Statistical Associated-Fluid Theory

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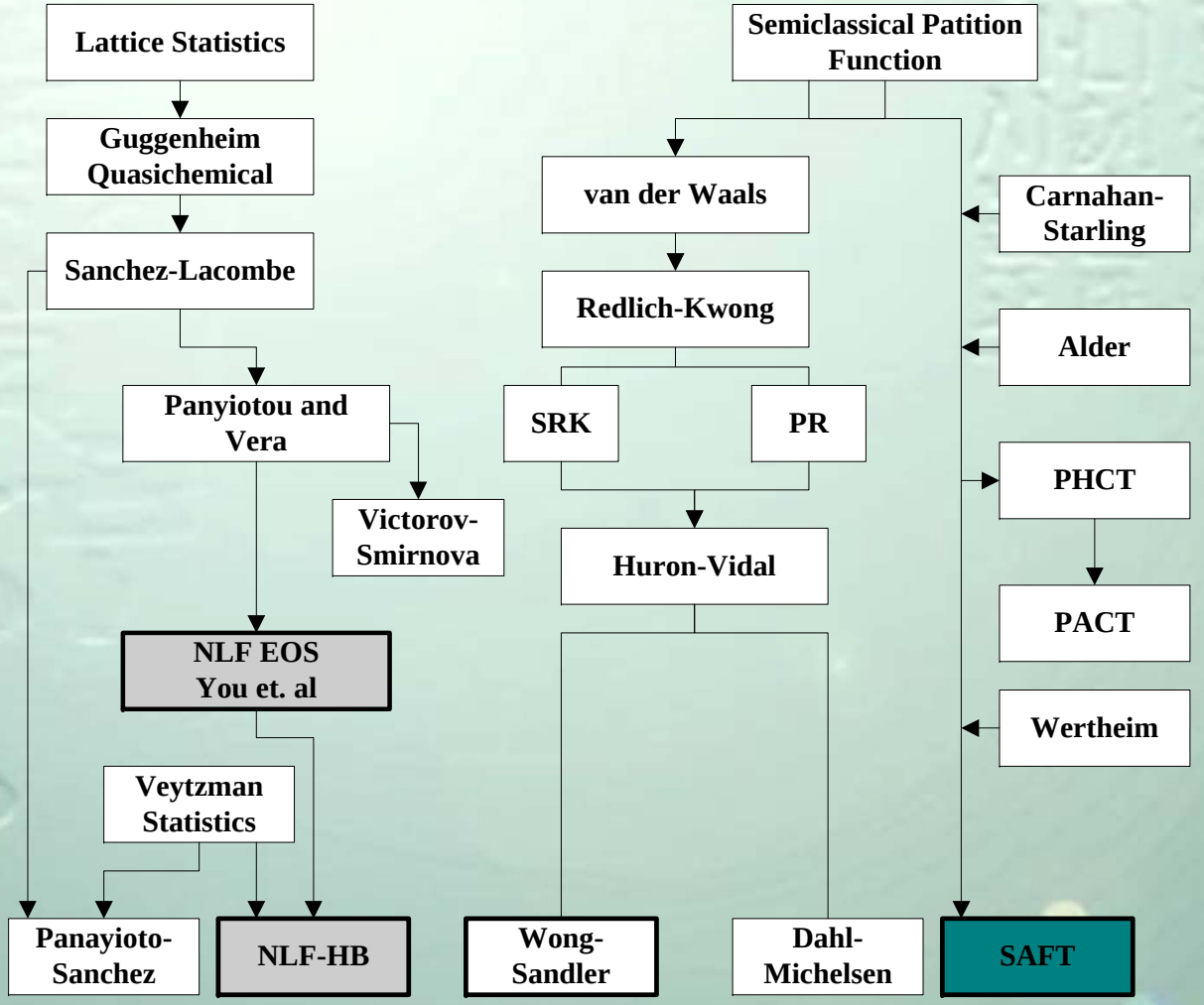
Motives

- Molecular association profoundly affects phase behavior and transport properties of fluid mixtures.
  - Supercritical conditions and high pressure systems
  - Phase equilibria of polymers
  - Phase equilibria of associating mixtures (alcohols, acids)
  - Simultaneous representation of VLE and H^E
- There have been many attemps to model the association effects on fluid phase equilibria.
- **The Statistical Associated-Fluid Theory** (SAFT) is based on the first – order perturbation theory of Wertheim (1987).

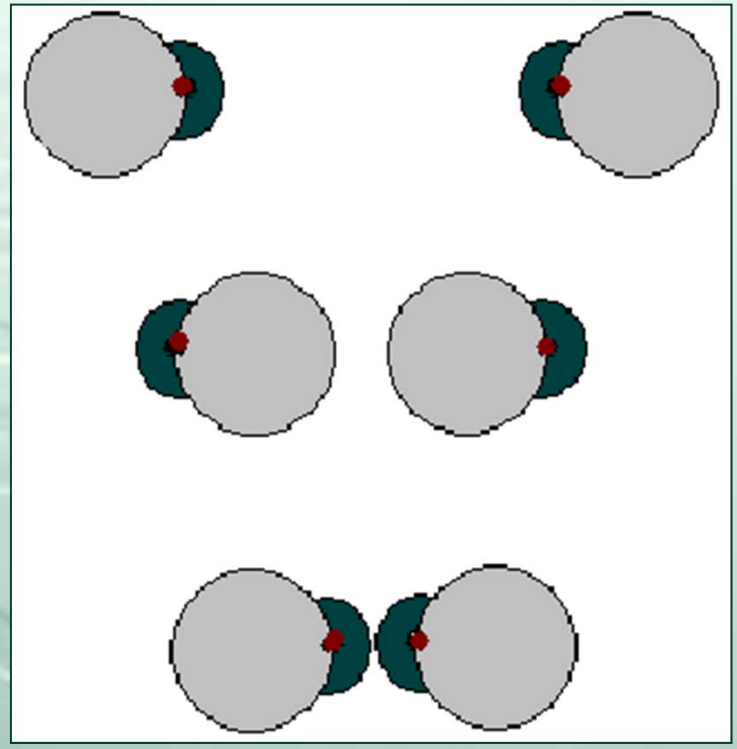
EOS Models – Historical Review



The Classes of EOS Models

- ***Based on Semi-Classical Partition Function***
  - Cubic Equation of State and Other van-der Waals based EOS
  - Radial Distribution Function Approaches
    - **PHCT (1978), PACT (1985)**
    - **SAFT (Huang and Radosz, Chapman, 1990)**
- ***Based on Lattice Statistical-mechanical theory***
  - **NLF -EOS proposed by You,Yoo and Lee (1993)**
  - **Hydrogen Boding proposed by Veytzman (1990) + Lattice EOS**

Model of hard spheres with a single associating site A



Wrong Distance

Wrong Orientation

Site-Site Attraction

Three steps to form chain molecules and association complexes

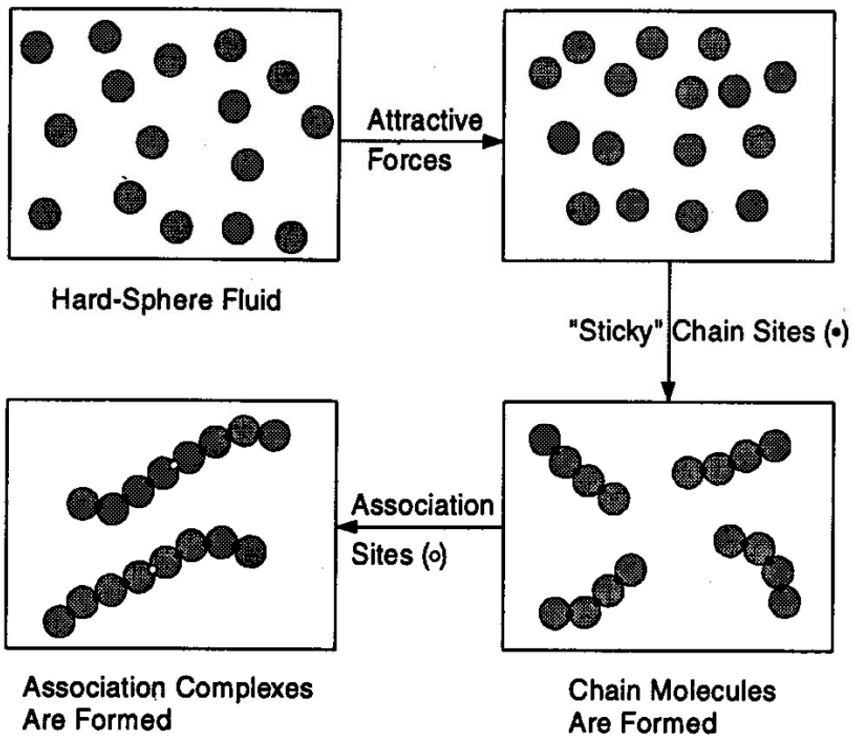
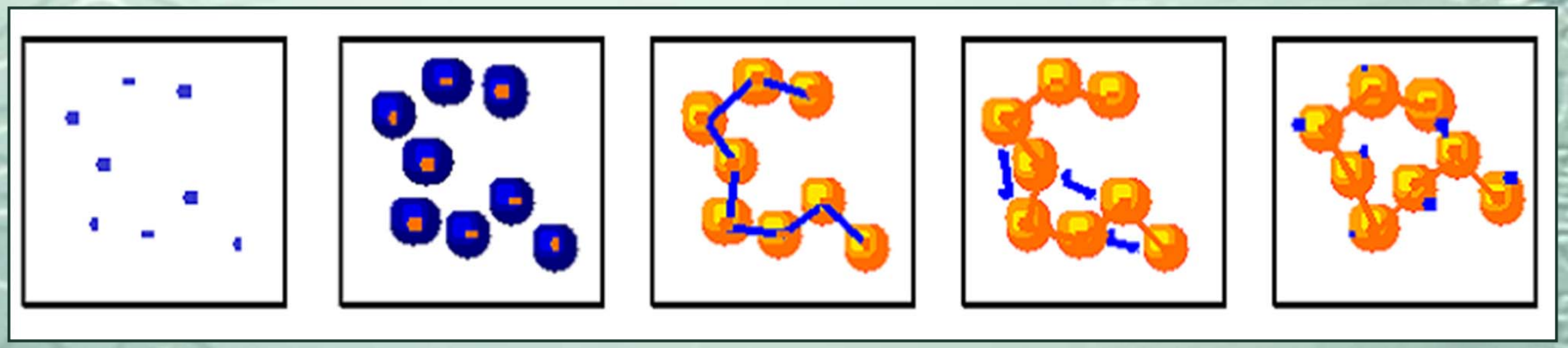


Figure 7-30 Three steps to form chain molecules and association complexes from hard spheres in the SAFT model.

SAFT EOS

: Huang and Radosz, Chapman (1990)

: SAFT EOS can be represented as a sum of Helmholtz energies



$$a = a_{\text{ideal gas}} + a_{\text{hard sphere}} + a_{\text{chain}} + a_{\text{dispersion}} + a_{\text{association}}$$

SAFT EOS

EOS

$$Z = 1 + Z_{hs} + Z_{chain} + Z_{disp} + Z_{assoc}$$

Hard Sphere Term

$$Z_{hs} = \frac{6}{\pi N_A \rho}\left[\frac{\xi_0\xi_3}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{(3-\xi_3)\xi_2^3}{(1-\xi_3)^3}\right] \qquad \xi_k = (\pi N_A \rho / 6)\sum_i x_i r_i (d_i)^k$$

Chain Term

$$Z_{chain} = \sum_i x_i (1-r_i) L(d_i)$$

$$L(d_i) = \frac{2\xi_3 + 3d_i\xi_2 - 4\xi_2^3 + 2d_i\xi_2^2 + 2\xi_3^3 + d_i^2\xi_2^2\xi_3 - 3d_i\xi_2\xi_3^2}{(1-\xi_3)(2-4\xi_3 + 3d_i\xi_2 + 2\xi_3^2 + d_i^2\xi_2^3 - 3d_i\xi_2\xi_3)}$$

Dispersion Term

$$Z_{disp} = r\sum_n \sum_m mD_{nm}(u/kT)^n \left(\xi_3 / \xi_{3cp}\right)^m$$

Association Term

$$Z_{assoc} = \rho \sum x_i \left[\sum \left(1/X^{S_i} - 1/2\right)\left(\partial X^{S_i} / \partial \rho\right)\right]$$

$$X^{S_i} = \left(1 + N_A \sum_j \sum_{Y_j} x_j \rho X^{Y_j} W_{ij}\right)^{-1}$$

SAFT prediction

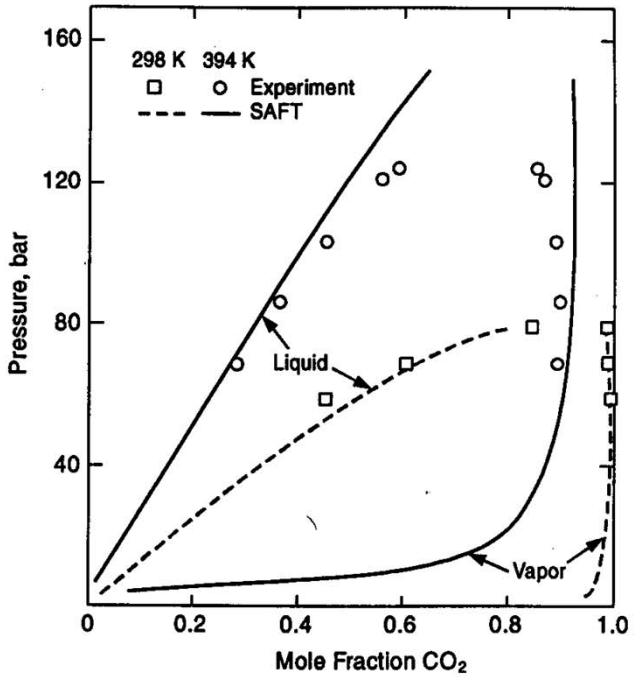
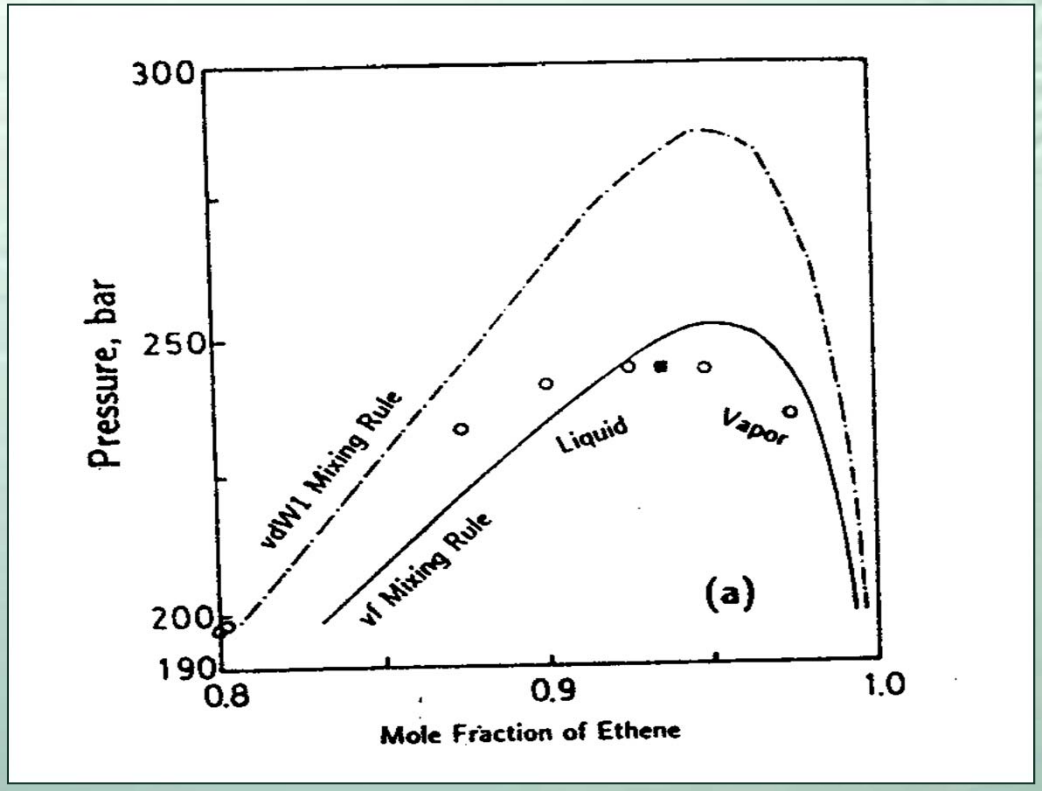


Figure 7-33 Vapor-liquid equilibria at 298 K and 394 K for the system CO_2/2-propanol. SAFT calculations were performed with the volume-fraction mixing rule (Huang and Radosz, 1991).

Prediction
[vdW1 and vf mixing rules]



Comparison

[Pure Component Parameters]

EOS Models	Parameters	T Dependency	Procedure To Get Parameters
**** Non-specific interaction***			
SAFT	$r_i, \varepsilon_i, \sigma_i, e$	Independent	Using vapor pressure and liquid density
NLF-HB	r_i, ε_{ii}	Dependent	Using vapor pressure and liquid density
**** Specific interaction (Hydrogen bonding)***			
SAFT	$\varepsilon^{S_iY_j}, \kappa^{S_iY_j}$	Independent	Required for individual species and additional bond formation
NLF-HB	U^{HB}, S^{HB}	Independent	Depends on the type of hydrogen bond

Comparison

[Mixing rule and binary interaction parameters]

	SAFT	*NLF-HB*
Basis of Mixing Rule	**Vdw / VF mixing rule Results are affected by the choice of mixing rule**	**Do not require empirical mixing rule**
No. of Binary Parameters	**1 (k_{ij})**	**1 (k_{ij})**
Cross Association	**Additional cross association parameters (2)**	**Can be assumed(2)**

Computational Aspects

	PVT Behavior	Computation speed	Remark
SAFT	Complex	Slow	Extra computation time for balance equation solving when two or more types of association
NLF-HB	Relatively simple	Relatively fast	

Conclusions

- **The Statistical Associated-Fluid Theory** (SAFT) is based on the first – order perturbation theory of Wertheim (1987).
- The essences of this theory is that the Helmholtz energy is given by a sum of expressions to account not only for the effects of repulsion and dispersion forces but also for association and/or solvation.
- The SAFT EOS has been applied successfully to describe thermodynamic properties and phase behavior of pure fluids and fluid mixtures containing small, large, non-associating and associating molecules, including supercritical and near-critical solutions of polymers.
- However, the SAFT EOS cannot be used for liquid-liquid equilibrium in aqueous systems at normal temperature.

References

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