# Introduction to Polymer Physics
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## Lecture-23
## Structure of Polymer Chain, Introduction to Monte Carlo Simulations of Polymer Chains

Welcome, so in the last class we have discussed the scattering theory in very brief and then what we said is we can find a number density correlation function and if I Fourier transform it I will get a structure function that we can get by scattering experiments. So now I will go further from that point and define what is known as the pair distribution function and then we will derive expressions for the pair distribution function using the polymer chain and then I will show how the structure functions will look like for the case of a polymer chain.

So what we had discussed is the number density correlation function that is equal to-

$$C_{nn}\left(\vec{x}_1,\vec{x}_2\right)\rightarrow\left\langle n\left(\vec{x}_1\right)n\left(\vec{x}_2\right)\right\rangle$$

After Fourier Transform we get-

$$I\left(\vec{q}\right)\rightarrow\left\langle n\left(\vec{q}\right)n\left(-\vec{q}\right)\right\rangle$$

So now I will define the pair distribution function, we had already discussed what does the function look like for the case of a liquid, solid and gas but now I will basically derive in two steps. So I will first define it as the functions g of two positions $X_1$ and $X_2$ that is the probability of finding a particle at $X_2$ if a particle is at $X_1$ and then I will explain when does it reduces to just one variable.

So let us define the pair distribution function-

$$\left\langle n\left(\vec{x}_1\right)\right\rangle g\left(\vec{x}_1,\vec{x}_2\right)\left\langle n\left(\vec{x}_2\right)\right\rangle=\left\langle\sum_{\left(\alpha\neq\alpha'\right)\left(\alpha,\alpha'\right)}\delta\left(\vec{x}_1-\vec{x}_\alpha\right)\delta\left(\vec{x}_2-\vec{x}_{\alpha}'\right)\right\rangle$$

$$For\,\alpha=\alpha'=\delta\left(\vec{x}_1-\vec{x}_\alpha\right)\delta\left(\vec{x}_2-\vec{x}_\alpha\right)$$

$$¿\left\langle n\left(\vec{x}_1\right)n\left(\vec{x}_2\right)\right\rangle-\left\langle n\left(\vec{x}_1\right)\right\rangle\delta\left(\vec{x}_1-\vec{x}_2\right)$$

So g of x1 x2 the way we have not defined when we exclude the case $\alpha \neq \alpha'$ is the probability of finding different particle at $X_2$ if a particle is at $X_1$. So the g ($X_1X_2$) is the probability of finding a different particular at $X_2$ if a particle is at $X_1$. So the detail here that we don't really look at a particular position but a small volume around that position just to make sure that we cover the entire space. So when I say at $X_2$ it really means a small volume around $X_2$ which we can write as-

$$\vec{x}_2-\frac{\delta\vec{x}_2}{2};\vec{x}_2+\frac{\delta\vec{x}_2}{2}\vee d\vec{x}_2$$

So we can make 2 approximations here when we are looking at a homogenous fluid. So homogenous fluid will have the same ensemble average density that is when we have discussed this for the case of liquid. This is ensemble average is –

$$Ensemble\ Average=\frac{N}{V}\left(it\ is\,a\ constant\right)$$

The second approximation is that, we did not look like look at the g of ($X_1$, X2) but we can look at g of ($X_1$ -$X_2$) what essentially it means is known as translational invariance that applies for homogenous fluid and the idea is that I do not need to look at every possible pairs of positions but we can look at only distances between the two positions.

So now we can show the structure function was the Fourier transform of the number density correlation function in the same way that is structure factor which was an intensive measure so we divided the structure function by N or V to get the structure factor. The structure factor is related to the Fourier transform of the pair distribution function again pair distribution function is like a normalised version of the number density correlation function just like this structure function factor is normalised form of the structure function. So the relation that I will not derived is I can write the structure factor as the following is form of homogenous fluid-

$$S(\vec{q}) = \langle n \rangle \left[ 1 + \langle n \rangle \int g(\vec{x}) e^{-i\vec{q}\cdot\vec{x}} d\vec{x} \right]$$

Here this is the average number density.

Now if the fluid is also isotropic then all the three directions are identical. So in that case we can actually replace-

$$g(\vec{x}) \cong g(|\vec{x}|) = g(r)$$

This is called the radial distribution function, which we have already shown for the case of the liquid and gas when we have been discussing the form of the pair distribution function for that liquid and gas we looked at absolute value of x along the x axis and for the case of solid we chose to use the actual value of x that's the vector value just because the gas and the liquid is assumed to be isotropic.

So now let us see how this g of r scale in the case of polymer solution, we will start with a polymer chain in a dilute solution. In this case the statistics will be similar to the polymer chain. So we have derived so for a polymer chain in the dilute case the number of segments at a distance r that is –

$$n(R) \approx M = R^{\frac{1}{\nu}}$$

Where ν will be the coefficient I get differently for the random walk, self-avoiding walk and collapse chain case. So if I know the number of segments at a distance r from a given segment or bead the number density that we see within the small volume pair will give me a measure of the virial distribution function.

Other way to say that is let us say if I keep as central at centre the particle which I want to keep as reference and if I look at a volume r around it assume my sphere of volume r around it and if I am interested in a number of particles present in that volume at location r that is you may be interested in a spherical shell that is-

$$g\left(r\right) \quad \frac{\delta n\left(r\right)}{4\pi r^{2}\delta r}$$

So if we look at the spherical shell that is at distance r and we are looking at a shell of thickness delta r, so as I said earlier that we are interested in a small volume at distance r. So then the g of r would scale like the number density that is present inside this particular shell of thickness delta r and that would then become the number of segments present in that volume that I represent using delta r/the volume of that segment which we can represent in more rigorous way as-

$$g\left(r\right) \quad \frac{4}{3}\pi\left[\left(R+\frac{\delta R}{2}\right)^{3}-\left(R-\frac{\delta R}{2}\right)^{3}\right] \quad 4\pi r^{2}\delta R \quad \frac{1}{4\pi r^{2}}\frac{dr}{dr} \quad \frac{n}{r^{3}}\vee\frac{n}{r^{d}}$$

Where d is dimensionality and we know what the N is scaling like-

$$g\left(r\right) \quad r^{\frac{1}{\nu}-d}$$

Now we will associate this with fractal dimension df and we get-

$$g\left(r\right) \quad r^{\left(d_{f}-d\right)}$$

If I do a Fourier transform of this then I will not divide it what we get is-

$$S\left(q\right) \quad \left(qb\right)^{\frac{-1}{\nu}} \equiv S\left(q\right) \quad \left(qb\right)^{-d_{f}}$$

So now again we can do it for different cases because we know the ν values corresponding to them. For example if I am doing in three dimensions then for θ solvent when we have ideal chain ν=1/2, g of r will scales like $r^{2-3}$ that is $r^{-1}$ and s of q will scale like $q^{-2}$ . In a good solvent ν is 3/5. So g of r will scale like $r^{-4/3}$ and s of q will scale like $q^{-5/3}$, in the bad solvent the chain is collapsed we get ν=1/3 and g of r scale like 1 and s of q scaling like $q^{-3}$.

So, this tells me the behaviour with q now there is a point to note here that my q goes like 1/λ and λ sets the characteristic length scale that I am looking at. So if I look at smaller q value that gives me the behaviour at longer length scales. If I look at the larger q values that gives me the behaviour at smaller length scales. So essentially when the length scale λ become comparable to the chain radius it is no longer a fractal as soon as we look at this length scales higher than the chain dimensions because the whole idea of self-similarity and fractal nature will apply to segments of the chain not the whole chain.

So whatever we have derived will be only true at length scales that is r values significantly lower than the $R_g$ value, at larger length scales we will have slightly different behaviour that we will not derive. So in this way we have a systematic way starting from the fractal dimension of the polymer chain that we have derived in different condition by Fourier transforming we get what do we expect in the s of q and I have said earlier s of q is the experimental output from the scattering experiment. So we have a way to verify from experiment whether this is scaling is observed or not in the particular case or vice versa by looking at the scattering plot we can identify whether we are in a good solvent regime or bad solvent regime or a theta solvent regime.

This is like a way to look at the structure of the chain and this adds to the size and shape characterization that we have discussed earlier. So with this now I want to take to another dimension of things that is all these are like theoretical is tough and for many cases that we have shown we can do very nice derivations. But we can also get these results and actually more results if I also employ simulations. In that case let we can actually see what the polymer chain looks like in different solvent and we can have a more accurate way in a sense to get the scaling laws because the simulations will not have some of the assumptions that the Flory theory made for example we assume that the concentration of segments are uniform, the inter connectivity of the segments were ignored for the purpose of interaction energy and elastic energy was taken for an ideal chain even though the chain was not ideal.

So if I do a simulation we can relax to assumptions and try to get best scaling law more accurately and in fact it turns out the simulations itself are not very difficult to perform. So we already had discussed the simulations in the case of ideal chain earlier where I said I can generate many confirmations of a polymer chain get there for example the end-to-end distance squared values taken ensemble average over many confirmations and then we can get the scaling laws that we got by the theory.

Now I want to extend the idea to the cases where we do have an excluded volume interaction, simulations can be of two types- the most common type in polymer literature is the Monte Carlo simulation at least for the toy models we have discussing and then there is other class that is molecular dynamics simulations. Actually there are many other methods that have been developed either as some sort of extension of these two methods or methods of their own.

So I will discuss the Monte Carlo simulation molecular dynamics simulations in somewhat more details. So I want to first give you again the idea of how the Monte Carlo simulation works and then we will see how we apply on a polymeric system.

So the basic idea of a Monte Carlo simulation is the following, we start with a configuration of system that is we start with the polymer chain in fact the Monte Carlo is a very general and the key idea is that we start with simulation box that is representative of the entire system I am considering. So for example if in reality we have polymer chains contained in the beaker the case I was telling you when I was discussing the effect of concentration. So it is probably not worth it and it is probably very expensive to come to do experiment the simulations over the entire beaker. So we will not do simulations over the entire beaker, we will do simulations over a smaller volume within the beaker that represents the condition in the beaker.

The simulation box is not the same as the experimental container that we are using, simulation box is something that represent the bulk behaviour that you see in the experiment. For example I can draw small volume inside my beaker and that volume will contain certain number of molecules and atoms and we will simulate that in the simulation and then we expect whatever behaviour we do get represents the behaviour of the bulk, the first thing is the simulation box should be significantly large that it is representative of what is going on in the system. At the same time it cannot be very high because if it is very high then the simulation becomes computationally expensive.

So I will use the word representative of the bulk system that is at least for the dilute concentrations we can hope to simulate only one polymer chain in a small simulation box and that will show the behaviour that we have got for the scaling laws polymer chains. If it is an in entangled systems on high concentrations maybe we need to take a larger volume considering more polymer chains but at least for the dilute case I am interested in this scaling law for a single polymer chain we can just make a simulation box that contain one chain in the system.

So let's say this is my simulation box and we have a chain contained in there let's say I am representing the polymer chain using the bead spring model. So we use the bead spring model, now if you recall from the Flory theory I represented the energy of the chain as sum of the elastic energy and the excluded volume energy.

$$\int ¿$$

$$U = U_{elastic} + U_{¿}$$

So in this case the elastic energy is because of the springs that connects the beads. So I am assuming that between every adjacent bead in the polymer segment we have a spring of certain spring constant K, for the Gaussian chain we have derived that the spring constant K of the spring goes like $k_BT$ but is general we can keep k value that is arbitrary for the simulation. So it can either be written as in terms of extension-

$$U(x) = \frac{1}{2} k x^2$$

$$¿\frac{1}{2} k (x - x_0)^2$$

This becomes equilibrium or average segment length. This takes care of the elastic parts, so now if you have for example n beads in the system you will have n-1 springs and we look at the spring energy of all those things that gives me the elastic energy. If I look at the interaction energy now the interaction energy can be present between every pair of beads in the system. So let us say if I look at a particular bead i here this bead interacts with 1, 2, 3, 4, 5 until all the beads that we have in the system. So the interaction energy in the two body interaction is-

$$U_{\int ¿^{(i,j)}}$$
$$\int ¿^{(i)} = \sum_{j=1}^{N} ¿$$
$$U_{¿}$$

U that represents the interaction between I and J. So we can write some sort of pair interactions and that’s way if I count all the pair interaction for pairs containing the particle we get the total energy due to interaction energy for that particular bead. So if I sum that over all the beads we get the total energy due to interaction in the system so-

$$\int ¿^{i} = \sum_{i=1}^{N} \sum_{j=1}^{N} U_{\int ¿^{(i,j)}}$$
$$U_{¿}$$
$$\int ¿ = \sum_{i=1}^{N} ¿$$
$$U_{¿}$$

So we have not yet said what that interaction energy form is but we know that we have to sum over all the pairs in the system. In fact to be precise we have to exclude the cases where j is not equal to I because there is no self-interaction considered. The interaction energy only happen between two beads which are distinct. In fact in many simulations it is preferable to also exclude the adjacent beads that is we also do not want j to be equal to i- 1 and j to be equal to i+1 because the interaction between adjacent beads are anyway captured using the spring force, but that depends on the model. The key ideas that we have to exclude the self-interactions and we may or may not exclude the interaction energy between the adjacent beads where the interaction energy is only referring to the non-bonded interactions the bonded is already considered in the first part.

So now the question is that how do I construct the form of this $U_{int}$ function, and that’s where there is a very famous potential that becomes very useful it is known as the Lennard-Jones potential. One of the first applications of potential was to explain real gases which is already is something that can give you Van der wall equation of state. The potential works like this, so I can look at $U_{int}$ between a pair of particles at a distance r as a function of r, now this particular interaction should possess certain features. First of all it should capture the range of interaction. So this particular potential is already for short ranged Van der wall interactions. So for example we have Van der wall attractions we know that it decays like $r^{-6}$. Now the issue is this if I just use this form then r=0 we will have in infinite interaction energy that would mean that all the beads will collapse into one ok. So this goes against the idea that the beads will contain certain amount of hard core that is giving rise to self- avoiding walk that we discussed in good solvent or excluded volume as we discussed in the Flory theory. So what we typically also want is want that at small distances there should be some repulsion which is referred as the hard core repulsion that prevents overlap of each because again if it is not found not present then the overlap of beads give rise to very high negative energy and if I do such a simulation I always go to one bead collapsing into all the beads collapse in 1 bead.

There is no specific form for this particular potential when I say no specific from there is no physical basis of choosing what the hard core repulsion should be, in practice it should be infinite at r = 0 and non-zero otherwise but that is difficult to difficult to handle. So it is preferable to have a very steep potential for the reasons you will see it works better than having an infinite energy hard core at r=0. So then I can construct what is known as the Lennard-Jones interaction as-

$$\int ¿^{LJ}(r)=4\in\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

$$U_{¿}$$

So in the particular expressions σ is sort of a length scale, σ is the value at which the ν interaction crosses 0 you can put in σ=r here we can see it goes to 0 and then if I look at the depth of the potential the depth is given by epsilon and I want to know where the minimum lies I can do minimization of u with respect to r which gives me-

$$\frac{du}{dr}=0$$

$$¿>\frac{-12\sigma^{12}}{r^{13}}+\frac{6\sigma^{6}}{r^{7}}=0$$

$$r^{¿}=2^{\frac{1}{6}}\sigma$$

So, beyond the value of r* we switch on the attractive Van der wall in this particular case below that we have a steep potential which becomes r distance σ which prevents the beads to overlap. So now of course the potential decays very rapidly and at higher r values pretty much the potential is very small. So come back to this point in a moment, but what we so far have is we have an elastic energy and we have a non-bonding interaction energy that is represented as a sum of the two body interactions and will look at all the pairs in the system excluding self-pairs.

So now the question is like how do I incorporate that energy in to the simulation the way of doing this is in the Monte Carlo method is the follow describe what the algorithm is and then we will discuss like why does it work. So Monte Carlo algorithm is the following and I am doing it for a polymer chain case again for a bead-spring model, but the idea itself is very general and we applied for many cases.

So we start with a chain confirmation and to begin with we do not know what the energy of confirmation is right. So it always starts with random confirmation and which will have certain positions of the beads. So let us say { $r_i$ } indicates the positions of the bead where the {} is a shortcut for the positions $r_1$ $r_2$ to say $r_m$.

$$\{\vec{r}_i\} \equiv (\vec{r}_1, \vec{r}_2, \ldots\ldots\ldots \vec{r}_m)$$

So now what we do, so now we do a trial displacement of a randomly chosen bead, so I can pick any of randomly from 1 to n and I will displace as from $r_i$ to sum $r_{i'}$ will come to like exactly we do the trial displacement. But let us say for the moments that we have chosen any particular bead randomly and then we try to displace from $r_i$ to $r_i$'.

$$\vec{r}_i \rightarrow \vec{r}_i'$$

Now that we comes now we compute the change in total energy due to the trial which is something like-

$$\Delta U = U(\{\vec{r}_i'\}) - U(\{\vec{r}_i\}) = (U\, includes\, both\, elastic \wedge Lennard\, Jones\, interaction)$$

So now we know that we have formed the trial and we have computed the energy chain to remove. So now here comes the main Monte Carlo logic that ultimately what do we want, we want the system to go towards the lowest free energy confirmation so we should accept moves which are going to lower energies and we should either reject the moves which are going to higher energy or at least accept with a lower probability because higher energy states are anyway not the ones that are present in equilibrium. So one of the standard method is we accept or reject the trial with some probability function so we do accept and reject and then we basically go to step 2 and continue until properties of interest converse.

So again the idea is that let us say I want to find end to end distance square of chain. I will start with random configuration I will do a trial displacement I will accept or reject based on the energy change we will have some probability to accept or reject based on energy change and then I will continue doing the simulation until whatever property I am interested in converse to a value that you we will call the equilibrium value of simulation.

So I will start from this particular point in the next class, thank you.