Introduction to Polymer Physics
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Lecture-15
Nonbonded Interactions, Hydrophobic and Hydrophilic Behaviour

In the last lecture we have briefly touched upon the idea of excluded volume interactions that is basically as we explained relates to the non-bonded interactions that varies with the actual physical distance between 2 points on the polymer chain. Now we will see like how does this change out scaling laws in that we have derived and we will talk about something known as a good solvent and a poor solvent in more detail.

So, let us just do a quick recap, so what we have said if I have a polymer chain then the 2 points along the polymer chain can be very far along the contour. So, (s-s') can be much higher than 1, so but the physical distance is small and the idea here is that what do you mean by small, small meaning that whatever interactions we are considering should be important for that distance.

So, let us call the quantity r and we elaborate more on this, so the basic idea is that whatever interactions we talk about should be significantly higher than at least the thermal energy of molecules or segments. So, if it is if the interaction is smaller than the k_BT that is the scale of the thermal fluctuations then anyway those interactions can be considered to be relatively less important or unimportant but when the interactions are dominant than the (u of r) must be much higher than k_BT .

Essentially we can also think in terms of the competition between the enthalpy and entropic forces. So, the k_BT coming from the entropic forces that we have in the system, so if the interactions are smaller than k_BT or comparable to k_BT we can say that it is entropy dominated. On the other hand if the interactions are higher than k_BT actually significantly higher than we can say it is enthalpy dominated.

So now before going into the specifics of what the interactions are, let us just start to visualise what exactly will happen if there are interactions present between segments far off along the chain. For example in the last class we discussed that what if there is a negative charge and a positive charge present in the polymer chain. The coulomb interactions are not the only one there can be for example hydrogen bonding, we can have van der wall interactions whatever right. But what will they do, so we can actually classify the interaction at least in 2 broad classes, 1 classes the interactions are attractive, the segments have a tendency to come together or they are repulsive the segments repel each other like in the case of say –and – they are like charges, they repel each other. If it is – and + they want to come together okay and it is not very difficult to visualise what will happen if there are repulsions between segments. If there are repulsions then the segments want to be as far off as possible giving rise to more stretching of the polymer chain because segments want to be as far as possible. On the other hand if we have attractive interactions in segments want to be close together and then they form like collapsed structure.

So, the one thing that is not difficult to see is for repulsive interactions we have a stretched chain and for attractive interactions we have a collapsed chain. Now the point to be made here is the ideal chain model gave us the scaling for the end to end distance squared average to be like R_e^2 going to M and that model did not consider either an attractive interaction or a repulsive interactions. So, my ideal chain is somewhere between the 2 extremes my ideal chain is somewhere here which is not as stretched as we will have in the case of a repulsive interactions and it is not as collapsed as what we will have in the case of an attractive interactions.. So, we must have the scaling law that reflects this kind of phenomena that the end to end distance must be larger when we have repulsive interactions, the end to end interaction must be smaller when we have attractive interactions and this must be reflected in this and what we are going to derive now, what we will derive now is basically 3 scaling laws something like-

$$\left\langle R_e^2 \right\rangle \propto M \left(ideal\, chain - Gaussian\, Statistics \right)$$

$$\left\langle R_e^2 \right\rangle \propto M^{\frac{6}{5}} \vee M^{1.2} - \left(Stretched \vee Swollen\, Chain \right)$$

$$\left\langle R_e^2 \right\rangle \propto M^{\frac{2}{3}} \vee M^{0.67} - \left(Collapsed\, Chain \right)$$

So with this background we will actually discuss some models that predict his kind of a scaling laws but before that I want to introduce some history here that's very interesting. So, there was as scientist and I think I have mentioned his name in the very beginning of a class his name was Paul Flory he was an American chemist actually he is one of the pioneers of polymer physics. So, back in the 1940's he derived the scaling law at least for the case of the stretched chain and he had a very interesting and very elegant yet very simple theory based on a scaling ideas that gave rise to this particular relations. Much later in 1960's and 70's there was Sam Edwards and others in I would say 60's then De Gennes in I think 70's they actually worked on a more rigorous theoretical treatment of polymer physics, they made more elaborate models and based on that the latest reference I want to site is of a French scientist named Des Cloizeaux who did a much more detailed theory compare to what Paul Flory did but got the same answer that Paul Flory had that is not the best part of the story.

The best part of the story is the theory that Paul Flory used are essentially based on wrong assumptions, so what Paul Flory was fortunate in or probably he had this kind of a physical intuition that he made errors but the errors somehow fortunately or cancelled each other and so the end result was so perfect that not only it was demonstrated by many experimental systems they have been proved to be true by more elaborate theories. In fact what the Des Cloizeaux and others even De Gennes did was very small I would say less than 1 or 2 percent maximum 5% change in the scaling laws for the stretched chain system, the numbers were like 1.2 compare to 2*.588 that is around almost same as 1.2.

So, we will start with a background that the theory is based on wrong assumptions, we will not do the detailed theories of Des Cloizeaux just to tell the name the more detailed theory is known as Renormalisation group theory that is beyond the scope of this course. The physics students may have learnt about this in the condense matter physics classes or another classes, we will skip that detailed theory we will stick with the Paul Flory theory, it contains the essential ingredients it makes some flaws admittedly flaws means we know that this cannot work but still it gives you the correct result because of some fortunate cancellation of the errors we make and then we will take some extensions of Flory's ideas to describe the behaviour of the chains here.

So, before we proceed into the Flory's theory let me also introduce the idea of like how exactly these interactions are coming into the picture apart from the fact that you can have like a positive and negative charge or whatever, what is also extremely important is all these interactions depend on the solvent in question. So, the same polymer chain will behave differently in water as compared to say benzene or for a polar solvent as post to a non-polar solvent. So, whatever interactions we are talking about is very much solvent dependent that is one, the second thing is whatever interactions are we are talking about is very much temperature dependent, you already said that we want our interactions to be higher than k_BT that means the interactions must be higher than the entropic contribution to the energy for the interactions to have any significant effect. But now since k_BT is increasing with temperature we will also see that whatever effect we are going to have will depend on the temperature. The other way to say that is whatever measure of this non-bonded or excluded volume interactions will be dependent on both solvent and temperature.

When we have a stretch chain is also known as a "good" solvent, good meaning that in this particular solvent the polymer segments will have repulsive interactions and just to going up bit further into what we will discuss the chain does what is known as a self-avoiding walk that is somewhat sometimes abbreviated as a (SAW) and then R_e^2 is proportional to $M^{2/3}$ that is when we have a collapse chain. The first one is swollen, second one is collapsed that is known as a "bad" solvent or a poor solvent. And then if you agree with both good and bad then ideal chain must be in between the 2 extremes actually we refer the ideal chain as something known as a θ solvent.

So, we will talk about how the depend on the temperature a bit later but let us talk about the solvent first and just for instance we take an example of water and let us see like how exactly water can change the interaction between polymer segments. So, now think of a water molecule system, let u say you have a glass of water can you add a polymer chain into it if you want experimentalist you can quickly point out that we cannot add 1 polymer chain actually we will add many polymer chains. Let us say if I add 1 milligram or 1gram it will contain many polymer chains but let us say it is very dilute, so that we can look at a particular volume in the beaker. So we have a beaker full of water and we mix polymer by some stirrer and it becomes an experimental arrangement.

The polymer chains present in that droplet or the crystal whatever we have the form of a polymer we started with, it will get distributed. And if I zoom-in anywhere in the system what essentially we will have is a polymer chain that is present with water molecules. Let us say it is dilute will talk about concentrations of polymer solutions a bit later. So, let us say if it is dilute enough, so that if I take a particular volume of my beaker I will only see 1 polymer chain surrounded by solvent molecules, the water molecules are much smaller compare to the polymer molecule. Polymer molecule can have a molecular weight in thousands and water molecule has a molecular weight like 18. So, they can be like surround the polymer chains, so you will see many water molecules surrounding the polymer chain and far off you can have other polymer chain in the system.

So, what is happening let us first look at like what is happening at a local level and then we will think about like what is happening in the overall beaker. So, in the overall beaker the scenario we have if it is well dispersed is we have polymer chains let us say some of them which are surrounded by solvent molecules and it is like uniformly mixed we do not know if it is equilibrium because we have shaken it and it is like right there..

So, now few things can happen, the first possibility is that the polymer chain likes water molecule and by like it means it has some sort of favourable interaction with the water molecule and that is when we call a polymer to be hydrophilic, philic stands for love, hydro for water, so if it is hydrophilic that means polymer likes water and if it is hydrophobic then the polymer hates water, both this cases the hydro part is water and the philic part is stands for like and phobic stands for hate okay. So, likes means it has some sort of a favourable interactions.

So, let us see like what was the scenario before we added the polymer and after we added the polymer. So, before we added the polymer since the water is a liquid it contains every water molecules is forming a hydrogen bond with other water molecules on an average every water molecule is forming like 3 hydrogen bonds with the neighbouring water molecules. Every water molecules on and average wants to form 3 hydrogen bonds because that is giving us the minimum energies state in thermodynamics sense and this is what is the origin behind the liquid state. If I go to vapour do not have a hydrogen bond, if you go to ice we have even larger number of hydrogen bond actually 4 and a hydrogen bonds are actually more frozen in a case of ice.

So, now I have added a polymer chain into it, now for the polymer chain to be dissolved in water what has to happen is the water molecules have to give up their hydrogen bonds. So, let's say now polymer comes then of course this hydrogen bond has to be sacrificed, so earlier it was coming 3 at least those in the vicinity of the polymer chain will have lesser number of hydrogen bonds with other water molecules. And of course they will not like it, because I just said the very greedy for the hydrogen bonds they will only like it in the situation where polymer has something to offer.. So, let us say if the polymer offers to form a hydrogen bond with a water molecule let us say it has certain group let us say it has some group let us say O-H and O-H forms a hydrogen bond with O, so in that situation water molecule has given up a hydrogen bond with other water molecule. But now it has formed a new hydrogen bond with a polymer chain. So the total number of hydrogen bonds of water molecule remains unchanged. So, that means that if the polymer likes to hydrogen bond with water it can dissolve in the water easily because water molecules can give up their hydrogen bond with other water and take the polymers hydrogen bonds okay so in that situation we do not have any problem.

But let us say the polymer does not have anything to offer let us say polymer does not want to participate in to a hydrogen bond with water molecule because it does not have any electron donors. In that case now the water molecules will be unhappy to accommodate the polymer there because they have to sacrifice the hydrogen bond with a water to accommodate the polymer chain and they do not get anything in return.

So, then in that case water molecules will try to maximize their contact with other water molecules because they do not want to form contact with the polymer. So, if the polymer is hydrophilic in that sense we will have more polymer water contact and if it is hydrophobic then we will have lesser polymer water contact. Because as I just explained in the first case every time the polymer forms a contact with a water molecules the contact can be let us say a hydrogen bond. The water molecule does not have to sacrifice a hydrogen bond it can give up a hydrogen bond with other water molecule and form with the polymer chain. The hydrogen bond with the polymer chain is relatively stronger compared to the hydrogen bond with the water. And I am only giving an example of a hydrogen bond we can think about other kinds of interactions that will give rise to the similar behaviour. And we can extend the idea of other kinds of solvents as well, the key point is that whenever something is a liquid if the solvent molecules have some interactions between them. So, a polymer can be accommodated if polymer has to offer some interaction to the solvent, if we have a polymer solvent interaction in that case we have in general sense we can say a solvent philic polymer otherwise it is solvent phobic polymer.

So, now let's imagine that what will happen in these 2 cases, in the first case the polymer chain would like to be stretched because in the stretched case it can form more and more contacts, this is a hydrophilic case. So, in this case it is perfectly no problem water molecules can surround the polymer chain because polymer likes water. On the other when it is hydrophobic then the best case situation is water molecules will remain as it is and the polymer is simply ask to precipitate or collapse. Because when the polymer is collapsed then you form fewer contacts of polymer with water and in then that case the water molecules have to sacrifice lesser number of hydrogen bonds.

So, now let us take it a bit further and go back to the beaker, so let us say if the polymer chain was hydrophilic then we can have different polymer chains floating around they are happy with their water partners and they do not worry about the other polymer chains outside in the system. On the other hand if you have a polymer chain that is hated by the water molecules there, they want to avoid contacts with them it will be better for the polymer chains to come together. Because in that situation water molecules have to form have to sacrifice even lesser number of hydrogen bonds.. So, in that case what we see is a precipitation of the polymer chains together what you will have in the case of a hydrophobic polymer is the polymer chains will simply settle at the bottom. And the water molecules will still fill the beaker, on the other hand for this is for the hydrophobic case this is what we know as precipitation and in the hydrophilic case it is perfectly fine for the polymer chains to float around because they are loved by the water molecules.

So, long story short, the idea is that if 2 people are enemy of the same person they have to become friends together, it is not because they have some inherent attraction between them like these polymer chains here they do not have any inherent attractions between them that can be possible. But since both hate water or both are hated by the water they have to come together and become friends because they are not being accommodated by water molecules they do not want to leave their water partners.

On the other hand if you have hydrophilic polymers they are very friendly with polymer with water molecules. So, water molecules are happy to accommodate them so, effectively the polymers need not come together. Because they are very happy in their company of water molecules. In the other way to state that is the polymer molecules will not like to come together because they have to sacrifice the contacts with water which is anyway favourable because they have hydrogen bonding, so why will they come together. So, essentially the interactions between the polymer molecules that we see is not necessarily the interactions between molecules as such they arise from interactions of polymer with the solvent. If polymer likes the solvent, polymer effectively repel other polymers, if polymer hates the solvent the polymer effectively attracts other polymer. And that is why we use the word good solvent and a bad solvent, when a solvent is good polymer likes it or the solvent like the polymer and when the solvent is bad or poor it is opposite.

Now just like think of a situation that if I now raise the temperature what will happen. If I now raise the temperature entropy will dominate, an entropy always favours a mixed state, so think of like dissolving anything that is insoluble in water let us say sugar in water and you make tea always do at higher temperature, that’s because of solubility of sugar in water is higher at higher temperature because entropy always favours mixed state or homogeneous states. And entropy always increase with temperature. So whatever we have said about polymer solvent interactions it has to be affected by the temperature because the hydrogen bonding or any interactions will have a temperature component in to them that is one way to state.

The other way state that is the ratio of that interaction with the thermal energy k_BT of course always depends on temperature because thermal energy has the k_BT that is the temperature inside there. Okay, that is why we use the word good, bad solvents it has to do with the nature of solvent and it has to do with the temperature as well that we will elaborate in the coming lectures.

So, I will stop with this and we can go with Flory theory in the next class.