Introduction to Polymer Physics
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Lecture-43
Rouse Model- III

Welcome in the last lecture we have started discussing the derivation of solution of the Rouse Model and we have been like halfway through so we will complete the derivation in this lecture. So, just too briefly recap, we are talking about the discrete to continuous transformation of the bead spring model. So, we have a contour variable n = 0 to N and we talk about the position of a segment r (n, t) and the random force acting on the segment like this and then the original equation is a partial differential equation-

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

With boundary conditions $\frac{\partial \vec{r}}{\partial n} = 0 \, when \, n = 0 \vee N$ then we did linear transformation and derived the equation i.e.

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

$$\zeta_p \frac{d\vec{X}_p}{dt} = -k_p \vec{X}_p + \vec{f}_p \wedge f_p = \frac{\zeta_p}{\zeta}\int_0^N dn \, \phi_{pn} \vec{F}_r(n,t)$$

So, that is where we are so far so now take it further, so now we have also obtained A value that is-

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

And

$$A^2 = \frac{\frac{k_p}{k}}{\frac{\zeta_p}{\zeta}} = \left(\frac{p\pi}{N}\right)^2 so\, k_p = k\frac{\zeta_p}{\zeta}\left(\frac{p\pi}{N}\right)^2$$

So, we have we have found the k_p the only thing is that the ζ_p is still to be found arbitrarily. So, if the whole procedure seems to be somewhat confusing to you keep in mind that we are only trying to write the PDE into a set of ODE's we do not really care about getting a unique value of the X_p and therefore we do not really care about a unique value of the of the constants we have like k_p and ζ_p. So, they are arbitrary as long as to satisfy the ordinary differential equation okay. So, even though we have established this equation the ζ_p can also be chosen arbitrarily.

So, how do we get how do we get ζ_p is the following so we choose ζ_p such that we have-

$$\langle f_{px}(t) f_{px}(0)\rangle = 2\zeta_p k_B T\delta(t)$$

Since,

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

And therefore if we are interested in something like $f_{p\alpha}$ (t) fq_β (0). I am doing in somewhat general terms ultimately as we want autocorrelation but we are doing in general terms α and β represent the coordinate directions and p and q represents the indices of the solutions that I am looking at different values of p essentially. So this would then be equal to-

$$\langle f_{p\alpha}(t) f_{q\beta}(0)\rangle = \frac{\zeta_p\zeta_q}{\zeta^2 N^2}\int_0^N dn \int_0^N dn \cos\left(\frac{p\pi n}{N}\right)\cos\left(\frac{q\pi m}{N}\right)\langle F_{r\alpha}(n,t) F_{r\beta}(m,0)\rangle$$

We are looking at, not really the whole vector but the alpha and beta components of these vectors. So, we can write this as-

$$\langle F_{r\alpha}(n,t) F_{r\beta}(m,0)\rangle = 2\zeta\, k_B T\delta(t)\delta_{\alpha\beta}\delta(n-m)$$

because if it is a different direction then the forces random forces are uncorrelated only when they are in the same direction the forces are correlated and then we also have a delta of n -m because at different points along the contours as long as the distance is not 0 the Fr values are uncorrelated.

And then this term I can write using the formula for cos (A + B) and cos (A – B) as-

$$\cos\left(\frac{p\pi n}{N}\right)\cos\left(\frac{q\pi m}{N}\right)=\frac{1}{2}\left[\cos\left\{\frac{p\pi n}{N}+\frac{q\pi m}{N}\right\}+\cos\left\{\frac{p\pi n}{N}-\frac{q\pi m}{N}\right\}\right]$$

So, now this looks somewhat complicated but we wrote it just because we wanted in general form. But now you can see that we are integrating over delta of n – m, so if I integrate over m I can replace n by m inside the integral and I can remove the integral over m. So, I will essentially take this away and I will replace m by n there and essentially then what we have is-

$$\langle f_{p\alpha}(t) f_{q\beta}(0)\rangle=\frac{\zeta_p\zeta_q}{2N^2\zeta^2}\int_0^N dn\left[\cos\left\{\frac{(p+q)\pi n}{N}\right\}+\cos\left\{\frac{(p-q)\pi n}{N}\right\}\right]2\zeta k_B T\,\delta(t)\,\delta_{\alpha\beta}$$

So, now we can go on and look at the integration, we have now integration over cosine functions. So, if I look at the integration over the cosine functions this would give me on integration other things are anyway constant this will give me-

$$\left[\cos\left\{\frac{(p+q)\pi n}{N}\right\}+\cos\left\{\frac{(p-q)\pi n}{N}\right\}\right]=\left[\frac{\sin\left\{\frac{(p+q)\pi n}{N}\right\}}{\frac{(p+q)\pi}{N}}\right]+\left[\sin\frac{\left\{\frac{(p-q)\pi n}{N}\right\}}{\frac{(p-q)\pi}{N}}\right]$$

Now if you notice here the second term will always be 0 as long as p is not equal to q because we will have something that is a multiple of nπ or π. So, this will be not equal to 0 only when p = q and in that case too we have to take a limit using the lapels rule and if I look at that then I can write this as something like if I let-

$$Let\ p-q=r\ then$$

$$\lim_{r \to 0} \frac{\sin\left(\frac{r\pi n}{N}\right)}{\frac{r\pi}{N}} = \lim_{r \to 0} \frac{\cos\left(\frac{r\pi n}{N}\right) \cdot \frac{\pi n}{N}}{\frac{\pi}{N}} = n$$

Now if I look at the first term now it is always 0 except when p + q = 0 now since p and q are both positive integers this means this is not equal to 0 when p = q = 0 and in that case this = N when p = q = 0, so as a shortcut I can look at this entire term and I can write as the first term as something like N multiplied by δp0 δpq, δpq means it is only nonzero when p = q and δp0 means it is only nonzero 1 p = 0. So, if I multiply both it means the condition p = q = 0 and the second term is N multiplied by δpq, so we have N multiplied by 1 + δp0 δpq.

$$N\delta_{p0}\delta_{pq} + N\delta_{pq} = N(1+\delta_{p0})\delta_{pq}$$

So, now I will plug that back in this equation and I will have a simplified relation which would be-

$$\langle f_{p\alpha}(t) f_{q\beta}(0)\rangle = \frac{\zeta_p^2}{N^2\zeta^2}(1+\delta_{p0})N\delta_{pq}\zeta k_B T \delta_{\alpha\beta}\delta(t)$$

So, this is what it becomes you can see that two has cancelled here that is why we do not have a prefactor in this in this equation. And now you also have a cancellation of N ζ and we get something like ζ_p^2 by N ζ in there. So, now since I am interested in fpx (t) fpx (0), $\delta_{pq} = 1$ because I have set p = q and $\delta_{\alpha\beta}$ is also =1 because we only are looking at x coordinates. So, we have-

$$\langle f_{px}(t) f_{px}(0)\rangle = \frac{\zeta_p^2}{N\zeta}(1+\delta_{p0})k_B T \delta(t)$$

So, now we have demanded that-

$$\langle f_{px}(t) f_{px}(0)\rangle = 2\zeta_p k_B T \delta(t)$$

Now we will look at two different cases- when p = 0 then,

$$\frac{\zeta_p^2}{N\zeta}(1+\delta_{p0})=\frac{N\zeta^2}{N\zeta}\cdot 2=2N\zeta=2\zeta_p$$

Case -2 when p $\neq 0$ then,

$$\frac{\zeta_p^2}{N\zeta}(1+\delta_{p0})=\frac{(2N\zeta)^2}{N\zeta}=4N\zeta=2\zeta_p$$

So, with that I now have the complete representation of the Rouse Model into a series of ordinary differential equations where we know how to get the constants k_p and ζ_p okay. So, we will start from this point in the next lecture and then try to illustrate that how this kind of math become useful to us because of course it is complicated we are trying to write a partial differential equation into a series of ordinary differential equation of course we said that PDE's are difficult to solve then compare toward ODEs but of course we could have done a numerical solution. So, there must be some other advantage of going in this particular means and that is what we will demonstrate in the next lecture.

Thank you.