Basic Statistical Mechanics
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Lecture - 56
Polymers in Solution and Polymer Collapse Part 2

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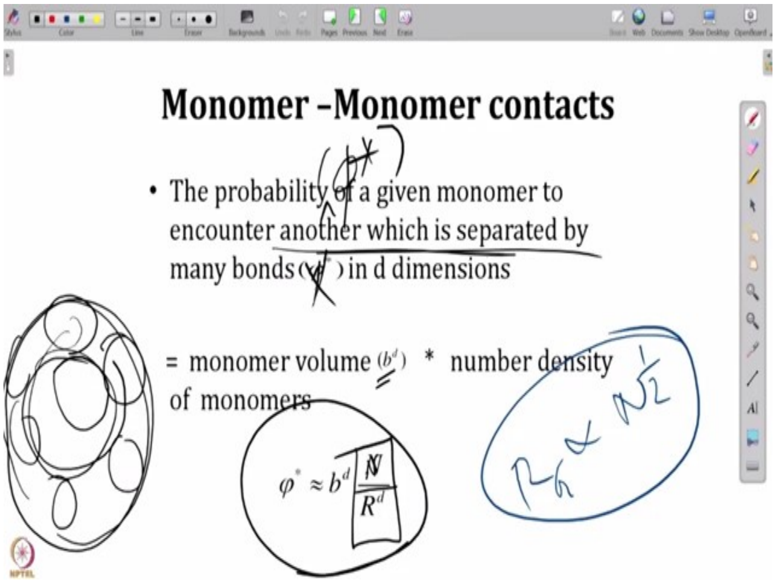

Monomer -Monomer contacts

- The probability (φ^*) of a given monomer to encounter another which is separated by many bonds (N) in d dimensions

= monomer volume (b^d) * number density of monomers

$$\varphi^* \approx b^d \boxed{\frac{N}{R^d}}$$

$R_G \propto N^{\frac{1}{2}}$

So there are some simple calculations now we will be doing which will be telling us certain scaling relations which plays a very important role in because the size is so big and since there are so much you know correlations between this polymer chain, it makes sense to talk in terms of certain very simple to find out how different properties of the polymer scales with the size N, like we already found that the size R_G scales as $N^{1/2}$.

But now that is when the monomers do not interact at all. However in a real world the monomers interact with each other particularly when they kind of a collapse state like in protein or in many other polymers in a polymer in a poor solvent and they collapse and that means it brings a little bit of the structure of liquids, it brings to us the I have to talk of local correlations;

I have to talk of the local density and local volume and but however at the same time I do not want to give up the beauty or that this scaling relation that polymer is famous for and that polymer really that really works. So the large size of the polymer at the same time can be again exploited to get these sudden ideas about the size. So in the Gaussian chain polymer the freely jointed chain polymer that Flory polymer. So these are all the same name that;

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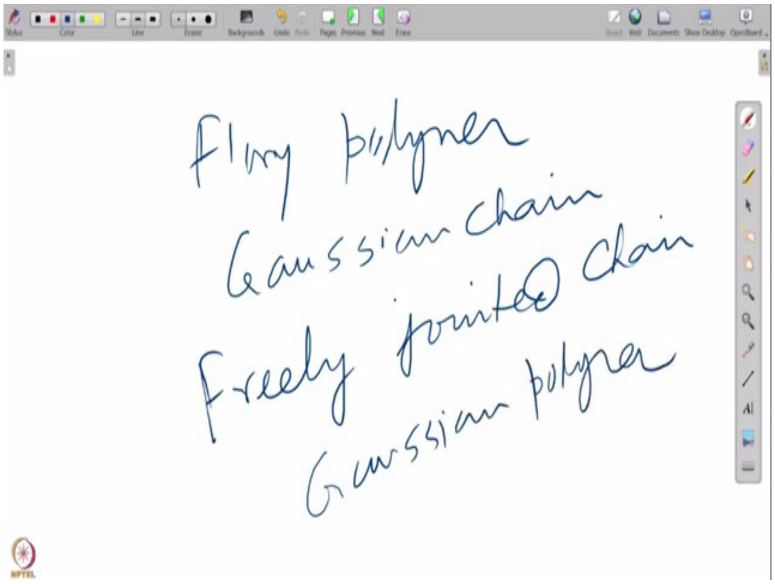

Flory polymer
Gaussian chain
Freely jointed chain
Gaussian polymer

Flory polymer, then Gaussian chain, then freely jointed chain, these are all Gaussian polymer. They are all the same things that we talk about that, so it is essentially means that polymers monomers do not interact with each other. So one of the major thing of that;

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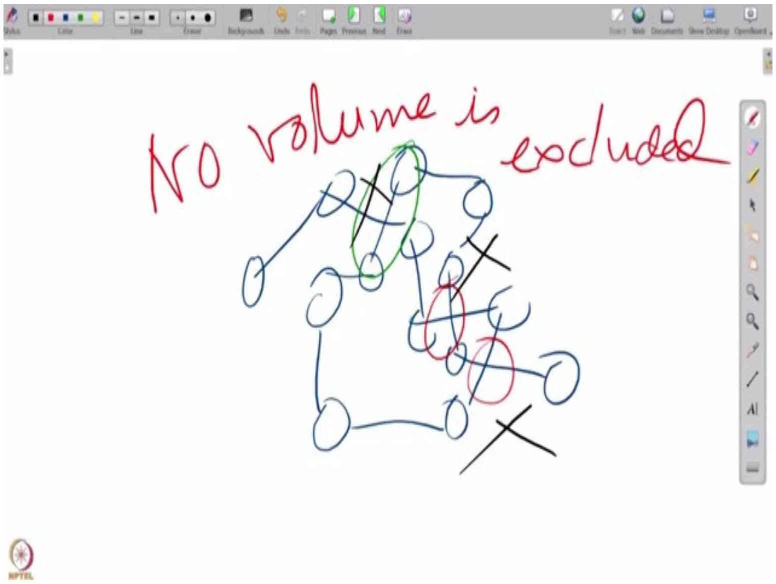

No volume is excluded

So these kind of thing, so this is allowed, so as a result in a freely jointed chain all these crossings are allowed that means no volume is excluded. But real world of course you cannot do that, in real world you cannot do that this is not allowed. It might seem that it is a small thing.

But no, these excluded volume interactions that the some volume is excluded plays a very important role. But how do I talk about it at the same time I do not want to talk up the completely the probabilistic description because this is many body system which has lots of randomness that brings us very close to the concept of liquids. That so they, so the concept that we developed in theory of liquids like distribution function you already used.

Which is like the distribution function of liquids but also the concept of density and arrangement these kind of things can be used in polymer and that is what we are going to do next.

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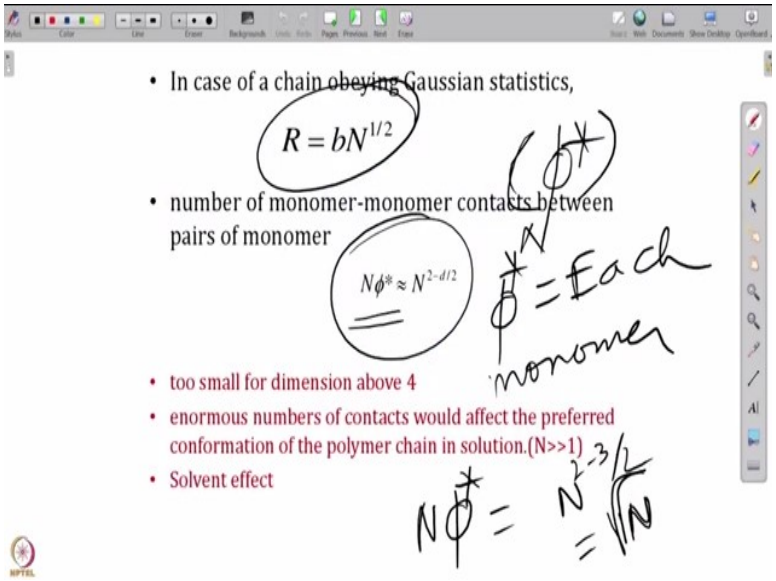

- In case of a chain obeying Gaussian statistics,

$$\boxed{R = bN^{1/2}}$$

- number of monomer-monomer contacts between pairs of monomer

$$\boxed{N\phi^* \approx N^{2-d/2}}$$

- too small for dimension above 4
- enormous numbers of contacts would affect the preferred conformation of the polymer chain in solution.(N>>1)
- Solvent effect

(ϕ^*)

ϕ^* = Each monomer

$$N\phi^* = N^{2-3/2} = \sqrt{N}$$

So and that is done by saying okay, that we know this, let us see Gaussian chain but number of monomer-monomer contacts, we are now going to talk of monomer-monomer interaction. Number of monomer-monomer contacts between two things are, can be shown I had, the proof of that I do not know where that is appeared. So number of contact, ϕ^* is the number of contact.

So ϕ^* is the number of contacts made by each monomer. So then $N\phi^*$ is the number of contacts made by

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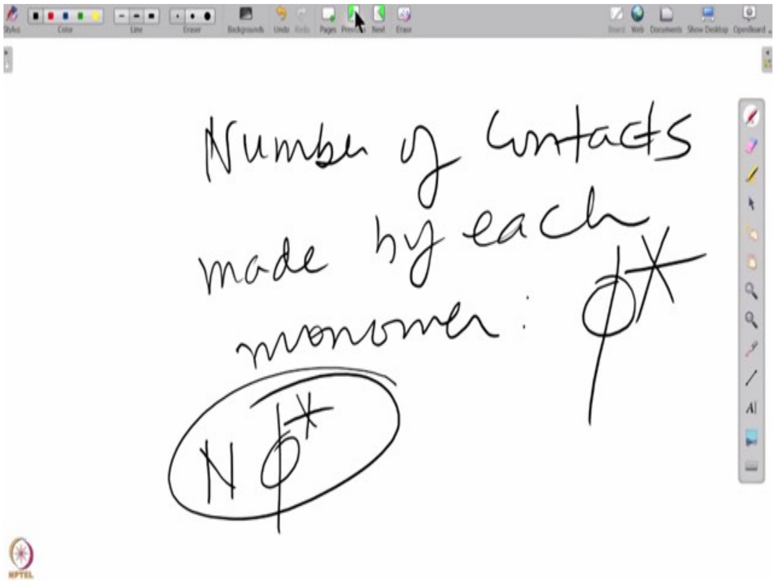

Number of contacts made by each monomer: ϕ^*

$\boxed{N\phi^*}$

each monomer is ϕ^*. So total number of contacts the N monomer is $N\phi^*$. This is very important and I will just show you how important it is. So probability of a given monomer is ϕ^* that a given monomer encounters another monomer. So this is not the number but probability but we are going to the number took from that.

So how does that come? It will come because it will be just like a liquid state that there is a volume of a monomer just like in liquid state. I have a volume of a monomer, just like liquid state and then the volume of the monomer which I can take like that with excluded volume then the number of molecules they are the contact within the same in liquid state in a shell will be the density.

So then average density of the polymer which is same as the density of the liquid is total number of monomers divided by the volume of the monomer. So volume of the monomer is R^d. So in these the dimension, this is something which is in polymer is more common now not in Flory's time, Flory would have put $d = 3$ everywhere.

But in a physics literature d when is very popular and favourite is $d = 4$ because at $d = 4$ we get a Gaussian polymer. So one can do the calculations about dimension 4 by making introduce a constant called ε and which is the comes from critical phenomena and dimension group and then ε is $d-4$ and so, or $4-d$ and d is 3 so ε becomes 1 and you could do a calculation, this is a lot of fun one does but we do not need to worry about it.

So if the monomer volume B is for bit, the B that is introduced because in physics kind of language this is nothing but it a bit, many times the chemists do not like to consider monomer as a bit because we delete monomers all the time and but Physics is nothing but bit and the neglects model. So the beat B, so B^3 size of the bit R, R^3 but the R is kept for the end-to-end distance.

So this is the volume of a monomer, then volume of the monomer into the density and density is total number of monomers divided by the volume which is R^d , R^3. We have the ϕ^* then we can show since $R = bN^{1/2}$, I can combine it before and it becomes $N^{1-\frac{d}{2}}$ and $N\phi^*$, the total number of contacts in my entire polymer chain is $N^{2-\frac{d}{2}}$.

Now this is very interesting, for three dimensions then I have $N^{2-\frac{3}{2}}$ is $\sqrt{N}$. So number of contacts is enormous. So again if I take 100 million which is a very good number and for polymers then 100 million means 10^8. So I have 10^4 contacts, there were 10,000 contacts and contacts cannot be allowed. So you immediately see that if I exclude the contacts then size of the polymer will increase.

So the simple analyst tells me the Gaussian polymer chain is inadequate, they random walk model. So what is a polymer chain are doing is nothing but doing the random walk, that is why this is the result that we get into size is same as that of random walk that how much it random walker will go in N step is exactly, this distance is $\sqrt{N}$ which is the size of the polymer. However if you now make the random walker, no you cannot visit the sides you have already visited once.

You are excluded from that. Then the random walker has to take new and new sides. As a result the end-to-end distance, the distance that random walker will go now will become larger and that has a tremendous implication in these things and that will do now. So I go back again, so I have considered a ϕ^* probability of a monomer is encountering another monomer and that is monomer size is b^d and density is N / R^d then $N\phi^*$ is total number.

So then they become N^2 and then N^2 and this R comes on the up. So I get $d / 2$. Let us go ahead that the things that we have done.

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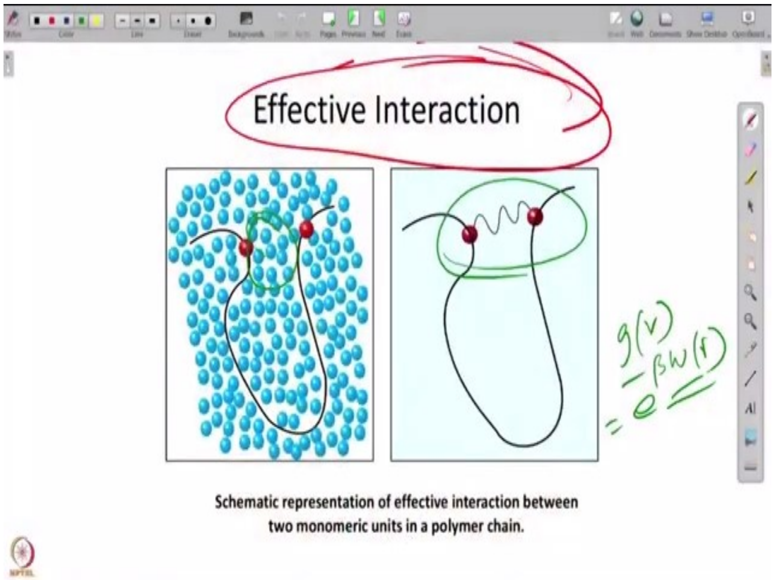

Effective Interaction

$g(r) = e^{-\beta w(r)}$

Schematic representation of effective interaction between two monomeric units in a polymer chain.

So is if there is one more thing that comes, in addition to this excluded volume interaction there is another term that is very popular.

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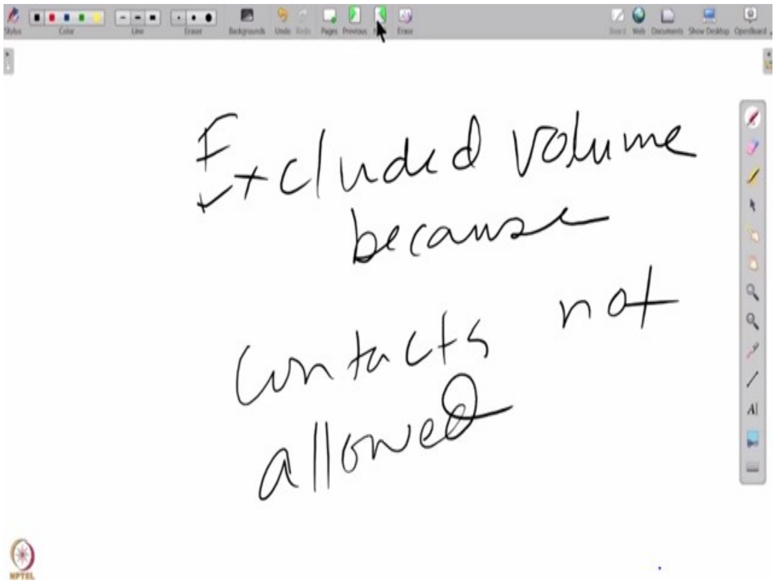

Excluded volume because contacts not allowed

So the I want to add here, so excluded volume, because contacts not allowed. You might think it is a small thing but it is not because there are large numbers of contacts. Then another thing is a different thing is the effective interaction that is used and that is this thing that means in polymer you put polymer in liquid then this is a very good example of saying that there is a chain, polymer chain any kind of deduced kind of a description but it captures these things.

And they say these are water molecules or ethanol molecules because polymers are not soluble in water so maybe they are ethanol molecules or methanol. Ethanol is a very good solvent for polymers. I am not interested in the water molecules or ethanol molecules; I am interested in the polymer configuration. However, this polymer is solvated by these water molecules but I want to have a description where these not there.

Because it is too difficult to bring all these because the polymer is as big as I told you 100 million monomers a huge high. If I have to put it in a solvent you know what I do want to do theory of simulation. I will have billions and billions of water molecules, I need trillion water molecule cells it that is not possible and also does not make sense because they seem to polymers seem to behave in certain way.

So you want the concept that came in that one say that what happened if I could have average an implicit solvent. Implicit solvent means I will remove the water molecules, behave as if it is a continuum and then I will have interaction these two guys who otherwise are not interacting but they will be interacting because of the interaction just like we discussed in liquid state, interaction.

They are proceeding through intervening in molecules just as a liquid state and actually the all the concept of the liquid state comes to polymer very handy. Then I remove the water molecule, this state I have an effective interaction between these two states which is somewhat longer distance and you know there is of course this hard sphere interaction is fall some interact with short lengths but, in long distance there could be at attractive interaction.

So this effective interaction is the thing to find common but we can again look into a liquid state theory. If we can get a radial distribution function between them $g(r)$ between this monomer and monomer polymer then I know I have can write $g(r) = e^{-\beta w(r)}$, then $w(r)$ is the potential of mean force and is the effective interaction. So that is the same kind of game we play that we are removing the water molecules.

And we are replacing that all the complexity are taken into account by potential of mean force or an effective interaction between them or the indirect interaction in the theory of liquid state. We remember what we did in the derivation of Percus-Yevick equation or direct correlation function and the indirect; one which is again goes through this potential of mean force. So we are essentially introducing a potential of mean force.

So effective interaction is a very important role played, it is introduced by Flory. So if the solvent is such that it does not like the polymer then the water molecule strong were will go away and the polymer will collapse. However, if they like then they will be in at it is inside and then the polymer will swell. So in a good solvent good for the polymer like ethanol is good for many things.

Then the polymer will swell, and then they do not want to cross each other. So they will almost mimic what is the stronger explicit volume of interaction and size of polymer goes up and that is a very important thing. So good solvent is where the size is large. However, if you put for example; a lot of water which does not like the hydrophobic interaction because like the polymer then polymer will collapse.

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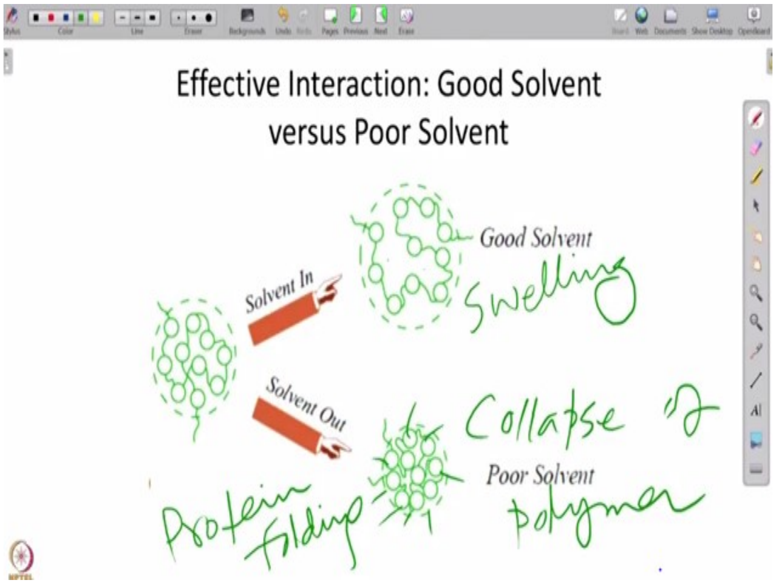

Effective Interaction: Good Solvent versus Poor Solvent

And this is shown here that good solvent, this is a good solvent then water all everywhere water molecules comes in and then you get a swelling polymer, very important phenomena. However, if the solvent is out if they do not like each other poor solvent then it collapse. Protein folding which is a very is essential hydrophobic collapse. So these collapse of polymer is like hydrophobic collapse that is so important in protein folding.

Except in protein folding we do not have a homo-polymer what we are discussing here all the monomers are the same that is called homo-polymer but protein is a hetero-polymer and the collapse of protein in a poor solvent is so because protein folding we do in water much of the studies or at least largely water and there are other part also but that is what makes. When protein folds all the inside all the things are the hydrophobic core like alanine, vanillin, phenylalanine and outside here all the hydrophobic things;

That is essentially architecture of protein which is the polymer or intermolecular size polymer. But many of the things that we learned in polymer both are used in understanding protein folding and many other things. So polymer is a very important for because of the biopolymers also. But I want to emphasize that the concept of liquid state, the densities N / R^d and then monomer-monomer contact and all these things actually are very useful in the polymer.

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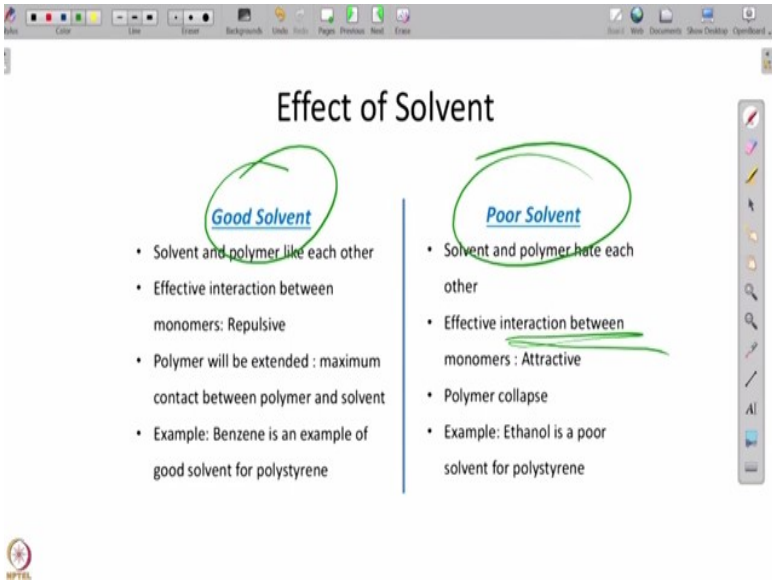

Effect of Solvent

Good Solvent

- Solvent and polymer like each other
- Effective interaction between monomers: Repulsive
- Polymer will be extended : maximum contact between polymer and solvent
- Example: Benzene is an example of good solvent for polystyrene

Poor Solvent

- Solvent and polymer hate each other
- Effective interaction between monomers : Attractive
- Polymer collapse
- Example: Ethanol is a poor solvent for polystyrene

So then the is a important thing of the good solvent and the poor solvent that effective interaction is repulsive good solvent this interaction is attractive. So we now have to think of how to describe at interaction between the polymers and that was also Flory did. So if I had the interaction between polymers I can do statistical mechanics, now I can bring in the whole apparatus of liquid state and that has been done. So then how do I talk of the interaction between the polymers?

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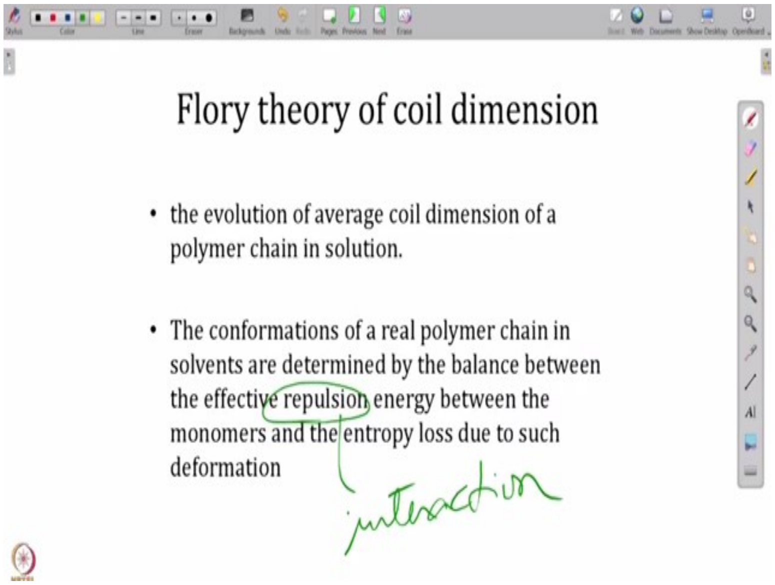

Flory theory of coil dimension

- the evolution of average coil dimension of a polymer chain in solution.
- The conformations of a real polymer chain in solvents are determined by the balance between the effective repulsion energy between the monomers and the entropy loss due to such deformation

interaction

This is the following way; this Flory used it again to develop the interactions and the evolution of the coil dimension of polymer**.** Now this is a bit, this not effective repulsion energy, actually effective interaction energy that we will see that it can be both positive and negative. It can be both attractive and effective.

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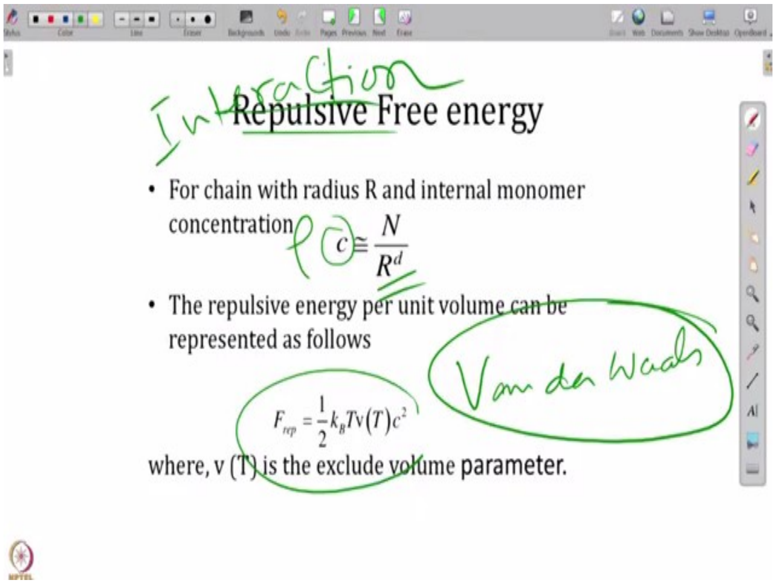

Interaction ~~Repulsive~~ Free energy

- For chain with radius R and internal monomer concentration ρ $c \cong \frac{N}{R^d}$
- The repulsive energy per unit volume can be represented as follows

$$F_{rep} = \frac{1}{2}k_B T v(T) c^2$$

where, v (T) is the exclude volume parameter.

Van der Waals

So, an interaction or effective interaction energy that is very important, effective interaction energy that you see. As we just discussed before that the density or concentration, I can as well called density ρ but concentration c is total number of monomers divided by the volume R^d, d is a dimension. Now I can now make the following answers; these just a completely Van der Waals.

That attraction is the or interaction between two polymers, that is exactly what the free energy contribution of Van der Waals because of attraction comes exactly, if you carry out the free energy calculation of, which was given in my book, that it is $\frac{1}{2}\rho^2$ and ρ is the density. So here c is the monomer density and so the interaction c^2. Now Flory did something amazing, up to this is just Van der Waals.

c^2 is $\rho^2 \frac{1}{2} k_B T$, $k_B T$ is introduced by hand and $v(T)$ is a parameter which is a Flory parameter X^2 many, many Flory polymerase X^2 follow.

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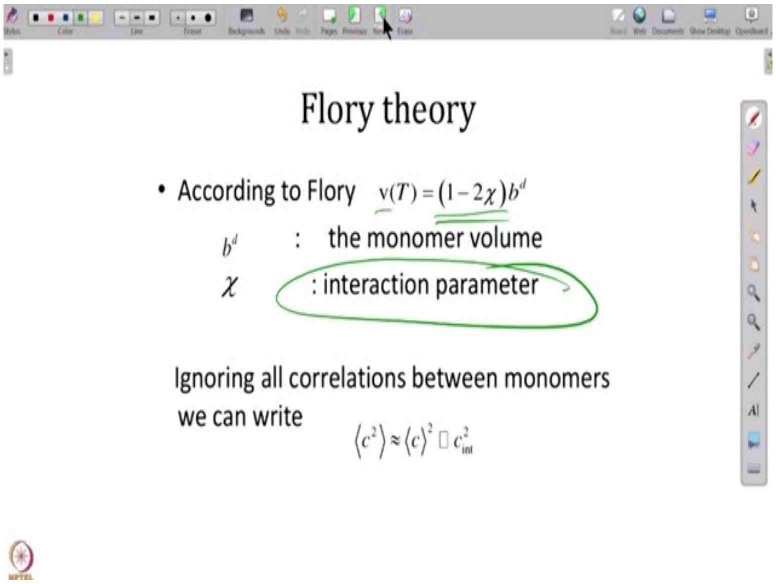

Flory theory

- According to Flory $v(T) = (1 - 2\chi)b^d$

b^d : the monomer volume

χ : interaction parameter

Ignoring all correlations between monomers we can write $\langle c^2 \rangle \approx \langle c \rangle^2 \square c_{\text{int}}^2$

Now what Flory did he said okay, this $\nu(T)$ that I have can be both positive and negative if this is what I say is wrong is equal to repulsion interaction. If $\nu(T)$ is negative then I get attraction and that is Van der Waals but if $\nu(T)$ is positive I get repulsion and that is just the beauty. So now Flory introduced a frame as parameter again called Flory parameter that is the exactly that quantity $(1-2\chi)$.

And he derived an expression for χ later which exactly works out according to these. So when χ is greater than $1/2$, then this is negative and is attraction but when χ is small, then it is repulsion. So this interaction parameter χ simulates when the monomers attract each other and monomers repel each other and then we know monomers attract each other in a poor solvent.
So χ becomes large in a poor solvent.

But χ becomes small in a good solvent. Then in the molecule we pay monomers repel each other and they swell. This is a beauty of this description.

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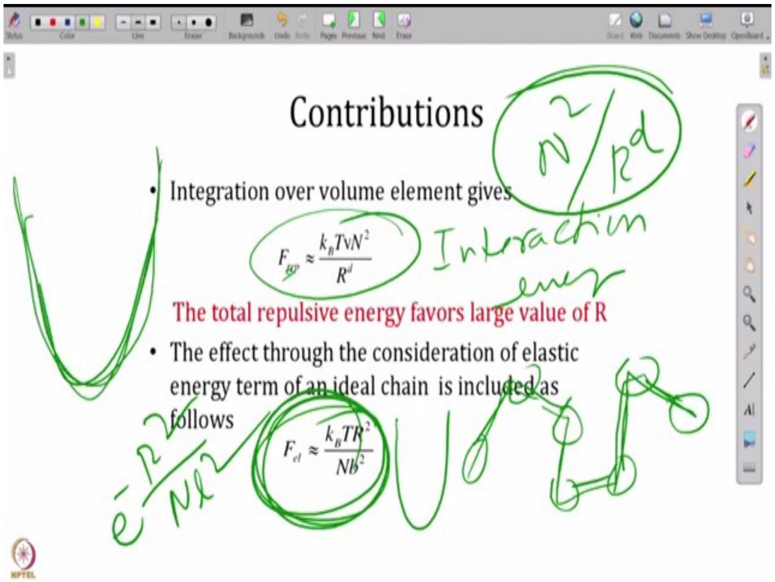

Contributions

- Integration over volume element gives

$$F_{rep} \approx \frac{k_B T v N^2}{R^d}$$

The total repulsive energy favors large value of R

- The effect through the consideration of elastic energy term of an ideal chain is included as follows

$$F_{el} \approx \frac{k_B T R^2}{N b^2}$$

So then one does a little bit more, these interaction of this is just what I wrote down these free energy is do we just say total volume because that is monomer-monomer in a volume V^d total volume if I do interaction then I get. These are interacting over the total volume and I will get the another volume is proportional to be a size R^2 and c^2 as N / R^d. So when I put these things I get N^2 as I said I get these quantity as the interaction energy, both attraction and repulsion.

So I get may be N^2 / R^d term. We are done in 2 minutes and then effect through the consideration of, then however I am interesting thing is that in the polymer I cannot just swell it because there is an elasticity that is the chain. So is an elastic, I cannot add too much and then that is a proportional to R^2. There is a potential energy which is like harmonic.

And that term the elastic term goes like R^2, because elasticity and one can show it because this essentially comes from e^{-R^2/Nl^2}. So this elastic part is comes completely very easily from the Gaussian distribution. So Gaussian chain has a referential size and that is an entropic effect. So this entropic effect give rise to elasticity because it is the favourable size is there. If you go out from that you have to pay, if you come close to that you have to pay.

So is the harmonic potential that harmonic potential is the coming of the central limit theorem and that you have to add.

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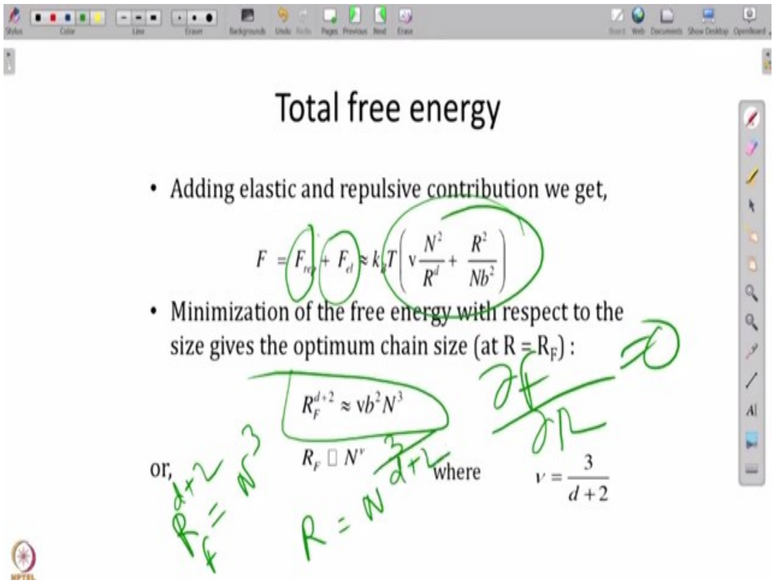

Total free energy

- Adding elastic and repulsive contribution we get,

$$F = F_{rep} + F_{el} \approx k_B T\left(v\frac{N^2}{R^d} + \frac{R^2}{Nb^2} \right)$$

- Minimization of the free energy with respect to the size gives the optimum chain size (at $R = R_F$) :

$$R_F^{d+2} \approx v b^2 N^3$$

or, $R_F \sim N^{\nu}$ where $\nu = \frac{3}{d+2}$

So you have to add the interaction energy and the elastic energy and this is the total free energy has a size R. Now you minimize that and you get good low and behold**,** one of the most beautiful result of polymer science, if you minimize that you say $\frac{\partial F}{\partial R} = 0$, then you get $R_f^{d+2} \sim N^3$ and you get $R_f \sim N^{3/(d+2)}$.

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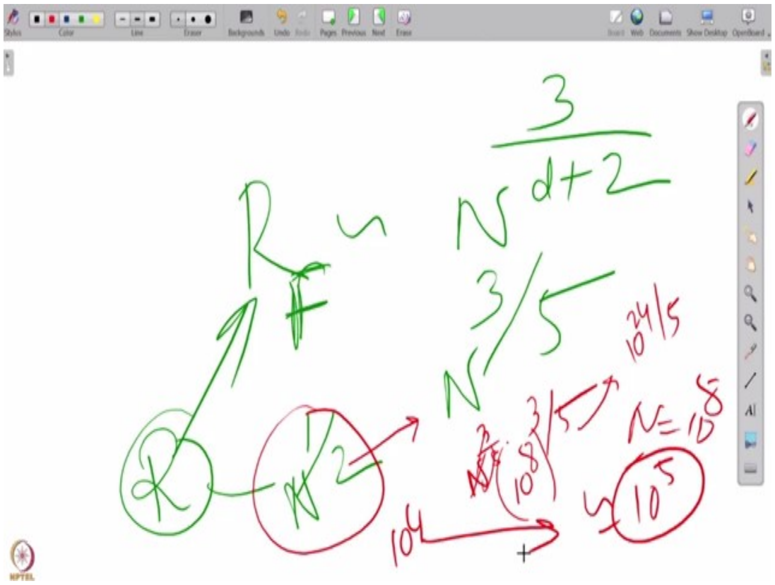

So that introduce an exponent that $R_f \sim N^{3/(d+2)}$. So because of interaction the excluded volume the Gaussian polymer size R get modified to R_f and d is 3 N so $N^{3/5}$. So R goes as $N^{1/2}$. So because of interaction $N^{1/2}$ swells to $N^{3/5}$. If I go with my $N = 10^8$ then that is 10^4 and now if I have to do then $\left(10^8\right)^{3/5}$ then I see that it is $10^{24/5}$ that is almost 10^5. So I see a 10 fold increase, a little less 8 but actually, huge increase in the size of the polymer because of the interaction between the polymers. So this is one of the most beautiful results of polymer science that size of the because of the interactions which is a contribution of the interaction between the polymers mediated to the solvent and the elastic part.

An elastic part is from the Gaussian chain that I can model the Gaussian chain. As per independence goals Gaussian chain independence is okay but the size now changing. So effective interaction renormalizes the size and gets to a beautiful new result and this is for Flory's $R_f \sim N^{\nu_f}$. This is the result Flory is $R_f \sim N^{\nu_f}$ and ν_f is the Flory parameter $\nu_f = 3/(d+2)$. So Flory got everything correct, this is amazing Flory got everything correct.

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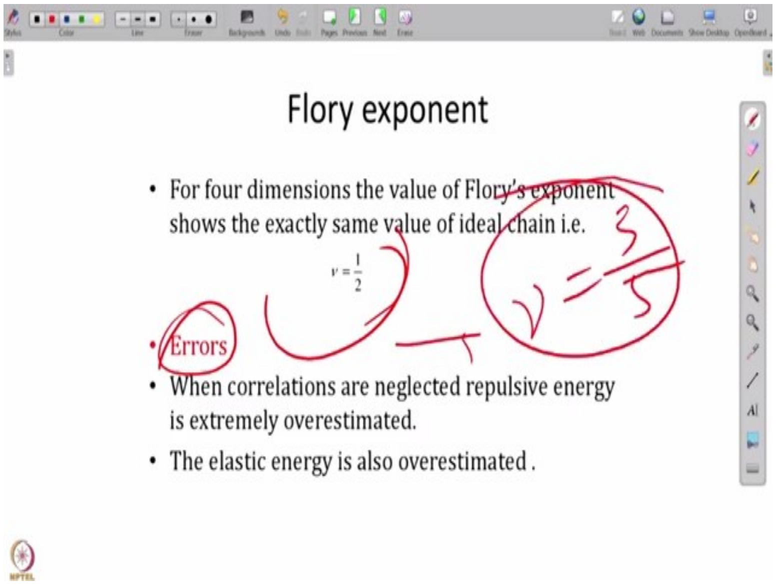

Flory exponent

- For four dimensions the value of Flory's exponent shows the exactly same value of ideal chain i.e.

$\nu = \frac{1}{2}$

$\nu = \frac{3}{5}$

- Errors
- When correlations are neglected repulsive energy is extremely overestimated.
- The elastic energy is also overestimated .

Flory exponent we got that mu equal to this is ideal chain $\nu = 1/2$ and that is underestimated this error, and then it goes over to $\nu = 3/5$ for 3 dimensions;

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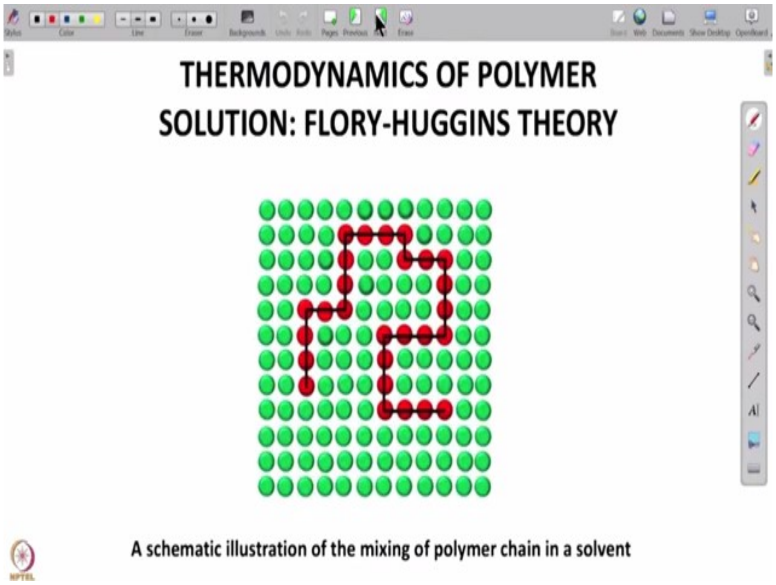

THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

A schematic illustration of the mixing of polymer chain in a solvent

And this is the sum thermodynamics from solution and for Flory theory will do in the next class. For the time will stop and the next the more things more work of Flory and beautiful work of Flory continues the saga of Flory's contribution continually do Flory thermodynamics of polymer solution Flory on his theory, then we will do sol-gel transition was also done by Flory. So, these two will be the next class. I hope you enjoyed this beautiful class.