}_m+\vec{f}_m(t)\right)$$

It corresponds to a Zimm model in θ solvent okay. So, now we can solve the equation that we have derived. Again the solution becomes somewhat tedious so I will only take you through the main points in the derivation and explain you the key results that we make or the key assumptions that we make in this scheme.

So, we start from the point that the mobility matrix is given by the Oseen tensor-

$$\acute{H}_{nm}=\frac{1}{8\pi\eta_s|\vec{r}_{nm}|}\left|\acute{I}+\hat{r}_{nm}\hat{r}_{nm}\right|$$

Now r is the distance between n and m bead. This $|\vec{r}_{nm}|=\left|\acute{I}+\hat{r}_{nm}\hat{r}_{nm}\right| for\, the\, case\, n\neq m.$ And for case n = m we have-

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

So, to proceed what we do here is you keep in mind that there are many beads. So, every bead is interacting with many other beads in the solution. So, of course we have to solve for many mobility tensors, mobility matrices. We make an approximation here that is called the pre averaging approximation which goes like this. The pre averaging approximation that is I will approximate the mobility matrix H_{nm} as the integral over the r_n values the set of values representing positions of each of the beads in the system multiplied by the H_{nm} multiplied by the probability to get that particular distribution-

$$Pre\,averaging\ Approximation : \acute{H}_{nm} = \int d\{\vec{r}_n\}\, P(\{\vec{r}_n\}, t)$$

And of course we are going to use the equilibrium- Gaussian distribution that we have derived and then this quantity is assumed to be equal to the pre averaged H_{nm} and that is given by-

$$\acute{H}_{nm} \cong \langle \acute{H}_{nm} \rangle = \frac{1}{8\pi\eta_s} \left\langle \frac{1}{|\vec{r}_{nm}|} \right\rangle \langle \hat{r}_{nm}\hat{r}_{nm} + \acute{I} \rangle = \frac{\acute{I}}{6\pi\eta_s} \left\langle \frac{1}{|\vec{r}_n - \vec{r}_m|} \right\rangle$$

So, we have replaced the mobility matrix that is appearing first by the Oseen tensor but then we noted that we have to compute many of these distances so we use the pre averaged over sum and then we use the fact that the distribution of the bead positions are given by the Gaussian distribution. So, I will use the fact that the P is a Gaussian function. And if I do that essentially what do I get, is-

$$\langle \acute{H}_{nm} \rangle = \int_0^\infty dr\, 4\pi r^2 \left[\frac{3}{2\pi |n-m| b^2} \right]^{\frac{3}{2}} \exp\left[\frac{-3r^2}{2|n-m| b^2} \right] \frac{\acute{I}}{6\pi\eta_s r}$$

$$¿ \frac{\acute{I}}{(6\pi^3 |n-m|)^{\frac{1}{2}} \eta_s b} = h(n-m)\acute{I}$$

As we had the pre averaged value of the mobility tensor and there is some function of n - m multiplied by the identity matrix I, so using this particular expression what I can then get-

$$\frac{\partial \vec{r}_n}{\partial t} = \sum_m \acute{H}_{nm} \cdot \left(k \frac{\partial^2}{\partial m^2} \vec{r}_m + \vec{f}_m(t) \right)$$

So now I have so we use the identity matrix that basically gets rid of the dot from the expression and then we had this entire thing-

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

So, just to give you a brief review of what we have done so far, we started with the Langevin equation for the interacting Brownian particle. It is different from the free particle case in the sense that the force acting on the particle also affects other particles in the system then we have been looking at this for the ideal chain case where the only force acting on the bead is the spring force due to the neighboring beads that is the case of a polymer chain and then we have made an approximation similar to what we have made earlier in the rouse model that we get a finite difference like form in the expression of the force and then we think of the continuous analogue of the discreet bead spring model. Using that I get the expression that I have-

$$\frac{-\partial U}{\partial \vec{r}_m} \approx k \frac{\partial^2 \vec{r}(n,t)}{\partial m^2}$$

Then we try to solve the Zimm model and I only hinted at the main steps in solution. So we started from the Oseen tensor that we have derived by Stokes approximation for the mobility matrix we have used the pre averaging approximation that is we approximate the mobility matrix by its average value that we get by integrating keeping in mind the probability distribution of the beads in a polymer solution that at equilibrium that is given by the Gaussian distribution for an ideal chain and using that after some mathematical manipulation I have got a function of (n – m) that is a function of the distance along the contour multiplied by the identity matrix. This is a basically a diagonal matrix that we have got mobility matrix may have contained an off diagonal term but since we have averaged it we get a diagonal matrix and if I plug that in back in here we do get the expression that you can see in the towards the end and I want to start from this particular point in the next lecture.

Thank you