Introduction to Polymer Physics

Prof. Dr. Prateek Kumar Jha
Department for Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture-16

Definition of Excluded Volume: Good, Bad, and Theta Solvent

In the last class we have been talking about the excluded volume interaction that is just to remind you very quickly is when the interactions vary with the physical distance not the distance along the contour. So we are looking at let us say 2 segments which are far along the contour (m-n) is much higher than 1 but they are close together and I have already pointed out that ultimately what matters is the interactions between the segments at this distance should be comparable to or higher than the thermal energy. If it is smaller than we do not care about it, so we got this R then whatever interaction you will define we wanted to be higher than the thermal energy of the system.

So in this class I will take this further, the first idea I want to introduce is why do we call these interaction as excluded volume interaction and then we will do a small explanation of first what types it can be we already said it can be attractive or repulsive. But will take it slightly further, and then finally we will drive what is known as a virial Expansion starting from this particular point.

So the first thing is I want to give it a particular expression for the interaction and I can choose any particular energy scale it doesn't really matter if I divide this by $k_B T$ or anything. So I can start with any scale and let us say I am defining in this particular way-

$$\int \text{¿}\left(\vec{r}_m-\vec{r}_n\right)=k_B T\,\tilde{v}\left(\vec{r}_m-\vec{r}_n\right)$$

$$U_{\text{¿}}$$

So I chose $k_B T$ as a scale and then since we have taken $k_B T$, $k_B T$ already has units of energy, so whatever else we have is some dimensionless parameter that we don’t know, but it depends on the distance so it will be dimensionless function to be more precise.

So now if the attractions are repulsive then what essential it means is this number v ($\tilde{v}$) has to be higher than 0, if the attractions are attractive this number should be less than 0. Other way to say it like it they are attractive they want to come together that is give rise to the lowering of energy if they are repulsive if they are if they come together that give rise to an increase in energy. So depending on that we are assigning a sign to the ($\tilde{v}$).

So if I define in this particular way let us say this is my R ($r= r_m-r_n$) and I am doing versus say the absolute value of the r. So, let us say I do it here, I assume that it only depends on the distance. We can talk about specifics later, but most interactions only depend on the distance not the distance vector like coulomb interaction only depends on the distance. So now if it is higher than 0 we can say it is repulsive and if it is less than 0 we can say that it is attractive and then how fast or slow the interaction depends on r define what is known as a long range interaction or short range interaction. For example the Coulomb interaction between like charges is repulsive and it decays like 1/r the r is this. The actual formula just to recall also contains some constants and the charges but we are looking at how the interaction scales with R.

Similarly if it is attractive like this it is like plus minus or minus plus in the same thing it also decays like 1/r. Now 1/r is of course not a very rapid decay if it goes to double the distance the interaction is half, if it makes it four times the interactions is like ¼ you know about functions that decay faster than this like exponential of something they decay much faster than compared to 1/r, of course if I take of higher powers of r 1/r to the power square that will decay faster compared to 1/r because if I say double the distance the interaction now will be one fourth as opposed to ½ in the case of 1/r.

So there is something known as the Van der walls interaction that is present even between neutral molecules and they are known to decay by 1/r to the power 6 that really means a very rapid decay. Now they can also in principle be both attractive and repulsive but mostly we talk about attractive Van der wall and they are like. So now if you think about it since we have said already that the interactions must be higher than k_BT for them to have any effect. So what it means in turn is let us say after certain distance this interaction 'u' becomes less than k_BT then after this distance we should not worry about that interaction that essentially means is this is a short range interaction because after a particular point the energies will become smaller than k_BT and this will happen much earlier in this case than compared to the coulomb interaction. So for the coulomb we can call it as long range interaction.

We also have talked about short range and long range interactions in the context of the ideal chain models. But told that time the range referred to the distance along the contour not the physical distance. So now and after this point when we say a short range and long range we are referring to the actual physical distance not the distance along the contour.

In the short range interaction case that is really falling of very sharply in the limit of like very rapid decay we can really approximate this as like a delta function. the delta function is in this case is the case of repulsive interaction because anyway for r=0 it is very high that means as soon as the polymer chains or segments cross we have a very high interaction and then otherwise it is 0 because anyway after some distance is going to fall off and the decay is very rapid. The decay is anyway very rapid compared to say long range interaction. So we can approximate using a data function We can call this a delta function and then in reality it was something that was rapidly decaying but now we can approximate as delta function. When the chains cross then only it will be considered for the purpose of excluded volume, if it is not crossing that means we will not consider.

Now before we proceed from here just keep in mind that when the chains cross it is you know making any kind of a physical error in terms of stating. It is not like 2 atoms are sitting on each other. As we have discussed earlier what it really means is two segments of the polymer chain has come together now individually both these segments are in different confirmation. So we don't have a 1-1 overlap of atoms we have an overlap of different conformations. What we have is like the segments represent different confirmation that is one point to make here. The other point to make here is how much do we care because we are doing a very toy like model we care about scaling laws, we know that at molecular level these models will not really work there is resolution not to the level of atoms, but they still give you good scaling law so we have to live with these kind of assumptions.

So as I have already said this v can be approximated to be a delta function where this function is essentially not equal to 0. Now we have:

$$\tilde{v}\left(\vec{r}_m-\vec{r}_n\right) \cong \delta\left(r_m-r_n\right)$$

This is what meant here that integration of the delta function is equal to 1 over the entire space, so since this going to has a unit of volume, this has a unit of 1/volume because 1 is dimensionless, so this entire thing delta has a unit of 1/volume, it must be multiplied with something of having the unit volume because we know ($\tilde{v}$) is dimensionless. Ok. So for the same reason we multiply with parameter V which has a unit of volume ok, just to explain the point again because it is very important, first we write the ($\tilde{v}$) that we got or we started with the expression of the interaction energy, first we say that the interaction are short ranged this assumption will not work for coulomb interactions for example, but they will work for Van der walls interactions. First we assume it is can be approximated by a delta function then we said that the delta function in three dimensional space will have a unit of 1/volume but ($\tilde{v}$) should have a dimensionless units must be dimension less, so you must have to multiply the delta function with something that has a unit of volume and we call that particular quantity V as our excluded volume. So in some sense we can think of it physically as some volume around the segment where the interactions become effective between the segment means we can we can think of like let us say if I start at segment m and I go to a small distance I will see some Van der Wall that is higher than $k_B T$, if I go to longer distances the interaction is present but that is smaller than $k_B T$.

So we can think of smaller volume around the segment m for which the interaction are substantial that particular volume we can think of as the excluded volume, but the analogies ends here because it is not always excluded the parameter V as you will see can be both positive and negative because ($\tilde{v}$) can of course be both attractive and repulsive.

So for v higher than 0 that is for the excluded volume parameter we call the system in the good solvent regime because that is when we have repulsive interactions and for v less than 0 we call it a bad or poor solvent. Now it is anybody's guess of what we can do for the case of ideal chain, it is not good, nor bad so it has to be something like v=0 and that is what we call as theta solvent or theta conditions.

So now will talk in terms of parameter v that has a unit of volume and we will see what will happen or positive v negative v, zero v and so on and just keep in mind that this has a unit of volume because the delta function had a unit of 1/volume.

It refers to some sort of and volume around every segment which are somewhat excluded in the sense that the interactions are effective there but then the interactions can be both positive and negative and so it is not that the polymer molecules cannot come there the segments cannot come there and so on. So now that was between one pair of segment m and n ok. So now if I look at the total interaction energy that is present in the chain by virtue of this excluded volume interaction. Then you must have to in to integrate the energy we have got between m and n for basically the index going from 0 to capital M that is the number of segments. Because that will look at all possible pairs of segment in the system. So the total interaction energy will be equal to-

$$\int \text{¿}=k_B T\frac{v}{2}\int_0^M dn\int_0^M dm\,\delta\left(\vec{r}_n-\vec{r}_m\right)$$

$$U_{\text{¿}}$$

Here, we have to define 2 dummy variable and n and m both are going from 0 to M that is along the contour, and then we had a delta I V as to be constant is moved outside the integration and we have a factor of 2 because if I am doing an integration twice from 0 to M we are looking at basically every pair twice. So it will now let say M and N will come twice one as MN next time as an NM. So that is why we divide by 2 in the integration.

So now we can also define something known as the local concentration of segments and the quantity is defined as-

$$C(\vec{r})=\sum_{n=1}^{M}\delta(\vec{r}-\vec{r}_n)=\int_{0}^{M}dn\,\delta(\vec{r}-\vec{r}_n)$$

It means if I look at any particular point in space and let us say it is r, then the number of segments passing through this particular point will be sum over all the delta functions where I basically iterate over every segment and see whether it is at r or not. So if more segments are passing through a point we say the concentration there is higher. Here we think concentration as the number per unit volume every time we count we increase the number and delta function already has a unit of 1/volume that is how we get the concentration.

So now again in this discrete space this can be 0 to again when we replace the summation by the integration over the contour that we can do for large M this is. So now I am going to use an identity here that will really make things more convenient from now. As we can write –

$$\int \text{¿}=k_B T\frac{v}{2}\int_{0}^{M}dn\int_{0}^{M}dm\int d\vec{r}\,\delta(\vec{r}-\vec{r}_n)\,\delta(\vec{r}-\vec{r}_m)$$

$$U_{\text{¿}}$$

$$\vec{r}_n=\vec{r}_m=\vec{r}$$

As I integrate over all possible values of r the product of these 2 that $r=r_n$ and $r=r_m$ delta functions, then the particular product is basically correspond to $r_n=r_m$ and since it integrate over the entire space this captures all the possible values of this position.

So now if I use this particular relation here so if I see here I can move the integration with r outside, something that we have been doing we have been interchanging the signs of integration keeping in mind that we want to figure out which order is more convenient for us. So in this case you will have-

$$\int \text{¿} = k_B T \frac{v}{2} \int d\vec{r} \int dn\, \delta(\vec{r}-\vec{r}_n) \int dm\, \delta(\vec{r}-\vec{r}_m) = k_B T \frac{v}{2} \int d\vec{r}\, c(\vec{r})^2$$

$$U_{\text{¿}}$$

So, that really means that the interaction energy that we have got goes like the squares of the concentration.

What I will do in the next lecture is to say that we have made assumption here that this only a 2 body interaction, in reality we can have a three body interaction or 4 body interaction and what this amount to is what is known as the virial equations that we will derive and based on that we can then do the Flory theory and derive the scaling laws for the good solvent case and the bad solvent case.

So I will stop here, thank you.