Polymer Process Engineering

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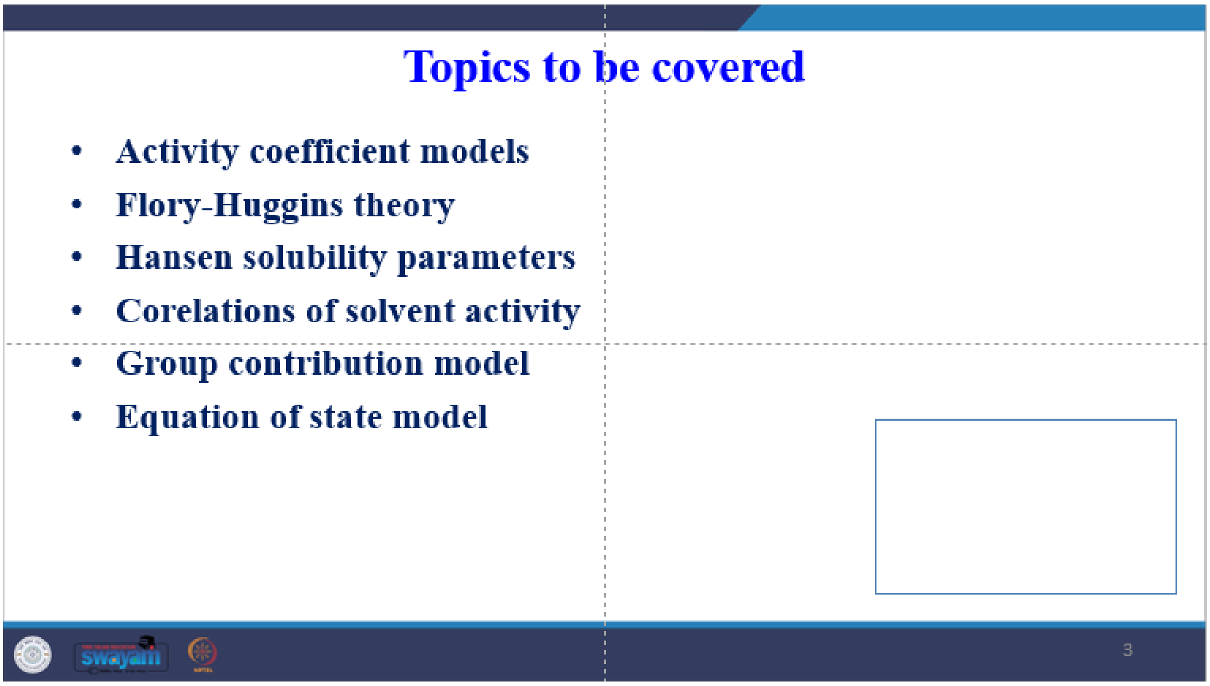
Lecture – 08

Thermodynamics of polymer systems-III

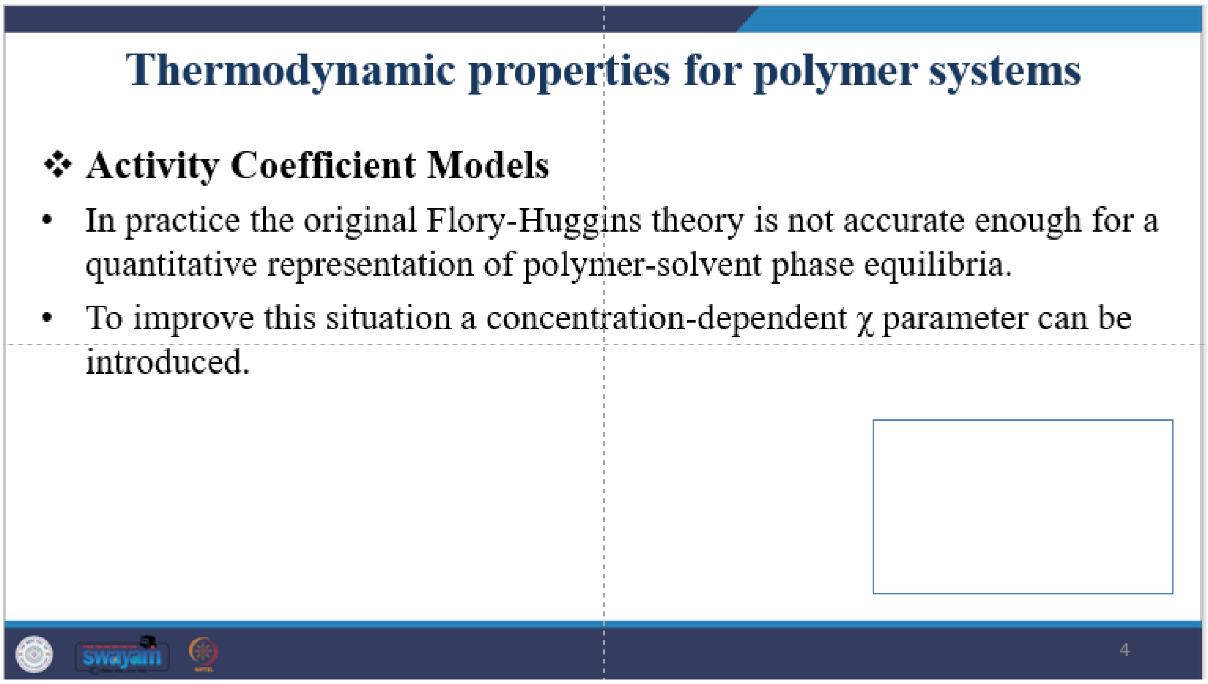
Hello friends, welcome to the thermodynamics of polymeric system phase 3. In this lecture, we will discuss about the enthalpy entropy calculation for various polymeric systems. We discussed the phase behavior of polymeric systems, fugacity, activity, equilibrium conditions, theories, and various theories like Flory-Huggin's theories in the thermodynamic system. In this particular segment, we are going to discuss the activity coefficient models. We will discuss the Flory-Huggins theory. Then we will discuss Hansen solubility parameters, and the correlation of various solvent activities because solvents play a vital role in shaping polymers into useful products.



Topics to be covered

- Activity coefficient models
- Flory-Huggins theory
- Hansen solubility parameters
- Corelations of solvent activity
- Group contribution model
- Equation of state model

Then we will discuss about the group contribution model and equation of state models. Now the first is the activity coefficient model. Now the in practice, the original Flory-Huggins theory which is not accurate enough for a quantitative representation of polymer solvent phase equilibrium. Now to improve this situation, a concentration dependent Xi parameter can be introduced.

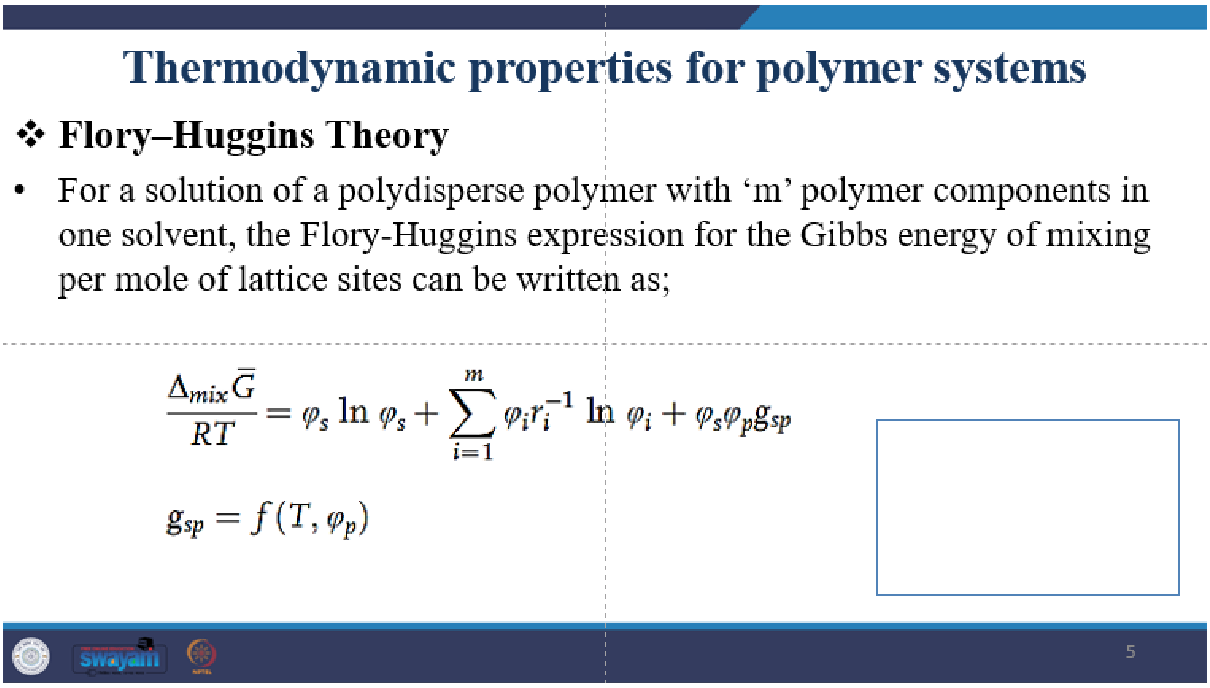


Thermodynamic properties for polymer systems

❖ **Activity Coefficient Models**

- In practice the original Flory-Huggins theory is not accurate enough for a quantitative representation of polymer-solvent phase equilibria.
- To improve this situation a concentration-dependent χ parameter can be introduced.

Now for this the Flory-Huggins they proposed the things and for a solution of a polydisperse polymer with M polymer component in one solvent, the Flory-Huggins expression for the Gibbs energy of the mixing per mole of lattice site. This can be written as delta G for mixing over RT is equal to psi s ln plus summation i shi i r i inverse ln shi i plus shi s shi p G sp and G sp is equal to is a function of temperature and shi p. Now the sum is only over the polymer component shi i is the segment fraction of polymer component i. So, this can be shi p is equal to summation of i is to summation from i is equal to 1 to M shi i is equal to 1 minus shi s. Now to avoid any kind of a confusion with the polymer solvent interaction parameter of the symbol G sp is used instead of shi which is independent of concentration.



Thermodynamic properties for polymer systems

❖ **Flory–Huggins Theory**

- For a solution of a polydisperse polymer with ‘m’ polymer components in one solvent, the Flory-Huggins expression for the Gibbs energy of mixing per mole of lattice sites can be written as;

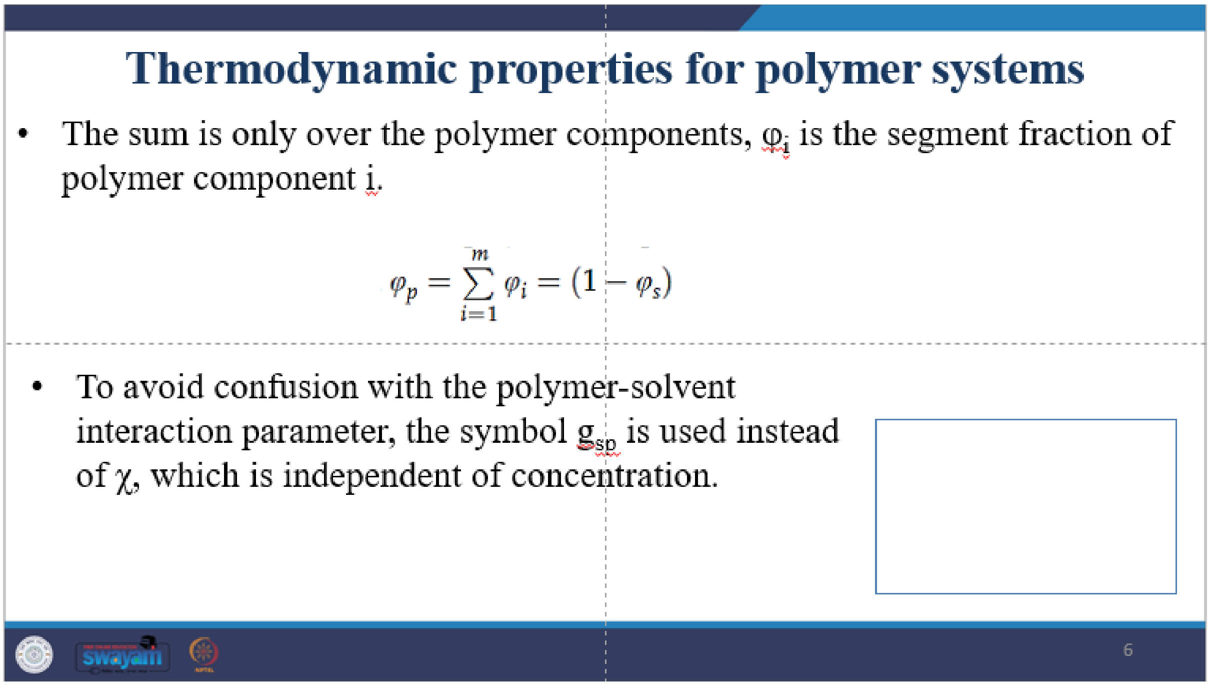
$$\frac{\Delta_{mix}\bar{G}}{RT} = \varphi_s \ln \varphi_s + \sum_{i=1}^{m} \varphi_i r_i^{-1} \ln \varphi_i + \varphi_s \varphi_p g_{sp}$$

$$g_{sp} = f(T, \varphi_p)$$

$$\frac{\Delta_{mix}\overline{G}}{RT} = \varphi_s \ln \varphi_s + \sum_{i=1}^{m} \varphi_i r_i^{-1} \ln \varphi_i + \varphi_s \varphi_p g_{sp}$$

$$g_{sp} = f(T, \varphi_p)$$

Now this G sp is equal to a plus b over t plus c t plus d shi p plus e shi p square. Now G sp is equal to a plus b plus c over t 1 minus d shi p. Now G sp is equal to a plus b t plus c ln t over 1 minus d shi p. Now this ln X s gamma s is equal to ln shi s plus 1 minus 1 over R n shi p plus G sp minus shi s del G sp over del shi p i p square. Now this ln X i gamma i is equal to ln shi i plus 1 minus R i shi p over R n minus R i shi s plus R i G shi p shi i square.



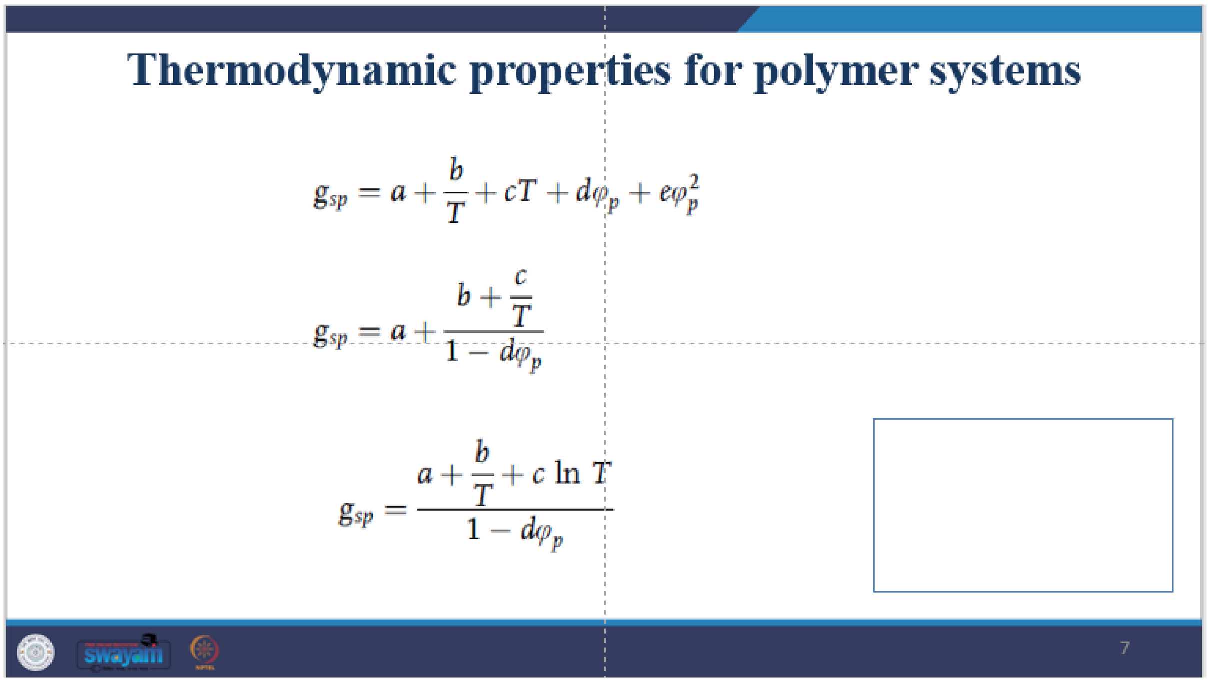
Thermodynamic properties for polymer systems

- The sum is only over the polymer components, φ_i is the segment fraction of polymer component i.

$$\varphi_p = \sum_{i=1}^{m} \varphi_i = (1 - \varphi_s)$$

- To avoid confusion with the polymer-solvent interaction parameter, the symbol g_{sp} is used instead of χ, which is independent of concentration.

$$\varphi_p = \sum_{i=1}^{m} \varphi_i = (1 - \varphi_s)$$



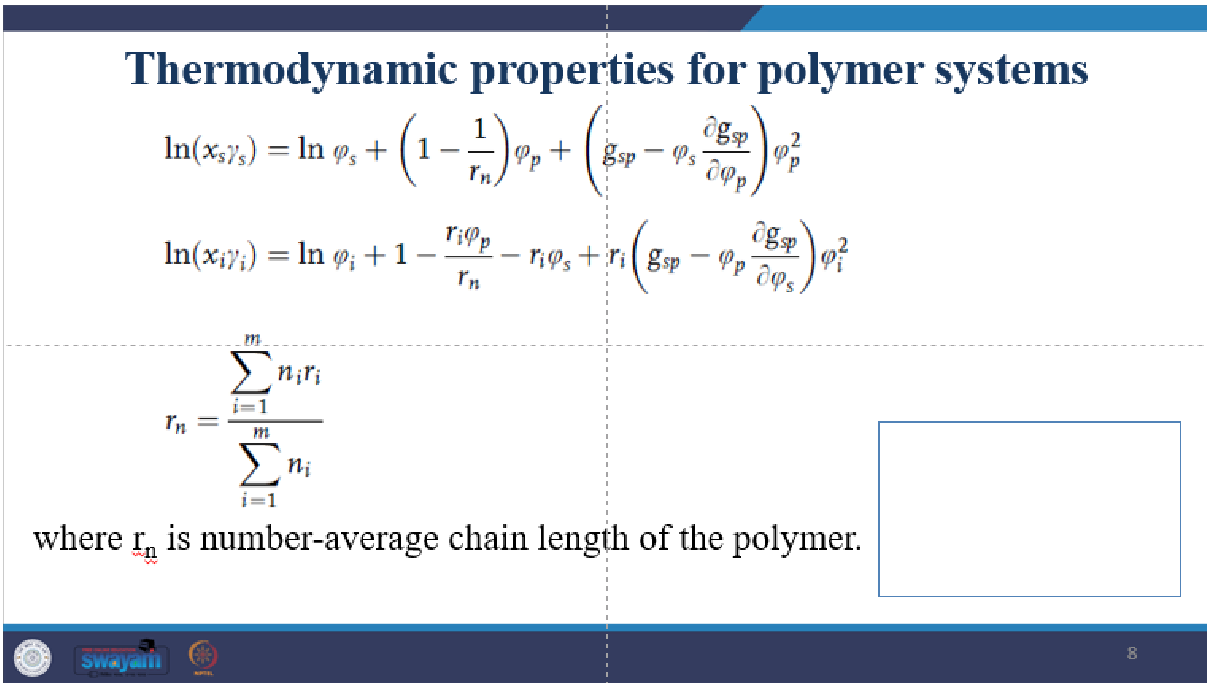
Thermodynamic properties for polymer systems

$$g_{sp} = a + \frac{b}{T} + cT + d\varphi_p + e\varphi_p^2$$

$$g_{sp} = a + \frac{b + \frac{c}{T}}{1 - d\varphi_p}$$

$$g_{sp} = \frac{a + \frac{b}{T} + c \ln T}{1 - d\varphi_p}$$

Now R n is equal to n i R i over i is equal to 1 m summation from i is equal to 1 to m n i where R n is number average chain length of polymer. Now Henson solubility parameter according to the regular solution theory of Hildebrand The xi parameter can be approximated by is v s over R t del s delta s minus delta p square where v s is the molar volume of the solvent, delta s is the solubility parameter of solvent and delta p is the solubility parameter of polymer. Now this Henson suggested the refining of the solubility parameter theory and introduction of the contribution from the dispersive interaction d and the polar interaction p and hydrogen bond formation that is H b. So, this can be represented as v s over R t delta s d delta p square plus delta s delta s h b and xi is equal to alpha v s R t delta s minus delta p plus 0.25 delta s minus delta p plus 0.



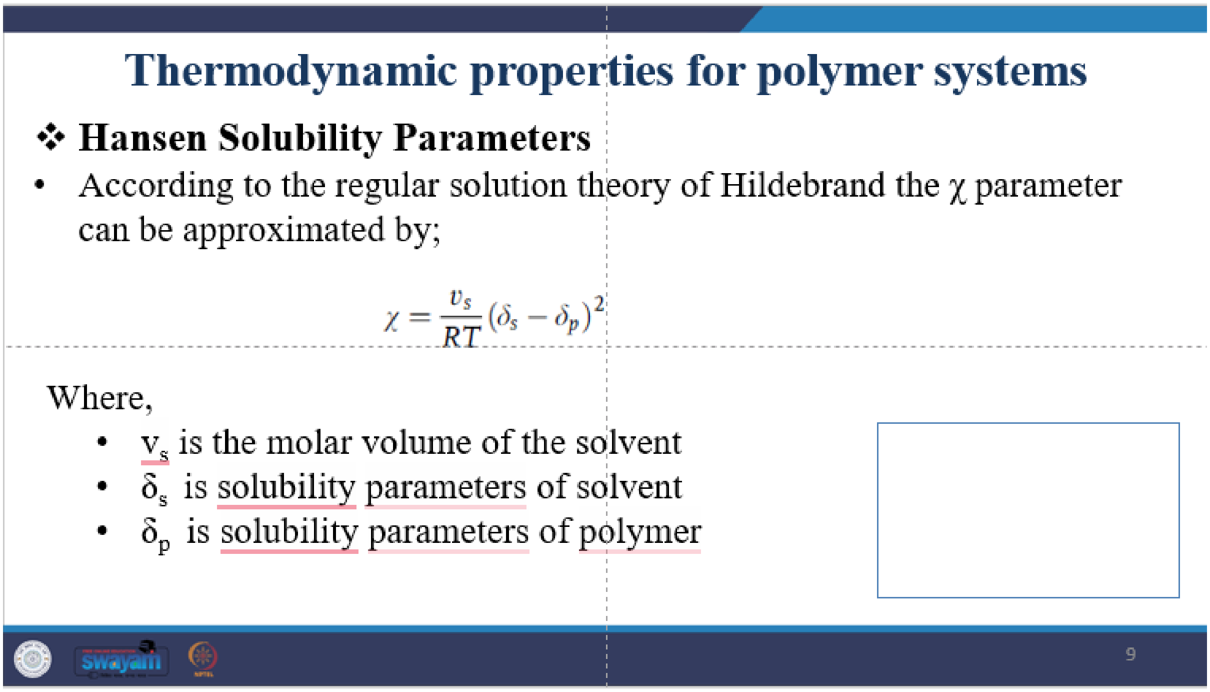
Thermodynamic properties for polymer systems

$$\ln(x_s\gamma_s) = \ln \varphi_s + \left(1 - \frac{1}{r_n}\right)\varphi_p + \left(g_{sp} - \varphi_s \frac{\partial g_{sp}}{\partial \varphi_p}\right)\varphi_p^2$$

$$\ln(x_i\gamma_i) = \ln \varphi_i + 1 - \frac{r_i\varphi_p}{r_n} - r_i\varphi_s + r_i\left(g_{sp} - \varphi_p \frac{\partial g_{sp}}{\partial \varphi_s}\right)\varphi_i^2$$

$$r_n = \frac{\sum_{i=1}^{m} n_i r_i}{\sum_{i=1}^{m} n_i}$$

where r_n is number-average chain length of the polymer.



Thermodynamic properties for polymer systems

❖ Hansen Solubility Parameters

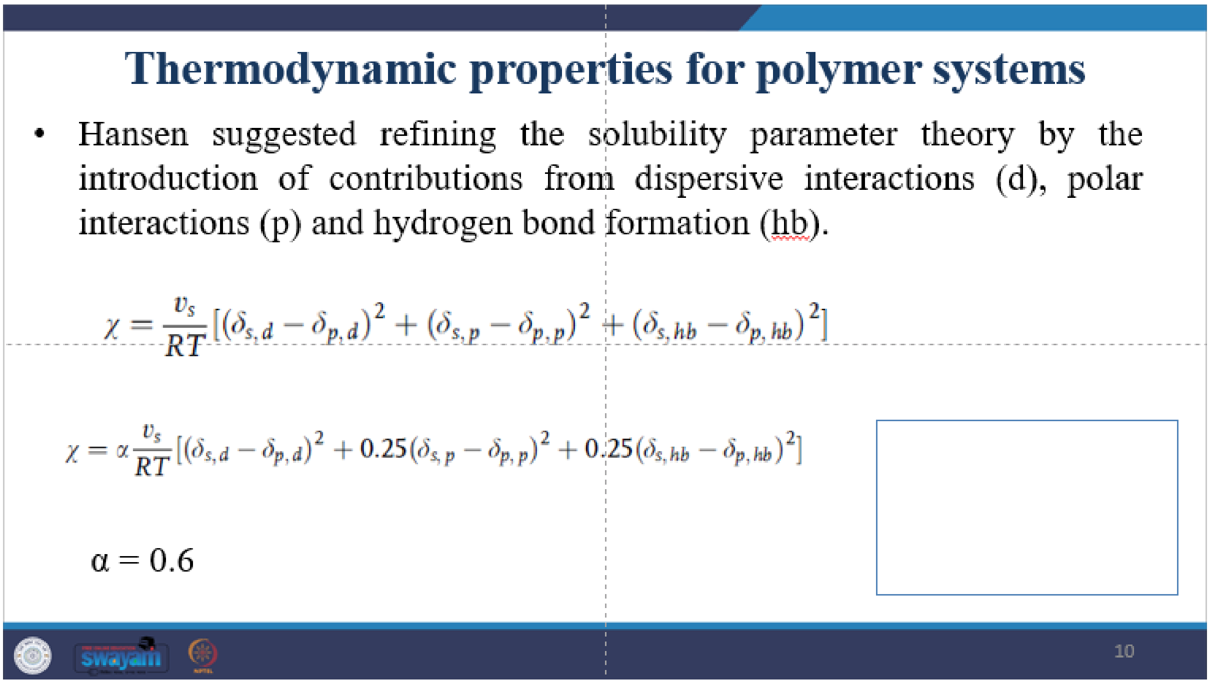
- According to the regular solution theory of Hildebrand the χ parameter can be approximated by;

$$\chi = \frac{v_s}{RT}(\delta_s - \delta_p)^2$$

Where,

- v_s is the molar volume of the solvent
- δ_s is solubility parameters of solvent
- δ_p is solubility parameters of polymer

$$\chi = \frac{v_s}{RT}(\delta_s - \delta_p)^2$$



Thermodynamic properties for polymer systems

- Hansen suggested refining the solubility parameter theory by the introduction of contributions from dispersive interactions (d), polar interactions (p) and hydrogen bond formation (hb).

$$\chi = \frac{v_s}{RT}[(\delta_{s,d} - \delta_{p,d})^2 + (\delta_{s,p} - \delta_{p,p})^2 + (\delta_{s,hb} - \delta_{p,hb})^2]$$

$$\chi = \alpha\frac{v_s}{RT}[(\delta_{s,d} - \delta_{p,d})^2 + 0.25(\delta_{s,p} - \delta_{p,p})^2 + 0.25(\delta_{s,hb} - \delta_{p,hb})^2]$$

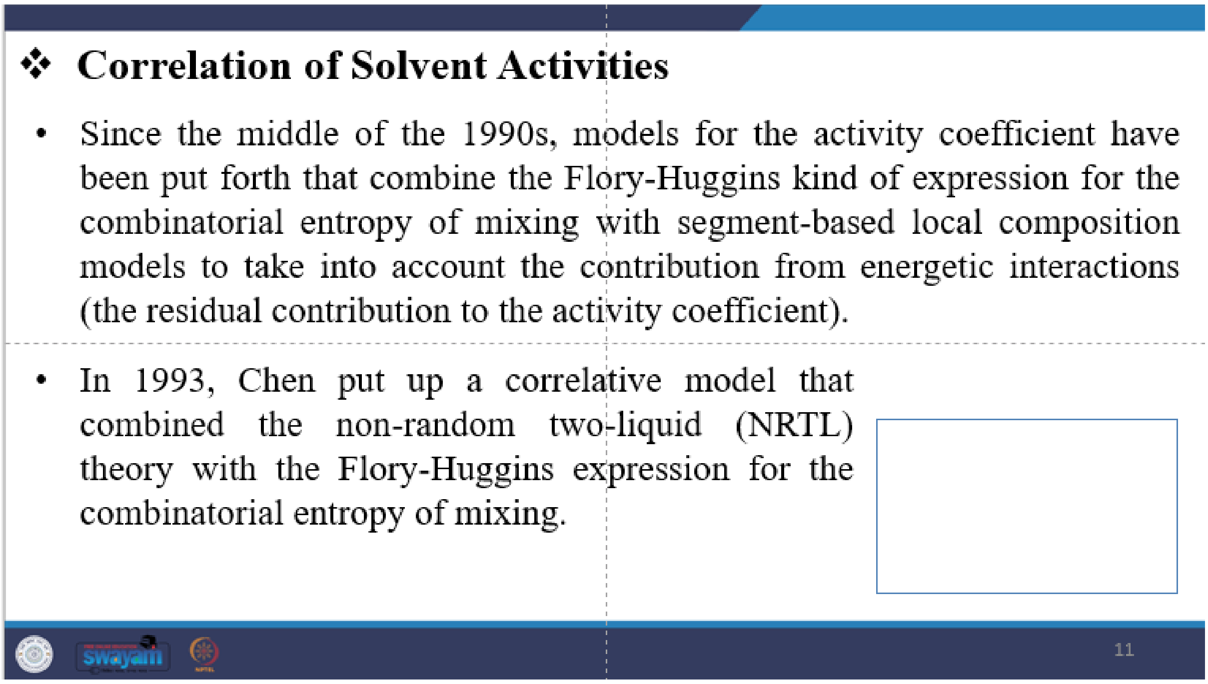
$\alpha = 0.6$

$$\chi = \frac{v_s}{RT}[(\delta_{s,d} - \delta_{p,d})^2 + (\delta_{s,p} - \delta_{p,p})^2 + (\delta_{s,hb} - \delta_{p,hb})^2]$$

$$\chi = \alpha\frac{v_s}{RT}[(\delta_{s,d} - \delta_{p,d})^2 + 0.25(\delta_{s,p} - \delta_{p,p})^2 + 0.25(\delta_{s,hb} - \delta_{p,hb})^2]$$

$\alpha = 0.6$

25 delta s h b minus delta p h b alpha is equal to 0.6. Now since the middle of 1990 is the model for the activity coefficient have been put for that combine the Flory Huggins kind of expression for the combinational entropy of mixing and the segment based local composition model to take into account the contribution from energetic interaction. In 1993 Chen they put up a correlative model of combined non-random two liquid NRTL theory with the Flory Huggins expression for the entropy change. Now correlation of solvent activity, now in place of NRTL theory Pedrosa he suggested unique quack theory in 2004.



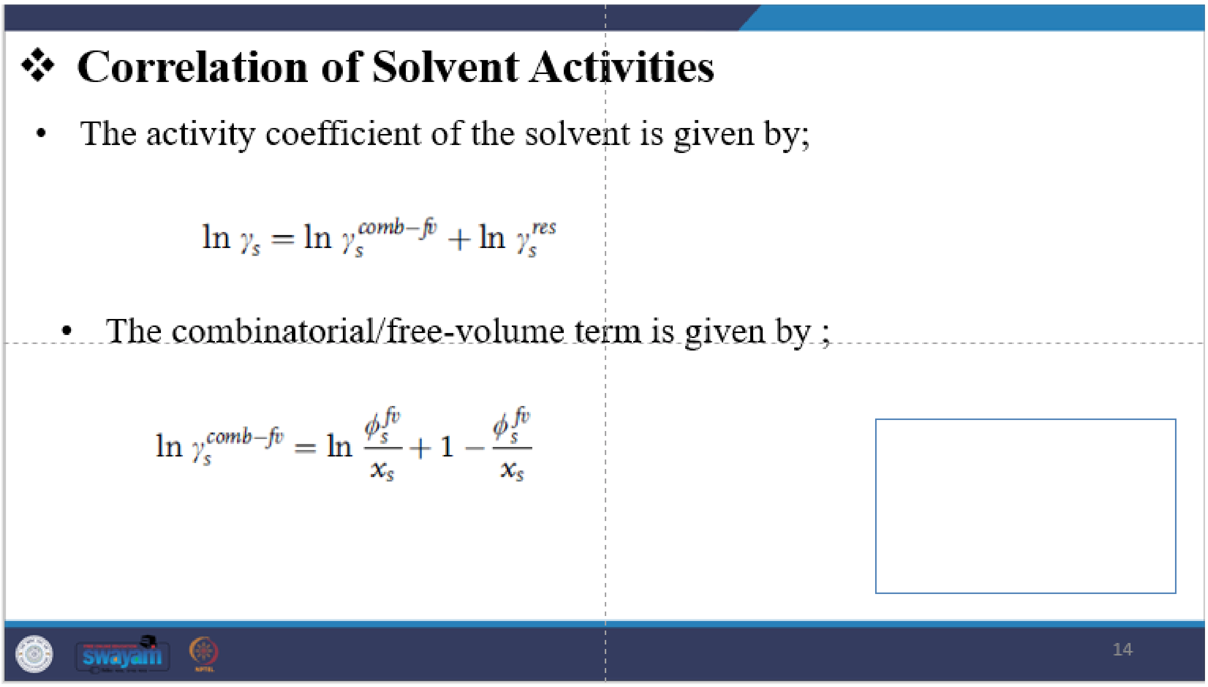
❖ Correlation of Solvent Activities

- Since the middle of the 1990s, models for the activity coefficient have been put forth that combine the Flory-Huggins kind of expression for the combinatorial entropy of mixing with segment-based local composition models to take into account the contribution from energetic interactions (the residual contribution to the activity coefficient).
- In 1993, Chen put up a correlative model that combined the non-random two-liquid (NRTL) theory with the Flory-Huggins expression for the combinatorial entropy of mixing.

Now using the database of 70 low pressure VLE system they examined the different combinations of contributions and residual contributions. Now as an illustration we will provide the expression for the activity coefficient of the solvent for a model that combines the segment based NRTL residual term along with the p free volume term and the contributions and the free contributions they are combined in the p free volume combinatorial term. The activity coefficient of the solvent is given by ln gamma s is equal to ln gamma s plus ln minus residual. Now this combinatorial free volume term is given by ln gamma s combinatorial free volume is equal to ln phi s this fugacity over plus 1 minus phi s X. Now the free volume fraction this phi f v is calculated as X i V i f v over summation j X j V i f v.

$$\ln \gamma_s = \ln \gamma_s^{comb-fv} + \ln \gamma_s^{res}$$

$$\ln \gamma_s^{comb-fv} = \ln \frac{\phi_s^{fv}}{x_s} + 1 - \frac{\phi_s^{fv}}{x_s}$$



❖ Correlation of Solvent Activities

- The activity coefficient of the solvent is given by;

$$\ln \gamma_s = \ln \gamma_s^{comb-fv} + \ln \gamma_s^{res}$$

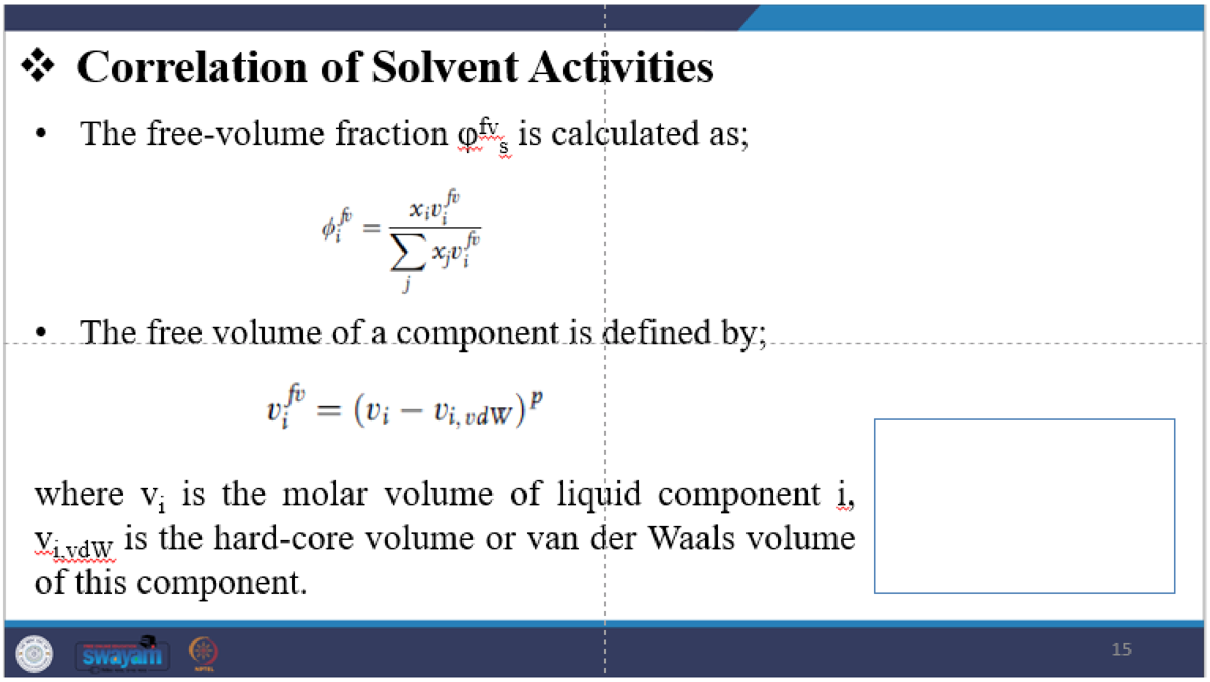
- The combinatorial/free-volume term is given by ;

$$\ln \gamma_s^{comb-fv} = \ln \frac{\phi_s^{fv}}{x_s} + 1 - \frac{\phi_s^{fv}}{x_s}$$

The free volume of the component is usually defined by V i f v is equal to minus V i V d w where this V i is the molar volume of the liquid component i and this V i V d w is the hard core volume or wonder volume of this particular segment. Now p correction factor which is which can be calculated as p is equal to 1 minus V s over V p. So, the residual term can be given as ln gamma s residual q s X p square tau p s over X s plus X p g p s square plus tau s p g s p square over X p plus X s g s p tau e to the power aij R T and Gi a is equal to e to the power minus alpha tau ij where a s p and a p s are adjustable inter interaction parameter and a is the n R T L non-random parameter which is fixed as by the Pedroza at point 4. Now so X i is equal to X i q i over summation j X j q j and q i is equal to R i 1 minus 2 alpha 1 minus 1 upon R i where X i is the effective mole fraction of the segment of a species i and q i is the effective segment number of a species i R s is equal to 1 and rp is equal to R. Now group contributions method this can be used to forecast the thermodynamic properties.

$$\phi_i^{fv} = \frac{x_i v_i^{fv}}{\sum_j x_j v_i^{fv}}$$

$$v_i^{fv} = \left(v_i - v_{i,vdW}\right)^p$$



Correlation of Solvent Activities

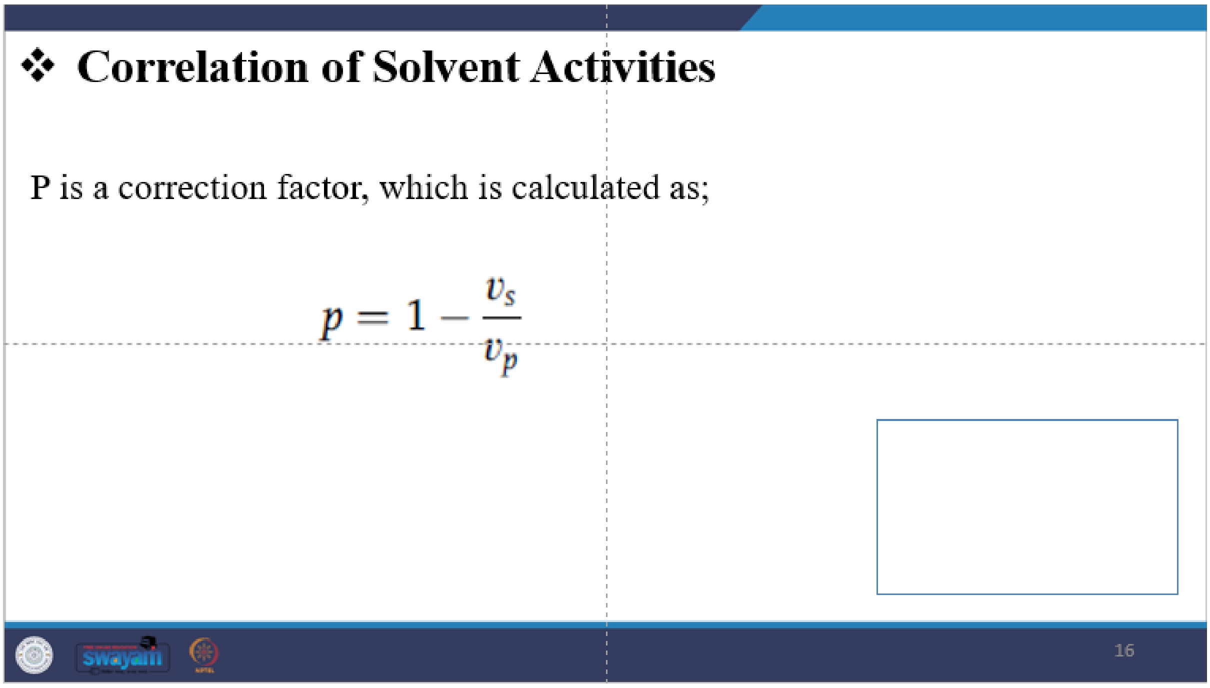
- The free-volume fraction φ^{fv}_s is calculated as;

$$\phi_i^{fv} = \frac{x_i v_i^{fv}}{\sum_j x_j v_i^{fv}}$$

- The free volume of a component is defined by;

$$v_i^{fv} = (v_i - v_{i,vdW})^p$$

where v_i is the molar volume of liquid component i, $v_{i,vdW}$ is the hard-core volume or van der Waals volume of this component.

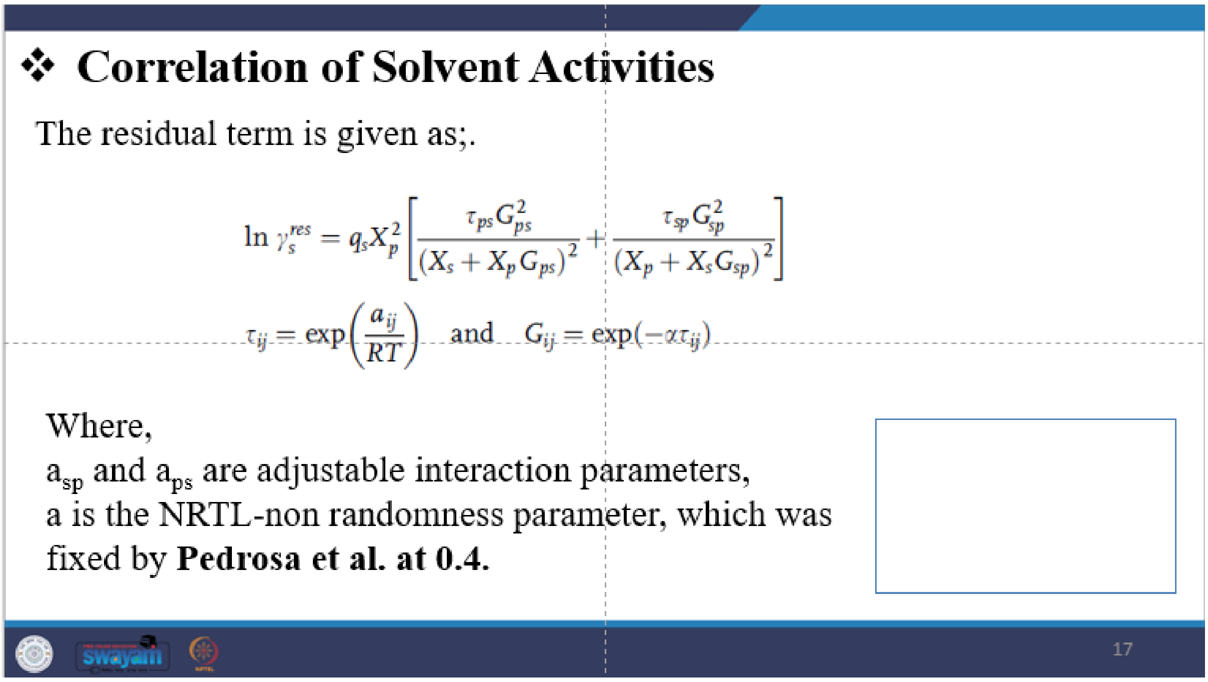


Correlation of Solvent Activities

P is a correction factor, which is calculated as;

$$p = 1 - \frac{v_s}{v_p}$$

$$p = 1 - \frac{v_s}{v_p}$$



❖ Correlation of Solvent Activities

The residual term is given as;.

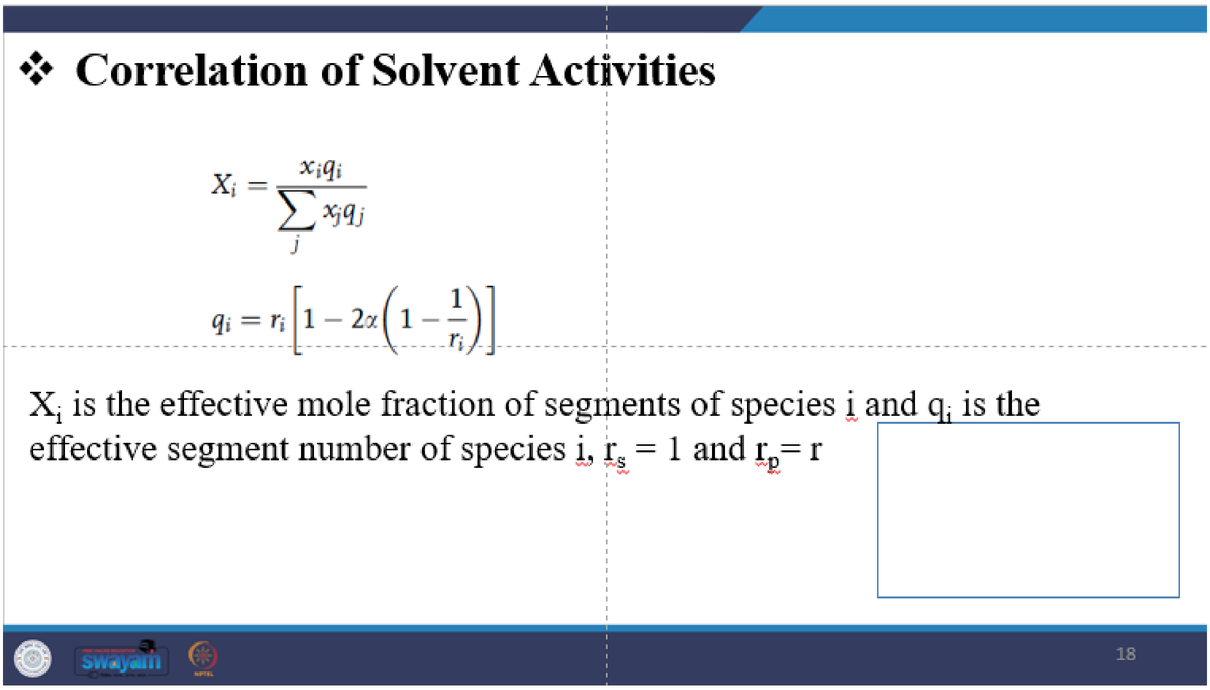
$$\ln \gamma_s^{res} = q_s X_p^2 \left[\frac{\tau_{ps} G_{ps}^2}{(X_s + X_p G_{ps})^2} + \frac{\tau_{sp} G_{sp}^2}{(X_p + X_s G_{sp})^2} \right]$$

$$\tau_{ij} = \exp\left(\frac{a_{ij}}{RT}\right) \quad \text{and} \quad G_{ij} = \exp(-\alpha \tau_{ij})$$

Where,
a_{sp} and a_{ps} are adjustable interaction parameters,
a is the NRTL-non randomness parameter, which was fixed by **Pedrosa et al. at 0.4.**

$$\ln \gamma_s^{res} = q_s X_p^2 \left[\frac{\tau_{ps} G_{ps}^2}{(X_s + X_p G_{ps})^2} + \frac{\tau_{sp} G_{sp}^2}{(X_p + X_s G_{sp})^2} \right]$$

$$\tau_{ij} = \exp\left(\frac{a_{ij}}{RT}\right) \quad \text{and} \quad G_{ij} = \exp(-\alpha \tau_{ij})$$



❖ Correlation of Solvent Activities

$$X_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

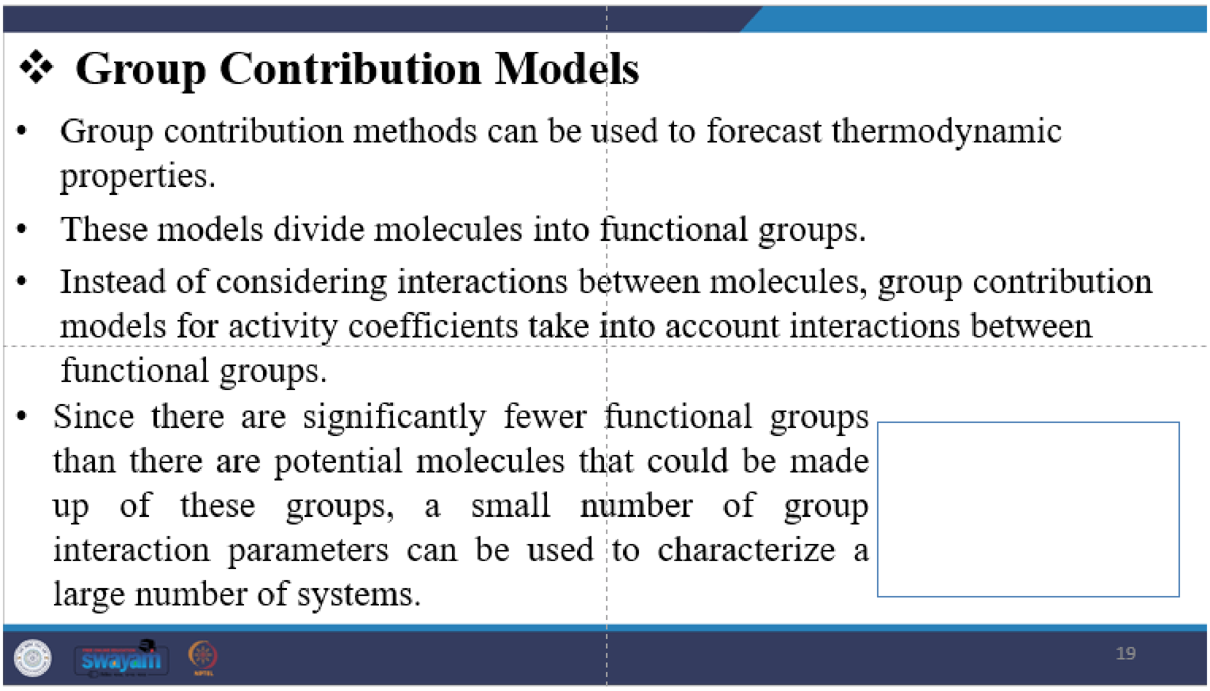
$$q_i = r_i \left[1 - 2\alpha \left(1 - \frac{1}{r_i} \right) \right]$$

X_i is the effective mole fraction of segments of species i and q_i is the effective segment number of species i, $r_s = 1$ and $r_p = r$

$$X_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

$$q_i = r_i\left[1 - 2\alpha\left(1 - \frac{1}{r_i}\right)\right]$$

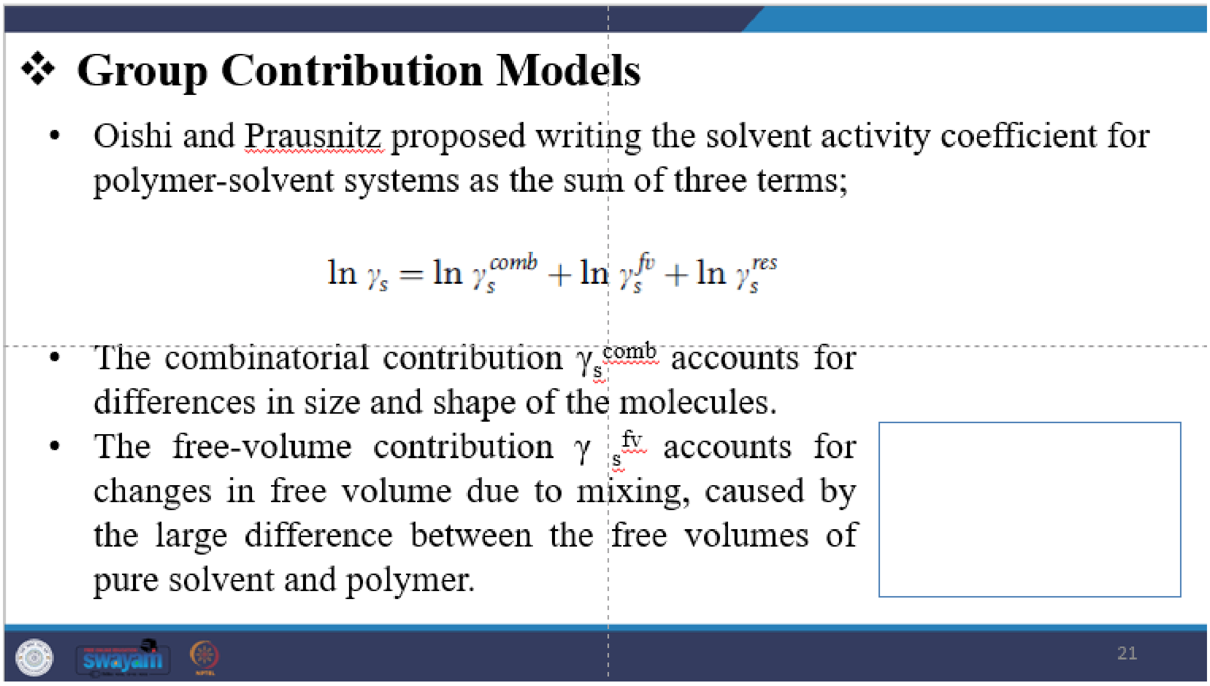
Now, these models divide molecules into functional groups. Now, instead of considering the interaction between the molecules group contribution model for activity coefficient, consider the interaction between the functional groups. So, there are significantly fewer functional groups then there are potential molecules that could be made up of these groups. A smaller number of group interaction parameters can be used to characterize a large number of systems. The regression of experimental data is how these group interactions were discovered.



❖ Group Contribution Models

- Group contribution methods can be used to forecast thermodynamic properties.
- These models divide molecules into functional groups.
- Instead of considering interactions between molecules, group contribution models for activity coefficients take into account interactions between functional groups.
- Since there are significantly fewer functional groups than there are potential molecules that could be made up of these groups, a small number of group interaction parameters can be used to characterize a large number of systems.

So, the group contribution approaches are thus entirely predictive. The group contribution approach for activity coefficient is typically less accurate than the correlative models since specify the particular specifics of the molecule structure are not considered. So Oishi they had all they proposed the writing of a solvent activity coefficient for the polymer-solvent system, and they are the sum of the terms like ln gamma s ln plus ln gamma s fugacity plus ln gamma s for the residual. The combinatorial contribution of this gamma accounts for the difference in the size and shape of the molecules. The free volume contribution of gamma then for the fugacity accounts for the change in the free volume due to mixing, and that is caused by the large difference between the free volume of pure solvent and polymers.



❖ Group Contribution Models

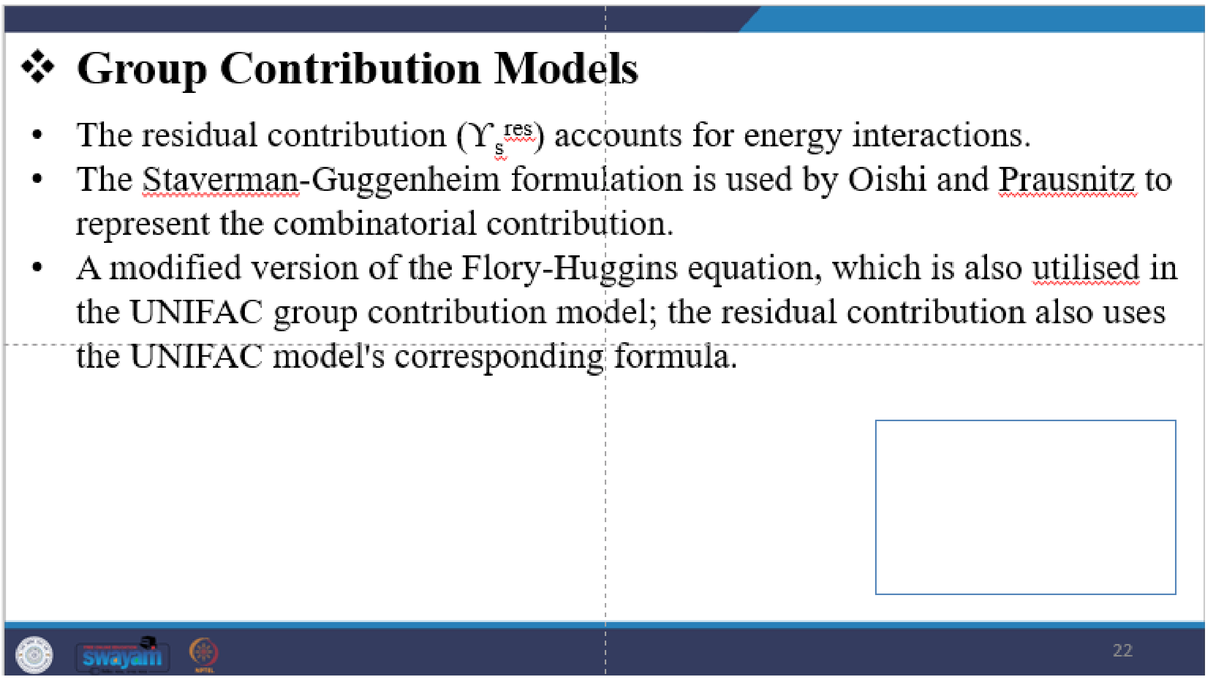
- Oishi and Prausnitz proposed writing the solvent activity coefficient for polymer-solvent systems as the sum of three terms;

$$\ln \gamma_s = \ln \gamma_s^{comb} + \ln \gamma_s^{fv} + \ln \gamma_s^{res}$$

- The combinatorial contribution γ_s^{comb} accounts for differences in size and shape of the molecules.
- The free-volume contribution γ_s^{fv} accounts for changes in free volume due to mixing, caused by the large difference between the free volumes of pure solvent and polymer.

$$\ln \gamma_s = \ln \gamma_s^{comb} + \ln \gamma_s^{fv} + \ln \gamma_s^{res}$$

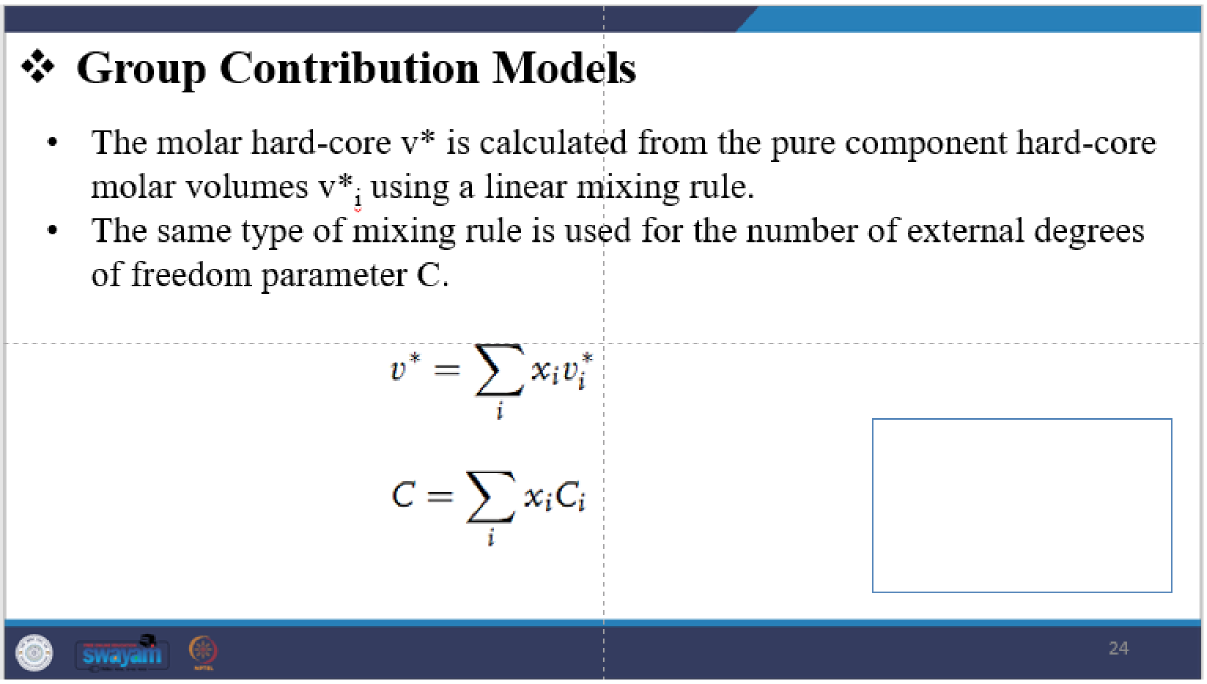
So, the residual contribution accounts for energy interaction, and some of the workers their formulation they use this Oishi to represent the combinatorial contribution. A modified version of Flory Huggins equation which is also utilized in the UNIFAC group contribution model. The residual contribution Also uses the UNIFAC models corresponding to the formula. The UNIFAC model residual contribution with temperature-dependent interaction parameters serves as a representation of the residual contribution. Now the liquid molar volume this requires for calculating the free volume of a component this can be determined experimentally by using the T-8 equation or by the Albro-Grupp contribution approach.



❖ Group Contribution Models

- The residual contribution (Υ_s^{res}) accounts for energy interactions.
- The Staverman-Guggenheim formulation is used by Oishi and Prausnitz to represent the combinatorial contribution.
- A modified version of the Flory-Huggins equation, which is also utilised in the UNIFAC group contribution model; the residual contribution also uses the UNIFAC model's corresponding formula.

So, the molar hard core we start this calculated from the pure component hard core molar volume using the linear mixing rule. Now what is this linear mixing rule this one can be represented mathematically like this X i C is equal to i X i C i. Now these same type of mixing rule is used for a number of approaches. Now the group contribution formula in these equations they are used to determine the pure component hard core volume and the C parameter. Now here this can be represented like this 21.

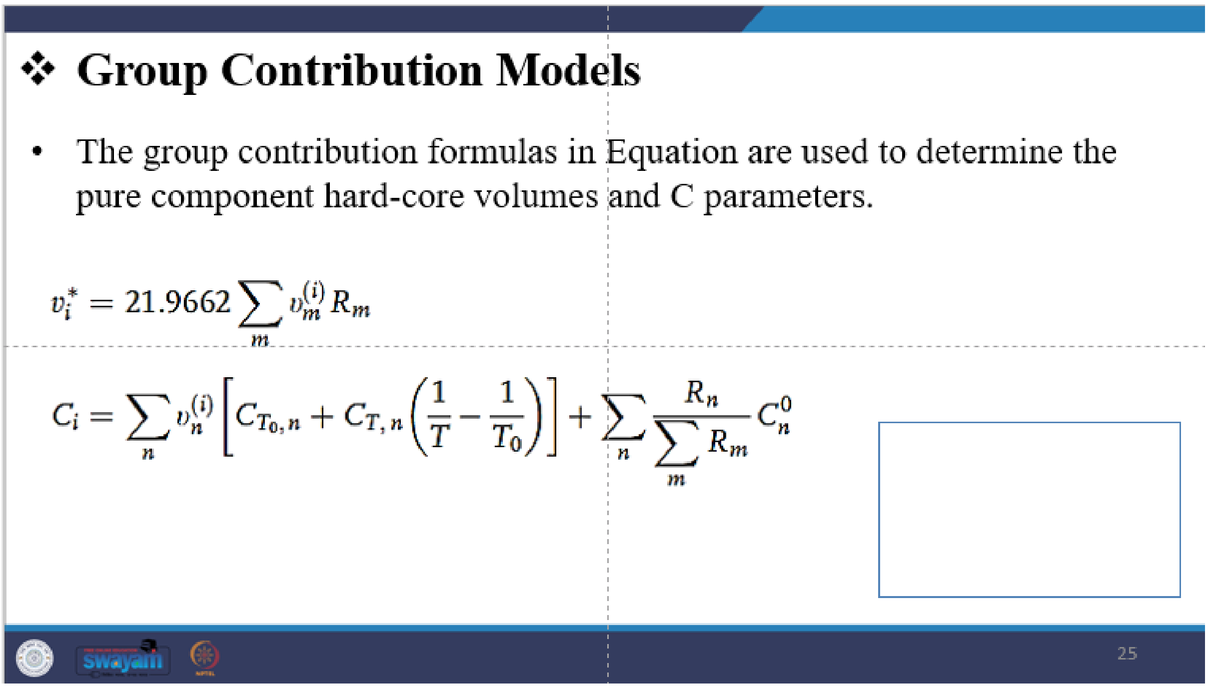


❖ Group Contribution Models

- The molar hard-core v* is calculated from the pure component hard-core molar volumes v^*_i using a linear mixing rule.
- The same type of mixing rule is used for the number of external degrees of freedom parameter C.

$$v^* = \sum_i x_i v_i^*$$

$$C = \sum_i x_i C_i$$



❖ Group Contribution Models

- The group contribution formulas in Equation are used to determine the pure component hard-core volumes and C parameters.

$$v_i^* = 21.9662 \sum_m \upsilon_m^{(i)} R_m$$

$$C_i = \sum_n \upsilon_n^{(i)} \left[C_{T_0,n} + C_{T,n} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] + \sum_n \frac{R_n}{\sum_m R_m} C_n^0$$

$$v^* = \sum_i x_i v_i^*$$

$$C = \sum_i x_i C_i$$

$$v_i^* = 21.9662 \sum_m v_m^{(i)} R_m$$

$$C_i = \sum_n v_n^{(i)} \left[C_{T_0,n} + C_{T,n} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] + \sum_n \frac{R_n}{\sum_m R_m} C_n^0$$

9662 summation of m V m i R m and C i is equal to the summation of n V n C t naught n plus C t n 1 over t minus 1 over t naught is equal to this summation n R n over summation m R m C n naught. Now here, the V i is the number of groups of type in n molecules i t naught is the reference temperature R n is the normalized volume of the group n used in the UNIFAC model. Now the attraction term sometimes E_{attr} is related to the UNIFAC model and Z is the lattice country coordination number chosen to be equal to 10 and q i the surface area of the molecule i which is given by this attraction term is equal to summation i half Z q i X i plus summation j theta j e to the power delta minus delta over R t delta epsilon j i over summation k theta k exponential minus delta over R t minus 3 R l n 1 by 3 minus 1 summation i X i summation n V n C t n. Now q i this is can be represented as V n q n q n is the normalized to wander wall surface of group n as in the uni-fact and the interaction energy parameter this epsilon j i and epsilon delta epsilon j i is given by the equations epsilon over nu and delta epsilon i j is equal to epsilon i j minus i i. Now where this epsilon naught j i is given by j i j epsilon n m and epsilon n m is equal to minus epsilon n epsilon m to the power half plus delta epsilon n m.

$$E^{attr} = \sum_i \frac{1}{2} z q_i x_i \left[\varepsilon_{ii} + \frac{\sum_j \theta_j \exp(-\Delta\varepsilon_{ji}/RT)\Delta\varepsilon_{ji}}{\sum_k \theta_k \exp(-\Delta\varepsilon_{ki}/RT)} \right] - 3R \ln\left(\frac{\tilde{v}^{1/3} - 1}{\tilde{v}} \right) \sum_i \left(x_i \sum_n v_n^{(i)} C_{T,n} \right)$$

❖ Group Contribution Models

- The attraction term E_{attr} is related to the UNIFAC mode, z is the lattice coordination number, chosen to be equal to 10, and q_i, the surface area of molecule i, is given by

$$E^{attr} = \sum_i \frac{1}{2} z q_i x_i \left[\varepsilon_{ii} + \frac{\sum_j \theta_j \exp(-\Delta\varepsilon_{ji}/RT)\Delta\varepsilon_{ji}}{\sum_k \theta_k \exp(-\Delta\varepsilon_{ki}/RT)} \right] - 3R \ln\left(\frac{\tilde{v}^{1/3}-1}{\tilde{v}}\right) \sum_i \left(x_i \sum_n v_n^{(i)} C_{T,n} \right)$$

❖ Group Contribution Models

$$q_i = \sum_n v_n^{(i)} Q_n$$

Q_n is the normalized van der Waals surface of group n, as in UNIFAC. The interaction energy parameters ϵ_{ji} and $\Delta\epsilon_{ji}$ are given by Eqs

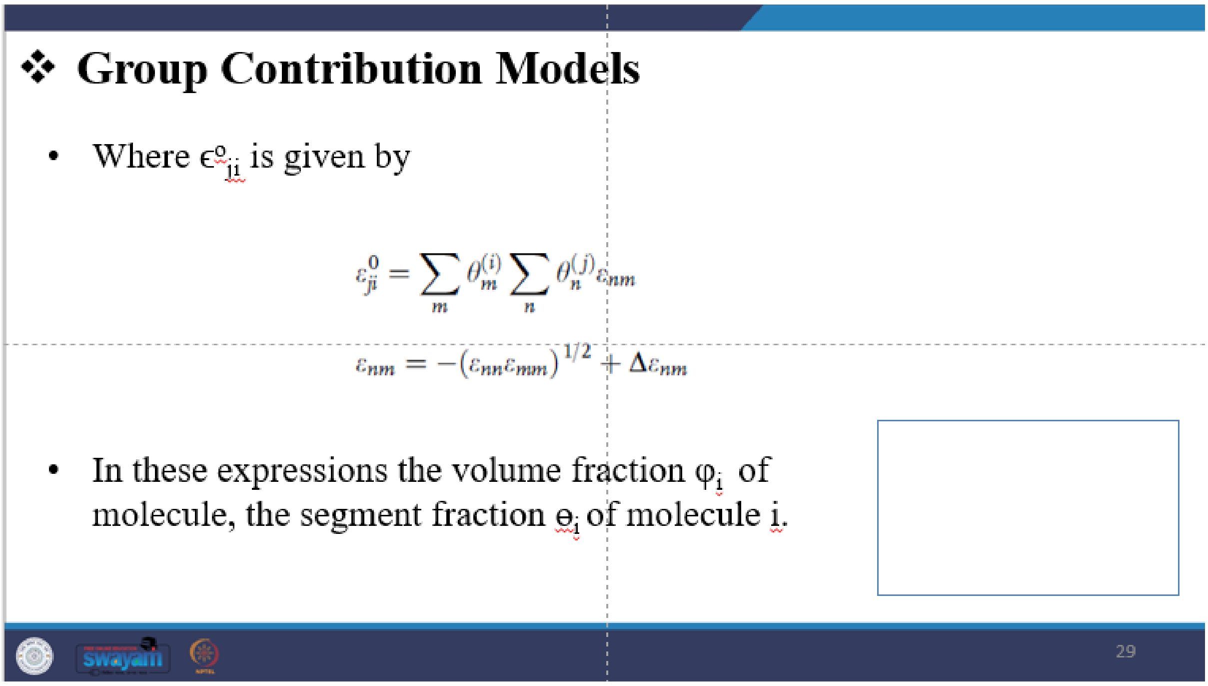
$$\varepsilon_{ij} = \frac{\varepsilon_{ij}^0}{\tilde{v}} \quad \text{and} \quad \Delta\varepsilon_{ij} = \varepsilon_{ij} - \varepsilon_{ii}$$

$$q_i = \sum_n v_n^{(i)} Q_n$$

$$\varepsilon_{ij} = \frac{\varepsilon_{ij}^0}{\tilde{v}} \quad \text{and} \quad \Delta\varepsilon_{ij} = \varepsilon_{ij} - \varepsilon_{ii}$$

$$\varepsilon_{ji}^{0} = \sum_{m} \theta_{m}^{(i)} \sum_{n} \theta_{n}^{(j)} \varepsilon_{nm}$$

$$\varepsilon_{nm} = -\left(\varepsilon_{nn}\varepsilon_{mm}\right)^{1/2} + \Delta\varepsilon_{nm}$$



❖ Group Contribution Models

- Where ϵ^{o}_{ji} is given by

$$\varepsilon_{ji}^{0} = \sum_{m} \theta_{m}^{(i)} \sum_{n} \theta_{n}^{(j)} \varepsilon_{nm}$$

$$\varepsilon_{nm} = -\left(\varepsilon_{nn}\varepsilon_{mm}\right)^{1/2} + \Delta\varepsilon_{nm}$$

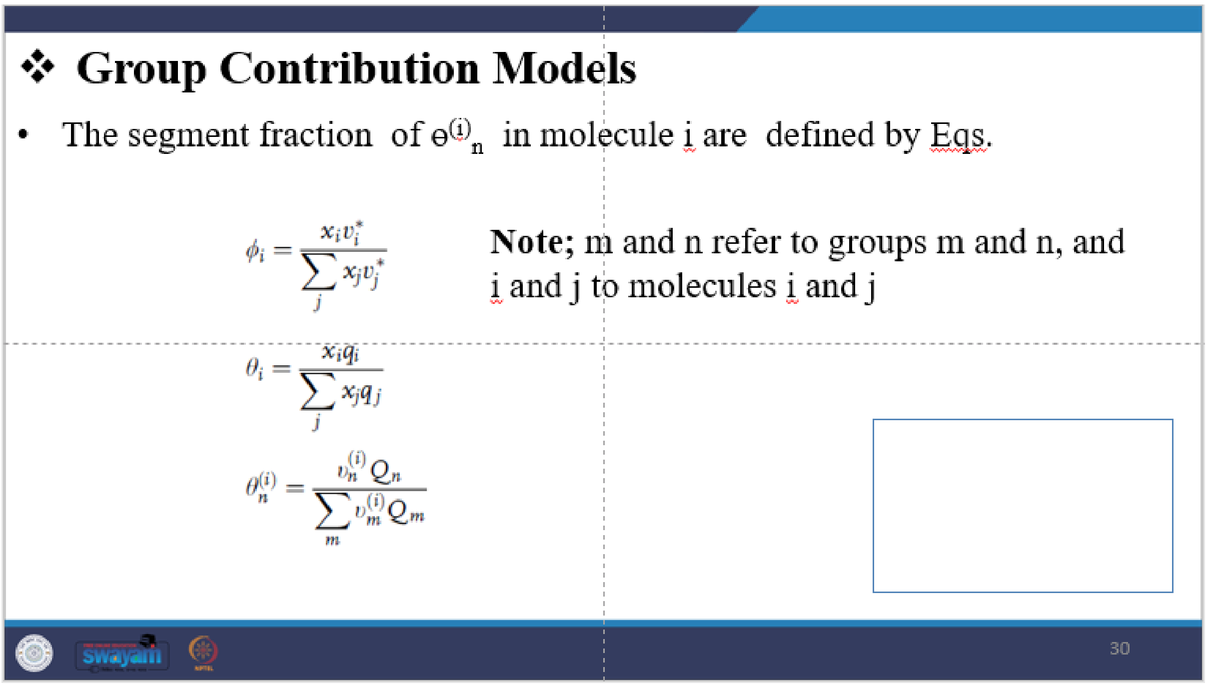
- In these expressions the volume fraction φ_i of molecule, the segment fraction θ_i of molecule i.

These expressions the volume fraction psi of the molecule and the segment fraction theta i of the molecule i. Now the segment fraction in the theta n in the molecule they are defined by the equation phi i is equal to X i V i star over j X j V j the reference then theta i is equal to X i q i over summation j X i q j then theta n i is equal to V n i q n over summation m V m i into q m. The resulting expression for the free volume contribution and the residual contribution in the activity coefficient is given by ln m i is equal to 3 1 plus c i l n 1 by 3 minus 1 over minus c i l n V i over V and l n gamma i residual is equal to 1 over to Z q i 1 over R T epsilon minus epsilon i i V i plus 1 minus l n summation j theta j e to the power minus delta epsilon j i over R T minus summation j theta j e to the power minus delta epsilon j i over R T over theta k e to the power minus delta epsilon k i over R T. This is summation. Now, this graph comprises or compares the experimentally determined solvent activity of the system for the polypropylene oxide benzene at 347.85.

$$\phi_i = \frac{x_i v_i^*}{\sum_j x_j v_j^*}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

$$\theta_n^{(i)} = \frac{v_n^{(i)} Q_n}{\sum_m v_m^{(i)} Q_m}$$



❖ Group Contribution Models

- The segment fraction of $\theta^{(i)}_n$ in molecule i are defined by Eqs.

$$\phi_i = \frac{x_i v_i^*}{\sum_j x_j v_j^*}$$

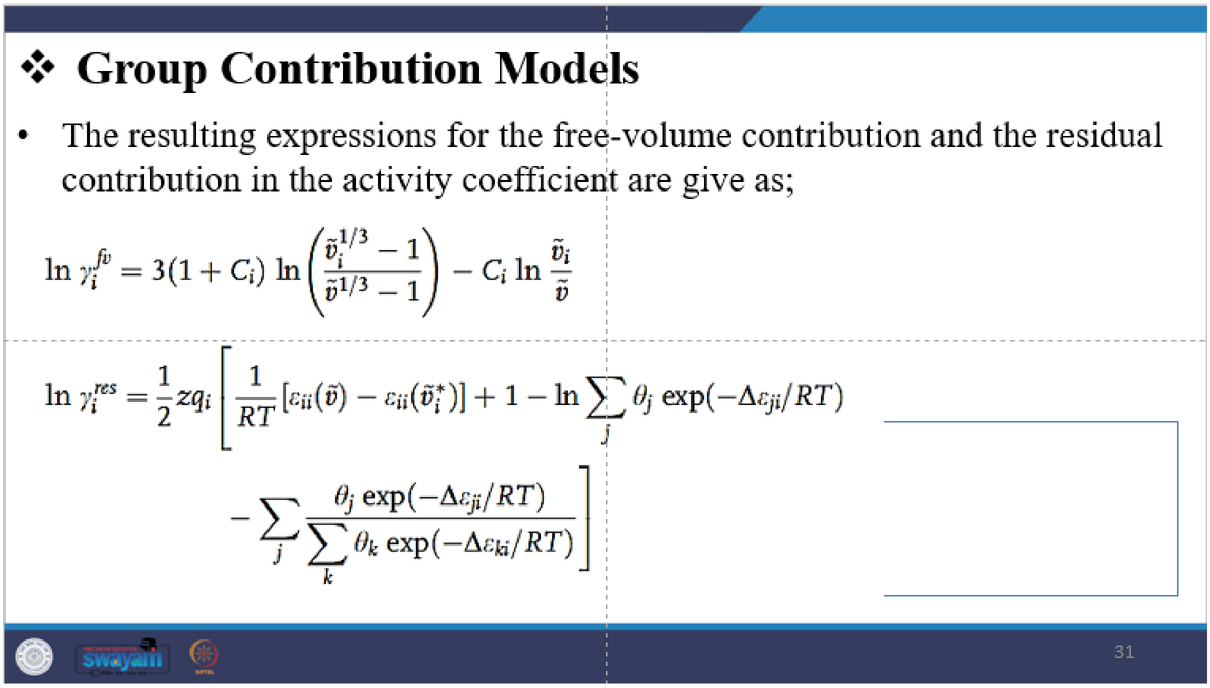
Note; m and n refer to groups m and n, and i and j to molecules i and j

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

$$\theta_n^{(i)} = \frac{v_n^{(i)} Q_n}{\sum_m v_m^{(i)} Q_m}$$

$$\ln \gamma_i^{fv} = 3(1 + C_i) \ln \left(\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}^{1/3} - 1} \right) - C_i \ln \frac{\tilde{v}_i}{\tilde{v}}$$

$$\ln \gamma_i^{res} = \frac{1}{2} z q_i \left[\frac{1}{RT} [\varepsilon_{ii}(\tilde{v}) - \varepsilon_{ii}(\tilde{v}_i^*)] + 1 - \ln \sum_j \theta_j \exp(-\Delta\varepsilon_{ji}/RT) \right.$$
$$\left. - \sum_j \frac{\theta_j \exp(-\Delta\varepsilon_{ji}/RT)}{\sum_k \theta_k \exp(-\Delta\varepsilon_{ki}/RT)} \right]$$

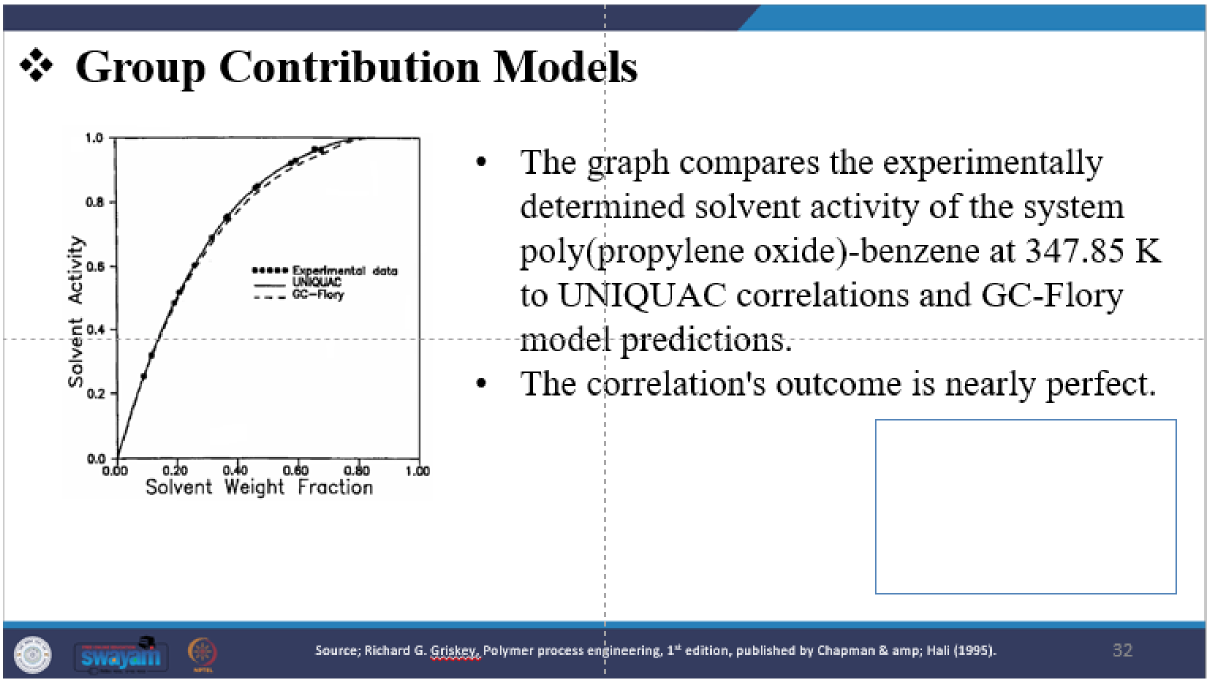


❖ Group Contribution Models

- The resulting expressions for the free-volume contribution and the residual contribution in the activity coefficient are give as;

$$\ln \gamma_i^{fv} = 3(1+C_i)\ln\left(\frac{\tilde{v}_i^{1/3}-1}{\tilde{v}^{1/3}-1}\right) - C_i \ln\frac{\tilde{v}_i}{\tilde{v}}$$

$$\ln \gamma_i^{res} = \frac{1}{2} z q_i \left[\frac{1}{RT}[\varepsilon_{ii}(\tilde{v}) - \varepsilon_{ii}(\tilde{v}_i^*)] + 1 - \ln \sum_j \theta_j \exp(-\Delta\varepsilon_{ji}/RT) - \sum_j \frac{\theta_j \exp(-\Delta\varepsilon_{ji}/RT)}{\sum_k \theta_k \exp(-\Delta\varepsilon_{ki}/RT)} \right]$$



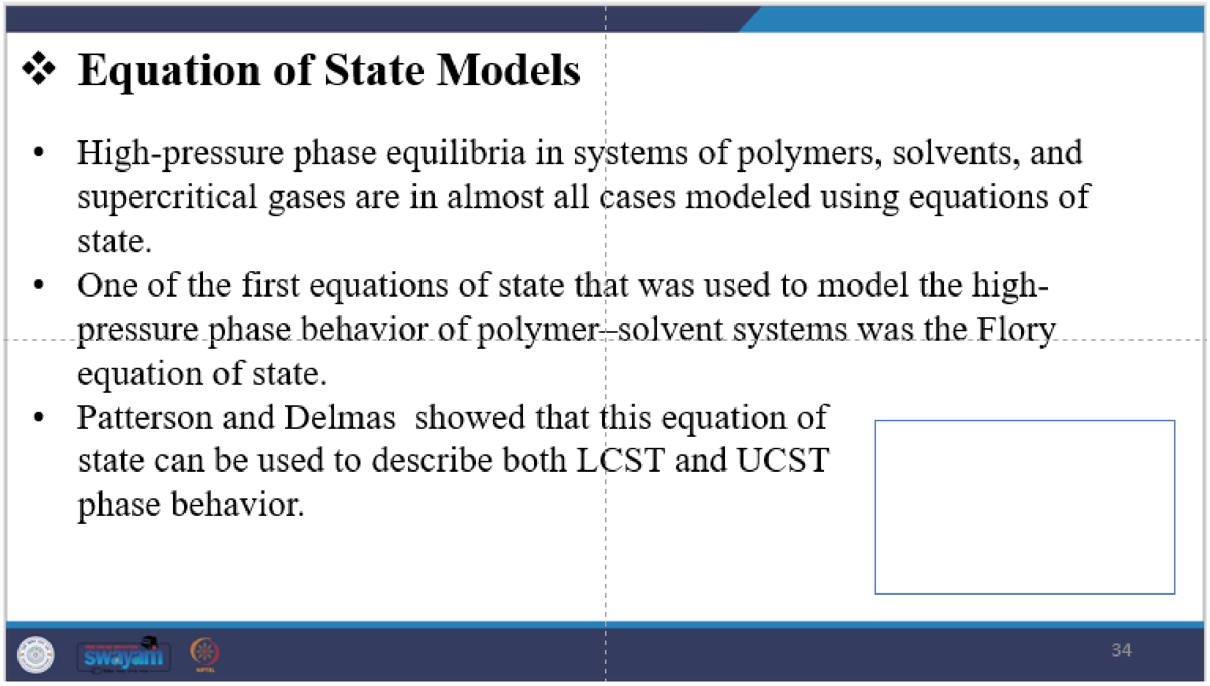
❖ Group Contribution Models

- The graph compares the experimentally determined solvent activity of the system poly(propylene oxide)-benzene at 347.85 K to UNIQUAC correlations and GC-Flory model predictions.
- The correlation's outcome is nearly perfect.

Source; Richard G. Griskey, Polymer process engineering, 1st edition, published by Chapman & amp; Hall (1995).

Kelvin at UNIFAC correlation, and this correlations outcome is nearly perfect. And this particular graph illustrates the agreement between the predictions made by this group contribution flow remodel for the homopolymer solvent system and experimental solvent activity coefficient at infinite dilution. Now, let us talk about the equation state model. The high-pressure phase equilibria in system of polymeric system or solvent and supercritical gases they are almost in all cases modelled using the equation of state. So, one of the first equation of state that was used to model the high-pressure phase behaviour of polymer solvent system was the flow equation of state.

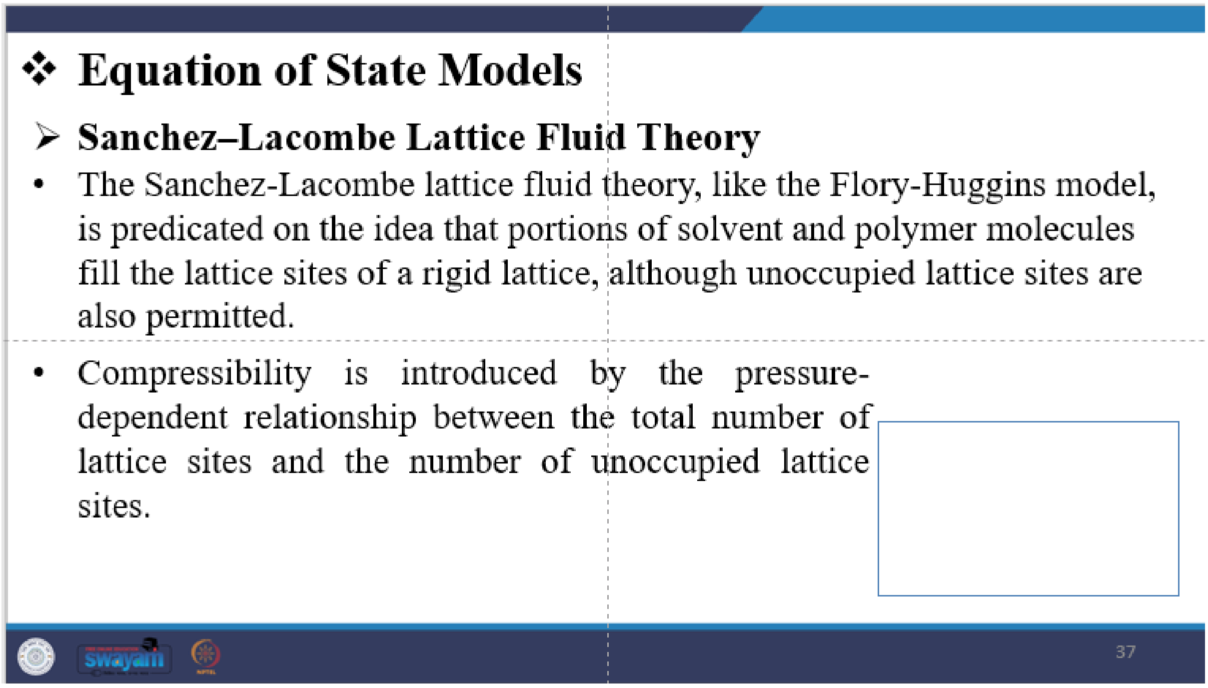
And Patterson and Delmas they showed the equation of state can be used to describe both LCST and UCST phase behaviour. And some of the co-workers they created the perturbed hard chain theory. It can be used to model the phase behaviour of mixture for small and big molecules including the polymer across a wide range of pressure and temperature. Now, this can be seen as an advance over the method of Flory and co-worker. Now, basically there are two equation of state methods the relatively simple that is Sanchez Locombe Lattice Fluid Model and statistical associated Flory Fluid Theory that is which has now become one of the standard equations of state for the polymeric system.



❖ Equation of State Models

- High-pressure phase equilibria in systems of polymers, solvents, and supercritical gases are in almost all cases modeled using equations of state.
- One of the first equations of state that was used to model the high-pressure phase behavior of polymer–solvent systems was the Flory equation of state.
- Patterson and Delmas showed that this equation of state can be used to describe both LCST and UCST phase behavior.

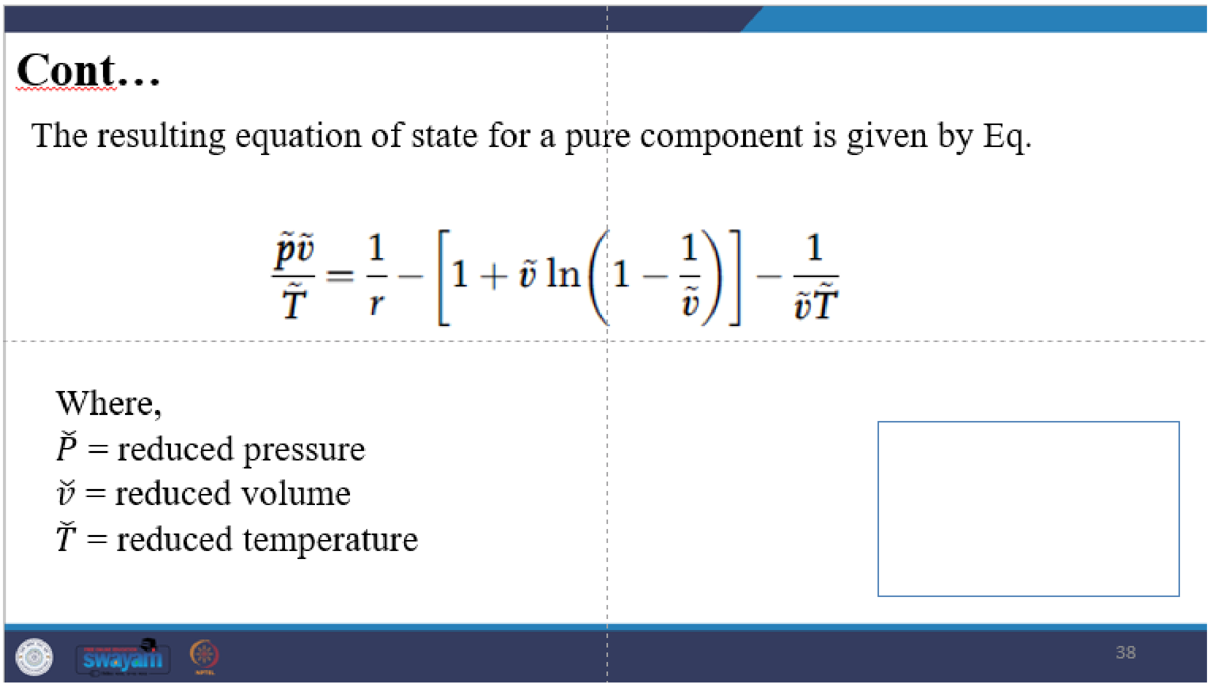
Now, Sanchez Locombe Lattice Fluid Theory this theory like the Flory Huggins model it is predicting the idea of portion of solvent and polymer molecule to fill the lattice sites of a rigid lattice although unoccupied lattice sites are also permitted. Now, the compressibility is also introduced by the pressure dependent relationship between the total number of lattice sites and number of unoccupied lattice sites. So, the resulting equation for the pure component is given by p v over t is equal to 1 over r minus 1 plus v ln 1 minus 1 v 1 over v t where p is the reduced pressure this one and this is the reduced volume and this is the reduced temperature.



❖ Equation of State Models

➢ Sanchez–Lacombe Lattice Fluid Theory

- The Sanchez-Lacombe lattice fluid theory, like the Flory-Huggins model, is predicated on the idea that portions of solvent and polymer molecules fill the lattice sites of a rigid lattice, although unoccupied lattice sites are also permitted.
- Compressibility is introduced by the pressure-dependent relationship between the total number of lattice sites and the number of unoccupied lattice sites.



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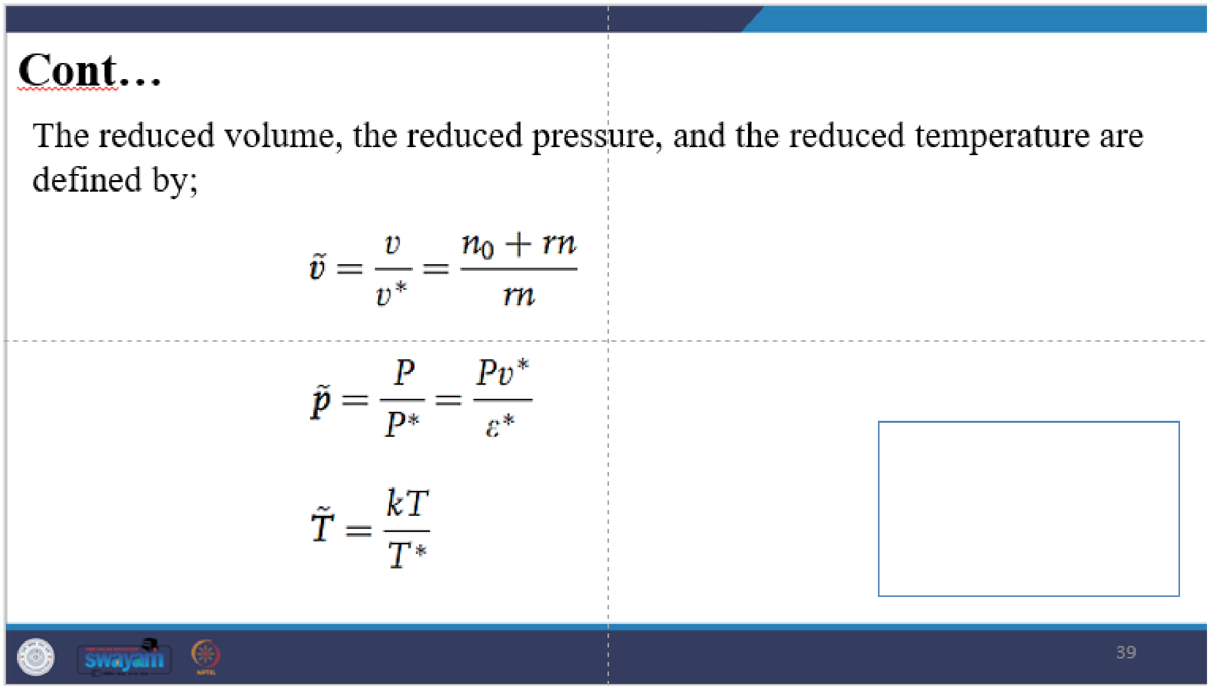
The resulting equation of state for a pure component is given by Eq.

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{1}{r} - \left[1 + \tilde{v}\ln\left(1 - \frac{1}{\tilde{v}}\right)\right] - \frac{1}{\tilde{v}\tilde{T}}$$

Where,
$\breve{P}$ = reduced pressure
$\breve{v}$ = reduced volume
$\breve{T}$ = reduced temperature

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{1}{r} - \left[1 + \tilde{v}\ln\left(1 - \frac{1}{\tilde{v}}\right)\right] - \frac{1}{\tilde{v}\tilde{T}}$$

Now, the reduced volume and a reduced pressure and this can be defined as bar v is equal to v over v standard which is equal to n naught plus r n over r n and reduced pressure can be defined as p over this standard pressure this is p v standard pressure silent and this reduced temperature is defined as k t over t star. The parameters with this standard is called the characteristics parameter and the practice r of the number of segments per molecule epsilon this is the interaction energy parameter and v star is the molar volume of the lattice site they are used as the independent pure component parameter and n is the number of moles of the component and n naught is the number of moles of vacant lattice site.



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The reduced volume, the reduced pressure, and the reduced temperature are defined by;

$$\tilde{v} = \frac{v}{v^*} = \frac{n_0 + rn}{rn}$$

$$\tilde{p} = \frac{P}{P^*} = \frac{Pv^*}{\varepsilon^*}$$

$$\tilde{T} = \frac{kT}{T^*}$$

$$\tilde{v} = \frac{v}{v^*} = \frac{n_0 + rn}{rn}$$

$$\tilde{p} = \frac{P}{P^*} = \frac{Pv^*}{\varepsilon^*}$$

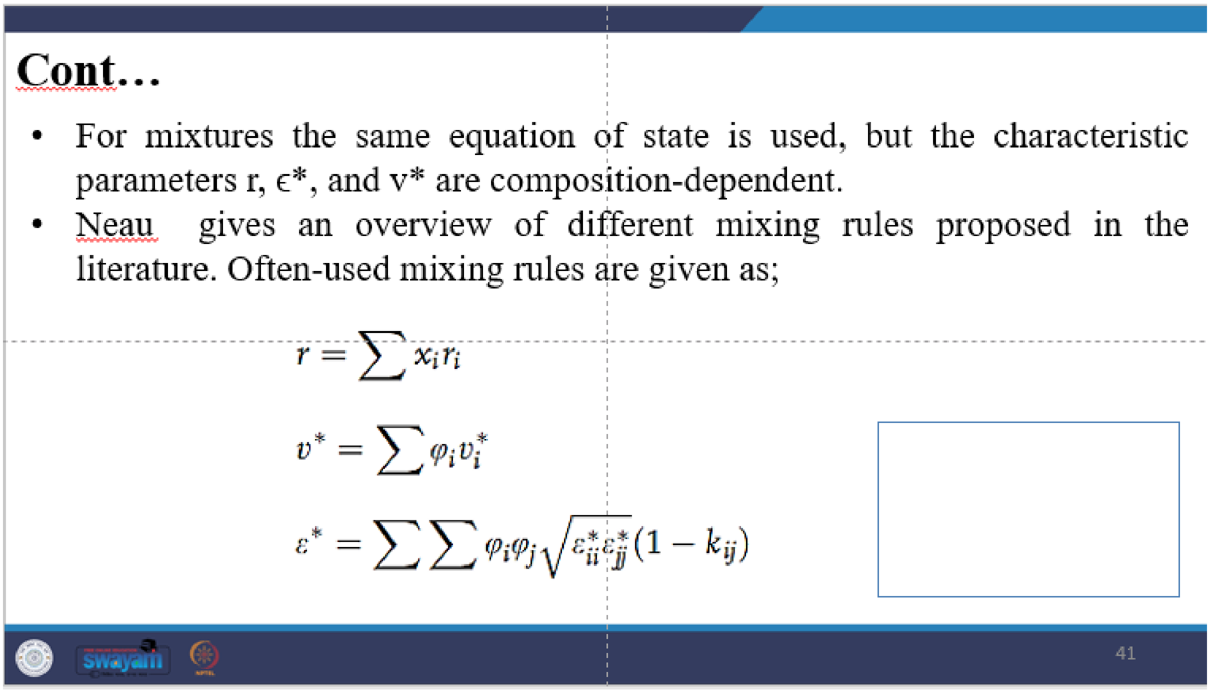
$$\tilde{T} = \frac{kT}{T^*}$$

Now, for mixture of same equation of state is used, but the characteristics parameter r epsilon star and v star are composition dependent. So, the new this give an overview of different mixing rule proposed and the literature and often used mixing rules this can be given as r is equal to summation of x i r i v star is given as psi i v i and epsilon star is given as summation of psi i psi j roots of epsilon j epsilon i i at the standard condition then epsilon j j its standard condition 1 minus k i j. Now, this kij is the adjustable binary interaction parameter which equals to 0 for i is equal to j. Now, the segment fraction of j i for the component psi is given by psi i is equal to x i r i over summation x i r i. Now, according to new the correct expression for the fugacity coefficient of the model given by ln psi i is equal to minus ln z plus r i minus 2 1 over v t minus ln 1 minus 1 over v plus z minus 1 over x j r j into n r over v star del v over del n i n j is not equal to n i minus 1 over v t into n r over epsilon del epsilon star over del n i n j is not equal to n i.

$$r = \sum x_i r_i$$

$$v^* = \sum \varphi_i v_i^*$$

$$\varepsilon^* = \sum \sum \varphi_i \varphi_j \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*}(1 - k_{ij})$$



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- For mixtures the same equation of state is used, but the characteristic parameters r, ϵ*, and v* are composition-dependent.
- Neau gives an overview of different mixing rules proposed in the literature. Often-used mixing rules are given as;

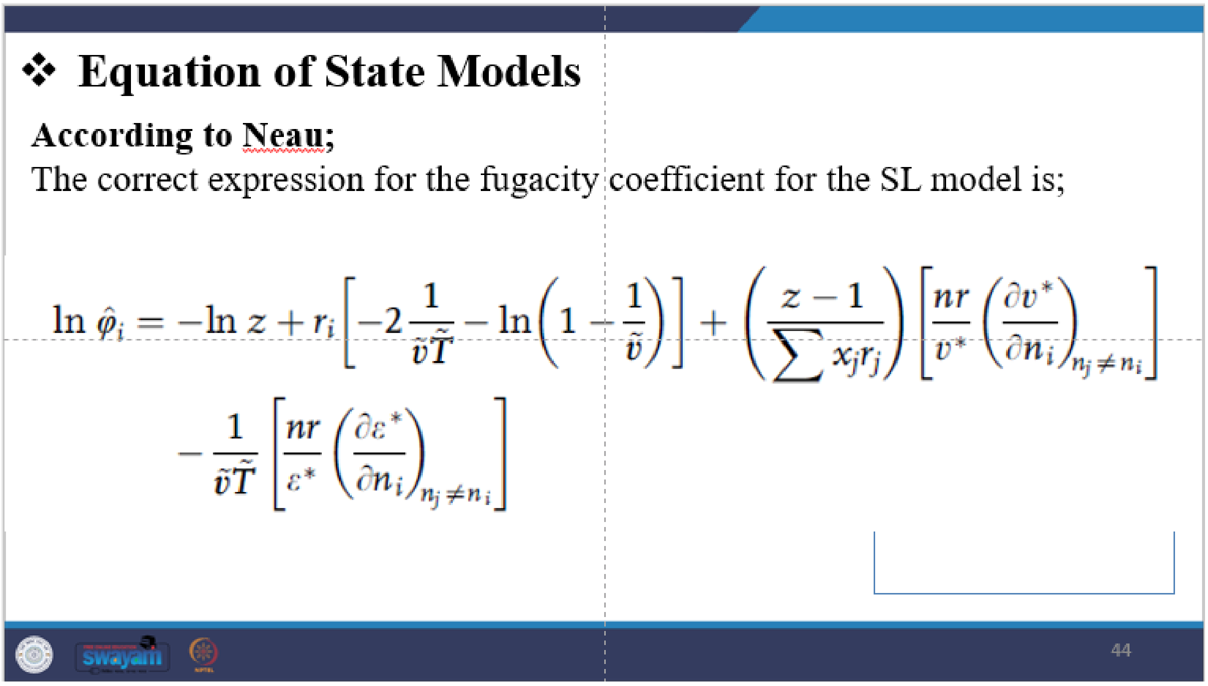
$$r = \sum x_i r_i$$

$$v^* = \sum \varphi_i v_i^*$$

$$\varepsilon^* = \sum \sum \varphi_i \varphi_j \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*}(1 - k_{ij})$$

$$\varphi_i = \frac{x_i r_i}{\sum x_i r_i}$$

$$\ln \hat{\varphi}_i = -\ln z + r_i\left[-2\frac{1}{\tilde{v}\tilde{T}} - \ln\left(1 - \frac{1}{\tilde{v}}\right)\right] + \left(\frac{z-1}{\sum x_j r_j}\right)\left[\frac{nr}{v^*}\left(\frac{\partial v^*}{\partial n_i}\right)_{n_j \neq n_i}\right] - \frac{1}{\tilde{v}\tilde{T}}\left[\frac{nr}{\varepsilon^*}\left(\frac{\partial \varepsilon^*}{\partial n_i}\right)_{n_j \neq n_i}\right]$$



❖ Equation of State Models

According to Neau;

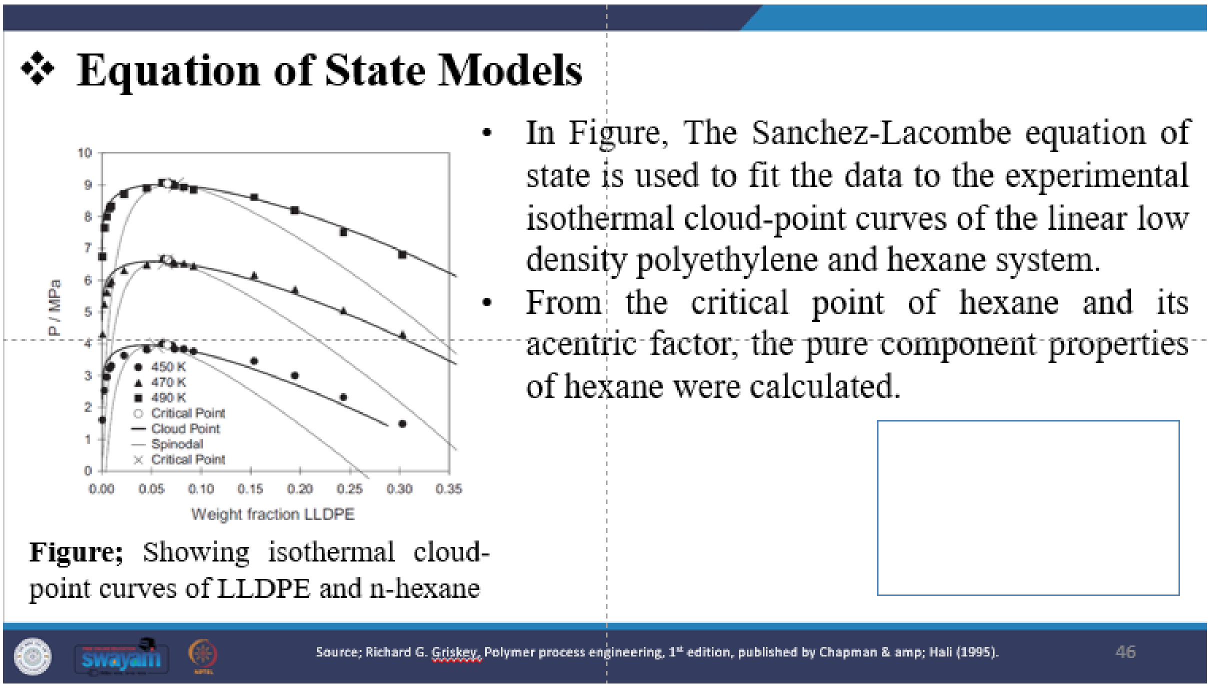
The correct expression for the fugacity coefficient for the SL model is;

$$\ln \hat{\varphi}_i = -\ln z + r_i\left[-2\frac{1}{\tilde{v}\tilde{T}} - \ln\left(1 - \frac{1}{\tilde{v}}\right)\right] + \left(\frac{z-1}{\sum x_j r_j}\right)\left[\frac{nr}{v^*}\left(\frac{\partial v^*}{\partial n_i}\right)_{n_j \neq n_i}\right] - \frac{1}{\tilde{v}\tilde{T}}\left[\frac{nr}{\varepsilon^*}\left(\frac{\partial \varepsilon^*}{\partial n_i}\right)_{n_j \neq n_i}\right]$$

Now, the compressibility factor because sometimes it is always required to assess the deviation from the ideal behaviour this can be given by p v over R T that is reduced pressure reduced volume and reduced temperature R.

$$z = \frac{Pv}{RT} = \frac{\tilde{p}\tilde{v}}{\tilde{T}}r$$

Now, in this particular figure the Sanchez-Lokambe equation of state is used to fit the data for to the experimental isothermal cloud point curves in the linear low density. Now, the p v t data and the data shown in this particular graph they are simultaneously fitted to yield the polymers pure component properties and the equations that were resolved there were those of Koch and Henderman described the temperature they had the linear relationship with the binary interaction parameters.

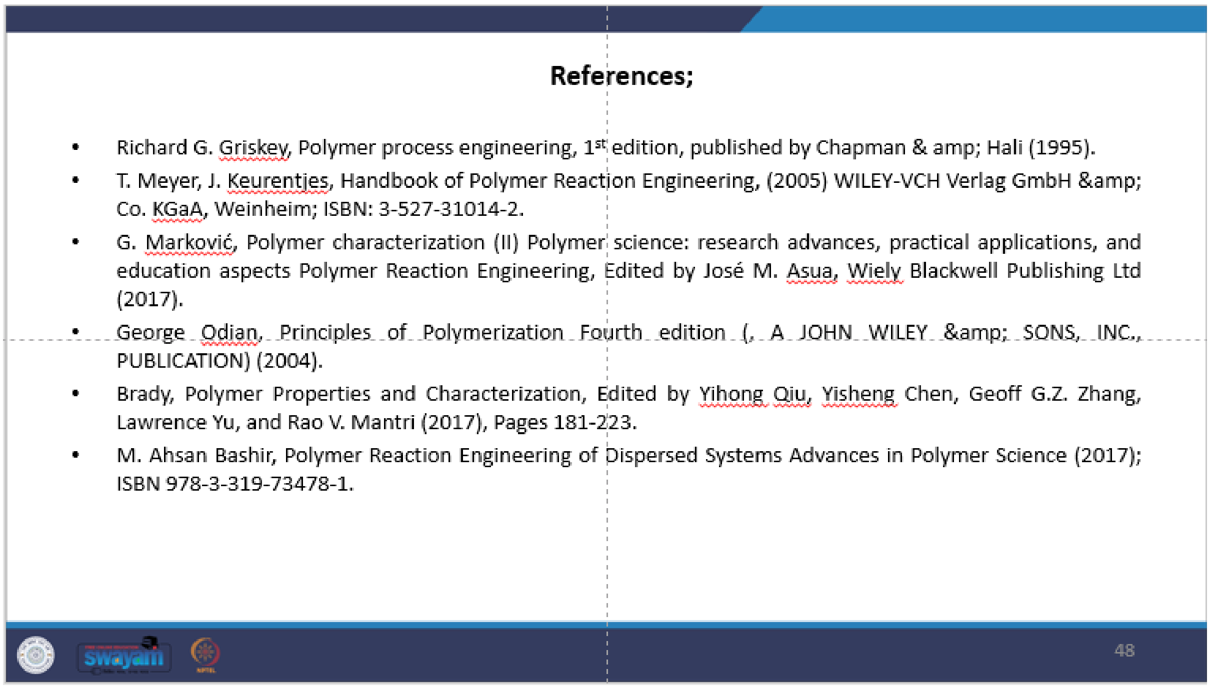


❖ Equation of State Models

- In Figure, The Sanchez-Lacombe equation of state is used to fit the data to the experimental isothermal cloud-point curves of the linear low density polyethylene and hexane system.
- From the critical point of hexane and its acentric factor, the pure component properties of hexane were calculated.

Figure; Showing isothermal cloud-point curves of LLDPE and n-hexane

Source; Richard G. Griskey, Polymer process engineering, 1st edition, published by Chapman & amp; Hali (1995).



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So, dear friend, in this particular segment, we discussed the different model for the polymeric system, and we see how this equation of state play a vital role in predicting the thermodynamic behaviour of the polymeric system. We have enlisted several references you can utilize these references as per your need. Thank you very much.