Introduction to Polymer Physics
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Lecture-17
Virial Expansion, Flory Theory for Good Solvent

In the last class we have been discussing about excluded volume interaction and we have been looking at what is known as two body interaction and today we will take it further derive the virial equation that I have been telling you about and then we go to the Flory theory that gives us the scaling laws for the good solvent case and the poor solvent case.

So what we have covered earlier is the excluded volume interactions which if you remember refer to the non-bonded interactions that depends on the physical distance between two segments as an opposed to the distance along the contour that we have discussed in the ideal chain models. So the basic idea was like this, so if you have 2 segments of a chain let us say m and n here and of course this is contour variable going from 0-m. In that case we said that we can define the local concentration that is-

$$c(\vec{r}) = \sum_{i=1}^{M} \delta(\vec{r} - \vec{r}_i)$$

Where $\int \delta(\vec{r})\, d\vec{r} = 1$

It has to satisfy the condition of normalisation.

So that essentially means that every time in a particular segment i is at a position r we add something of the order of 1/V and if I sum over all the segments we get the numbers per unit volume and that characterize the concentration or the number density as you want to call it and based on that assuming that we have only short range interactions that is to exclude the case of long range coulomb interactions so short range interactions decay rapidly. In that case we can approximate the interactions again by a delta function and based on that what we have derived is the total interaction energy is given by-

$$\int ¿(\vec{r}) = \int dr \left[\frac{1}{2} v\, k_B T\, c(\vec{r})^2\right]$$

$$U_{¿}$$

Where, $\int dr = \int dxdydz$ and v= excluded volume.

So now this particular interaction that we have discussed is basically what is referred as a 2 body interaction that is we look at pairs of segments which can be nearby or in the same position if I approximate the interactions by a delta function, but in fact this can be the case that three segments come together close to each other in that case we have to think about a three body interaction.

So the idea is something like this. So now instead of this 2 there can be three guys referred as M, N and P they are close together and they will interact. This three body interaction is not the same always as the sum of the two body interaction. So the interaction between M, N and P is not same as the sum of interactions mn, np and mp and this is what we referred to as a three body interaction. So again since we have assume that this is not coulombic so we cannot take an example of coulomb interaction really but it is easier to think in terms of charges. So if we have say two charges together they attract but if there are three charges together then we form like what is known as a triplet of charge that is not the same as the sum over 3 triplets. So we can extend the idea also to short range interactions and this is what is referred as a three body interaction.

So in this particular case we can extend the derivation we have done earlier for 2 body interaction and note that now for the 3 body case so let me refer the earlier one has 2 body just like we have done earlier. Now we will have something of this order-

$$\int ¿^{3\,body}=\int\left[\frac{1}{6}w\,k_B Tc(\vec{r})^3\right]d\,\vec{r}$$

$$U_{¿}$$

$$\int ¿(\vec{r})=\int dr\left[\frac{1}{2}v\,k_B Tc(\vec{r})^2+\frac{1}{6}w\,k_B Tc(\vec{r})^3\right]$$

$$U_{¿}$$

So essentially then if I account for both of these then we get and in fact just like we talked about the three body interaction, we can think of all the of like the 4 body interaction, 5 body interaction and so on. And as we go to say 4 body interaction we will have ‘c’ to the power 4, in 5 body interaction we have ‘c’ to the power 5 in that. So what we are writing is sort of a series in the powers of concentration and this is what is known as Virial expansion that is one of the most common tactic in thermodynamics to look at that the interaction between objects.

So now one thing to note here is if the interaction are short range then if I go to the higher powers of concentrations we will get a smaller number. 2 body is more dominant simply because there is more possibility of having pairs as oppose to triplets, similarly there is more possibility of having triplets as a oppose to 4 objects remains together or quad rids so as to speak and so it must be like a decaying series.

It turns out that this is not the case when we have like long-range interactions it doesn’t form like decaying or convergent series that is why we have kept coulomb interaction out of question it is only true for short range interaction. So we will use this particular expression in addition to the elastic energy of polymer chain that we have derived earlier to build what is known as total energy of the chain. So this is the interaction due to non-bonded interactions or excluded volume interactions and then we also have some elastic energy purely due to in entropic reasons because as the number of segments increases the number of confirmation increases the entropy increases, so essentially it is a competition of two interactions in the system we can think of excluded volume also as a enthalpic interaction and if we remember from thermodynamics we are interested in quantities like Gibbs free energy change defined as the change in the enthalpy -T delta s where delta s is chain in entropy. So this will come from the elastic energy and this will come from the excluded volume interactions.

So now we will discuss what is known as the Flory theory based on this particular idea before we do that I want to remind you that the parameter V is a function of the solvent nature as we have discussed in the case of water extensively and it is also a function of temperature simply because as we raise temperature the entropy will increase and interactions weaken particularly hydrogen bonds as we discussed in the case of water as solvent.

So we can define the parameter V as some constant multiplied-

$$v = v^0\left[1 - \frac{\theta}{T}\right]$$

This works in many cases and this will be of course equal to 0 at T=theta which plays why we call ideal chain as a theta solvent and of course this will be higher than 0 for T higher than theta. This is what is referred to a good solvent in which case I will get a swollen or stretched chain and this is also referred as a self-avoiding walk, and then finally it can be less than 0 for attractive interactions for T less than theta this is known as bad solvent and this is give rise to collapsed chain which is having a smaller value of size that compare to ideal chain and of course swollen chain.

So what we will now look using the Flory theory is we look at the size of a chain, but we will not do it very rigorously, we will make a what is known as an scaling estimate. So in place of looking at the end to end distance or the radius of gyration of specific conformations and then doing an ensemble average, we will characterize the size of the chain as some quantity ‘r’ which of course correspond to ensemble average in a rigorous description, but since we are doing I would say an approximate scaling theory we are not doing a very rigorous kind of derivation. So we will basically refer to some measure of size of the chain. You can think of this r being the square root of the mean squared average of radius of gyration, we also think in terms of end to end distance frankly the way the theory is being built does not really going to details about what exactly the size is how it is defined. It characterizes I would say and characteristic size of the chain and how it is changing with solvent.

So now with this in mind we can start building the total energy of the chain in terms of the two interactions we have discussed. One is elastic energy and one is the interaction energy, so I can say total energy of chain by the way we are now doing Flory theory and we are first doing it for the case V higher than 0 that is good solvent. So total energy of the chain U is comprised of the elastic energy and interaction energy due to excluded volume that we have just derived. So now there is a small detail here that whenever we say that the energy is sum of the two contribution. We are actually making an approximation that is known as additivity approximation which is not again rigorously valid and the reason is this that if for example of chain has a non-bonded interaction then the elastic energy will not be same as that in the case of an ideal change it will not be as streched as ideal chain would because it has either repulsive on an attractive interaction. So basically what it means is the elastic energy is not completely decoupled with the interaction energy.

In reality by writing any kind of questions we are excluding any sort of coupling between two different types of interactions. The other way to think about it is in terms of degrees of freedom. So the elastic energy will give rise to certain degree of freedom of chain so we can do some kind of stretching that correspond to a degree of freedom. We can also do at a level of a segment for those degree of freedom do not really do really depend on the interaction energy as well, but what we say is the degree of freedom because of elastic energy is independent of the degree of freedom due to interaction energy. So we are going in details here, but this is one of the first approximate that Flory made in his theory. Although this is not the most serious one will come to the most serious approximation.

$$\int \text{¿}(additive\,approximation)$$

$$U=U_{elastic}+U_{\text{¿}}$$

So now what Flory said is the elastic energy is the same like it is for the ideal chain which means that the elastic energy scales like-

$$U_{elastic} \quad \frac{R^2}{Mb^2} \, here \; M = number \; of \; segments$$

We do not worry about the pre factors here, there was a pre- factor of 3/2 if you recall since we are doing is scaling so we do not care about the protectors, we only care about how the r scales with n or m, and actually we are using m always. So let us go back the m, m is the number of segments. so although chain has an non-bonded interaction we still are thinking of it as having the elastic energy component same as that of an ideal chain and then separately we look at the excluded volume interaction, so here again in fact we should do the integration that we have discussed earlier that's right here we will make 2 approximations to make things easier to avoid any kind of integration.

The first approximation is that V is higher than 0 and the first term is much higher than the remaining terms to only consider the first term to be the dominance term and will drop everything else that is the first approximation. The second approximation is we will not worry about the connectivity of the polymer chain for the purpose of considering the excluded volume interaction. So what this means is of course my chain looks like this it occupies some volume the volume of course in three dimensions scale like r^q , so you can think of like an sphere has a volume of 4/3 πr^3, we do not care about the pre-factors again. So the volume is scaling like r^3 and in that volume I assume that the segments are uniformly distributed. That means you do not care about the fact that that full polymer chain is connected and it is not same as a uniform distribution of segment, other segments cannot be like anywhere it has to be connected to the previous segment, but we assume that this is the case, we assume that these segments are present in this volume and there is no connectivity between them and in that case we can say that concentration is actually uniform that means concentration is same everywhere and then it must go like m/r cube that is a number of segments per unit volume again do not care about it.

$$c(\vec{r}) \approx \tilde{c} \quad \frac{M}{R^3} \left(excluded \; volume \; interaction \; which \; ignores \; connectivity \right)$$

Now, before we go further let us look at like what sort of errors we are making here. So as I already said that an ideal chain and a self-avoiding walk or a good solvent case polymer chain differ in the stretching of the polymer chain and in the case of self-avoiding walk we can expect that the chain is more streched if the chain is more streched, then the elastic energy if I really would have considered in the non-bonded interaction would have been higher and in fact by assuming it to be an ideal chain we are under estimating the elastic energy. So the elastic energy is underestimated which means-

$$U_{elastic} \quad \frac{R^2}{Mb^3}\left(this\,expression\,is\,underestimated\right)$$

We assume that the concentration is uniform basically what we are doing is we are overestimating the energy and the reason being that another segment let us see if I look at a particular segment it cannot be the case that the other segments are uniformly distributed of course the next segment has to be the close but if I go farther along the contour they have to be farther from this particular segment. There is no way that we can have a uniform distribution of segments around it to, so we always overestimate excluded volume from what it should be. So

$$c(\vec{r}) \approx \tilde{c} \quad \frac{M}{R^3}\left(this\,expression\,is\,overestimated\right)$$

Now as I have already told you earlier Flory was very lucky in a sense that the errors that results from the under estimation of elastic energy and over estimation of excluded volume they both cancel out perfectly for I would say very mysterical reasons and he was able to get the correct scaling law.

So now I can write my interaction energy also assuming that the first term is the dominant here. This will become, so I will first approximate as only the first term in the virial expansion and then I will use the idea that the concentration is assumed to be uniform. So in that case-

$$\int \text{¿} \approx \frac{1}{2}\int d\vec{r}\, v\, k_B T c(\vec{r})^2 \approx \frac{1}{2}\cdot R^3 v\, k_B T\left(\frac{M}{R^3}\right)^2 \quad v\, k_B T\frac{M^3}{R^3}$$

$$U_{\text{¿}}$$

Again we drop the pre-factor 1/2 since we do not care about the pre-factors in this scaling law. So now we are left with the elastic energy and the interaction energy both scaled in this particular way in terms of M and R, M is the number of segments R is the size. And I can write the total energy as –

$$U \quad k_B T\left[\frac{R^2}{M b^2}+\frac{v M^3}{R^3}\right]$$

So now we use the idea that the chain will like to minimise its energy that is a standard thermodynamic approximation things like to go towards the minimum of free energy. And I can do that by taking a derivative with respect to ‘r’ the size will be such that will meaning the free energy and that we can get-

$$\frac{\partial U}{\partial R}=0\, therefore,$$

$$\frac{2R}{M b^2}-\frac{3 v M^2}{R^5}=0$$

Since $R^5 \quad v M^3, R \quad v^{\frac{1}{5}} M^{\frac{3}{5}} so\, R^2 \quad M^{\left(\frac{6}{5}\right)}$

If I compare that with ideal chain it was an R square going like m in this case we get a higher power meaning that the chain will be more stretched as compared to the ideal chain. So this is what we have got for the good solvent case.

Now let us see how thinks workout for the bad solvent case ok. So for the bad solvent case now the v is actually less than 0 ok. So now in this case you can see that v to the power 1/5 will give you an imaginary answer ok and that’s where you can find that r cannot be imaginary because size has to be a real number. So something goes a miss in the derivation and what went wrong really is that we have missed the three body interaction that can be important for the collapse chain for the simple reason that is a chain is like collapse there is more possibilities of 3 body interactions or three body contacts than compared to the case when the chain is streched.

So we will have now try to include the 3 body interactions and then see what kind of scaling laws we get here. So again I want to point out before I going further one important thing here that whatever approximations we are making in a sense are motivated by experimental results or some kind of a physical intuition, so although it may seem like some sort of arithmetic manipulation it can be verified or it should be verified by some experiments are the physical intuition that we have and only then the scaling theory can succeed. Ok, it is not always that whatever assumptions we have made will succeed in the representation of system and then we have to go back and revise our estimate because essentially what we have been doing is trying to revise or approximate or simplify the rigorous integrations that we had earlier derived that also had certain assumptions present but we have further simplified by simply dropping the integration and choosing to do a pure scaling analysis. So in that sense we have to be very careful that we do not go wrong in the intuition that we started with or we should always plan to do experiments to back up our theory and indeed that has been done by Flory by experiments as well, so we will return to the case of v less than 0, in the next lecture where we also will include the three body interactions that we have missed earlier in the good solvent case.

Thank you.