# Introduction to Polymer Physics
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## Lecture-44
## Rouse Model- IV

Welcome in the last lecture we have been discussing the solution of Rouse Model and we have almost written the partial differential equation that we had in terms of ordinary differential equation. So, today I will take it further and talk about the physical significance of the solutions that we have written for the $X_p$ that is my variables that appear in the ordinary differential equation.

So, essentially what we have done is for the discrete to continuous for the continuous analogue of the bead spring model I am not writing the partial differential equation but the 1 dimensional analogue that we have been working on where we have obtained the value of ζ.

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

$$\zeta_0 = N\zeta \wedge \zeta_p = 2N\zeta$$

It is different for p = 0 and everywhere else and then we can also get the expression for $k_p$ using the expression I have derived this is equal to the following-

$$k_p = \frac{2k p^2 \pi^2}{N}$$

Now you can note here that we do not write a separate equation for p = 0 because if I put p = 0 here it is anyway 0 so the pre factors does not really matter for p = 0 case. So, now you can recall that for an ideal chain the k value was derived to be-

$$ideal\,chain\,k = \frac{3k_B T}{b^2}$$

And therefore for ideal chain we can write $k_p$ as-

$$k_p = \frac{6 k_B T p^2 \pi^2}{N}$$

So, let us first look at what advantage we get from here, the one clear thing you can see from here if you recall the Brownian motion of a free particle the equation we had something like this-

$$\textit{Brownian motion of free particle}: \frac{d\vec{X}}{dt} = \frac{-k}{\zeta}\vec{X} + \vec{F}_r$$

And now the equation we have written of course this is for different values of p looks very similar in form to what we had for the Brownian equation further for the Brownian motion of a free particle okay. So, therefore all the kind of math we did for the displacement correlations functions and so on for the free particle case will apply in this case for particular values of p. So, in the in the free particle case there is only one x but now we have multiple values $x_0$, $x_1$, $x_2$ they correspond to different values of p. But for each of those p values the mathematical form is similar to what we had for the Brownian motion of free particle.

So, what essentially it means if I start thinking at an intuitive level is we are writing the model of a polymer chain as many equations for different p values where each of the p values give rise to an equation that is similar to the free particle case that is the first thing that we see here. Let us say if I am interested in the correlation functions for the displacements. Now I can talk about displacements in different values of $X_p$ for different p that is x0, x1 and so on.

Let us say for example for p = 0 what we can get as the auto-correlation would be equal to-

$$\left\langle \left( \vec{X}_0(t) - \vec{X}_0(0)_\alpha \right) \left( \vec{X}_0(t) - \vec{X}_0(0) \right)_\beta \right\rangle = \zeta_{\alpha\beta} \frac{2 k_B T}{\zeta_0} T$$

Where $\zeta_0$ is of course and $N\zeta$ as you can see the $\frac{2k_BT}{\zeta}$ was like a diffusion coefficient in that case. Now we have a $\zeta_0$ appearing there for a particular p value. So, for every p value we can think of a diffusion coefficient for that particular p value. In general for p higher than 0 we can say or also q higher than 0 we can write this as-

$$\langle \vec{X}_{p\alpha}(t)\vec{X}_{q\beta}(0)\rangle = \delta_{pq}\delta_{\alpha\beta}\frac{k_BT}{k_p}e^{-\left(\frac{t}{\tau_p}\right)}$$

Where $\tau_p = \frac{\zeta_p}{k_p} = \frac{\tau 1}{p^2} \wedge \tau_1 = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}(for\, the\, case\, of\, ideal\, chain).$

That is to say if I look at the displacement correlation functions in terms of these solutions $X_p$ that I will refer to them as Rouse modes. These correlations decay exponentially with the time scale $\tau_p$ and that time scale basically decreases as I increase the values of p okay. So, the decay is faster if I go to larger values of p and decay is slower if I go to lower values of p that is the first thing that we see.

The next thing is what is more important and that is that once we have got these values of $X_p$ so I have transformed my 'r' that was representing the positions along the contour to $X_p$ I can do vice-versa so I can start from $X_P$ and get the 'r' that is called the inverse transform. I can write this as-

$$Inverse\, Transform: \vec{r}(n,t) = \vec{X}_0 + 2\sum_{p=1}^{\infty}\vec{X}_p\cos\left(\frac{p\pi n}{N}\right)$$

So, using the value of $X_p$, I can get the values of r and you can also note that $X_p$ basically go from 1 to infinity that means we can have infinite Rouse modes that are present in the system ok. So, let us see why this is the case, so we can prove we can prove this statement for inverse transform by using the definition of the $X_p$ that we started with after derivation of the basis function we had got something like this right. The proof is-

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

$$\text{¿}\int_0^N dn \frac{1}{N}\cos\left(\frac{p\pi n}{N}\right)\left[\vec{X}_0 + 2\sum_{q=1}^{\infty}\cos\left(\frac{q\pi n}{N}\right)\right]$$

$$\text{¿}\frac{1}{N}\int_0^N dn\cos\left(\frac{p\pi n}{N}\right)\vec{X}_0 + \frac{2}{N}\sum_{q=1}^{\infty}\int_0^N dn\cos\left(\frac{p\pi n}{N}\right)\cos\left(\frac{q\pi n}{N}\right)\vec{X}_q$$

Now we will replace using the rule that we have discussed earlier cause cos(A + B) + cos (A – B) by 2-

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

Now if I integrate I get-

$$\frac{1}{N}\vec{X}_0 \sin\frac{\left(\frac{p\pi n}{N}\right)}{\frac{p\pi}{N}} J$$

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N for p = 0 is 0 otherwise we have-

$$\text{¿}\vec{X}_0\delta_{p0} + \frac{1}{N}\left[\sin\frac{\left(\frac{(p+q)\pi n}{N}\right)}{\left(\frac{(p+q)\pi}{N}\right)} + \sin\frac{\left(\frac{(p-q)\pi n}{N}\right)}{\left(\frac{(p-q)\pi}{N}\right)}\right]\vec{X}_q$$

So, of course both of these are only nonzero when p = q and as we have done earlier this becomes-

$$\text{¿}X_0\delta_{p0} + \frac{1}{N}\sum_{q=1}^{\infty}(\delta_{p0}+1)N\delta_{pq}$$

Since we start from q = 1 and we have a $\delta_{pq}$ inside, so $\delta_{p0}$ is not a possibility because we have taken that separately. So, what we have here is-

$$\text{¿}\vec{X}_0\delta_{p0}+\sum_{q=1}^{\infty}\vec{X}_q\delta_{pq}=\vec{X}_p$$

So, this is how we have shown that the inverse transform follows the relation that we have provided here by using the definition of the transform itself. So, now we know that if I know the $X_p$ I can get r and if I know r I can get $X_p$ so it is perfectly the kind of transformation I wanted. So, I only need to solve for $X_p$ and I can get the r values and I can get the chain configuration if I am solving the Rouse modes the solutions $X_p$ ,the only thing is that it is infinite such solutions that we have to solve for.

Now what I am going to demonstrate is we do not really need to solve for this infinite solutions. Each of these individual solutions also have a meaning embedded in them and that we can see if I if we do certain examples try to get some quantifiers of polymer chain and see how does that relate to the Rouse modes that we have described.

So, let us say for example I am interested in the center of mass, if I am interesting center of mass then it is of course given by simply the integration of r over N the whole contour and divided by N that gives me the center of mass i.e.

$$Center\ of\ Mass:\vec{r}_{cm}(t)=\frac{1}{N}\int_0^N dn\,\vec{r}(n,t)$$

And then if I simply plug in the definition of inverse transform we get the following-

$$\text{¿}\frac{1}{N}\int_0^N dn\left[\vec{X}_0+2\sum_{p=1}^{\infty}\vec{X}_p\cos\left(\frac{p\pi n}{N}\right)\right]$$

$$\text{¿}\vec{X}_0+\frac{2}{N}\sum_{p=1}^{\infty}\vec{X}_p\sin\frac{\left(\frac{p\pi n}{N}\right)}{\left(\frac{p\pi}{N}\right)}$$

The first term here simply gives me $X_0$ because integration over N gives me capital N it cancels out. The second term here gives me the integration which is anyway going to be 0 because we have started from p not equal to 0 we start from p = 1. So, what I get from here is my center of mass simply is the first or $0^{th}$-

$$\vec{r}_{cm}(t)=\vec{X}_0$$

Therefore, the center of mass refers to the 0th Rouse mode of the system. So, without even solving for all the Rouse modes even if I get the 0th Rouse mode that already has a meaning to it, it tells me about the center of mass of the polymer chain. So, now we can think about other quantifiers and see like what they become. Let us say for example I am interested in the diffusion coefficient. To get the diffusion coefficient we want to start with the mean square displacement.

The mean square displacement we can define for the entire chain more specifically maybe we want to define for the center of mass. If I want to define the mean square displacement of center of mass, it already captures the net diffusion of polymer chain. So, let us say for example if my polymer chain goes from one point to other then I can characterize the overall diffusion by looking at the center of mass here over two points.

The net motion of center of mass characterize the overall diffusion of the polymer chain. Note that I am not putting the center of mass on the polymer chain itself because by definition the center of mass can be anywhere on the chain it need not it any anywhere in this space where the polymer chain is present it need not lie on the polymer chain or any particular segment because of the relation that we are using to get the center of mass it does not require that we have to place the center of mass on the polymer chain itself. I can define this as-

$$\left\langle \left(\vec{r}_{cm}(t)-\vec{r}_{cm}(0)\right)^2 \right\rangle = \sum_{\alpha=x,y,z} \left\langle X_{0\alpha}(t)-X_{0\alpha}(0) \right\rangle$$

$$¿3\cdot\frac{2k_BT}{N\zeta}t=\frac{6k_BT}{N\zeta}t$$

And if I compare to the relation that we derived for 3 dimensions Einstein relation in 3D what we can get is for a polymer chain the net diffusion is given as simply-

$$\langle r^2\rangle=6Dt$$

$$D=\frac{k_B T}{N\zeta} \vee D \propto \frac{1}{N}$$

That is if I increase the number of segments the diffusivity decreases. Although it is qualitatively true, it turns out that the scaling is not perfectly correct the scaling changes with different solvents. And scaling changes also due to factors that I called hydrodynamic interactions that we discuss later and for that we have a model called Jim model but nonetheless it already captures the basic feature that the diffusion coefficient will decrease if I increase the number of segments on the polymer chain which is indeed true and the longer polymer chains have lesser diffusivity because they will diffuse more slowly in the system. So, now let us look at some other quantity that we are used to.

Let us say for example I am interested in the end to end distance. So, the end to end distance is for our polymer chain going from n = 0 to n = N is simply-

$$\vec{R}_e(t)=\vec{r}(N,t)-\vec{r}(0,t)$$

And as we know

$$\vec{r}(n,t)=\vec{X}_0+2\sum_{p=1}^{\infty}\vec{X}_p\cos\left(\frac{p\pi n}{N}\right)$$

So we get-

$$\vec{R}_e(t)=2\sum_{p=1}^{\infty}\vec{X}_p\left[\cos(p\pi)-1\right]$$

The term $\cos(p\pi)=(-1)^p$ so if you notice here all the even terms will cancel out because for even terms we have cos p Ⅲ - 1 = 0 only the old terms will remain. So, this is going to be-

$$\text{¿}2\sum_{p:odd}\vec{X}_p(-2)=-4\sum_{p:odd}\vec{X}_p$$

That gives me the end to end distance vector.

If I am interested in the correlation time correlation of $R_e$ ultimately I am interested in-

$$\left\langle \vec{R}_e(t)\vec{R}_e(0)\right\rangle = 16\sum_{p:odd}\left\langle \vec{X}_p(t)\vec{X}_p(0)\right\rangle$$

And this we have already established will decay exponentially and then it is going to be something like-

$$\text{¿}16\sum_{p:odd}^{\infty}\frac{3k_BT}{k_p}e^{\frac{-t}{\tau_p}}$$

Here $\tau_p = \frac{\tau_1}{p^2}$

So, now you can notice here that only the first term will be the one that will be dominant because the exponential actually decreases as we go to progressively higher values of p. Let us say for example we go for p = 3 then we have exponential of -9 times what we had in the case of p = 1, so, exponential decay very fast for higher values of p. So, p = 1 is the dominant term that we will see in here. So p = 1 is dominant what this means is the first Rouse mode essentially captures the time correlation of $R_e$.

So, in summary what we have shown so far is we have assigned two meaning to the Rouse modes 0th Rouse mode correspond to the center of mass of a polymer chain. 0th Rouse mode also gives us the net diffusion coefficient of a polymer chain. The first Rouse mode tells me about the time correlation of the end to end displacement and we take the idea further and discuss on the physical significance of Rouse modes in a bit more detail in the next lecture.

With that I conclude here, thank you.