Equations of State for the Calculation of Fluid-Phase Equilibria

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Introduction

- Advantages of using Equation of State(EOS)
  - Wide ranges of temperature and pressure
  - Application of mixtures of diverse components
  - Various phase equilibria without any conceptual difficulties

- This work
  - An overview of recent progress in EOS
    - Simple empirical EOS
    - Theoretically-based EOS
  - Relationships between different EOS
  - Role of molecular simulation data

EOS for simple molecules

- van der Waals EOS (vdW) (1873)

$$Z = \frac{V}{V-b} - \frac{a}{RTV}$$

  - Hard-sphere (repulsive) + Attractive intermolecular interactions
  - A qualitative description of phase transitions
  - Inadequate to critical properties and phase equilibria

- Requirement of modifications of attractive and repulsive terms

EOS for simple molecules
Modification of Attractive term

- Benedict-Webb-Rubbin EOS (1940)

$$Z = 1 + \left(\frac{B_0 RT - A_0 - C_0 / T^2}{RTV} \right) + \left(\frac{bRT - a}{RTV^2} \right) + \frac{\alpha a}{RTV^5}$$
$$+ \frac{c}{RT^3 V^2} \left(1 + \frac{\gamma}{V^2} \right) \exp\left(- \frac{\gamma}{V^2} \right)$$

  - Disadvantage
    - Requirement of plentiful, accurate PVT and VLE data for parmamter estimation
    - Difficulty of extension to mixtures

EOS for simple molecules
Modification of Attractive term

- Redlich-Kwong EOS (1949)

$$Z = \frac{V}{V-b} - \boxed{\frac{a}{RT^{1.5}(V+b)}}$$

$$a = 0.4278 R^2 T_c^{2.5} / P_c$$

$$b = 0.0867 R T_c / P_c$$

  - Significant improvement over the vdW EOS
  - The impetus for many further empirical EOS

EOS for simple molecules

Modification of Attractive term

- SRK (1972)

$$Z = \frac{V}{V-b} - \frac{a(T)}{RT(V+b)}$$

$$a(T) = 0.4274\left(\frac{R^2T_c^2}{p_c}\right)\left\{1 + m\left[1 - \left(\frac{T}{T_c}\right)^{0.5}\right]\right\}^2$$

$$m = 0.480 + 1.57\omega - 0.176\omega^2$$

$$b = 0.08664RT_c / p_c$$

  - Prediction of phase behavior of mixtures in the critical region and improvement of accuracy of critical properties

EOS for simple molecules

Modification of Attractive term

- Peng–Robinson (1976)

$$Z = \frac{V}{V-b} - \frac{a(T)V}{RT\left[V(V+b)+b(V-b)\right]}$$

$$a(T) = 0.45724\left(\frac{R^2T_c^2}{p_c}\right)\left\{1+k\left[1-\left(\frac{T}{T_c}\right)^{0.5}\right]\right\}^2$$

$$k = 0.37464 + 1.5422\omega - 0.26922\omega^2$$

$$b = 0.07780RT_c / p_c$$

  - Slight improvement of the predictions of liquid volumes
  - Superior to the VLE in hydrogen and nitrogen containing mixtures (Han et al., 1988)

EOS for simple molecules
Modification of Attractive term

- The advantages of SRK and PR EOSs
  - Easy representation of the relation among temperature, pressure, and phase compositions in multicomponent systems
  - Only requirement of the critical properties and acentric factor
  - Little computing time
- Overestimation of saturated liquid volumes.

EOS for simple molecules
Modification of Attractive term

Redlich-Kwong (RK) (1949)	$\frac{a}{RT^{1.5}(V+b)}$	Kubic (1982)	$\frac{a(T)V}{RT(V+c)^2}$
Soave (SRK) (1972)	$\frac{a(T)}{RT(V+b)}$	Patel-Teja (PT) (1982)	$\frac{a(T)V}{RT[V(V+b)+c(V-b)]}$
Peng-Robinson (PR) (1976)	$\frac{a(T)V}{RT[V(V+b)+b(V-b)]}$	Adachi et al. (1983)	$\frac{a(T)V}{RT[(V-b_2)(V+b_3)]}$
Fuller (1976)	$\frac{a(T)}{RT(V+cb)}$	Stryjek-Vera (SV) (1986a)	$\frac{a(T)V}{RT[(V^2+2bV-b^2)]}$
Heyen (1980) (Sandler, 1994)	$\frac{a(T)V}{RT[V^2+(b(T)+c)V-b(T)c]}$	Yu and Lu (1987)	$\frac{a(T)V}{RT[V(V+c)+b(3V+c)]}$
Schmidt-Wenzel (1980)	$\frac{a(T)V}{RT(V^2+ubV+wb^2)}$	Trebble and Bishnoi (TB) (1987)	$\frac{a(T)V}{RT[V^2+(b+c)V-(bc+d^2)]}$
Harmens-Knapp (1980)	$\frac{a(T)V}{RT[V^2+Vcb-(c-1)b^2]}$	Schwartzentruber and Renon (1989)	$\frac{a(T)V}{RT[(V+c)(V+2c+b)]}$

EOS for simple molecules
Modification of Repulsive term

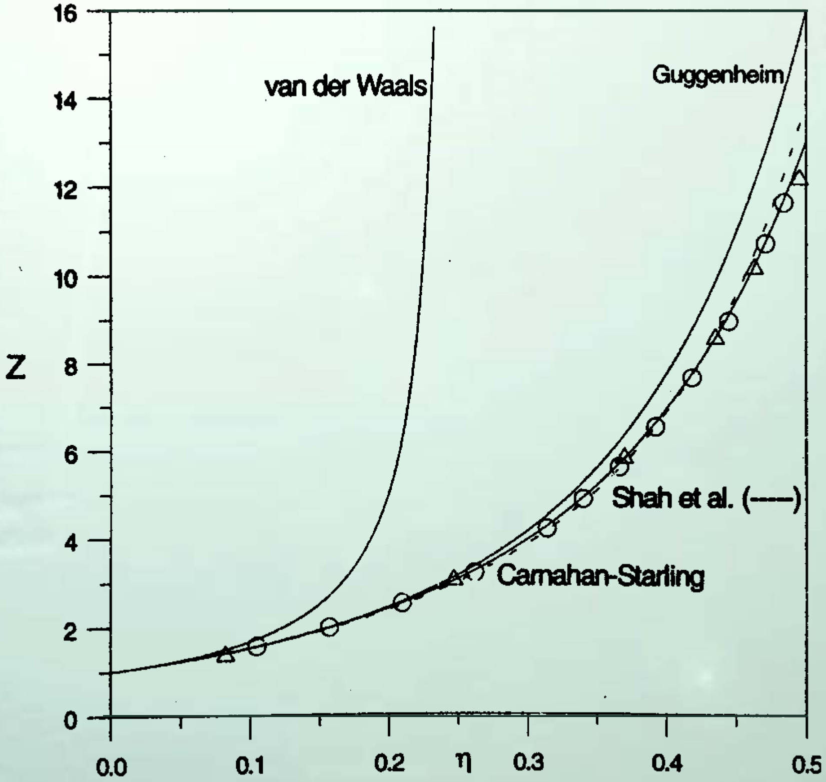
Equation	Repulsive Term (Z^{hs})
Reiss et al. (1959)	$\dfrac{1+\eta+\eta^2}{(1-\eta)^3}$
Thicle (1963)	$\dfrac{1+\eta+\eta^2}{(1-\eta)^3}$
Guggenheim (1965)	$\dfrac{1}{(1-\eta)^4}$
Carnahan-Starling (1969)	$\dfrac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$
Scott et al. (1971)	$\dfrac{RT(V+b)}{V(V-b)}$
Boublik (1981)	$\dfrac{1+(3\alpha-2)\eta+(3\alpha^2-3\alpha+1)\eta^2-\alpha^2\eta^3}{(1-\eta)^3}$

nonsphericity parameter(α)
for arbitrary geometry of molecules

- Reproducibility of complex phase transitions such as LLV equilibria.

EOS for simple molecules

Modification of Repulsive term



- Hard-sphere compressibility factors from different EOS with molecular simulation data

EOS for simple molecules

Combining modification of both attractive and repulsive terms

- Carnahan and Starling (1972)

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{a}{RT^{1.5}(V+b)}$$

  - The prediction of hydrocarbon densities and supercritical phase equilibria.

- Chen and Kreglewski (1977)

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \sum_i \sum_j jD_{ij} \left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j$$

  - The substitution of attractive term with the power series fit of MC data by Alder et al. (1972)
  - This attractive term is the inspiration for further development.

EOS for simple molecules

Combining modification of both attractive and repulsive terms

- Shah et al. (1994)

$$Z = \underbrace{\frac{V}{V - k_0\alpha} + \frac{\alpha k_1 V}{(V - k_0\alpha)^2}}_{\text{Repulsive}} - \underbrace{\frac{aV + k_0\alpha c}{RT(V + e)(V - k_0\alpha)}}_{\text{Attractive}}$$

  - Requirement of 3 properties of fluids : Tc, Vc, and acentric factor
  - Quartic equation, but it behaves like cubic equation.
  - Lin et al. (1996)
    - Extension to polar fluids.
    - Need of dipole moment

EOS for Chain Molecules

Perturbed hard chain theory

- Prigogine (1957)
  - Rotational and vibrational motions are depend on density

    => EOS and configurational properties are affected.

$$Q = \frac{V^N}{N!\Lambda^{3N}} \left(\frac{V_f}{V} \right)^N \left[\exp\left(\frac{-\phi}{2kT} \right) \right]^N (q_{r,v})^N$$

$$q(r,v) = q_{ext}(v) q_{\mathrm{int}}(T) = \left(\frac{V_f}{\Lambda^3} \right)^{c-1} q_{\mathrm{int}}(T)$$

EOS for Chain Molecules
Perturbed hard chain theory

- Beret and Prausnitz (1975)
  - Development of PHCT EOS
  - More accurate expressions for repulsive and attractive partition functions
  - Meeting the ideal gas law at low densities
    - Deficiency in Prigogine's theory

$$V_f = V \exp\left(\frac{\eta(3\eta - 4)}{(1-\eta)^2}\right) \text{ and } q_{ext}(V) = \left(\frac{V_f}{V}\right)^{c-1}$$

EOS for Chain Molecules

Perturbed hard chain theory

- Equation of State

$$Z = 1 + c\frac{4\eta - \eta^2}{(1-\eta)^3} + \frac{\varepsilon q}{kTV}(rv^0)\sum_{n=1}^{4}\sum_{m=1}^{M}\left(\frac{mA_{nm}}{\tilde{v}^{m-1}}\right)\left(\frac{1}{\tilde{T}^{n-1}}\right)$$

- Parameters : $rv^0, \varepsilon q / k, c$

- Sucessful in calculating the various properties of fluids and phase equilibria

- A practical limitations as a result of the use of Carnahan-Starling free-volume term and the Alder power series

- Simplifying the PHCT EOS

EOS for Chain Molecules

Simplified perturbed hard chain theory

- Kim et al. (1986)

$$Z = 1 + c\frac{4\eta - 2\eta^2}{(1-\eta)^3} - \frac{Z_m c V^* Y}{V + V^* Y}$$

$$Y = \exp\left(\frac{T^*}{2T}\right) - 1, \quad \eta = \tau V^* / V, \; T^* = \varepsilon q / ck$$

  - Parameters : c, T^*, V^*
  - The SPHCT EOS retains the advantages of the PHCT EOS.

EOS for Chain Molecules

Hard-sphere chain theory

- Wertheim's thermodynamic perturbation theory (TPT)
  - The association site are replaced by covalent, **chain-forming** bonds.

- Chapman et al. (1988) : Generalization of TPT

$$Z^{hc} = mZ^{hs} - (m-1)\left(1+\eta\frac{\partial \ln g^{hs}(\sigma)}{\partial \eta}\right)$$

  - Z^{hs} is Carnahan-Starling equation.
  - $g^{hs}(\sigma) = \frac{2-\eta}{2(1-\eta)^3}$

EOS for Associating Fluids

Statistical associating fluid theory (SAFT)

- Chapman et al. (1988, 1990)

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{seg}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT}$$

- $$\frac{A^{seg}}{NkT} = m\left(\frac{4\eta - 3\eta^2}{(1-\eta)^3} + \sum_i \sum_j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \right)$$
- $$\frac{A^{chain}}{NkT} = (1-m) \ln \frac{1-\eta/2}{(1-\eta)^3}$$
- $$\frac{A^{assoc}}{NkT} = \sum_\alpha \left[\ln X_\alpha - \frac{X_\alpha}{2} \right] + \frac{1}{2} M$$

EOS for Associating Fluids
Statistical associating fluid theory (SAFT)

- Huang and Radosz (1990)

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

- $$Z^{hs} + Z^{disp} = m\left(\frac{4\eta - 2\eta^2}{(1-\eta)^3} + \sum_i \sum_j jD_{ij}\left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j\right)$$

- $$Z^{chain} = (1-m)\frac{(5/2)\eta - \eta^2}{(1-\eta)[1-(1/2)\eta]}$$

- $$Z^{assoc} = \rho \sum_\alpha \left[\frac{1}{X_\alpha} - \frac{1}{2}\right]\frac{\partial X_\alpha}{\partial \rho}$$

EOS for Associating Fluids

Statistical associating fluid theory (SAFT)

- Development of variable SAFT model
  - Simplified SAFT : Fu and Sandler (1995)

$$Z^{disp} = -m \frac{Z_m V^* Y}{V_s + V^* Y}$$

  - Galindo et al. (1996) : The expression of Boublik for the hard-sphere contribution
  - LJ-SAFT (Banaszak et al., 1994), VR-SAFT (Gil-Villegas et al., 1997), and so on.

Comparing EOS

Interrelationships between different EOS

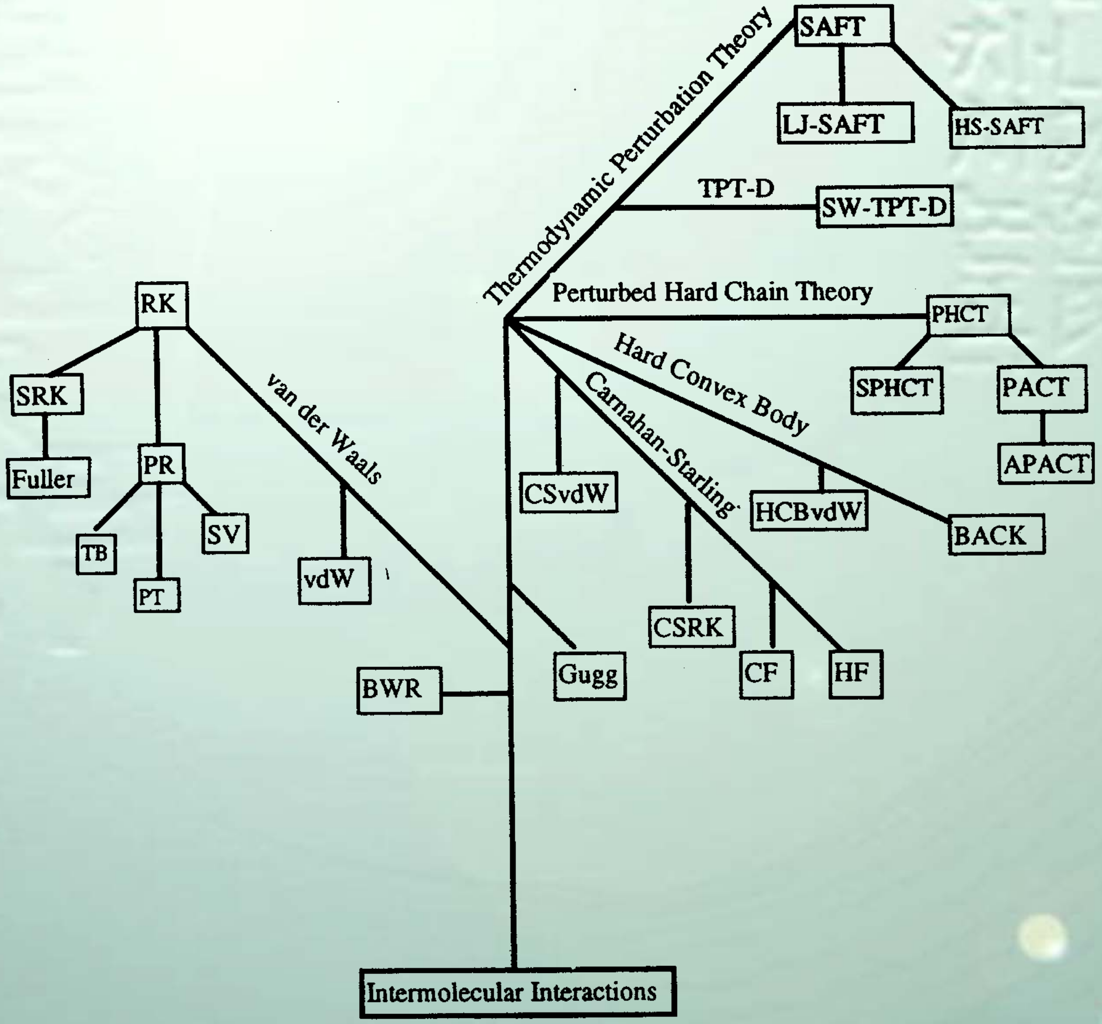
- New EOS
  - Modification of existing ones
  - Reuse of successful EOS to form a new EOS

- The branches in next figure show different ways of representing **intermolecular repulsion.**
  - van der Waals, Carnahan-Starling, HCB, PHCT, and TPT

- The precursor for the development of EOS
  - SRK in empirical EOS's
  - PHCT and SAFT in theoretical EOS's

Comparing EOS

Interrelationships between different EOS



Comparing EOS

Comparison with experiment

- Experimental data
  - The ultimate test of the accuracy of an EOS
  - No absolute quantitative judgments about the relative merits of competing EOS

- Why is an absolute quantitative judgments difficult?
  - EOS developers test their EOS against experimental data, but not offer an identical comparison with other EOS.
  - The accuracy of EOS is often dependent on highly optimized EOS parameters
  - EOS users adopt a favorite EOS with which they become expert in using.

Comparing EOS

Comparison with experiment

- The true value in using a theoretical EOS
  - Their improved ability to **predict** phase equilibria rather than merely **correlate** data.
  - Correlation of experimental data with PR/SRK at low pressure

    => Failure of the prediction of phase equilibria at high pressure
    - Breakdown of vdW repulsion term

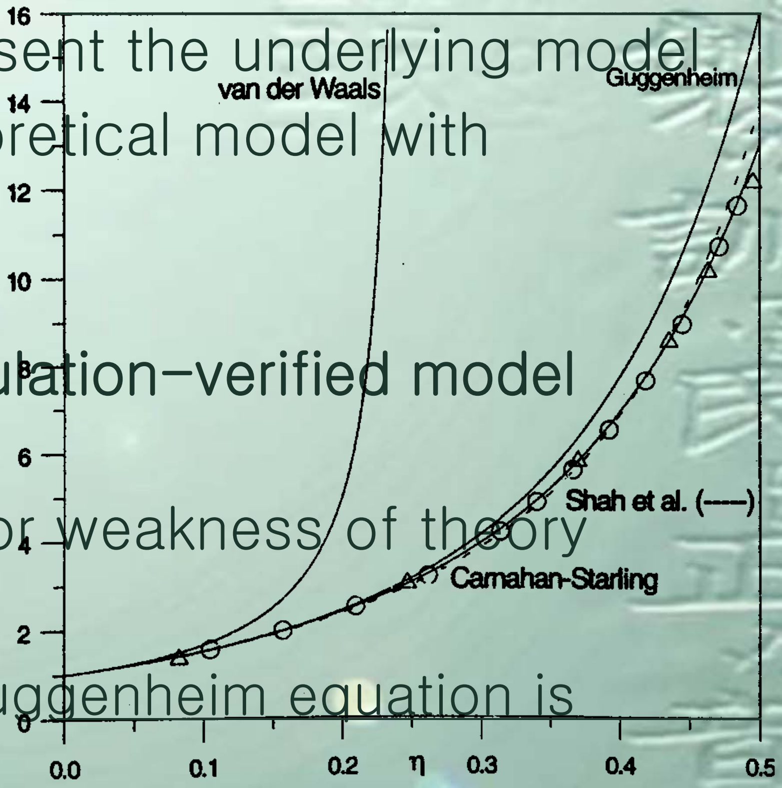
    => Using Carnahan-Starling or Guggenheim repulsion term
  - Ability of calculating full range of phase equilibria of mixtures.

- Theoretical EOS's, such as SAFT and PHCT are promising approaches.

Comparing EOS

Comparison with molecular simulation data

- Molecular simulation
  - Provision of exact data to test the accuracy of theory
  - Discrepancies between theory and MC
    =>Failure of theory to represent the underlying model
  - Direct comparison of a theoretical model with experiment
    => No useful information
  - Direct comparison of a **simulation-verified model** with experiment
    =>To indicate the strength or weakness of theory
  - Example => Show figure
    - Carnahan-Starling and Guggenheim equation is accurate !



Comparing EOS

Comparison with molecular simulation data

- Failure of accuracy in comparison of EOS with MC
  - Not merely due to the failure of theory to represent adequately the underlying model
  - Because of the limitations of theory to model the real molecules

Conclusion

- To meet the challenge posed by large and complicated molecules, EOS are being developed with an improved theoretical basis.
- These new EOS are playing an expanding role in the calculation of various phase equilibria.
- Molecular simulation have an ongoing and crucial role in the improvement of the accuracy of EOS