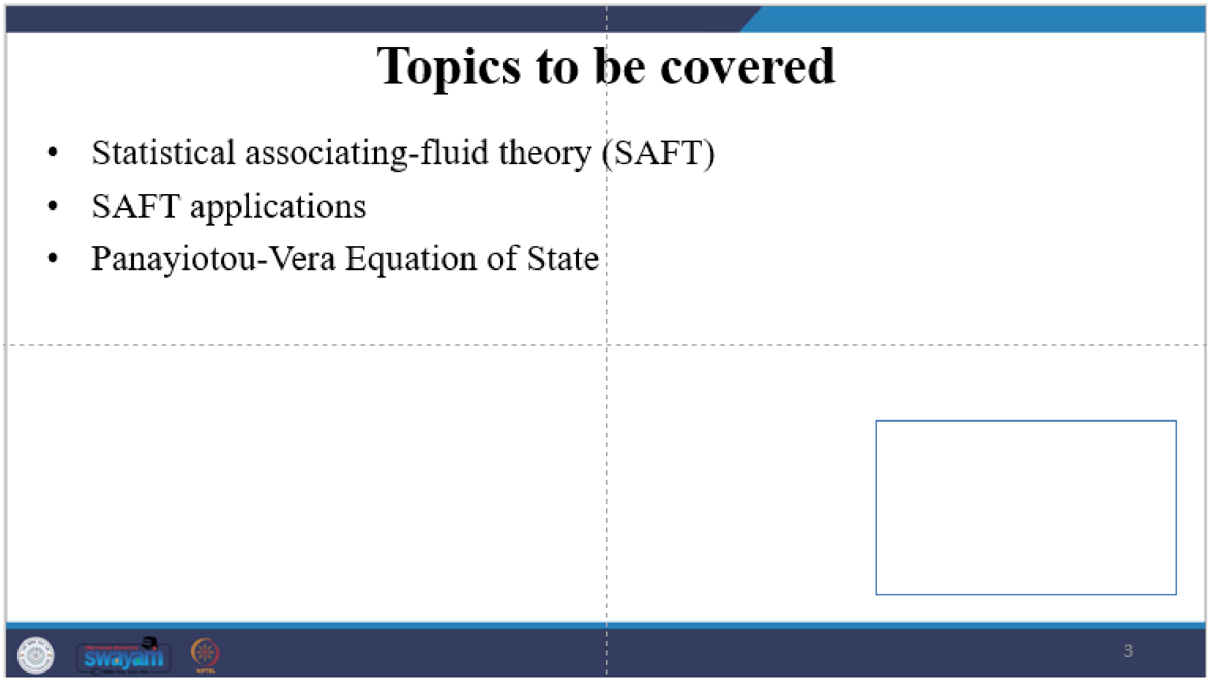
Polymer Process Engineering

Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology-Roorkee

Lecture – 09
Thermodynamics of polymer systems-IV

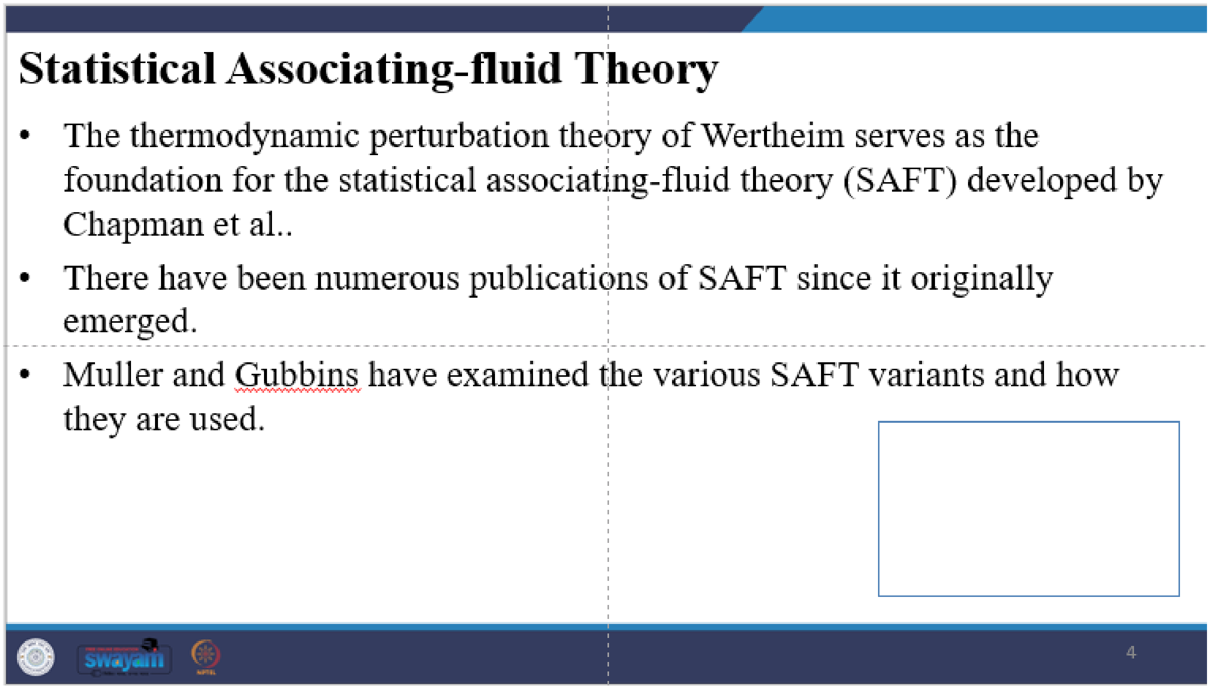
Hello friends, welcome to the fourth segment of thermodynamics of a polymeric system, under the edges of polymer process engineering. Now, in the previous lectures, we covered the activity coefficient models; we discussed the Flory Huggins theory because we were discussing the different thermodynamic models, that can predict the behavior of the polymeric system. We discussed the Hansen solubility parameters and developed the correlation for solvent activity. We discussed the group contribution model and discussed about the equation of a state model. In this particular segment, we are going to discuss the statistical associating fluid theory that is called SAFT.



Topics to be covered

- Statistical associating-fluid theory (SAFT)
- SAFT applications
- Panayiotou-Vera Equation of State

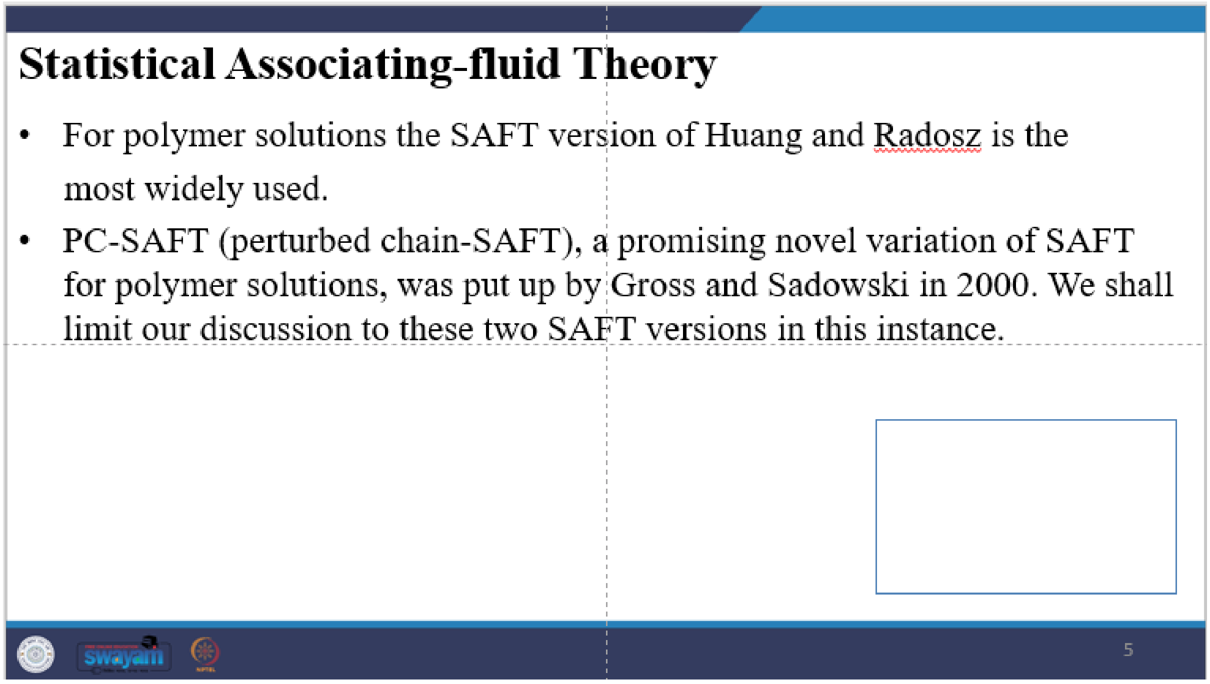
Then, we will discuss the shaft application, and we will discuss the Vera equation of state. Now, let us talk about the statistical associating fluid theory, the thermodynamic perturbation theory, which is given by various workers. These are the foundations of statistical associating fluid theory. This is developed by Chapman and co-workers.



Statistical Associating-fluid Theory

- The thermodynamic perturbation theory of Wertheim serves as the foundation for the statistical associating-fluid theory (SAFT) developed by Chapman et al..
- There have been numerous publications of SAFT since it originally emerged.
- Muller and Gubbins have examined the various SAFT variants and how they are used.

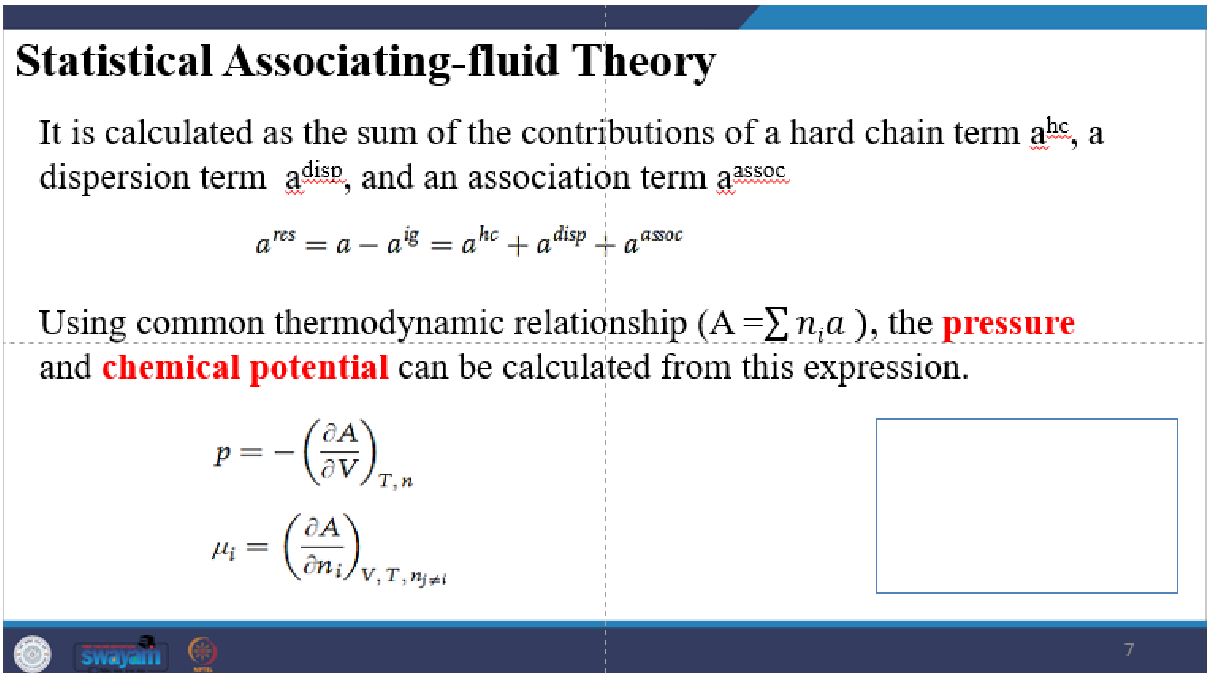
There have been several numerous publications in this SAFT theory, it originally emerged and Muller and Gabbins, they have examined the various SAFT variants and how they are used. Now, for polymeric solutions, the SAFT version of HONG and RADS is used to most widely. The PC-SAF, it is perturbed chain SAFT, a promising novel variation of SAFT for polymer solution. This was put by the Gross and Sadosky in 2000. Now, we shall limit our discussion because this is the latest one.



Statistical Associating-fluid Theory

- For polymer solutions the SAFT version of Huang and Radosz is the most widely used.
- PC-SAFT (perturbed chain-SAFT), a promising novel variation of SAFT for polymer solutions, was put up by Gross and Sadowski in 2000. We shall limit our discussion to these two SAFT versions in this instance.

So, we shall limit our discussion to these two SAFT versions in this particular instance. Now, both the equation of state can be expressed as distinct contributions to the Muller Helmholtz energy because of fundamental components are equal. The difference between the system Muller Helmholtz energy and its Muller Helmholtz energy in an ideal gas state under the same temperature, pressure, and composition is known as the Muller residual Helmholtz energy which is represented as A residual. Now, it is calculated as the sum of the contribution of hard chain terms a^{HC}, this is referred as a^{HC}, and a dispersion term adispersion and the associated term or association term A association. So, this can be represented as a minus a, a^{HC} plus a dispersion plus a.



Statistical Associating-fluid Theory

It is calculated as the sum of the contributions of a hard chain term a^{hc}, a dispersion term a^{disp}, and an association term a^{assoc}

$$a^{res} = a - a^{ig} = a^{hc} + a^{disp} + a^{assoc}$$

Using common thermodynamic relationship ($A = \sum n_i a$), the **pressure** and **chemical potential** can be calculated from this expression.

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,n}$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}}$$

$$a^{res} = a - a^{ig} = a^{hc} + a^{disp} + a^{assoc}$$

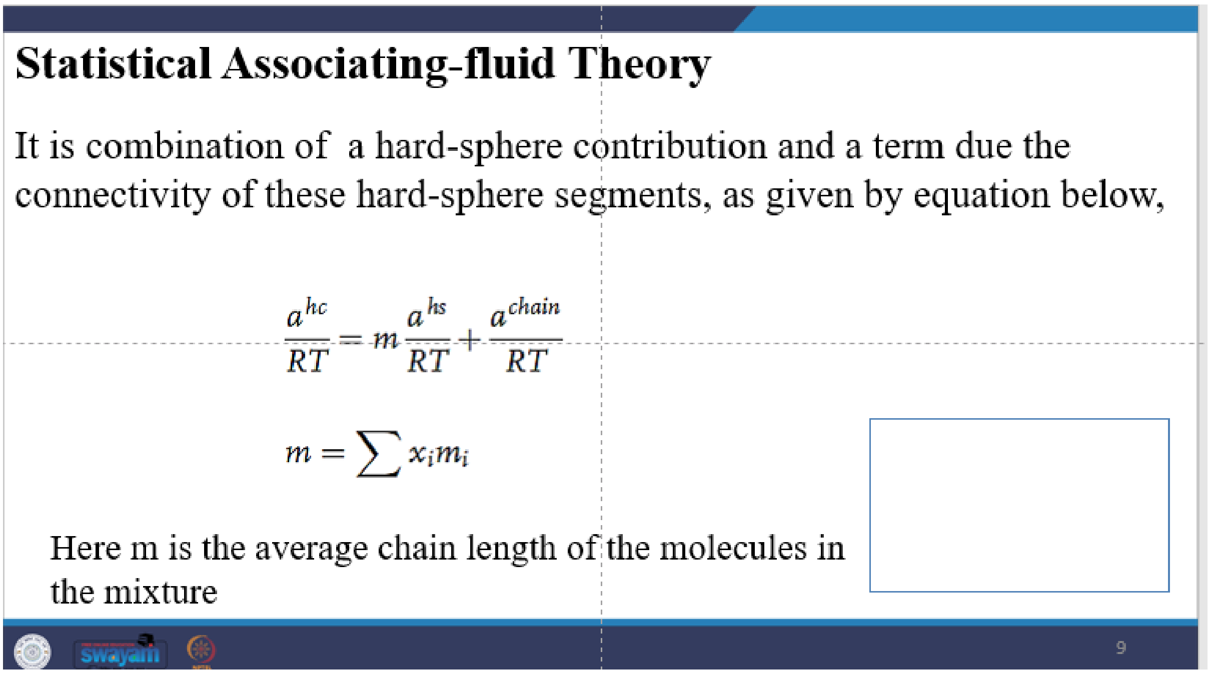
$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,n}$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}}$$

Now using the common thermodynamic relationship that is A is equal to summation n i A, the pressure and a chemical potential can be calculated from the expression which is we are going to write p is equal to minus del A over del v at constant temperature n and mu i that is the chemical potential del A over del n i v t. Now, the shaft and PC shaft that is hard chain term, this chain in the molecular model underlying the shaft is made up of two hard sphere segments, the covalent bond over these portions of hard sphere together and both shaft version hard sphere term is the result of two contributions. Now, the statistical associating fluid theory, it is the combination of hard sphere contribution and a term due the conductivity of these hard sphere segment which is given by AHC over RT this is equal to m AHS over RT plus A over RT and m is equal to psi m i, where m is the average chain length of molecule in the mixture. The hard sphere contribution AHS is shown by Boublik-Mansoori this hard-sphere contribution of state for a mixture of hard spheres. Now, this can be represented as AHS over RT 6 pi rho 2, 1, where psi r 2 square over 1 minus rho.

$$\frac{a^{hc}}{RT} = m\frac{a^{hs}}{RT} + \frac{a^{chain}}{RT}$$

$$m = \sum x_i m_i$$



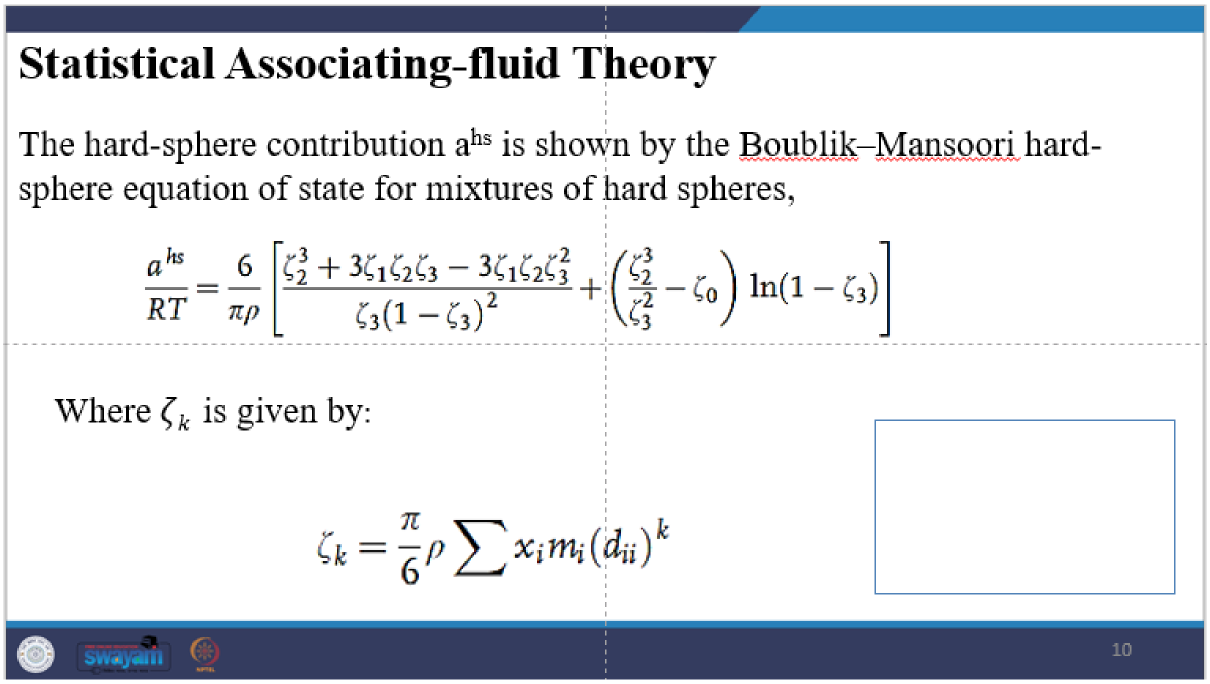
Statistical Associating-fluid Theory

It is combination of a hard-sphere contribution and a term due the connectivity of these hard-sphere segments, as given by equation below,

$$\frac{a^{hc}}{RT} = m\frac{a^{hs}}{RT} + \frac{a^{chain}}{RT}$$

$$m = \sum x_i m_i$$

Here m is the average chain length of the molecules in the mixture



Statistical Associating-fluid Theory

The hard-sphere contribution a^{hs} is shown by the Boublik–Mansoori hard-sphere equation of state for mixtures of hard spheres,

$$\frac{a^{hs}}{RT} = \frac{6}{\pi\rho}\left[\frac{\zeta_2^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2\zeta_3^2}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1-\zeta_3)\right]$$

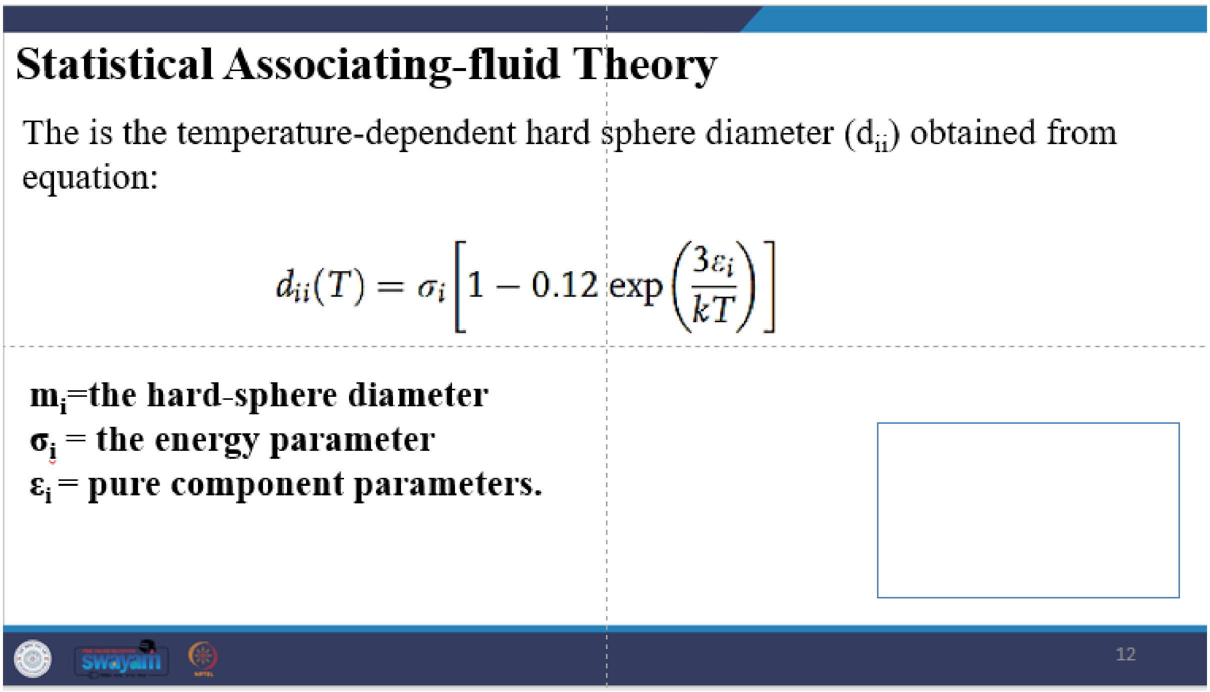
Where ζ_k is given by:

$$\zeta_k = \frac{\pi}{6}\rho\sum x_i m_i (d_{ii})^k$$

$$\frac{a^{hs}}{RT} = \frac{6}{\pi\rho}\left[\frac{\zeta_2^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2\zeta_3^2}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1-\zeta_3)\right]$$

$$\zeta_k = \frac{\pi}{6}\rho \sum x_i m_i (d_{ii})^k$$

To the whole power 2 plus psi at the initial then ln 1 minus this can be given by k is equal to pi over 6 rho summation of x i m i d i i to the power k. Now, this k can be pi is equal to 6 pi over 6 rho summation x i m i d i i k, where rho is the number density and d i i is the temperature-dependent hard sphere diameter. Now, this is the temperature-dependent hard sphere d i i obtained from the equation d i i t is equal to small theta i 1 minus 0.12 e to the power 3 epsilon i over k t, where this m i is the hard sphere diameter and theta i is the energy parameter and epsilon i is the pure component parameter. Now, the chain term this A chain is given by A chain is given by RT is equal to summation x i 1 minus m i ln g to the power h s, where this term is so-called hard sphere radial distribution function at close contact.



Statistical Associating-fluid Theory

The is the temperature-dependent hard sphere diameter (d_{ii}) obtained from equation:

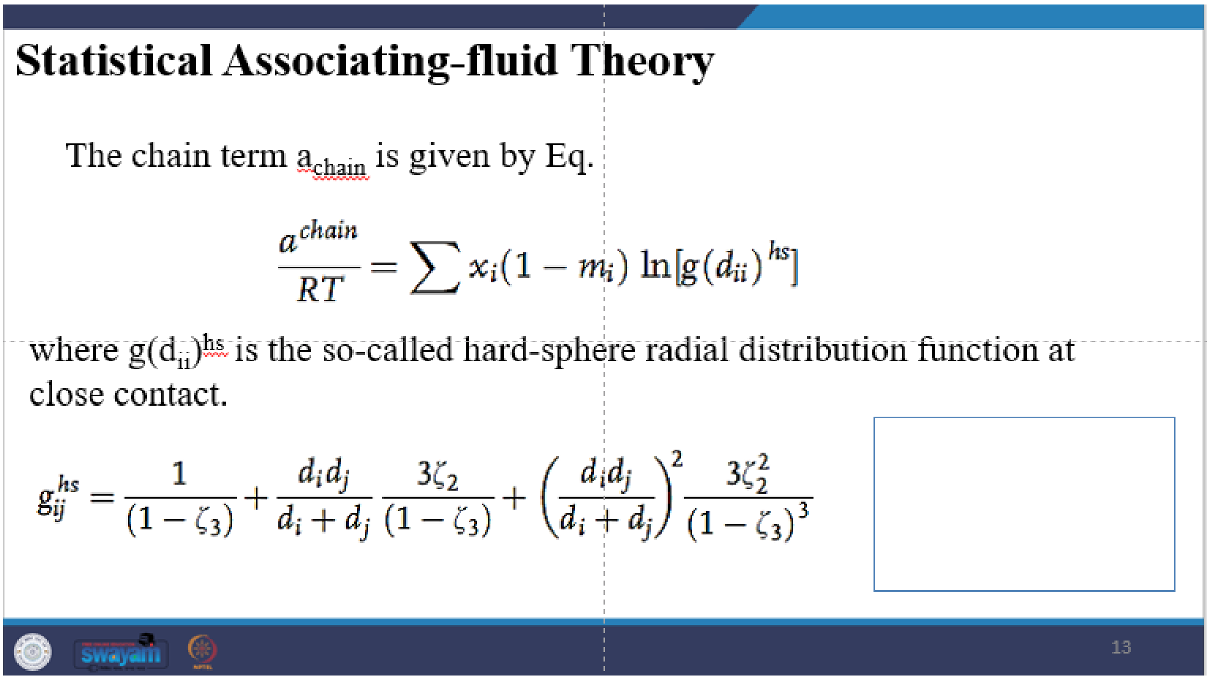
$$d_{ii}(T) = \sigma_i\left[1 - 0.12\exp\left(\frac{3\varepsilon_i}{kT}\right)\right]$$

m_i=the hard-sphere diameter
σ_i = the energy parameter
ε_i = pure component parameters.

$$d_{ii}(T) = \sigma_i\left[1 - 0.12\exp\left(\frac{3\varepsilon_i}{kT}\right)\right]$$

$$\frac{a^{chain}}{RT} = \sum x_i(1 - m_i)\ln[g(d_{ii})^{hs}]$$

$$g_{ij}^{hs} = \frac{1}{(1-\zeta_3)} + \frac{d_i d_j}{d_i + d_j}\frac{3\zeta_2}{(1-\zeta_3)} + \left(\frac{d_i d_j}{d_i + d_j}\right)^2 \frac{3\zeta_2^2}{(1-\zeta_3)^3}$$



Statistical Associating-fluid Theory

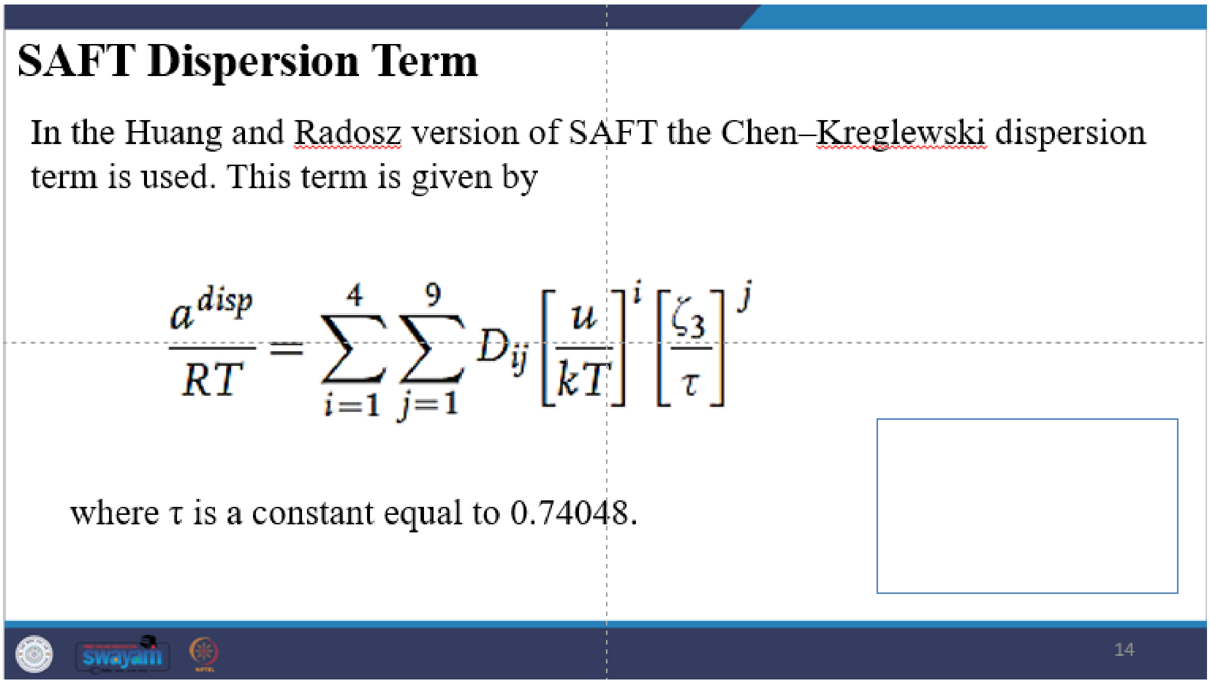
The chain term a_{chain} is given by Eq.

$$\frac{a^{chain}}{RT} = \sum x_i(1-m_i)\ln[g(d_{ii})^{hs}]$$

where $g(d_{ii})^{hs}$ is the so-called hard-sphere radial distribution function at close contact.

$$g_{ij}^{hs} = \frac{1}{(1-\zeta_3)} + \frac{d_i d_j}{d_i+d_j}\frac{3\zeta_2}{(1-\zeta_3)} + \left(\frac{d_i d_j}{d_i+d_j}\right)^2\frac{3\zeta_2^2}{(1-\zeta_3)^3}$$

Now, this g i j h s is equal to 1 over 1 minus d d i d j over d i plus d j plus d i d j over d i plus d j square 3 1 minus. Now, the Hong and Redo's version of this shaft chain shaft, the chain at all the dispersion term is used and this term is given by A dispersion over RT is equal to summation i from 1 to 4 j is equal to 1 to 9 d i j u k t to the i tau j where tau is a constant equal to 0.74048. Now, for mixture the wonder wall one fluid mixing rule or the volume fraction of the mixing can be used. The wonder wall mixing rules are given by this particular equation u over k t is equal to summation i and j x i x j u i j k t d i j over x i x j d i j 3. Now, here k i j is the adjustable binary interaction parameter and d i i is the hard sphere diameter.



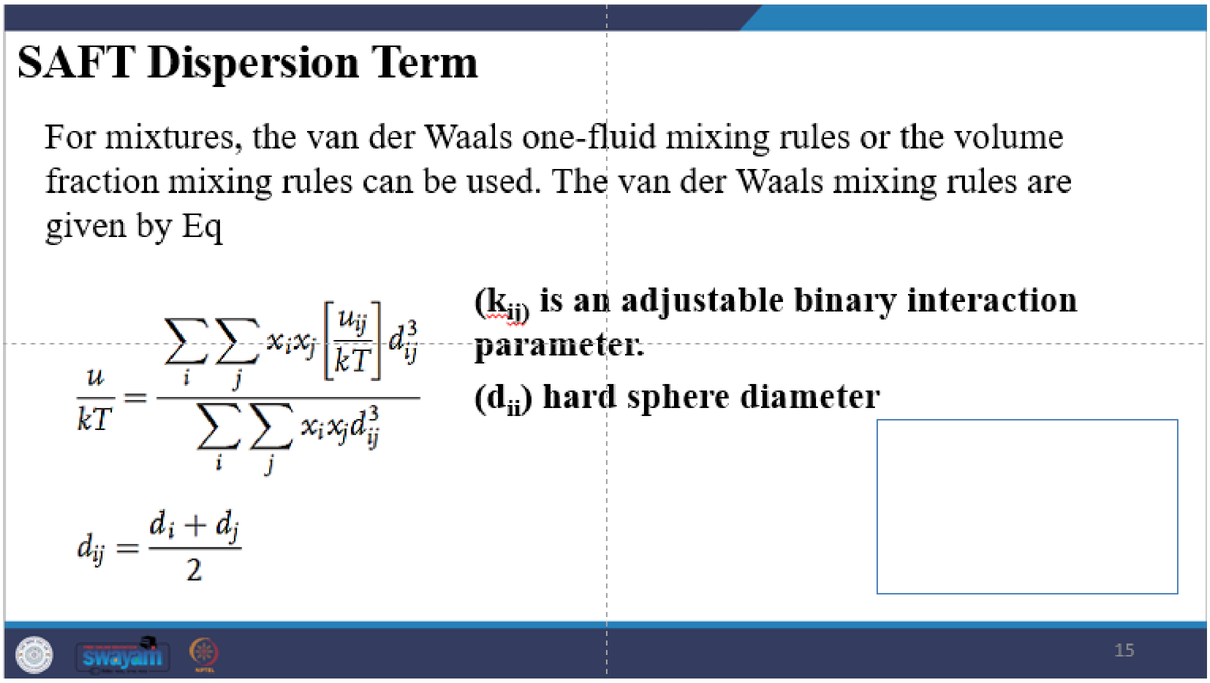
SAFT Dispersion Term

In the Huang and Radosz version of SAFT the Chen–Kreglewski dispersion term is used. This term is given by

$$\frac{a^{disp}}{RT} = \sum_{i=1}^{4}\sum_{j=1}^{9} D_{ij}\left[\frac{u}{kT}\right]^i\left[\frac{\zeta_3}{\tau}\right]^j$$

where τ is a constant equal to 0.74048.

$$\frac{a^{disp}}{RT} = \sum_{i=1}^{4}\sum_{j=1}^{9} D_{ij}\left[\frac{u}{kT}\right]^{i}\left[\frac{\zeta_3}{\tau}\right]^{j}$$



SAFT Dispersion Term

For mixtures, the van der Waals one-fluid mixing rules or the volume fraction mixing rules can be used. The van der Waals mixing rules are given by Eq

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j \left[\frac{u_{ij}}{kT}\right] d_{ij}^3}{\sum_i \sum_j x_i x_j d_{ij}^3}$$

$$d_{ij} = \frac{d_i + d_j}{2}$$

(k_{ij}) is an adjustable binary interaction parameter.

(d_{ii}) hard sphere diameter

$$\frac{u}{kT} = \frac{\sum_i \sum_j x_i x_j \left[\frac{u_{ij}}{kT}\right] d_{ij}^3}{\sum_i \sum_j x_i x_j d_{ij}^3}$$

$$d_{ij} = \frac{d_i + d_j}{2}$$

So, d i j is equal to d i plus d j over 2. Now, in shaft dispersion term represents the interaction between the individual segments, but in PC shaft the dispersion term represents the interaction of chains of segments. So, the expression A dispersion derived by the gross at all and this is the equation is given by A dispersion over RT is equal to A1 over RT plus A2 over RT. Now, this term in the right-hand side of the previous equation they are defined by the equation like A dispersion RT is equal to A1 over RT plus A2 over RT. Now, A1 over RT is equal to minus 2 pi rho m square u k t then i is equal to 0 6 a i m n i.

$$\frac{a^{disp}}{RT} = \frac{a_1}{RT} + \frac{a_2}{RT}$$

PC-SAFT Dispersion Term

- In SAFT the dispersion term represents the interactions between individual segments.
- But PC-SAFT the dispersion term represents the interactions of chains of segments.
- The expression for $\mathbf{a}^{\mathbf{disp}}$ derived by Gross and Sadowski is equation:

$$\frac{a^{disp}}{RT} = \frac{a_1}{RT} + \frac{a_2}{RT}$$

PC-SAFT Dispersion Term

The terms on the right-hand side of expression for $\mathbf{a}^{\mathbf{disp}}$ are defined by Eqs.

- ➢ **reduced fluid density η**
- ➢ **m number of segments**

$$\frac{a^{disp}}{RT} = \frac{a_1}{RT} + \frac{a_2}{RT}$$

$$\frac{a_1}{RT} = -2\pi\rho m^2\left(\frac{u}{kT}\right)\sigma^3\sum_{i=0}^{6} a_i(m)\eta^i$$

$$\frac{a_2}{RT} = -\pi\rho m\left[1 + m\frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-m)\frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{(1-\eta)^2(2-\eta)^2}\right]^{-1}$$

$$* \, m^2\left(\frac{u}{kT}\right)^2\sigma^3\sum_{i=0}^{6} b_i(m)\eta^i$$

$$\frac{a^{disp}}{RT} = \frac{a_1}{RT} + \frac{a_2}{RT}$$

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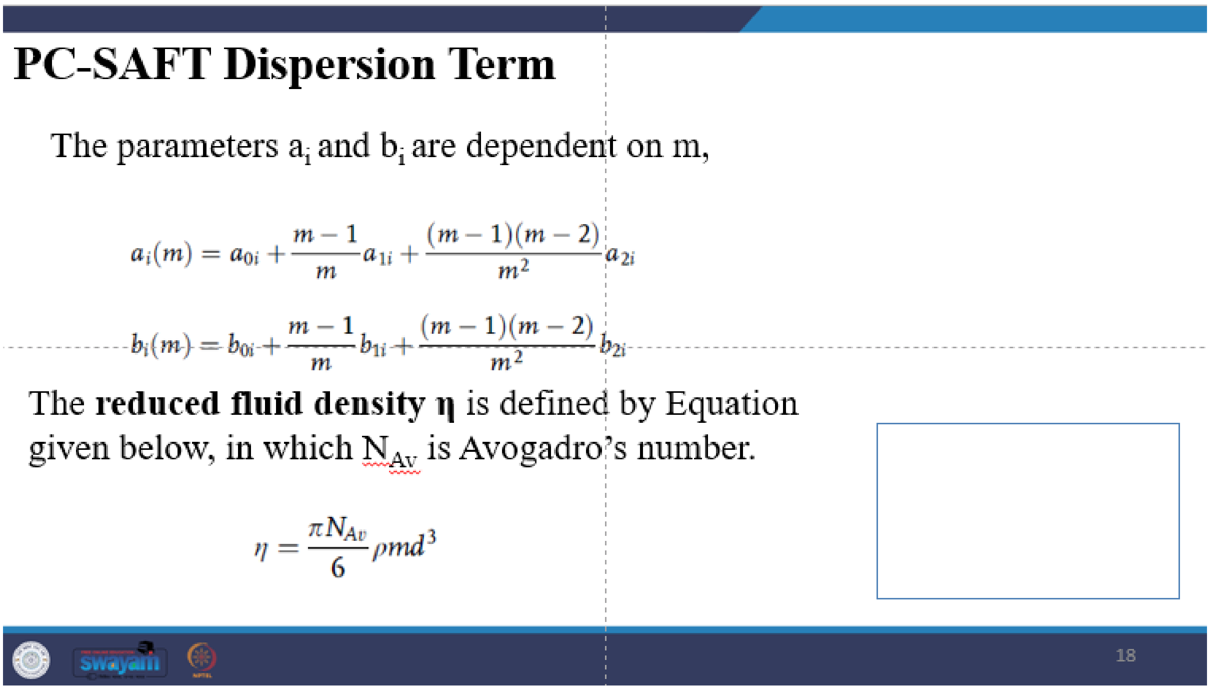
$$* \, m^2 \left(\frac{u}{kT}\right)^2 \sigma^3 \sum_{i=0}^{6} b_i(m)\eta^i$$



PC-SAFT Dispersion Term

The parameters a_i and b_i are dependent on m,

$$a_i(m) = a_{0i} + \frac{m-1}{m}a_{1i} + \frac{(m-1)(m-2)}{m^2}a_{2i}$$

$$b_i(m) = b_{0i} + \frac{m-1}{m}b_{1i} + \frac{(m-1)(m-2)}{m^2}b_{2i}$$

The **reduced fluid density η** is defined by Equation given below, in which N_{Av} is Avogadro's number.

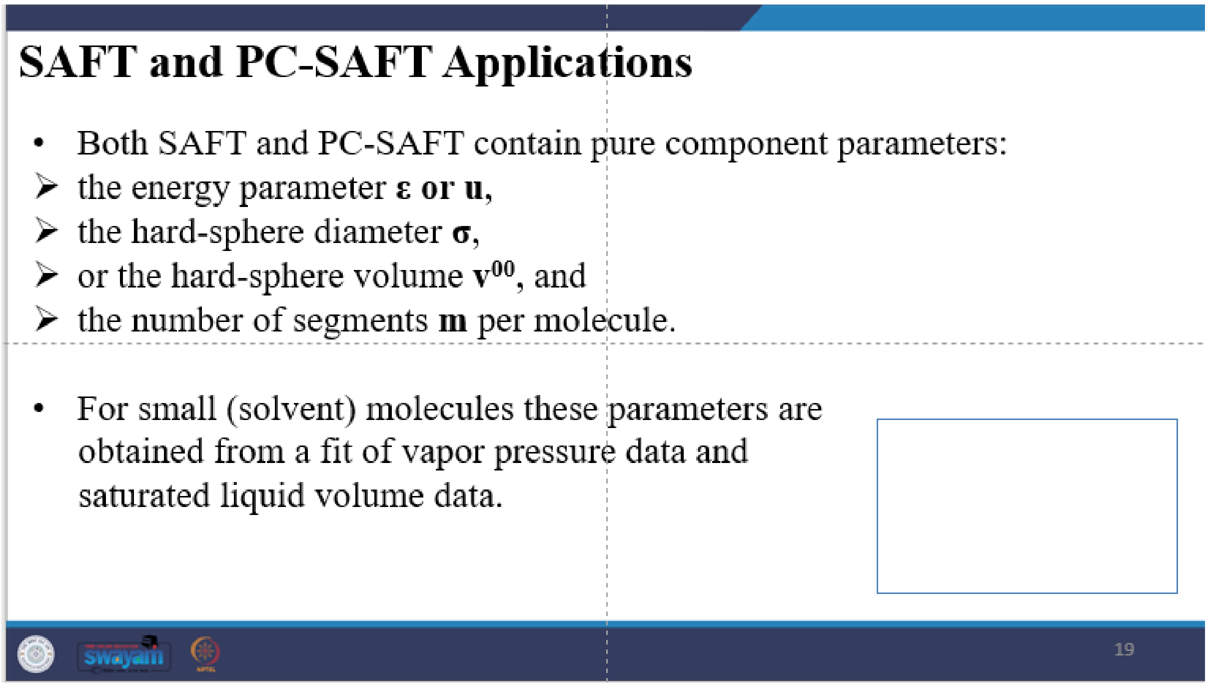
$$\eta = \frac{\pi N_{Av}}{6}\rho m d^3$$

$$a_i(m) = a_{0i} + \frac{m-1}{m}a_{1i} + \frac{(m-1)(m-2)}{m^2}a_{2i}$$

$$b_i(m) = b_{0i} + \frac{m-1}{m}b_{1i} + \frac{(m-1)(m-2)}{m^2}b_{2i}$$

$$\eta = \frac{\pi N_{Av}}{6}\rho m d^3$$

Now, A2 is over RT is equal to minus pi m 1 plus m 8 nita minus 2 squares over 1 minus beta to the power 4 plus 1 minus m into 20 nita minus 27 nita square plus 12 the cube minus 10 2 nita to the power 4 over 1 minus 2 minus square m square u over k t small theta cube i is summation i from 0 to 6 b i m n i. Now, the parameter a i and b i are dependent on a i m is equal to a plus m minus 1 over m a 1 i plus m minus 1 m minus 2 a 2 i and similarly b i plus m minus 1 b 1 i plus m minus 1 m minus 2 b 2 i. Now, the reduced fluid density nita is defined by the equation which which is given by the as per the following notation, nita is equal to pi n this is Avogadro's number over 6 rho m d cube. Now, both the shaft and PC shaft contains pure component parameters that is the energy parameter epsilon or u the hard sphere diameter small theta or hard sphere volume v i i and the number of segments m per volume for small solvent molecules. These parameters are obtained from a fit of vapour pressure data and saturated liquid volume data.

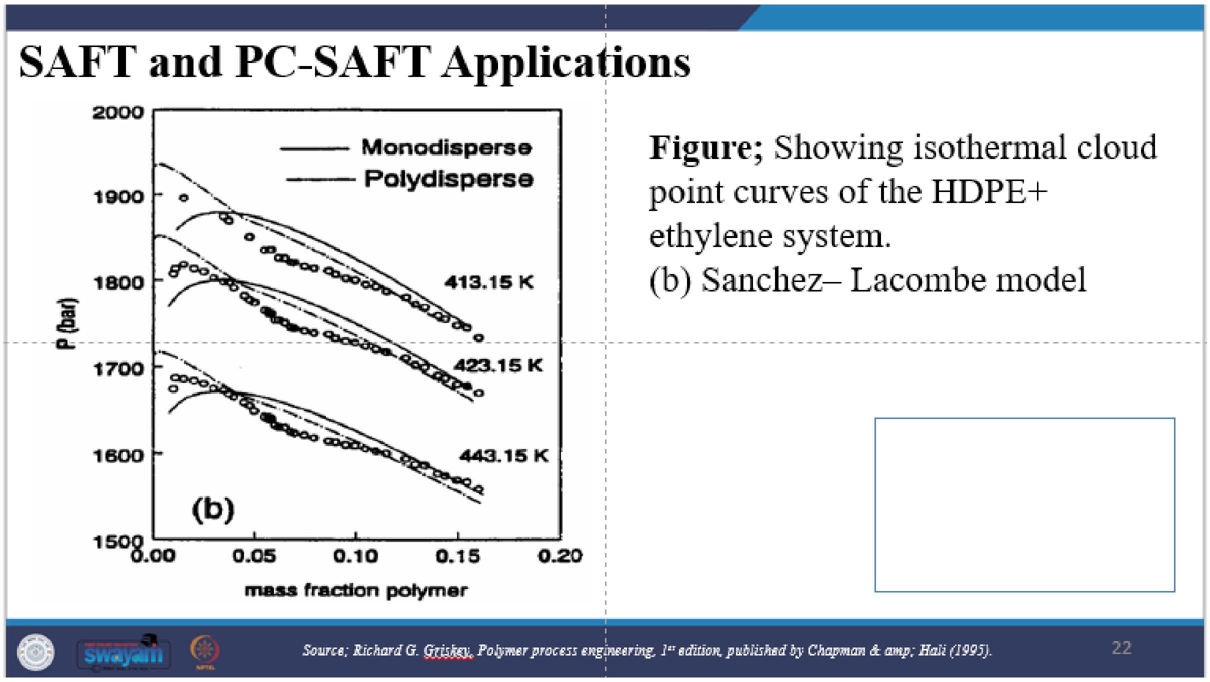


SAFT and PC-SAFT Applications

- Both SAFT and PC-SAFT contain pure component parameters:
  - the energy parameter **ε or u**,
  - the hard-sphere diameter **σ**,
  - or the hard-sphere volume $\mathbf{v}^{00}$, and
  - the number of segments **m** per molecule.
- For small (solvent) molecules these parameters are obtained from a fit of vapor pressure data and saturated liquid volume data.

Now, for pure component polymer parameters they are acquired from acquired from a fit to PVT data of a molten polymer and a binary phase equilibrium data because polymer cannot be fitted because they are having the lack of vapour pressure. For the description of a mixture one needs one binary interaction parameters k i j per binary which has to be fitted to a phase equilibrium data. Now, if necessary this k i j can be made temperature dependent and in general the phase equilibrium are very sensitive to the k i j value. Now, here this particular figure shows the isothermal cloud point curve of HDPE and ethylene system and here you see that this is a shaft model. Now, if we go to the other things like Sanchez-Lecombe model this particular curve shows the isothermal cloud point for HDPE plus ethylene system.

Now, in this particular graph the experimental results from the system of ethylene plus HDPE they are compared with the modelling result using shaft and Sanchez-Lecombe model. In both cases k i j is taken to be linearly dependent on temperature and due to the polydispersity of the polymer the cloud point curve shows a dip in which a critical point is located. Now, if in the modelling of the polymer it is assumed to be monodisperse this behaviour we cannot reproduce. The graphical demonstration of the previous figure this demonstrates that although the deviation they are bigger at high and low term polymer concentration both shaft and Sanchez-Lecombe model adequately describe the experimental phase behaviour and the same system this was modelled by Tumakaka using the shaft and PC shaft model. Let us talk about the other equation of state the equation of state based on the lattice hole theory this is theory and created by Penaju-Wu and Vera in 1982 this was comparable to the Sanchez and Lecombe equation of state.

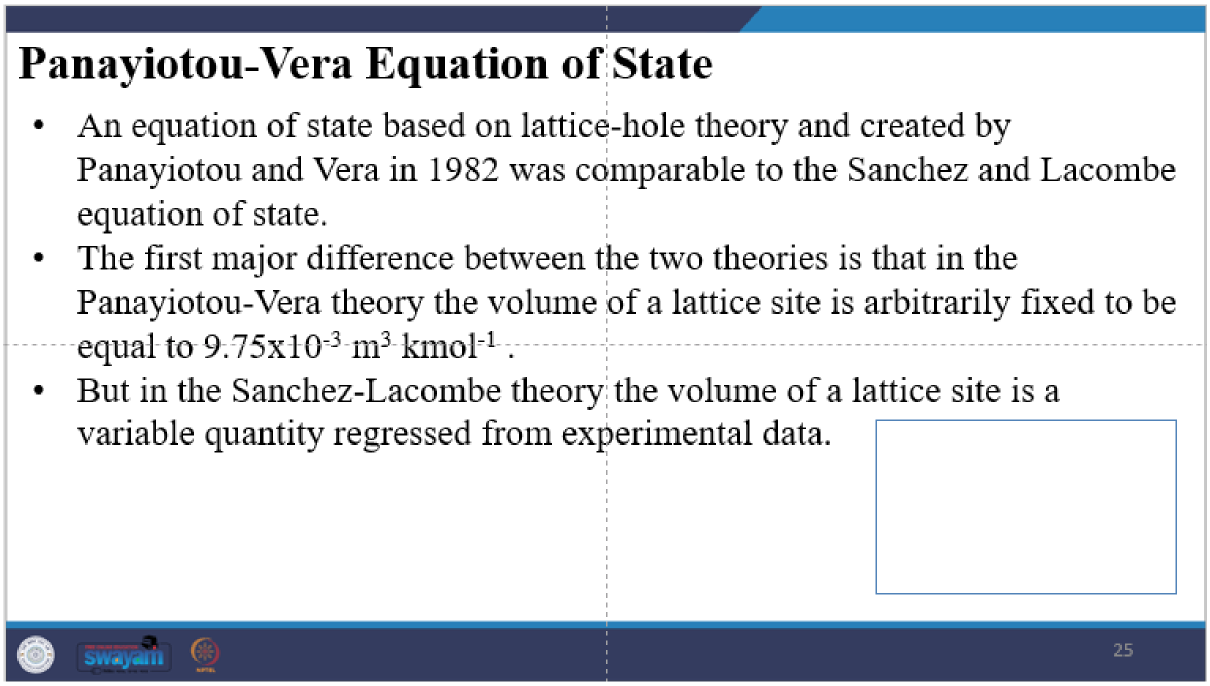


SAFT and PC-SAFT Applications

Figure; Showing isothermal cloud point curves of the HDPE+ ethylene system.
(b) Sanchez– Lacombe model

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

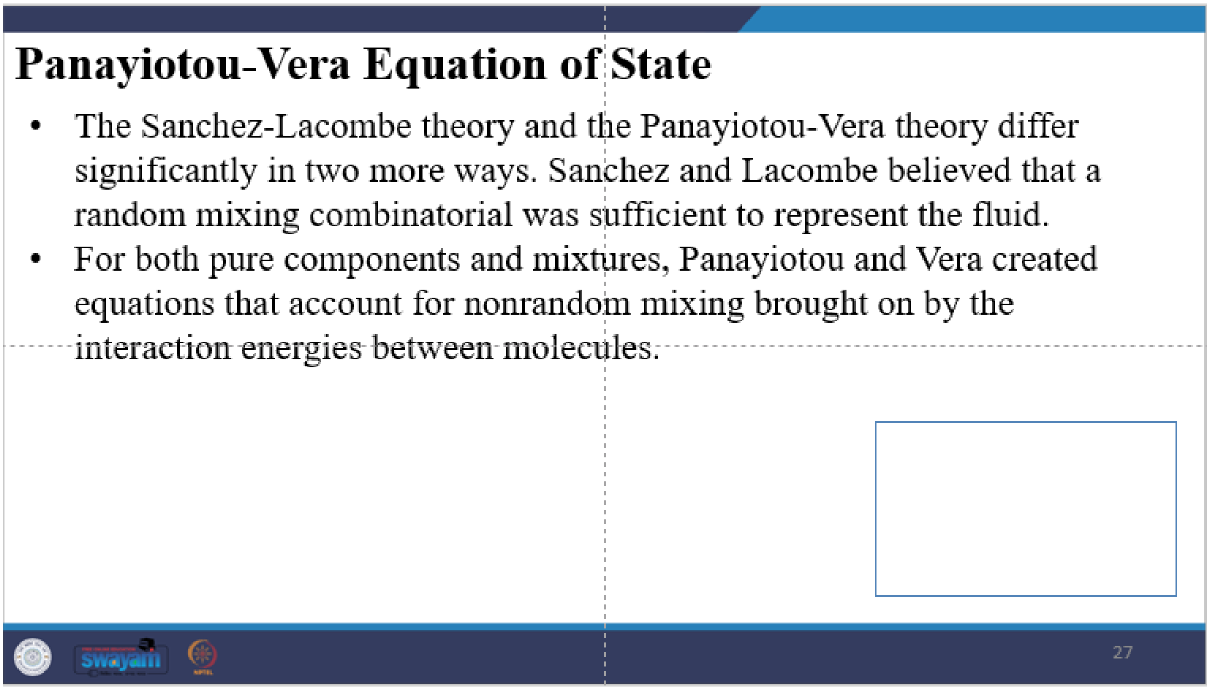
The first major difference between the two theories is that the Vera theory the volume of a lattice site is arbitrarily fixed to be equal to 9.75 into 10 to the power minus 3-meter cube per kilo mole. But in the Sanchez-Lecombe theory the volume of a lattice site is a variable quantity regressed from the experimental data. Now, fixing the volume of the lattice site this eliminates the need for a mixing rule for lattice site for mixture. The issue of having the various lattice volume for the mixture and the pure component this is resolved by using fixed lattice volume.



Panayiotou-Vera Equation of State

- An equation of state based on lattice-hole theory and created by Panayiotou and Vera in 1982 was comparable to the Sanchez and Lacombe equation of state.
- The first major difference between the two theories is that in the Panayiotou-Vera theory the volume of a lattice site is arbitrarily fixed to be equal to 9.75×10^{-3} m^3 $kmol^{-1}$.
- But in the Sanchez-Lacombe theory the volume of a lattice site is a variable quantity regressed from experimental data.

The volume should be chosen so that the lattice site and the smaller group of interest have nearly the same volume. Now, where at all they choose the value of 9.75 into 10 to the power minus 3-meter cube per kilo mole which accurately reproduce the pressure volume temperature data for polyethylene. So, all these things are case sensitive polyethylene polypropylene all these things are case sensitive. The Sanchez-Lecombe theory of and the Vera theory they differ significantly in two more ways.

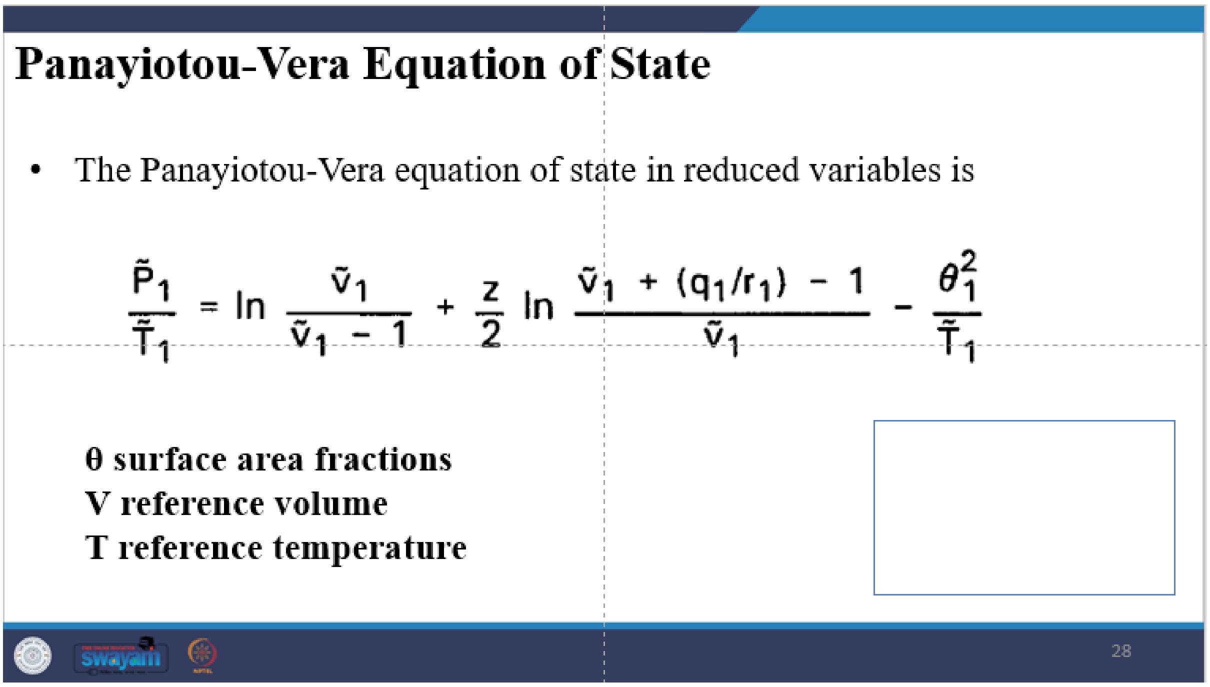


Panayiotou-Vera Equation of State

- The Sanchez-Lacombe theory and the Panayiotou-Vera theory differ significantly in two more ways. Sanchez and Lacombe believed that a random mixing combinatorial was sufficient to represent the fluid.
- For both pure components and mixtures, Panayiotou and Vera created equations that account for nonrandom mixing brought on by the interaction energies between molecules.

The Sanchez-Lecombe believe that a random mixing combinatorial was sufficient to represent the fluid for both component and a mixture and a Vera created the equation that accounts for non-random mixing brought on by the interaction energies between molecules. So, this Vera equation of a state in reduced variable this can be represented as p reduced over t 1 that is ln equal ln v 1 reduced over v 1 reduce minus 1 plus z over 2 ln v 1 reduce plus q 1 over r 1 minus 1 over v 1 reduced minus theta 1 over t 1 reduced. Now, theta is the surface area fraction, v is the reference volume and t is the reference temperature. Now, for modeling of the phase behaviour of copolymer solvent system the copolymer can be treated as a homopolymer with the effective pure component parameters. McCaughey and colleagues, they provided examples for this particular strategy.

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln \frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{z}{2} \ln \frac{\tilde{v}_1 + (q_1/r_1) - 1}{\tilde{v}_1} - \frac{\theta_1^2}{\tilde{T}_1}$$



Panayiotou-Vera Equation of State

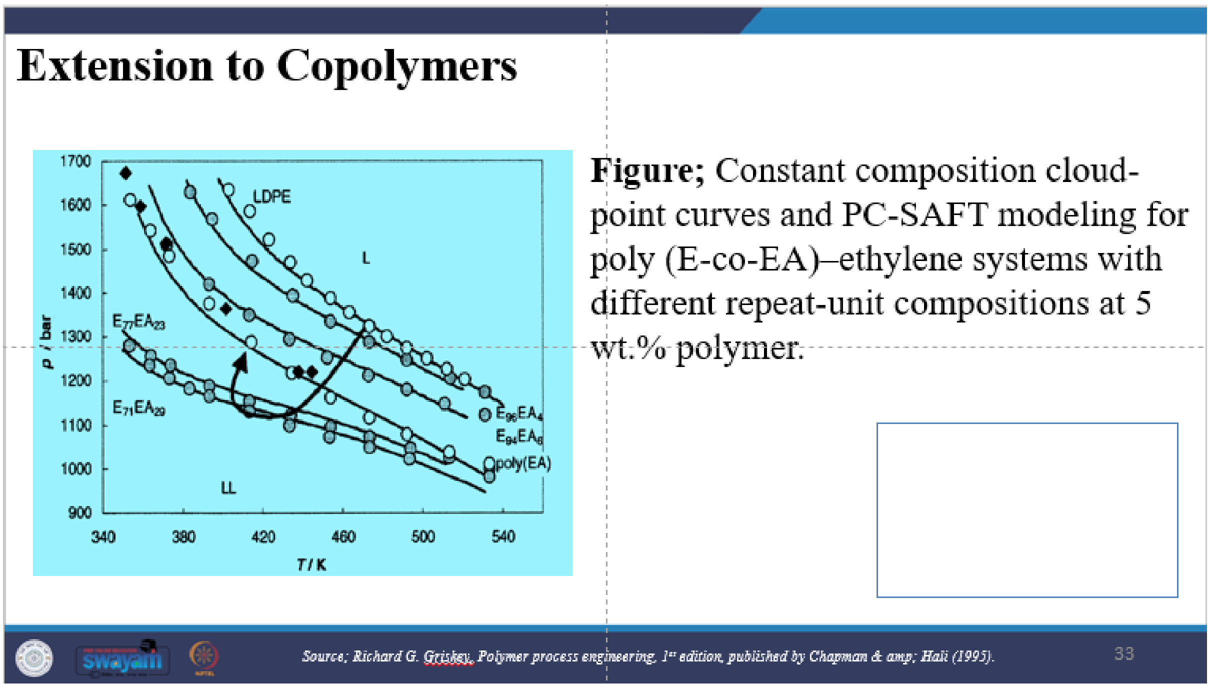
- The Panayiotou-Vera equation of state in reduced variables is

$$\frac{\tilde{P}_1}{\tilde{T}_1} = \ln \frac{\tilde{v}_1}{\tilde{v}_1 - 1} + \frac{z}{2} \ln \frac{\tilde{v}_1 + (q_1/r_1) - 1}{\tilde{v}_1} - \frac{\theta_1^2}{\tilde{T}_1}$$

θ surface area fractions
V reference volume
T reference temperature

The drawback of this strategy is that the characteristics of a pure component polymer depend on the nature and makeup of the copolymer. From binary polymer solvent phase equilibrium data pure component polymer properties are usually derived. Now, it is feasible to describe the phase behaviour of the same polymer in a different solvent using these parameters. The Redo's and the co-workers they use the copolymer shaft methodology in which the copolymer characteristics they are computed based on solely the copolymers molecular weight and structure and it is found to be the superior method. Now, there are 3 binary interaction parameters for A B type of copolymer.

The parameter governing the interaction between A segment and solvent molecule segment and B segment and solvent molecule segment and A and B segment interaction. So, the phase behavior of 2 homopolymer system can be used to determine the first 2 binary interaction parameters while some copolymer solvent data must be fitted to determine the third binary interaction parameter. Now, once these parameters are known, predictions can be made for a copolymer solvent system with the same type of copolymer but with a different copolymer composition. And this particular figure the constant temperature cloud point curves and PC-SAFT modeling of the polyethylene system with the different repeat units composition at 5 weight percent of the graduation of the polymer. Now, the model correctly predicts the change in the location of the cloud point with changing co-monomer concentration in the polymer.

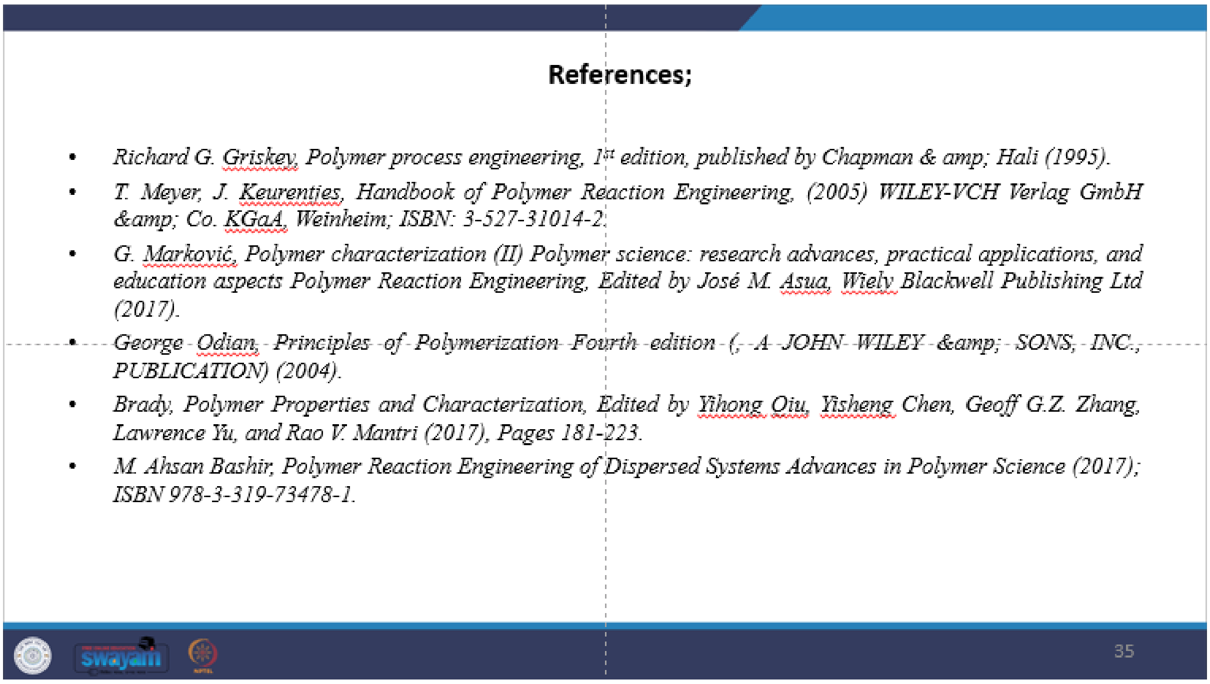


Extension to Copolymers

Figure; Constant composition cloud-point curves and PC-SAFT modeling for poly (E-co-EA)–ethylene systems with different repeat-unit compositions at 5 wt.% polymer.

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

Especially, it is interesting to see that the ethylene and polyethylene system in the curve of the cloud point pressure as a function of ethylene thiol-coal concentration in the polymer shows this is the minimum. So, dear friends in this particular segment we discussed the different models for the prediction of thermodynamic systems, and for convenience, we have enlisted a couple of references. Thank you very much.



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