Basic Statistical Mechanics

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Lecture - 58
Polymers in Solution and Polymer Collapse Part 4

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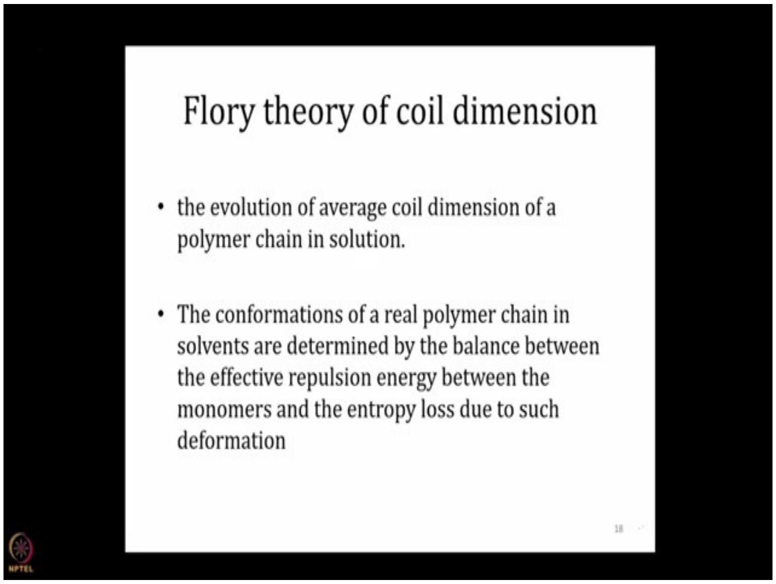

Flory theory of coil dimension

- 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

With this third lecture, we continue our study of polymer solutions. So now Flory said okay, there are two very interesting things there. One is if the polymer is a good solvent i.e., the monomers of the polymers do not like each other then we have effective repulsion between them. However, it cannot go on swell because when you increase remember the distribution is e^{-R^2} where R^2 comes because all the many configurations. What is the configuration of degree of freedom tells you it will tell you the entropy. Now you can see e^{-R^2} has a maximum. You have $\langle R \rangle = 0$ this is an average because many different orientations but, however, I also tells you, you cannot stretch it too far. This is called elasticity of the polymer.

So polymer loses lot of entropy if you stretch it. So these are two forces acting opposite to each other. One is that repulsion energy which tries to push it out but elasticity of the polymer which wants to keep it a certain size.

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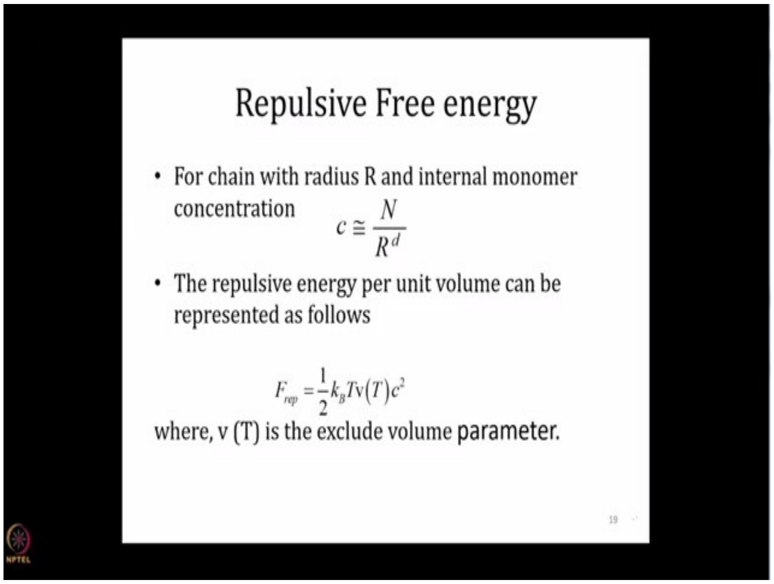

Repulsive Free energy

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

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

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

This is what Flory realized and did beautiful calculation. Internal concentration of the N/R^d as we discussed already. Then I can consider repulsion energy with this equation that a repulsive is $\frac{1}{2}k_B T\nu(T)c^2$. So this $\nu(T)$ is the effective parameter. This is essentially nothing but Van der Waals theory that we are doing. Here the important thing to know two terms $\nu(T)$, where $\nu(T)$ which is temperature dependent excluded volume parameter which is like very much like a parameters in Van der Walls theory. This says it is a volume parameter but it essentially takes care of the interaction energy. c is the concentration in number within a volume where volume is R^d. So this is repulsive energy.

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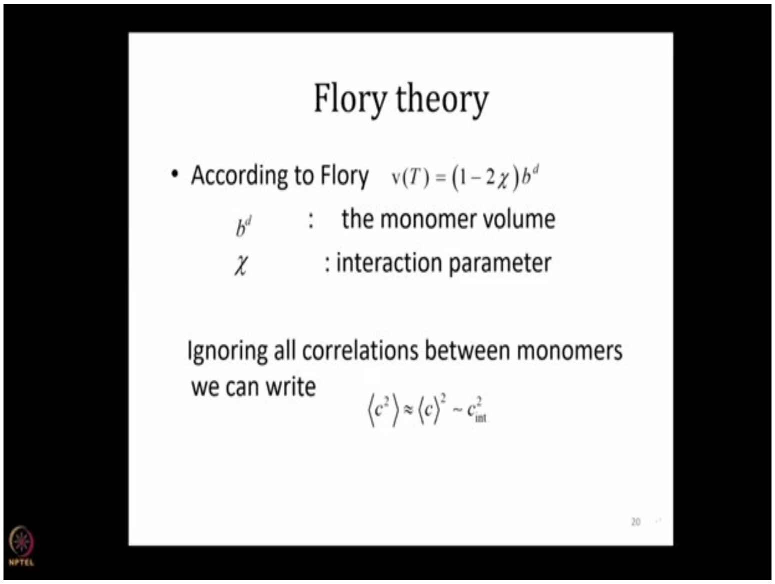

Flory theory

- 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 $\langle c^2 \rangle \approx \langle c \rangle^2 \sim c_{\text{int}}^2$

And Flory introduced this parameter $(1-2\chi)b^d$, but we will learn about it later. But it is just to show that it can go by there from plus to minus.

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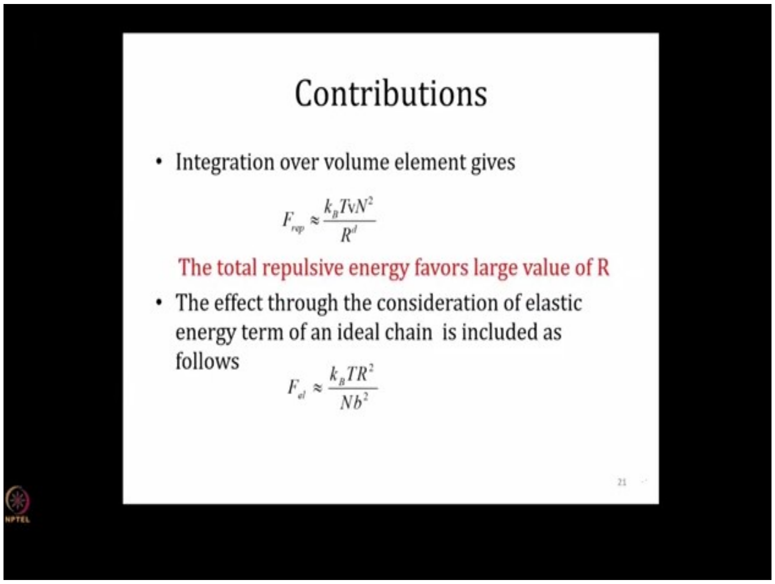

Contributions

- 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

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

And then integration over volume element. If I integrate over these volume element of these of this NR^d. Then I will get the total repulsion energy is N^2 because there is a coming with N here R^d. I take all the monomers then I get N^2. So integration of volume element essentially meaning taking of scope. The important thing is that repulsion energy scales as N^2 / R^d.

Now if take the elastic term, it is nothing but what is in the exponent of Gaussian distribution R^2 / Nb^2. That is what I had in the Gaussian distribution. So since Boltzmann distribution gives me a value of a quantity X, e^{-X/k_BT}. So I just rearranged terms I gave the elastic terms trivially a k_BTR^2 / Nb^2.

I have the repulsive term of N number of monomers connected in a polymer in a chain is $N^2 / R^d k_BTv$ and v essentially Van der Waals a. It plays a very similar role and comes up in a very similar way that we have already done Mayer's theory.

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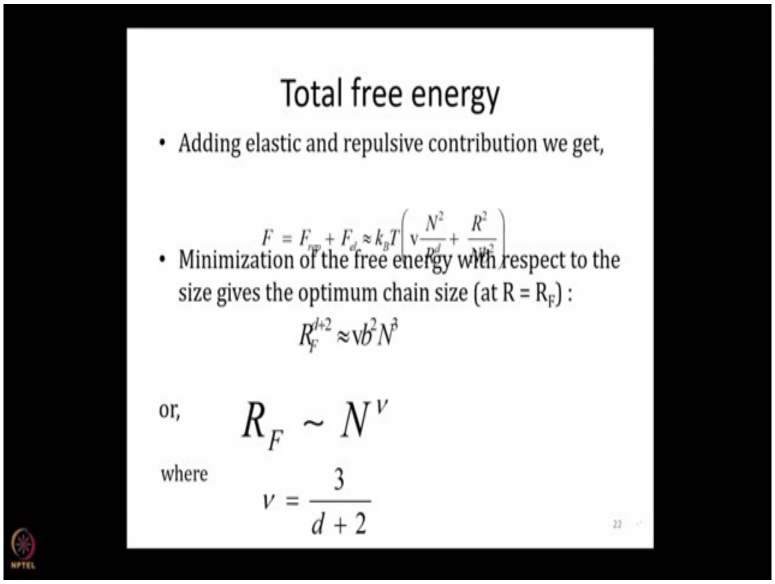

Total free energy

- Adding elastic and repulsive contribution we get,

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

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

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

or, $$R_F \sim N^{\nu}$$

where $$\nu = \frac{3}{d+2}$$

We add the two free energy repulsion and the elastic term which is related to attraction, which is kind of putting it closer together. When I add them I get this thing sorry it is a little bit, what do you read it screwed up equation by bN^2 / R^d, where just two terms are added. Now the important thing is that I minimize F with respect to R and then I get a beautiful result.

This is $\frac{dF}{dR} = 0$, then there is R^{d+1} it becomes and d terms become R. So R^{d+1} and R but they are in opposite side one is in the denominator and another is in the numerator. So when we rearrange the term then there is a negative term comes from N^2 / R^d and positive comes from second term.

Then we get R^{d+2} scales the N^3 and then you get the beautiful result R_f is for Flory, then N^{ν} the radius of Flory. ν is called Flory parameter which is $3/(d+2)$.

If d = 3, it becomes $3/5$ which is very important results. So suddenly you see in ideal polymer chain these end-to-end distance scales as $\sqrt{N}$ ($\nu = 1/2$). However, when you take an attraction and repulsion and all these things into an account and in a good polymer solvent then you get these are huge difference that was $\sqrt{N}$ because of $N^{3/5}$.

But when you go to d=4 another surprise an interesting it is $\frac{3}{6} = \frac{1}{2}$. So in 4 dimension that plays a very important role theoretically not much relevance in the real world but you get ideal chain behaviour partly because on your 4 dimension then the concentration of polymer is so much more volume around each polymer then this repulsive interactions are all these things are not that important.

That is where you get back the ideal polymer chain but 3 dimensions and 2 dimensions it is very different.

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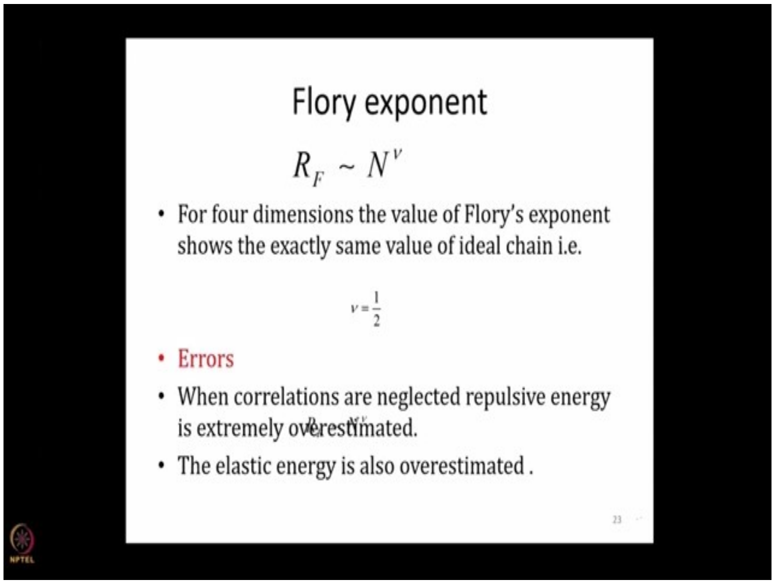

Flory exponent

$$R_F \sim N^{\nu}$$

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

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

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

Now these, we have discussed this also, but I like to emphasize it $R_f \sim N^{\nu}$ for ideal chains ν is half but it is not so in the real chain. In real chain it is very different.

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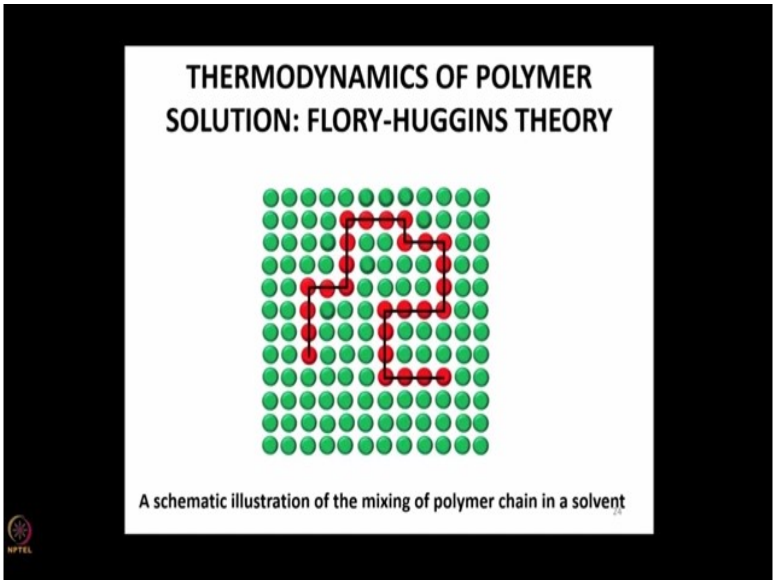

THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

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

Thermodynamics of a polymer solution you are did quite bit because at the end of the day it is the same thing that we will be having this take care of these two forces. One is the interaction the monomer solvent, when interaction that is one term, which is a Flory parameter χ that will come here. And we will be little bit quantified here and then we will do the mixing of polymer in a solvent. So solvent has to come in.

So in addition to the entropy that we talked about and Flory-Huggins that you will have one more entropy that the entropy, so basically the entropy term here is solvent.

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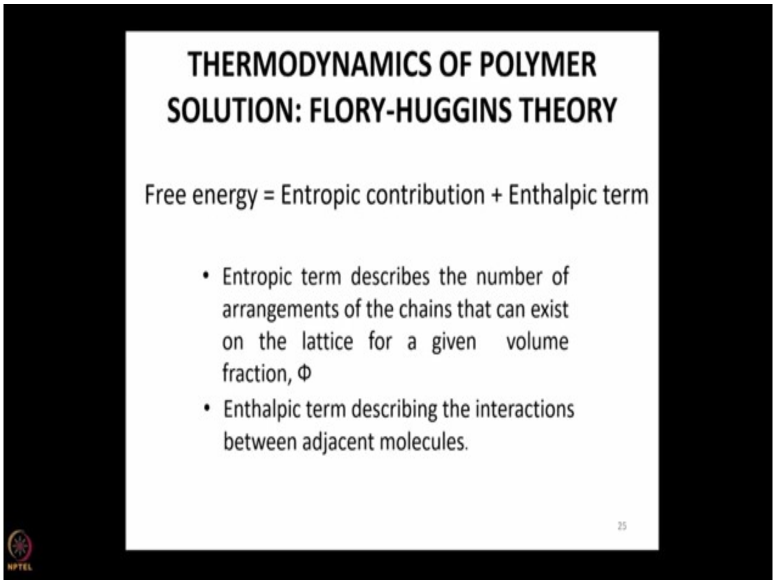

THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

Free energy = Entropic contribution + Enthalpic term

- Entropic term describes the number of arrangements of the chains that can exist on the lattice for a given volume fraction, Φ
- Enthalpic term describing the interactions between adjacent molecules.

So basically the entropy term here is essentially the arrangement of the polymer chains that exists. So what one consider in Flory Huggins theory, very famous theory; that one can consider as a lattice, and the lattice is, trivially mean polymer because polymer is so big much bigger than the solvent one can consider as, I told as N number and that since the size of the monomer is not important one can as well take the advantage of the lattice.

So now we can make estimates of how many ways I can put monomer of the polymer and the solvent molecules on a lattice. That will give an entropy term. There is an enthalpy term because with interactions between solvent molecules and solvent and polymer and monomer and monomer. So enthalpy we had three terms.

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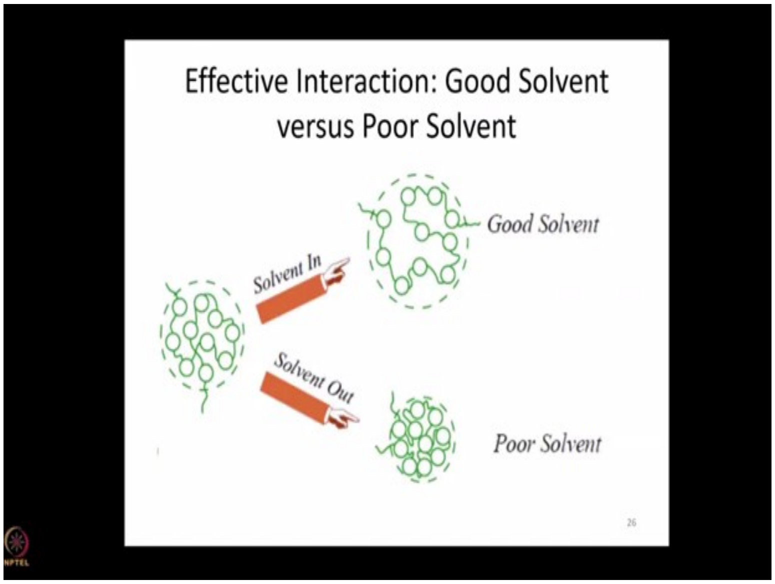

Effective Interaction: Good Solvent versus Poor Solvent

Now, we have already considered that the effective interaction of these kind of good solvent but, what we were doing is very similar but we are doing is a little bit more justification of the polymer or polymer solvent interaction. That is a little bit done better than quantify that is why other is nothing different from the what we did earlier or same minimization of free energy and everything will come.

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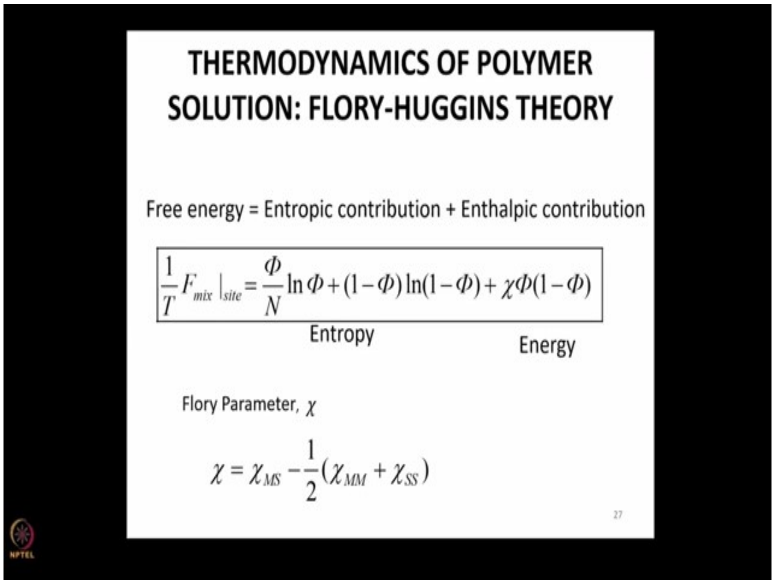

THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

Free energy = Entropic contribution + Enthalpic contribution

$$\boxed{\frac{1}{T}F_{mix}|_{site} = \underbrace{\frac{\Phi}{N}\ln\Phi + (1-\Phi)\ln(1-\Phi)}_{\text{Entropy}} + \underbrace{\chi\Phi(1-\Phi)}_{\text{Energy}}}$$

Flory Parameter, χ

$$\chi = \chi_{MS} - \frac{1}{2}(\chi_{MM} + \chi_{SS})$$

So when you do that we said how many ways I can put a polymer then you can see the first term and the second term on the right hand side. This is the free energy of mixing as the entropy term, that means how many ways I can place a polymers in our size N, polymer size N_P, N is the total number of sites and then and calculate that is entropy of mixing.

Because I am mixing solvent molecules and the polymer and I am laying down the polymers in the lattice. And how many ways I can do that essentially same as binary mixture entropy of mixing. When you do entropy of mixing in your thermodynamics in binary mixture. What do you do? You do $\frac{N!}{N_A!N_B!}$ and then that will gives you the Ω the total number of ways.

And then you take log of that, get the entropy by using Boltzmann formula and that gives you $x_1 \ln x_1 + x_2 \ln x_2$ you can also write $x_1 \ln x_1 + (1 - x_1)\ln(1 - x_1)$ because x_1 and x_2 are mole fractions together they become 1. It is a very similar thing here in polymer here, however, one has to take care of the fact that you have a polymer is a monomer and polymer constitute of many monomers.

The first term takes care of that fact. The second part is just the solvent part and ϕ is the volume. Through ϕ enters the size of the polymer. Now the important thing is χ the Flory parameter that is exactly the same thing we have in binary mixtures. And we did the binary mixtures or you are not you are looking right book for binary mixtures has been done in great detail.

That is AA interaction, AB interaction and BB interaction. When A and B like each other in this parameter that means monomer of the polymer and the solvent they like each other, then the χ term that you see over the first term on the right hand side will be negative and χ become negative. On the other hand if A and B are monomer of the polymer and of the solvent and they do not like each other and A and B like each other and AA like each other BB like each other, then this term is become, then χ becomes positive. So a good solvent χ is negative and the bad a solvent χ is positive. So through this parameter we essentially what Flory did use the ideas of entropy of mixing and the binary mixture theory. The non ideality parameter that we break down of Raoult’s law.

So the idea of this classical physical chemistry is combined with statistical mechanics or statistical concepts to develop this statistical thermodynamic theory of polymer solution, a very elegant and very simple way which has took the test of time.

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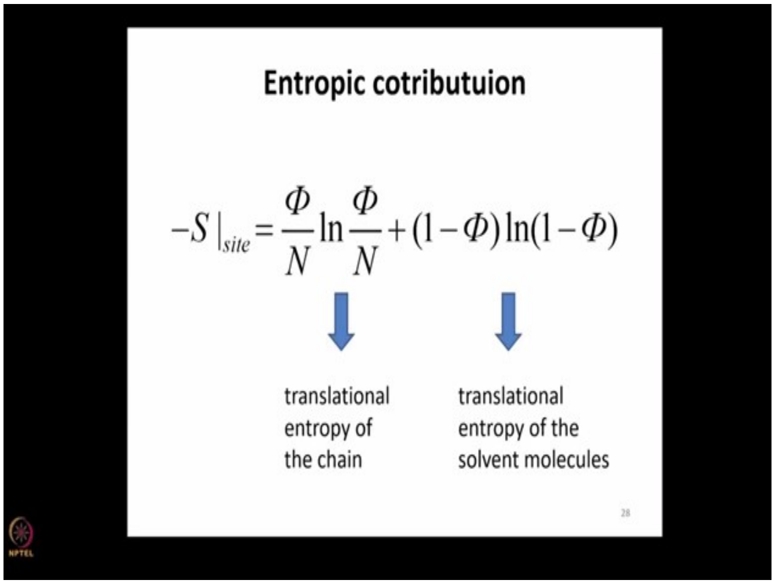

Entropic cotributuion

$$-S|_{site} = \frac{\Phi}{N}\ln\frac{\Phi}{N} + (1-\Phi)\ln(1-\Phi)$$

translational entropy of the chain

translational entropy of the solvent molecules

So this again, the same thing this is ϕ because I divide the total number of sites and then you get the entropy of the solvent as I said an entropy of the things, I am going to derivations you will find the derivations in many places including my book and also in Wikipedia.

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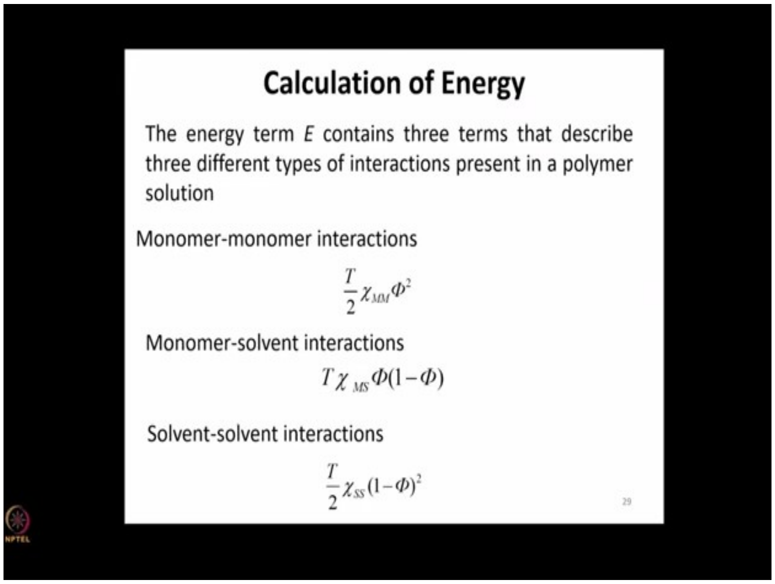

Calculation of Energy

The energy term E contains three terms that describe three different types of interactions present in a polymer solution

Monomer-monomer interactions

$$\frac{T}{2}\chi_{MM}\Phi^2$$

Monomer-solvent interactions

$$T\chi_{MS}\Phi(1-\Phi)$$

Solvent-solvent interactions

$$\frac{T}{2}\chi_{SS}(1-\Phi)^2$$

I calculate the entropy. Is the entropy of laying down the polymer of volume fraction ϕ

lattice of N side polymer interaction. That is why the first end of the denominator comes. Now monomer-monomer interaction as we just discussed the Van Der Waal, these k_BT, I put $k_B = 1$, $\frac{k_BT}{2}\chi_{MM}\phi^2$, where χ_{MM} is the Flory parameter for monomer- monomer.

Because monomer and solvent it is $\phi(1-\phi)$, because $(1-\phi)$ for solvent and solvent and solvent, solvent $(1-\phi)^2$. There are three terms. Next I add all these terms together. I keep in the down which is union. So I find out in that sense that is the maximum contribution comes from the one that I need is the monomer solvent interaction is $\phi(1-\phi)$.

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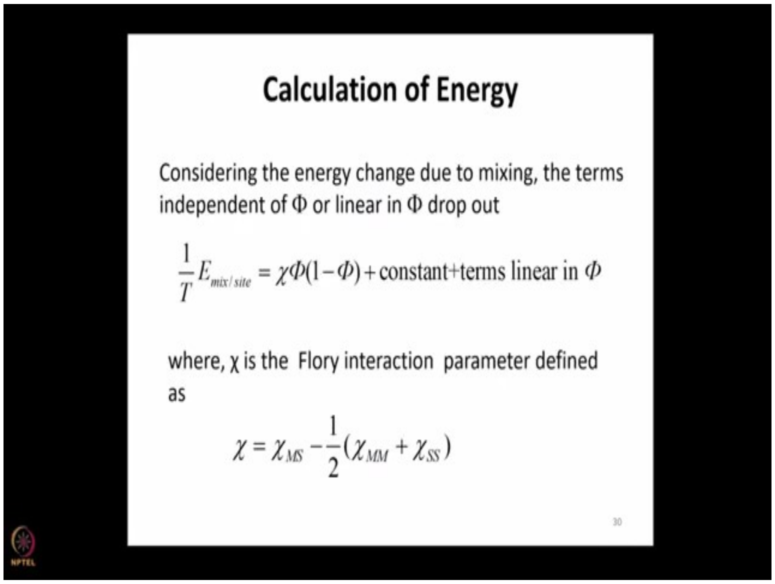

Calculation of Energy

Considering the energy change due to mixing, the terms independent of Φ or linear in Φ drop out

$$\frac{1}{T}E_{mix/site} = \chi\Phi(1-\Phi) + \text{constant+terms linear in } \Phi$$

where, χ is the Flory interaction parameter defined as

$$\chi = \chi_{MS} - \frac{1}{2}(\chi_{MM} + \chi_{SS})$$

So the first term becomes important term for me in this understanding the thermodynamics of polymer because solvent polymer integration is $\chi\phi(1-\phi)$. χ gives the relative interaction and $\phi(1-\phi)$ gives the probability that a monomer is interacting with a solvent molecule.

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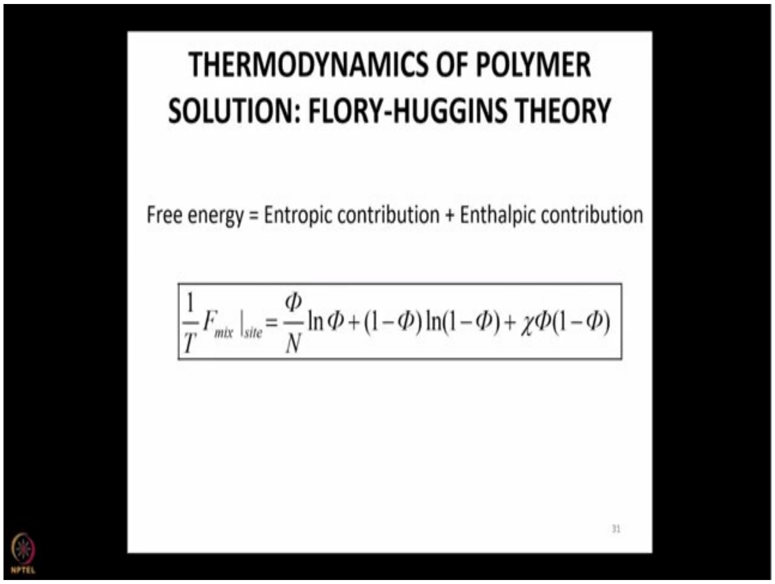

THERMODYNAMICS OF POLYMER SOLUTION: FLORY-HUGGINS THEORY

Free energy = Entropic contribution + Enthalpic contribution

$$\boxed{\frac{1}{T}F_{mix}|_{site}=\frac{\Phi}{N}\ln\Phi+(1-\Phi)\ln(1-\Phi)+\chi\Phi(1-\Phi)}$$

Then I add these all these things together and then I again minimize and when I minimize free energy and I get it theory of the polymer solution and that theory when I do with the value of χ is essential Van der Waals theory, that then explains this good solvent and bad solvent collapse in terms of these things. So, for the good solvent χ is negative but when it crosses over to poor solvent the χ is positive.

And this is exactly the thing that you get the free energy and then you find out what is this site and you find there is a crossover in the size from depending on the value of χ. This is the essentially free energy of bodies the thermodynamics of polymer solution on Flory Huggins theory and so polymer solution and Flory Huggins Theory whole details are worked out in my book I am sorry, we do not have, but we will try to put a slide there on these things slides, next slide is missing, so I would not be able to go there.

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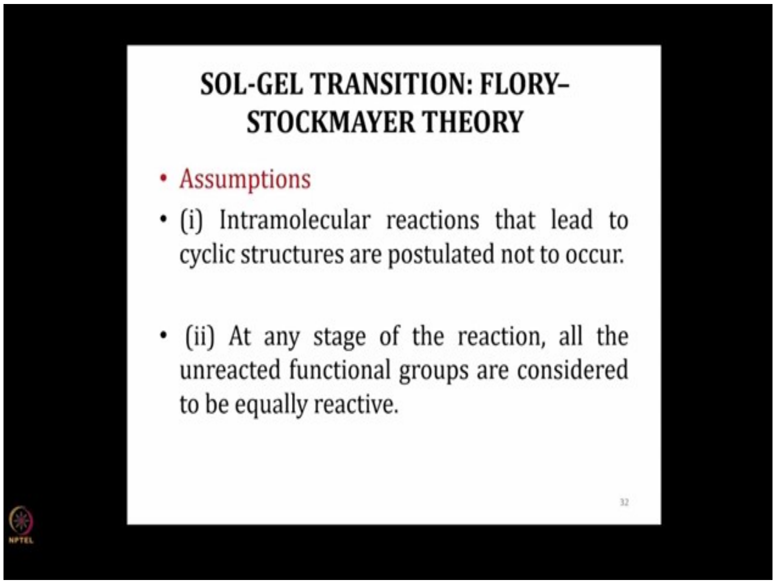

SOL-GEL TRANSITION: FLORY-STOCKMAYER THEORY

- Assumptions
- (i) Intramolecular reactions that lead to cyclic structures are postulated not to occur.
- (ii) At any stage of the reaction, all the unreacted functional groups are considered to be equally reactive.

But still I go into that which is the postulates of thermodynamics. This is the theory that we know experimentally when we find the transition that means when I add many important thing, we did sol-gel many of the applications of material. What do we do? We go on adding the concentration of these monomers and then we sometimes add some things to chill them together.

But what happened when monomer concentration goes beyond certain concentration or temperature is lowered. Then we find there is a dramatic phase transition that takes place from sol to gel and that is called the sol-gel transition is a very well-known phenomenon which is essentially very close what we do in Mayer's theory. So sol-gel transition is very similar to gas-liquid transition.

And the reason of my including in this course and also in the book is that show you how Mayer's theory is used. Mayer theory of 1937 and Flory did almost at the same time and Stock Mayer later in 1941, the same theory Stock Mayer was a student of Joseph Mayer. So basic idea that instead of Mayer clusters, we have real polymer clusters and remember the Mayer's theory who guys come close to each other and we have a Mayer function.

Here, we have the Mayer function placed by something called functionality F and polymers like nylon they are thread like they never form a gel, but they may become very long and it is important that they do not form a gel, for all our textiles, but in many other cases like rubber we want them to forming gel. That is the functional idea to get the tool**.** I briefly tell you now the method of sol-gel transition.

The basic idea is that I have a solution phase by viscosity is low and monomers are kind of disperse then they undergoing a polymerization and they form a giant molecule and they precipitated out. Reason it is important to understand it because this Sol-Gel transition, if we can control, we can control the property of the gel.

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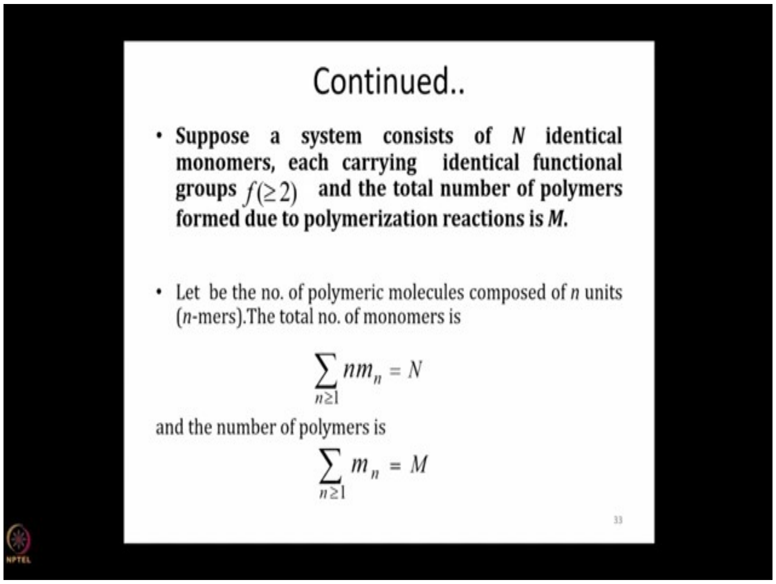

Continued..

- **Suppose a system consists of N identical monomers, each carrying identical functional groups $f(\geq 2)$ and the total number of polymers formed due to polymerization reactions is M.**
- Let be the no. of polymeric molecules composed of n units (n-mers).The total no. of monomers is

$$\sum_{n\geq 1} n m_n = N$$

and the number of polymers is

$$\sum_{n\geq 1} m_n = M$$

So these exactly it follows like Mayer’s theory this system one domain identical monomers and carrying identical functional groups. Monomers react with each other to that form a polymer and the functionality is F choosen very similar to be as a function also functions it gave. Now we have to say after some stages of the polymerization. We have nm, gives the number of monomer or size again and the sum of nm last equation in the bottom is the total number of polymers.

And, nm is the total number of monomers is exactly what we did, Mayer’s theory the nm is the number of n clusters in Mayer. So nm is total number of molecules or atoms. The system mean is nm also there; the M was the size of the polymer.

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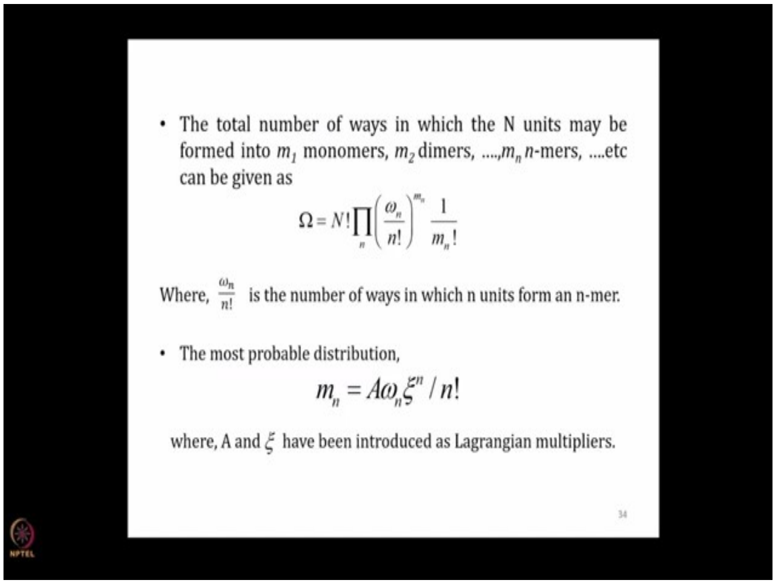

- The total number of ways in which the N units may be formed into m_1 monomers, m_2 dimers, ...,m_n n-mers, ...etc can be given as

$$\Omega = N!\prod_{n}\left(\frac{\omega_n}{n!}\right)^{m_n}\frac{1}{m_n!}$$

Where, $\frac{\omega_n}{n!}$ is the number of ways in which n units form an n-mer.

- The most probable distribution,

$$m_n = A\omega_n\xi^n / n!$$

where, A and ξ have been introduced as Lagrangian multipliers.

So the total number of ways, now we do exactly what Mayer did. So we can remember what we did in as partition function, here that is the number of ways I can form monomers. So this essentially our partition function Q. In this sol-gel transition, the interaction it is already taken into account by forming one of my board, as I told you that is essentially Mayer's function.

All we need to find out how many ways I can form this. Then that is that exactly Mayer's Theory $\omega_n / n!$, where ω_n is what you would called Mayer's cluster integrals. So it is exactly Mayer's partition function. Remember in Mayer's theory we did $\omega_n / n!$, in terms of reducible cluster integral in b_l. So that is now done in this case ω_n is evaluated directly and that is given here.

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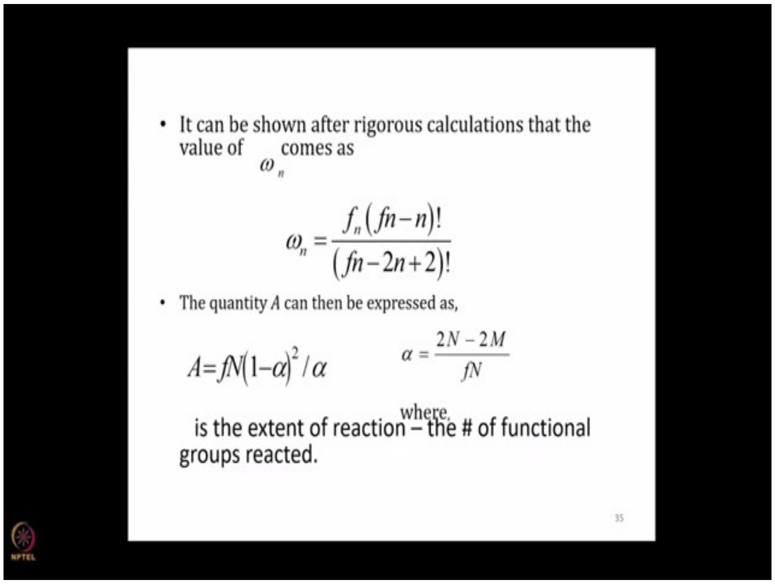

- It can be shown after rigorous calculations that the value of ω_n comes as

$$\omega_n = \frac{f_n(fn-n)!}{(fn-2n+2)!}$$

- The quantity A can then be expressed as,

$$A = fN(1-\alpha)^2/\alpha \qquad \alpha = \frac{2N-2M}{fN}$$

where, is the extent of reaction – the # of functional groups reacted.

Story goes it is following it is in the Mayer theory the relation between cluster integrals the Mayer did the expression of the Mayer cluster integral q in terms of reducible cluster b_l.

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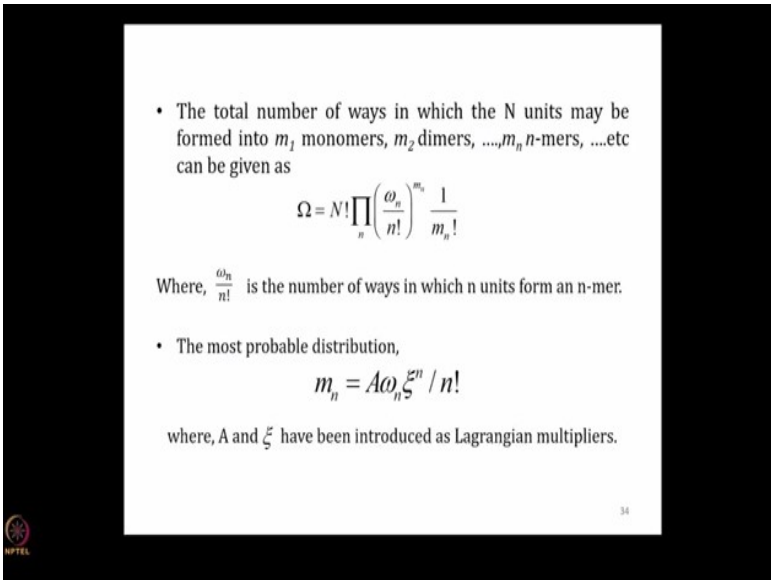

- The total number of ways in which the N units may be formed into m_1 monomers, m_2 dimers, ...,m_n n-mers, ...etc can be given as

$$\Omega = N!\prod_n \left(\frac{\omega_n}{n!}\right)^{m_n} \frac{1}{m_n!}$$

Where, $\frac{\omega_n}{n!}$ is the number of ways in which n units form an n-mer.

- The most probable distribution,

$$m_n = A\omega_n\xi^n/n!$$

where, A and ξ have been introduced as Lagrangian multipliers.

And the derivation of b_l in terms of β_k was highly non-trivial and that was done by his wife Joseph the Maria Goeppert Mayer got the Nobel prize later in Nucleation theory. Who was did not have a job because those it was just difficult for women to get a job. So and she came from America and then was in Colombia for some time they moved to Chicago.

In Chicago she was not having job in the beginning but it was the Maria Goeppert Mayer who helps Stock Mayer and which is in Stock Mayer, 1941 paper that is acknowledged. She also the one co-author of the paper. So those days the women many times did not get due credit they deserved that is something with no more famous scientists do not think it repeatedly brings out these days, then many of the things in those days were done actually by women and that were not given much credit.

So this is the expression in terms of the f and . There is a mistake. There are 2 factorial actually one factorial sign is missing. When you do that now you have to do exactly like in Mayer theory. You know why it is maximize, the Ω this is the thing in statistical mechanics. This is same as minimization of free energy.

Maximization Ω is same as maximization of entropy and that is same as minimization of free edge. When you do that I get a beautiful relation which is in terms of the most probable distribution which is actually parallels the Mayer m_l or Mayer theory. Where they comes in fugacity in a Mayer's theory here that quantity is by ξ. And beauty of that I can now evaluate A and ξ.

And the A is the following expression might you have $A = fN(1-\alpha)^2/\alpha$ and α is the extent of reaction very common in chemistry that means how many number of the functional groups react. So if I do not have a ring that is why absent of ring polymer cyclization comes as an hypothesis. So you can easily convince yourself α is the fraction of each reaction consumes two functional groups. That is why you see the factor of f , total number of functional moves the fN.

So the extent of reaction $\alpha = (2N-2M)/fN$ as the extent of reaction. When I do the minimization with Lagrangian multiplier then I get the $A = fN(1-\alpha)^2/\alpha$. So one does exactly Mayer's theory, one does the Lagrangian multiplier parellel all these things. There now I got the event nm^*.

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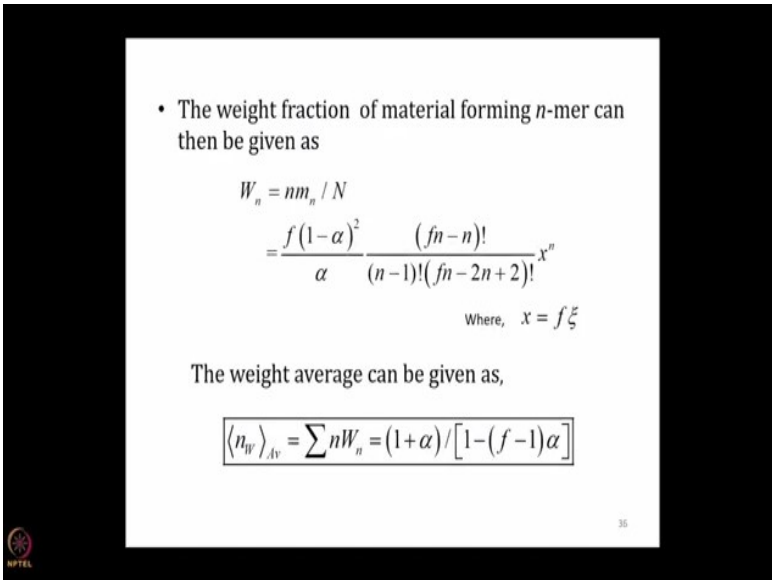

- The weight fraction of material forming *n*-mer can then be given as

$$W_n = nm_n / N$$

$$= \frac{f(1-\alpha)^2}{\alpha}\frac{(fn-n)!}{(n-1)!(fn-2n+2)!}x^n$$

Where, $x = f\xi$

The weight average can be given as,

$$\boxed{\langle n_W\rangle_{Av} = \sum nW_n = (1+\alpha)/\left[1-(f-1)\alpha\right]}$$

Now I can do some science. What we measure inany experiment like in viscosity is the weight average molecular weight that viscosity diverges. So first I define, I know fN so I do what is the weight fraction of an n-mer which is exactly like a n-mer an m_l in Mayer's theory. What is the weight of the gigantic cluster that is going to appear? Here what is the weight of n-mer there is a nm_n / N and then I put this nm expression in equation and I use the a here. Then I did very small transformation of variable ξ^n there is f^N comes that becomes x^n on the extreme right of my right hand side. $(f_n - n)!$. So I move on a little bit, this is f^n , that is subscription to the superscript is a the power. Then I get this equation. Then now whenever it is molecular weight if this W_n is a distribution.

So in order to get the normal distribution, I have to multiply by W_n and sum over all n. When I do that this sum can be done and this is one of their other truth the force and a beautiful result of statistical mechanics that I get this beautiful expression of weight average molecular weight which is observed by light scattering, observed by viscosity and all other experiments.

Now look at this beauty equation there is something very nice about this equation and some unusual when in the denominator on the right hand side extended reactions increases such that $\alpha(f-1)=1$, then the denominator diverges. So when the extent of reaction becomes $1/(f-1)$

That extent of reaction when monomers he had to the extend increase as it is going on reacting reaches $1/(f-1)$ that value any diverges.

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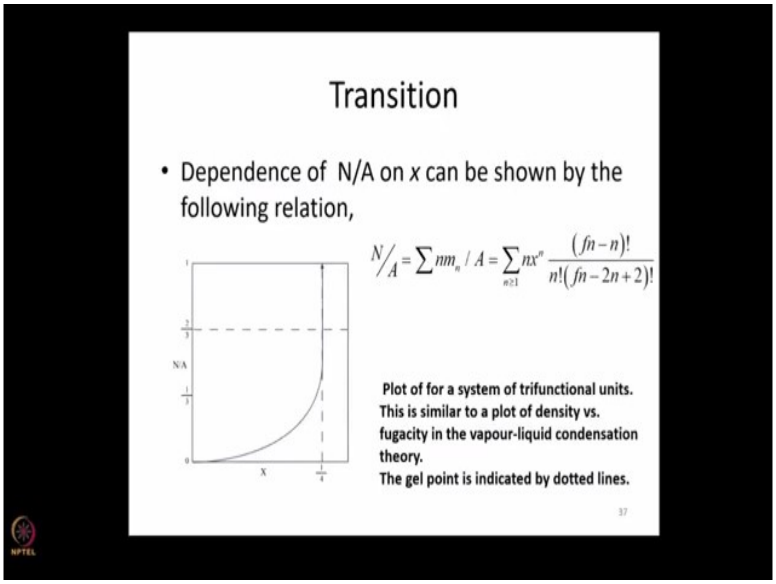

Transition

- Dependence of N/A on *x* can be shown by the following relation,

$$N/A = \sum nm_n / A = \sum_{n\geq 1} nx^n \frac{(fn-n)!}{n!(fn-2n+2)!}$$

Plot of for a system of trifunctional units. This is similar to a plot of density vs. fugacity in the vapour-liquid condensation theory.
The gel point is indicated by dotted lines.

And that is exactly what is shown here, that weight over molecular weight is undergoing a divergence. So, plot of a system of trifunctional unit where this b becomes this extend is divergence and extent of reaction. In trifunctional $f=3$. So 3- 1 is 2; so 2α, when α become 1/2 in for the trifunctional unit is divergence. This is where we find divergences to the thinks it is exactly like similar to density theory.

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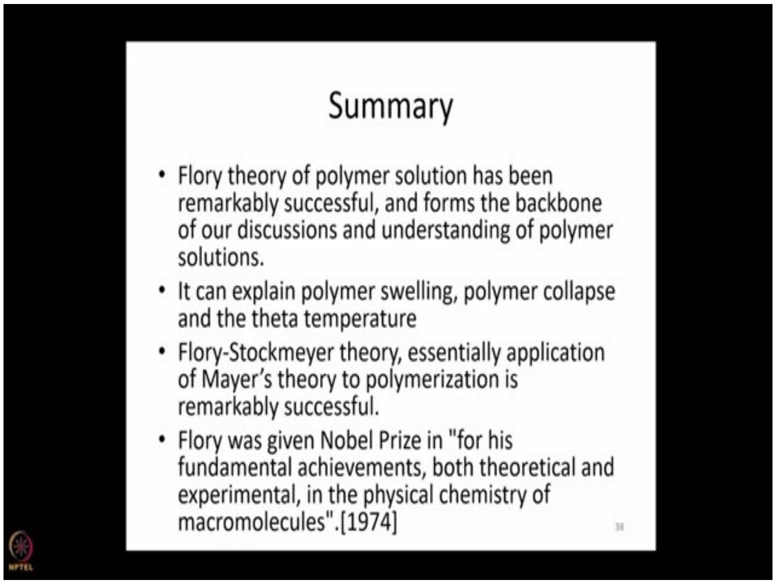

Summary

- Flory theory of polymer solution has been remarkably successful, and forms the backbone of our discussions and understanding of polymer solutions.
- It can explain polymer swelling, polymer collapse and the theta temperature
- Flory-Stockmeyer theory, essentially application of Mayer's theory to polymerization is remarkably successful.
- Flory was given Nobel Prize in "for his fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules".[1974]

Now, so summary of these so this is initially same as a appearance of liquid phase. This is one of the beautiful theory where Flory used it first then Stock Meyer did it. I just briefly summarize you polymer that we done. We have done the entire distribution and polymer size, then we have done theory of polymer solution, which has been remarkably successful and it can explain polymer swelling, it can explain polymer collapse, it can save this crossover from swelling to collapse and at the θ temperature.

And Flory- Stock Mayer theory of sol-gel transition essentially the application from a Mayer's theory to polymerization and Stock Mayer was a student of Mayer but also worked with Flory. But Flory already did that sol-gel transition, Flory did that before but Stock Mayer used to make it more rational by using the Mayer's theory and that is the theory very nice and as I told you Flory was given a single Nobel Prize in 1974.

People say Falcon Stains should have shared it but given the Flory's contribution so gigantic because he not only did the theory of polymer, size distribution, the theory of ideal polymer that is N^{ν} where $\nu = 3/5$ the theory of polymer solution which is Flory Huggins and sol-gel transition that is also Flory theory, that is probably was justified give Flory single Nobel Prize.

Summarize, I want to tell you that theory is usually almost like the one that we did in the course essentially is a celebration of Paul Flory who as I told you in the beginning was a remarkable human being who not only just did this wonderful work did it work in many other areas. The Flory theory that is why is also a very important and respected name in biology.

And he is a humanitarian did a lot of work for scientists in underdeveloped and countries under difficult conditions. So look up the Flory theory polymer, book of scaling concepts of physics which is takes many of deploring concepts to a much higher level. Last I see the one of the reason Flory was given in 1974, Nobel Prize it is know many of us know what was done before 1940s and 1950s.

Reason is that, in 1970s just after critical phenomena theory was developed by Karen Wilson we know Michael Fisher and all these people and that is the time, 1972 Keegan's did a wonderful calculation of polymers excluded volume. We mapped it into a magnetic problem and he essentially do renormalization group calculation of the polymer problem. Then, Michael Fisher extended that and they discover all the Flory equations.

All of them they discover mean square size scales as N^{ν} and $\nu = 3/5$ for 3 dimension and ½ for 2 dimension. Then they discover the θ solvent polymer collapse. So whole of Flory theory was developed and derived by using much sophisticated methods of polymer physics by John Michael fisher and some other people in France, Germany and that probably the realization that this work Flory did goes far beyond just polymer.

It is a beautiful theory of statistical mechanics; multiple contributions in statistical mechanics of interacting systems. I stop here today this is the last lecture on polymer and I strongly recommend you would read our book, my book and the other books also. I hope you enjoy it and thank you for your attention bye.