Introduction to Polymer Physics

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Lecture-41
Rouse Model- I

Welcome and in the last class we have been discussing the Brownian motion of a free particle in an external field and the motivation that I have already given you is that we want to use that to discuss the Brownian motion of polymer chains. We required an external field discussion because when we look at the motion of polymer segments the every bead experiences some spring force due to other neighboring beads and also it experiences the usual solvent drag and thermal motion of solvent molecules and therefore we have first discussed that how can we incorporate an external field into it and the same idea we are going to use to incorporate the effect of spring force and using that we can build the model of a polymer chain the Brownian motion mode of a polymer chain that is known as the Rouse model.

So, we will talk about the Rouse model. It is actually simply an extension of or I would say an application of the bead spring model that we already have discussed. So, you have beads connected by springs and I can represent the positions of beads as say r_0, r_1, r_2 to some say are r_n. Now they are in a solution and so of course they are surrounded by tiny solvent molecules although I say tiny even the beads are not very large themselves because otherwise the Brownian motion will not really occur or will not be significant in the system.

So, then the spring force between the beads is simply given as the - k the extension of that particular spring or we can talk about spring energy that is half k extension squared. So, between say two beads or better still we can say but for any bead that is located at r_n it experiences to spring forces due to the n + 1 bead and n - 1 bead which are located at r_{n+1} and r_{n-1}. So, if I talk of the spring energy that is present at r_n for bead 'n' that is because of the two neighboring beads that we have that we can write as-

$$U_{spring}(\vec{r}_n)=\frac{1}{2}k(\vec{r}_{n+1}-\vec{r}_n)^2+\frac{1}{2}k(\vec{r}_n-r_{n-1})^2$$

So, using that we can get the force that is-

$$\vec{F}(\vec{r}_n)=\frac{\partial U}{\partial \vec{r}_n}=-k(\vec{r}_n-\vec{r}_{n+1})-k(\vec{r}_n-\vec{r}_{n-1})$$

$$¿k[\vec{r}_{n+1}+\vec{r}_{n-1}-2\vec{r}_n]$$

So, now we have to be slightly careful for the beads at the end for the beads at the ends only one spring is coming r1. So-

$$U=\frac{1}{2}k(\vec{r}_1-\vec{r}_0)$$

$$\vec{F}=-k(\vec{r}_0-\vec{r}_1)$$

Similarly for the other end of chain-

$$\vec{F}=-k(\vec{r}_N-\vec{r}_{N-1})$$

So, now we have found the forces because of the springs all of them are the force only because of spring of course we have other forces in the system. So, let us go back to what we derived for in one dimension we had-

$$\frac{dx}{dt}=\frac{-1}{\zeta}\frac{\partial U}{\partial X}+v_r(t)$$

Where, $v_r(t)=\frac{F_r(t)}{\zeta}$

$$\langle v_r(t)\rangle=0$$

$$\langle v_r(t) v_r(t') \rangle = 2D\delta(t-t')$$

So, if I now extend it in the case of a polymer chain I have to write separate equation for each of the beads that is to say that we have to write equations for each beads. So,

For bead 'n' we have-

$$\frac{d\vec{r}_n}{dt} = \frac{+1}{\zeta}\vec{F}_{rn} + v_r(t)$$

For bead n = 1, 2 …n-1 we have-

$$\frac{d\vec{r}_n}{dt} = \frac{k}{\zeta}(\vec{r}_{n+1} + \vec{r}_{n-1} - 2\vec{r}_n) + v_r(t)$$

For bead n = 0 we have-

$$\frac{d\vec{r}_0}{dt} = \frac{-k}{\zeta}(\vec{r}_0 - \vec{r}_1) + v_r(t)$$

For bead n = N we get-

$$\frac{d\vec{r}_N}{dt} = \frac{-k}{\zeta}(\vec{r}_N - \vec{r}_{N-1}) + v_r(t)$$

So, there is one thing we can see here and that is that if I look at the term $(\vec{r}_{n+1} + \vec{r}_{n-1} - 2\vec{r}_n)$ this has the form of the second difference second derivative in the in the finite difference form and the term $(\vec{r}_0 - \vec{r}_1)$ & $(\vec{r}_N - \vec{r}_{N-1})$ has a form of first derivative in the finite difference form that is to say that if N is very large then as I was doing for the case of a polymer chain. I can approximate the bead spring model as a continuous contour and then instead of talking about the discrete differences we can talk about derivatives along the contour and second derivative along the contour and so on.

So, if I now approximate the model as a continuous model which is going from n = 0 to n = N and 'r' being now a function of the contour variable N then in that case-

$$\frac{\partial^2 \vec{r}}{\partial n^2} = (\vec{r}_{n+1} + \vec{r}_{n-1} - 2\vec{r}_n)\,(known\,as\,Central\,Difference\,Approximation)$$

It has to be divided by Δn^2 but Delta n = 1 in this case and increase in increments of 1 so we get this particular relation. And then we can write for the 2 ends as the first derivatives. So we have-

$$\frac{\partial \vec{r}}{\partial n} \cong \vec{r}_1 - \vec{r}_0\,(for\,n=0\,known\,as\,Forward\,Difference\,Approximation)$$

$$\frac{\partial \vec{r}}{\partial n} \cong \vec{r}_N - \vec{r}_{N-1}\,(for\,n=N\,known\,as\,Backward\,Difference\,Approximation)$$

So, now if I go back here the equations I have derived now I can write them in a continuous notation so this equation becomes-

$$\frac{\partial^2 \vec{r}}{\partial n^2} = (\vec{r}_{n+1} + \vec{r}_{n-1} - 2\vec{r}_n)$$

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

And then I can also modify the two equations at the boundaries again using those derivatives-

For n= 0 we have-

$$\frac{\partial r_0}{\partial t} = \frac{k}{\zeta}\frac{\partial \vec{r}}{\partial n}\bigg|_{n=0} + v_r(t)$$

And for bead n= N it is-

$$\frac{\partial \vec{r}_N}{\partial t} = -\frac{k}{\zeta}\frac{\partial \vec{r}}{\partial n}\bigg|_{n=N} + v_r(t)$$

So we can always do this but now you see that this problem because somewhat complicated because if this is my partial differential equation and these are my boundary conditions. Then these boundary conditions are in somewhat complicated form and it is not really easy to solve because boundary condition itself our ordinary differential equation. So, we will do a trick here and the trick is that if I look at these two ends they are essentially free ends and since they are free there is like nothing before them so the any gradient that is present there should vanish at the free end that we have that is the nothing before this nothing after that. If it was like clamped on say two walls then this is no longer true then the gradient will be present at the boundaries but in this case the gradients has to vanish at this at the end because it is a free end. So, what we assume is-

$$\frac{\partial \vec{r}}{\partial n} = 0 \, when \, n = 0 \wedge N$$

This is because the ends are ands are free there is no polymer chain if I go further from n = 0, nothing there at n = -1. Similarly nothing there for n = n + 1. So, there the gradient must has to vanish.

So, now I have the full statement of the Rouse model in continuous approximation and that is we have a partial differential equation (PDE) for r and t where what we are now solving is for the positions as a function of n and t and being a contour variable running for from n = 0 to n =N and the PDE we have something like this-

$$PDE \, \vec{r}(n,t) : \frac{\partial \vec{r}}{\partial t} = \frac{k}{\zeta} \frac{\partial^2 \vec{r}}{\partial n^2} + v_r(n,t)$$

So, of course if I look closely then the random force was of course different for different beads in the system and therefore the random force should also be a function of ‘n’ because since we have replaced the r ends by a continuous variable r, control function r which is a function of n and t the random force is also differ for every bead. So, they also have to be a function along the contour. So, they also have to be changing with n and t and therefore he will do not clearly stated earlier this has to be v_r as a function of n and t. So, for every value of n we have to find a new random function or it is a continuous random function that would change its value as n is changing.

With Boundary Condition- $\frac{\partial \vec{r}}{\partial n} = 0 \; at \; n = 0, N$

The above two equations become the statement of Rouse Model.

Now it turns out that this is a second order partial differential equation and it is somewhat difficult to solve. So, in the next class what I would discuss is we can write this equation equivalently in terms of a series of ordinary differential equations and those ordinary differential equations are easier to solve and then we can get solution in terms of what is known as Rouse modes which I will elaborate in the next lecture. So, they are we are going towards what is known as a normalized coordinate or a Rouse mode and you want to find solution in terms of them and that's where we will take the discussion in the next class. So, I want to stop here, thank you.