Introduction to Polymer Physics
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Lecture-42
Rouse Model- II

Welcome in the last class we have been discussing the Rouse model to discuss the motion of a polymer chain and we have started deriving the equation, first we wrote in discrete terms and then we wrote a continuous were some of it that is true for large number of segments and today we will go on solving the equation into what we know as the Rouse Modes.

So just to recap, the model we have been trying to build is the continuous analog of the bead spring model where we have a contour variable 'n' going from 0 to N and the position at any point is given as 'r' as a function of n and t and at that point we are having a random force F_r as a function of n and t. If I divide by ζ I call it a random velocity v_r this was the Rouse model and the equation was for r and t we are solving a partial differential equation. It is-

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

Where we have the boundary conditions at the two ends that the gradients of 'r' vanish at n = 0 and N.

$$BC:\frac{\partial \vec{r}}{\partial n}=0\ at\ n=0 \vee N$$

So, what we have is a partial differential equation and it is of course difficult to solve when we compare that to an ordinary differential equation. So, the method we adopt is we try to write this partial differential equation into a set of ordinary differential equations which are easier to solve and then I write the ordinary differential equations that we get as the Rouse Modes and using that we can get the solution of the Rouse Model. So, the goal here is to write equations in the form of ordinary differential equations like this because we know how to solve these equations and that is what this is what we have got for the Brownian motion of a free particle just like one is sphere in a solvent. So we write as-

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

And to do that of course you cannot work with just one ODE because the PDE is a higher dimensional equation you will have a series of ordinary differential equation that represents that. So, this equation that I have written is for P = 0, 1, 2 and so on. So, what I do is known as a linear transformation where the variable I have defined the X_p which is now a function of 't' alone is given as the integration over r and t multiplied by a function ϕ_{pn} that I would refer to as a basis function and so far I am not saying what the basis function is but the basis function must, must satisfy this particular relation for X_p t where X_p is a solution of the equation I have just written let us call that *.

$$\text{Linear Transformation}: \vec{X}_p(t) = \int_0^N dn\, \phi_{pn} \vec{r}(n,t)$$

Here ϕ_{pn} is a basis function.

So, now let us look at the equation that we have written-

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

So, now I have constants ζ_p that is a drag coefficient but it is changing for different values of P so we will assign a meaning to it in a moment. Similarly we have K_p analogous of a spring constant but defined for an ODE for a value of p. And similarly F_p is like a random force that is defined for the value of p and of course that is changing as I change the values of p we do not know what the values are yet we will derive the values that would give any meaning to this equation.

So, now since we have defined X_p as integral over n of ϕ_{pn} multiplied by r (n, t). We have-

$$\vec{X}_p = \int_0^N dn\, \phi_{pn} \vec{r}(n,t)$$

If I plug that in the in the equation above what we have is-

$$\zeta_p \frac{d\vec{X}_p}{dt} = \zeta_p \int_0^N dn \phi_{pn} \vec{r}(n,t)$$

Of course I can move the time integration inside the integral because the integral is over n not time and ϕ is assumed to be not a function of time it is only a function of p and N. So, we can write this as-

$$\zeta_p \frac{d\vec{X}_p}{dt} = \zeta_p \int_0^N dn \phi_{pn} \frac{\partial \vec{r}(n,t)}{\partial t}$$

Here, we have to be slightly careful here because outside its total derivative d by dt when it is moved inside then since r is a function of both N and t. I have moved to partial derivative. But this we already know from the original equation that $\frac{\partial r(n,t)}{\partial t} = \frac{k}{\zeta} \frac{\partial^2 r}{\partial n^2} + \frac{F_r(t)}{\zeta}$

So, now this is equal to-

$$\zeta_p \frac{d\vec{X}_p}{dt} = \zeta_p \int_0^N dn \phi_{pn} \frac{k}{\zeta} \frac{\partial^2 \vec{r}}{\partial n^2} + \zeta_p \int_0^N dn \phi_{pn} \frac{\vec{F}_r(t)}{\zeta}$$

So, we will first do the integration by part over the first term and then we worry about the second term here. So, let us look at the first term which contains an integral like this of course it has some pre factors we will worry about that later. So, we use the integration by parts and the rule is if we have a product of two functions integrated over the variable x then-

$$\int f(x) g(x) dx = f(x) \int g(x) dx - \int f'(x) g(x) dx dx$$

So this is the rule I am going to use here where and set our variables as-

$$f(x) = \phi_{pn} ; g(x) = \frac{\partial^2 \vec{r}}{\partial n^2} \wedge x = n$$

Now –

$$\int \phi_{pn} \frac{\partial^2 \vec{r}}{\partial n^2} dn = \left(\phi_{pn} \frac{\partial \vec{r}}{\partial n} \right)_0^N - \int \frac{\partial \phi_{pn}}{\partial n} \frac{\partial \vec{r}}{\partial n} dn$$

We will drop the first term as we know-

$$\frac{\partial \vec{r}}{\partial n} = 0 \, using \, boundary \, conditions$$

So we get-

$$¿ - \left(\frac{\partial \phi_{pn}}{\partial n} \vec{r} \right)_0^N + \int \frac{\partial^2 \phi_{pn}}{\partial n^2} \vec{r} \, dn$$

So, once we have derived the equation for one term there so I want to put it back into the expression that I had earlier-

$$\zeta_p \frac{d\vec{X}}{dt} = \frac{\zeta_p}{\zeta} \left[\int_0^N k \phi_{pn} \frac{\partial^2 \vec{r}}{\partial n^2} dn + \int_0^N \vec{F}_r(n,t) \phi_{pn} dn \right]$$

$$¿ \frac{\zeta_p}{\zeta} \left[- \left(k \frac{\partial \phi_{pn}}{\partial n} \vec{r} \right)_0^N + \int_0^N k \frac{\partial^2 \phi_{pn}}{\partial n^2} \vec{r} \, dn + \int_0^N \vec{F}_r(n,t) \phi_{pn} dn \right]$$

$$¿ - k_p \vec{X}_p + \vec{f}_p = -k_p \int_0^N dn \phi_{pn} \vec{r} + \vec{f}_p$$

Now there can be many possible solutions to this particular equation we will look at a particular solution because any of these solutions that satisfy the ordinary differential equation that I have just written will suffice for us it need not be a unique solution. It can be any solution because we are transforming the variable to get a linear ODE and there may not be a unique solution there can be multiple ways to linearize the PDE that we have. So, one possible way is we look at the term by term in the two expressions I have written. So, first of all I look at the last term in the two expressions and we get-

$$\vec{f}_p = \frac{\zeta_p}{\zeta} \int_0^N dn \, \phi_{pn} \vec{F}_r(n,t)$$

This is my first equation.

Now I look at the other terms and I get-

$$\frac{\zeta_p}{\zeta} k \frac{\partial^2 \phi_{pn}}{\partial n^2} = -k_p \phi_{pn}$$

So, this is one way of getting a solution for what we have written and again I want to emphasize that this is not a unique solution there may be other ways of solving it but this one will suffice because this already transformed the PDE to the ODE we want. We need not care about a unique solution we can get any solution that will work because any transformation is will work for us.

So, if I look at the above equation I can also write as something like this-

$$\frac{\partial^2 \phi_{pn}}{\partial n} = \frac{-\frac{k_p}{k}}{\frac{\zeta_p}{\zeta}}$$

Now you can see we have a partial differential equation in terms of the basis function that I am trying to solve for and we know the boundary condition that basis function also satisfies so using that we will solve for the basis function and using that basis function I can define the solution X_p t this is what we are going to do. So, let us get started so we have an equation of the form because all the constants that we have are assumed to be positive that is an assumption again-

$$\frac{\partial^2 \phi_{pn}}{\partial n^2} = -A^2 \phi_{pn}$$

Here $A = \frac{\left(\frac{k_p}{k}\right)}{\left(\frac{\zeta_p}{\zeta}\right)}$

The general solution of this will be

$$\phi_{pn} = \alpha\cos(An) + \beta\sin(An)$$

Where α and β are arbitrary constants you can verify this by doing the first derivative and the second derivative which is-

$$\frac{\partial \phi_{pn}}{\partial n} = -\alpha A\sin(An) + \beta A\cos(An)$$

$$\frac{\partial^2 \phi_{pn}}{\partial n^2} = -\alpha A^2\cos(An) - \beta A^2\sin(An) = -A^2\phi_{pn}$$

So, if I look at this general solution now and if I now use the first boundary condition at n = 0 we can put n = 0 here the sine term is anyway 0 the cos term will give me-

$$\phi_{pn} = \alpha\cos(An) + \beta\sin(An)$$

$$\frac{\partial \phi_{pn}}{\partial n} = 0 \; at \; n = 0 \; then \; \beta A = 0 \; so \; A = 0 \; which \, is \, a \, trivial \, solution$$

Because this will give me the k_p values to be 0. B A = 0 you can see A = 0 will be a trivial solution because this will give me the k_p values to be 0. So, we go for β= 0 then I will use the second condition at n = N, β is already gone we have from here αA sin AN = 0 of course A is not equal to 0 because it is a trivial solution, if we set A = 0 again we get a trivial solution. So, α= 0 is trivial. So, we set sin AN = 0 which gives me-

$$\sin(AN) = 0 \; so \; AN = p\pi$$

Therefore,

$$A = \frac{p\pi}{N}$$

Where p is again an integer going from 0, 1, 2 and so on.

So, using that now I have the solution for this equation that means now we have the basis function ϕ_{pn} and the basis function in our case is this-

$$\phi_{pn} = \alpha \cos\left(\frac{p\pi n}{N}\right)$$

Now the only issue is we do not know what α is now for any value of α we will have a linear transformation. So, it is up to us which α value we are going to choose. So, we will choose-

$$\alpha = \frac{1}{N}$$

Therefore,

$$\phi_{pn} = \frac{1}{N} \cos\left(\frac{p\pi n}{N}\right)$$

The reason why we have taken alpha is equal to 1 by N is because if you recall-

$$\vec{X}_p = \int_0^N dn\, \phi_{pn} \vec{r}$$

This dn is of the order of N, so if I multiply this with the quantity that is of the order of 1 by N the net quantity will be of the order of unity that is one justification why we are taking alpha = 1 by N because that gives me a quantity of the order of unity in the in the equation I have written for X_p.

So, just to conclude, so, we have now obtained the basis function ϕ_{pn} using that now I can get the solutions X_p which will then be used to solve the ordinary differential equations and by solution of those equations we can get the solution of the Rouse Model.

So, we continue from this point in the next lecture, thank you.