

Chapter 3 Equations of State

Equations of state play an important role in chemical engineering design and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures. Originally, equations of state were used mainly for pure components. When first applied to mixtures, they were used only for mixtures of nonpolar (Soave, 1972; Peng and Robinson, 1976) and slightly polar compounds (Huron et al., 1978; Asselineau et al., 1978; Graboski and Daubert, 1978). Since then, equations of state have developed rapidly for the calculation of phase equilibria in non-polar and polar mixtures. The advantage of the equations of state method is its applicability over wide ranges of temperature and pressure to mixtures of diverse components, from the light gases to heavy liquids. They can be used for the representation of vapour-liquid, liquid-liquid and supercritical fluid phase equilibria and they can be also applied to the gas, liquid and supercritical phases without encountering any conceptual difficulties.

Many equations of state have been proposed in the literature with either an empirical, semi-empirical or theoretical basis. Comprehensive reviews can be found in the works of Martin (1979), Gubbins (1983), Tsonopoulos and Heidman (1985), Han et al. (1988), Anderko (1990), Sandler (1994) and Donohue and Economou (1995).

The van der Waals equation of state was the first equation to predict vapour-liquid coexistence. Later, the Redlich-Kwong equation of state (Redlich and Kwong, 1949) improved the accuracy of the van der Waals equation by proposing a temperature dependence for the attractive term. Soave (1972) and Peng and Robinson (1976) proposed additional modifications for Redlich-Kwong equation to more accurately predict the vapour pressure, liquid density, and equilibria ratios. Carnahan and Starling (1969), Guggenheim (1965) and Boublik (1981) modified the repulsive term of van der Waals equation of state and obtained their accurate expressions for hard sphere fluid. Christoforakos and Franck (1986) modified both the attractive and repulsive terms of van der Waals equation of state.

In addition to modelling small molecules, considerable emphasis has been placed recently on modelling long molecules. Based on Prigogine's (1957) and Flory's (1965) theory, Beret and Prausnitz (1975) and Donohue and Prausnitz (1978) constructed an equation for molecules treated as chains of segments, Perturbed-Hard-Chain-Theory (PHCT). To overcome the mathematical complexity of PHCT, Kim et al. (1986) developed a simplified

version of PHCT (SPHCT) by replacing the complex attractive part of PHCT by a simpler expression. To take into account the increase in attractions due to dipolar and quadrupolar forces, Vimalchand and Donohue (1985) obtained fairly accurate multipolar mixture calculations by using the Perturbed Anisotropic Chain Theory (PACT). Ikononou and Donohue (1986) extended the PACT to obtain an equation of state which takes into account the existence of hydrogen bonding, that is the Associated Perturbed Anisotropic Chain Theory (APACT).

Advances in statistical mechanics and increase of computer power allowed the development of equation of state based on molecular principles that are accurate for real fluids and mixtures. Using Wertheim's theory, Chapman et al. (1990) and Huang and Radosz (1990) developed the Statistical-Associating-Fluid-Theory (SAFT) which is accurate for pure fluids and mixtures containing associating fluids. Recently, various modified versions, such as LJ-SAFT (Kraska and Gubbins, 1996a & b), SAFT-VR (Gil-Villegas et al., 1997), have been developed.

In this chapter we will review equations of state with particular emphasis on application to phase equilibrium and theoretically used equations of state. In general, equations of state can be classified as being a member of one of three families:

1. Equations of State for Simple Molecules
2. Equations of State for Chain Molecules
3. Equations of State for Associating Fluids

3.1 Equation of State for Simple Molecules

3.1.1 van der Waals Equation

The van der Waals equation of state, proposed in 1873 (Rowlinson, 1988), was the first equation capable of representing vapour-liquid coexistence:

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad (3.1)$$

where p represents pressure, T is temperature, V is volume and R is the molar gas constant. The parameter a is a measure of the attractive forces between the molecules and the parameter b is a measure of the size of the molecules (hard body term). Both adjustable parameters a and b can be obtained from the critical properties of the fluid. The van der Waals equation can be regarded as a “hard-sphere (repulsive) + attractive” term equation of state composed from the contribution of repulsive and attractive intermolecular interactions, respectively. It gives a qualitative description of the vapour and liquid phases and phase transitions (Van Konynenburg and Scott, 1980), but it is rarely sufficiently accurate for critical properties and phase equilibria calculations. A simple example is that for all fluids, the critical compressibility predicted by Eq.(3.1) is 0.375, whereas the real value for different hydrocarbons varies from 0.24 to 0.29. The van der Waals equation has been superseded by a large number of other, more accurate equations of state.

3.1.2 Modification of the Attractive Term

Many modifications of the attractive term have been proposed. Some of these are listed and compared in Table 3.1.

Benedict et al. (1940) suggested a multi-parameter equation of state, known as the Benedict-Webb-Rubin (BWR) equation

$$p = \frac{RT}{V} + \left(\frac{B_0 RT - A_0 - C_0/T^2}{V^2} \right) + \left(\frac{bRT - a}{V^3} \right) + \frac{aa}{V^6} + \left(\frac{c}{V^3 T^2} \right) \left(1 + \frac{g}{V^2} \right) \exp\left(-\frac{g}{V^2} \right) \quad (3.2)$$

where $A_0, B_0, C_0, a, b, c, \mathbf{a}, \mathbf{g}$ are eight adjustable parameters. The BWR equation could treat supercritical components and was able to work in the critical area. However, the BWR equation suffers from three major disadvantages. First, the parameters for each compound must be determined separately by reduction of plentiful, accurate pressure-volume-temperature (PVT) and vapour-liquid-equilibrium (VLE) data. Second, the large number of adjustable parameters makes it difficult to extend to mixtures. Third, its analytical complexity results in a relatively long computing time.

Table 3.1 Summary of Modification of Attractive term of van der Waals Equation

Equation	Year	Attractive term
Redlich-Kwong	1949	$\frac{a}{T^{0.5}V(V+b)}$
Soave	1972	$\frac{a(T)}{V(V+b)}$
Peng-Robinson	1976	$\frac{a(T)}{V(V+b)+b(V-b)}$
Fuller	1976	$\frac{a(T)}{V(V+cb)}$
Heyen (Sandler, 1994)	1980	$\frac{a(T)}{V^2+(b(T)+c)V-b(T)c}$
Schmidt-Wenzel	1980	$\frac{a(T)}{V^2+ubV+wb^2}$
Harmens-Knapp	1980	$\frac{a(T)}{V^2+Vcb-(c-1)b^2}$
Kubic	1982	$\frac{a(T)}{(V+c)^2}$
Patel-Teja	1982	$\frac{a(T)}{V(V+b)+c(V-b)}$
Adachi et al.	1983	$\frac{a(T)}{(V-b_2)(V+b_3)}$
Stryjek-Vera	1986a	$\frac{a(T)}{(V^2+2bV-b^2)}$
Yu and Lu	1987	$\frac{a(T)}{V(V+c)+b(3V+c)}$
Treble and Bishnoi	1987	$\frac{a(T)}{V^2+(b+c)V-(bc+d^2)}$
Schwartzentruber and Renon	1989	$\frac{a(T)}{(V+c)(V+2c+b)}$

Perhaps, the most important model for the modification of the van der Waals equation of state is the Redlich-Kwong (RK) equation (Redlich and Kwong, 1949). It retains the van der Waals hard-sphere term but a temperature dependence was introduced in the attractive term:

$$p = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad (3.3)$$

For pure substances the equation parameters a and b are usually expressed as

$$a = 0.4278R^2T_c^{2.5} / p_c \quad (3.4)$$

$$b = 0.0867RT_c / p_c \quad (3.5)$$

Carnahan and Starling (1972) used the Redlich-Kwong equation of state to compute the gas phase enthalpies for a variety of substances, many of which are polar and/or not spherically symmetric. Their results showed that the Redlich-Kwong equation is a significant improvement over the van der Waals equation. Abbott (1979) also concluded that the Redlich-Kwong equation performed relatively well for the simple fluids Ar, Kr, and Xe (for which the acentric factor is equal to zero), but it did not perform well for complex fluids with nonzero acentric factors.

The Redlich-Kwong equation of state can be used for mixtures by applying mixing rules to the equation of state parameters. It offered remarkable success in improving the van der Waals equation with a better description of the attractive term. Joffe and Zudkevitch (1966) showed that substantial improvement in the representation of fugacity of gas mixtures could be obtained by treating interaction parameters as empirical parameters. The results of the critical properties calculations for binary mixtures indicated that adjusting the value of binary interaction parameters in the mixing rules of the parameter a of the Redlich-Kwong equation of state could reduce the average error levels in the predicted critical properties for most binary mixtures. Spear et al. (1969) demonstrated that the Redlich-Kwong equation of state could be used to calculate the gas-liquid critical properties of binary mixtures. Chueh and

Prausnitz (1967a & b) also showed that the Redlich-Kwong equation can be adapted to predict both vapour and liquid properties. Several other workers (Deiters and Schneider, 1976; Baker and Luks, 1980) applied the Redlich-Kwong equation to the critical properties and the high pressure phase equilibria of binary mixtures. For ternary mixtures, Spear et al. (1971) gave seven examples of systems for which the gas-liquid critical properties of hydrocarbon mixtures could be calculated by using the Redlich-Kwong equation of state. The results showed that the accuracy of the Redlich-Kwong equation of state calculations for ternary systems was only slightly less than that for the constituent binaries.

The success of the Redlich-Kwong equation has been the impetus for many further empirical improvements. Soave (1972) suggested replacing the term $a / T^{0.5}$ with a more general temperature-dependent term $a(T)$, that is:

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (3.6)$$

where:

$$a(T) = 0.4274 \left(\frac{R^2 T^{c2}}{p^c} \right) \left\{ 1 + m \left[1 - \left(\frac{T}{T^c} \right)^{0.5} \right] \right\}^2 \quad (3.7)$$

$$m = 0.480 + 157\omega - 0.176\omega^2 \quad (3.8)$$

$$b = 0.08664 \frac{RT^c}{p^c} \quad (3.9)$$

ω is the acentric factor. To test the accuracy of Soave-Redlich-Kwong (SRK) equation, the vapour pressures of a number of hydrocarbons and several binary systems were calculated and compared with experimental data (Soave, 1972). In contrast to the original Redlich-Kwong equation, Soave's modification fitted the experimental curve well and was able to predict the phase behaviour of mixtures in the critical region. Elliott and Daubert (1985) reported an accurate representation of vapour-liquid equilibria with the Soave equation for 95

binary systems containing hydrocarbon, hydrogen, nitrogen, hydrogen sulfide, carbon monoxide, and carbon dioxide. Elliott and Daubert (1987) also showed that the Soave equation improved the accuracy of the calculated critical properties of these mixtures. Accurate results (Han et al., 1988) were also obtained for calculations of the vapour-liquid equilibrium of symmetric mixtures and methane-containing mixtures.

In 1976, Peng and Robinson (1976) redefined $a(T)$ as

$$a(T) = 0.45724 \left(\frac{R^2 T^{c2}}{p^c} \right) \left\{ 1 + k \left[1 - \left(\frac{T}{T^c} \right)^{0.5} \right] \right\}^2 \quad (3.10)$$

$$k = 0.37464 + 1.5422w - 0.26922w^2 \quad (3.11)$$

$$b = 0.07780 \frac{RT^c}{p^c} \quad (3.12)$$

Recognising that the critical compressibility factor of the Redlich-Kwong equation ($Z_c = 0.333$) is overestimated, they proposed a different volume dependence

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (3.13)$$

The Peng-Robinson (PR) equation slightly improves the prediction of liquid volumes and predicts a critical compressibility of $Z_c = 0.307$. Peng and Robinson (1976) gave examples of the use of the Peng-Robinson equation for predicting the vapour pressure and volumetric behaviour of single-component systems, and the phase behaviour and volumetric behaviour of binary, ternary and multicomponent system, and concluded that Eq.(3.10) can be used to accurately predict the vapour pressures of pure substances and equilibrium ratios of mixtures. The Peng-Robinson equation performed as well as or better than the Soave-Redlich-Kwong equation. Han et al. (1988) reported that the Peng-Robinson equation was superior for predicting vapour-liquid equilibrium in hydrogen and nitrogen containing mixtures.

The Peng-Robinson and Soave-Redlich-Kwong equations are widely used in industry. The advantages of these equations are that they can accurately and easily represent the relation among temperature, pressure, and phase compositions in binary and multicomponent systems. They only require the critical properties and acentric factor for the generalised parameters, little computer time and lead to good phase equilibrium prediction. However, the success of these modifications is restricted to the estimation of vapour pressure. The calculated saturated liquid volumes are not improved and are invariably higher than the measured data.

Fuller (1976) proposed a three parameter equation of state which has the form

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+cb)} \quad (3.14)$$

with the additional parameter added is denoted as c . At the critical point

$$\mathbf{b}_c = \frac{b}{V_c} \quad (T = T_c) \quad (3.15)$$

At the critical point it is found that

$$c(\mathbf{b}) = \frac{1}{\mathbf{b}} \left(\sqrt{\frac{1}{\mathbf{b}} - \frac{3}{4}} - \frac{3}{2} \right) \quad (3.16)$$

$$b = \Omega_b(\mathbf{b}) \frac{RT_c}{P_c} \quad (3.17)$$

$$\Omega_b(\mathbf{b}) = \mathbf{b} \frac{(1-\mathbf{b})(2+c\mathbf{b}) - (1+c\mathbf{b})}{(2+c\mathbf{b})(1-\mathbf{b})^2} \quad (3.18)$$

$$a(T) = \frac{\Omega_a(\mathbf{b})R^2T_c a(T)}{P_c} \quad (3.19)$$

$$\Omega_a(\mathbf{b}) = \frac{(1 + c\mathbf{b})^2 \Omega_b(\mathbf{b})}{\mathbf{b}(1 - \mathbf{b})^2 (2 + c\mathbf{b})} \quad (3.20)$$

$$\mathbf{a}^{1/2}(T) = 1 + q(\mathbf{b})(1 - Tr^{1/2}) \quad (3.21)$$

$$q(\mathbf{b}) = (\mathbf{b} / 0.26)^{1/4} m \quad (3.22)$$

$$m = 0.480 + 1.5740\mathbf{w} - 0.176\mathbf{w}^2 \quad (3.23)$$

$$Z_c(\mathbf{b}) = \frac{p_c V_c}{RT_c} = \frac{-(1 - \mathbf{b}c)(2 + c_c \mathbf{b}_c) - (1 + c_c \mathbf{b}_c)}{(2 + c_c \mathbf{b}_c)(1 - \mathbf{b}_c)^2} \quad (3.24)$$

Fuller's modification contain two features. First, the equation of state leads to a variable critical compressibility factor, and second, a new universal temperature function is incorporated in the equation making both the a and b parameters functions of temperature. Fuller's equation can be reduced to the Soave-Redlich-Kwong and van der Waals equations. If $\mathbf{b}_c = 0.259921$, then we have $c = 1$, $\Omega_a = 0.4274802$, $\Omega_b = 0.0866404$, $Z_c = 0.333$, and the Soave-Redlich-Kwong equation is obtained. If \mathbf{b}_c has a value of $1/3$, then $c = 0$, $\Omega_a = 0.421875$, $\Omega_b = 0.125$, $Z_c = 0.375$, and van der Waals equation is obtained.

Fuller (1976) reported that the proposed modification produced a root-mean-square error in saturated liquid volumes of less than 5%. In the majority of cases it also improved the vapour pressure deviations of the original Soave-Redlich-Kwong equation. The results of calculations indicated that this equation is capable of describing even polar molecules with reasonable accuracy.

Similar to Fuller's equation, Table 3.1 also shows that a feature of many of the empirical improvements is the addition of adjustable parameters. A disadvantage of three parameters (or more parameters) equation of state is that the additional parameters must be obtained from additional pure component data. They almost invariably require one (or more) additional mixing rules when the equation is extended to mixtures. The Peng-Robinson and Soave-Redlich-Kwong equations fulfil the requirements of both simplicity and accuracy since they require little input information, except for the critical properties and acentric factor for the

generalised parameters a and b . Consequently, although many equations of state have been developed, the Peng-Robinson and Soave-Redlich-Kwong equations are widely used in industry, and often yield a more accurate representation (Palenchar et al. 1986) than other alternatives.

3.1.3 Modification of the Repulsive Term

The other way to modify the van der Waals equation is to examine the repulsive term of a hard sphere fluid. Many accurate representations have been developed for the repulsive interactions of hard spheres and incorporated into the equation of state. Several proposals have been reported; some of them are summarised in Table 3.2.

Table 3.2 Summary of Modification of Repulsive term of the van der Waals Equation

Equation	Year	Repulsive term
Reiss et al.	1959	$\frac{RT(1 + y + y^2)}{V(1 - y)^3}$
Thiele	1963	$\frac{RT(1 + y + y^2)}{V(1 - y)^3}$
Guggenheim	1965	$\frac{RT}{V(1 - y)^4}$
Carnahan-Starling	1969	$\frac{RT(1 + y + y^2 - y^3)}{V(1 - y)^3}$
Scott	1971	$\frac{RT(V + b)}{V(V - b)}$
Boublik	1981	$\frac{RT(1 + (3a - 2)y + (3a^2 - 3a + 1)y^2 - a^2y^3)}{V(1 - y)^3}$

Among them, the most widely used equation is the Carnahan-Starling equation. Carnahan and Starling (1969) obtained an accurate expression for the compressibility factor of hard sphere fluids which compared well with molecular-dynamics data (Reed and Gubbins, 1973). The form is

$$Z_c = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \quad (3.25)$$

with $y = b / 4V$ and b is the volume occupied by 1 mol of molecules.

To improve the accuracy of the van der Waals equation, Carnahan and Starling (1972) substituted Eq.(3.25) for the traditional term $RT / (V - b)$ resulting in the following equation of state

$$p = \frac{RT(1 + y + y^2 - y^3)}{V(1 - y)^3} - \frac{a}{V^2} \quad (3.26)$$

Both a and b can be obtained by using critical properties ($a = 0.4963 R^2T_c^2/p_c$, $b = 0.18727RT_c/p_c$). Sadus (1993) has demonstrated that Carnahan-Starling equation can be used to predict the Type III equilibria of non-polar mixtures with considerable accuracy.

The Guggenheim equation (Guggenheim, 1965) is a simple alternative to the Carnahan-Starling. It also incorporates an improved hard-sphere repulsion term in conjunction with the simple van der Waals description of attractive interactions.

$$p = \frac{RT}{V(1 - y)^4} - \frac{a}{V^2} \quad (3.27)$$

The covolume ($b = 0.18284RT_c/p_c$) and attractive ($a = 0.49002 R^2T_c^2/p_c$) equation of state parameters are related to the critical properties.

The Guggenheim equation has been used to predict the critical properties of diverse range of binary mixtures (Hicks and Young, 1976; Hurle et al., 1977a & b; Hicks et al., 1977 & 1978; Semmens et al., 1980; Sadus and Young, 1985a & b; Waterson and Young, 1978; Toczylkin and Young, 1977, 1980a & b & c; and Sadus, 1992a & 1994). Despite the diversity of the systems studied, good results were consistently reported for the gas-liquid critical locus. The critical liquid-liquid equilibria of Type II mixtures was also represented adequately. In contrast, calculations involving Type III equilibria are typically only semi-quantitative (Christou et al., 1986) because of the added difficulty of predicting the transition

between gas-liquid and liquid-liquid behaviour. The Guggenheim equation has also been proved valuable in calculating both the gas-liquid critical properties (Sadus and Young, 1988) and general critical transitions of ternary mixtures (Sadus, 1992a).

Boublik (1981) has generalised the Carnahan-Starling hard sphere potential for molecules of arbitrary geometry via the introduction for a nonsphericity parameter (α). Svejda and Kohler (1983) employed the Boublik expression in conjunction with Kihara's (1963) concept of a hard convex body (HCB) to obtain a generalised van der Waals equation of state:

$$p = \frac{RT(1 + (3\mathbf{a} - 2)y + (3\mathbf{a}^2 - 3\mathbf{a} + 1)y^2 - \mathbf{a}^2 y^3)}{V(1 - y)^3} - \frac{a}{V^2} \quad (3.28)$$

Sadus et al. (1988) and Christou et al. (1991) have used Eq.(3.28) for the calculation of the gas-liquid critical properties of binary mixtures containing nonspherical molecules. The results obtained were slightly better than could be obtained from similar calculations using the Guggenheim equation of state. Sadus (1993) proposed an alternative procedure for obtaining the equation of state parameters. Eq.(3.28) in conjunction with this modified procedure can be used to predict Type III critical equilibria of nonpolar binary mixtures with a good degree of accuracy.

Sadus (1994) compared the compressibility factors predicted by the van der Waals, Guggenheim and Carnahan-Starling hard-sphere contributions with molecular simulation data (Alder and Wainwright, 1960, Barker and Henderson, 1971) for one-component hard-sphere fluid (Fig. 3.1). The results demonstrated that the hard-sphere term of Guggenheim equation is as accurate as Carnahan-Starling term at low to moderately high densities.

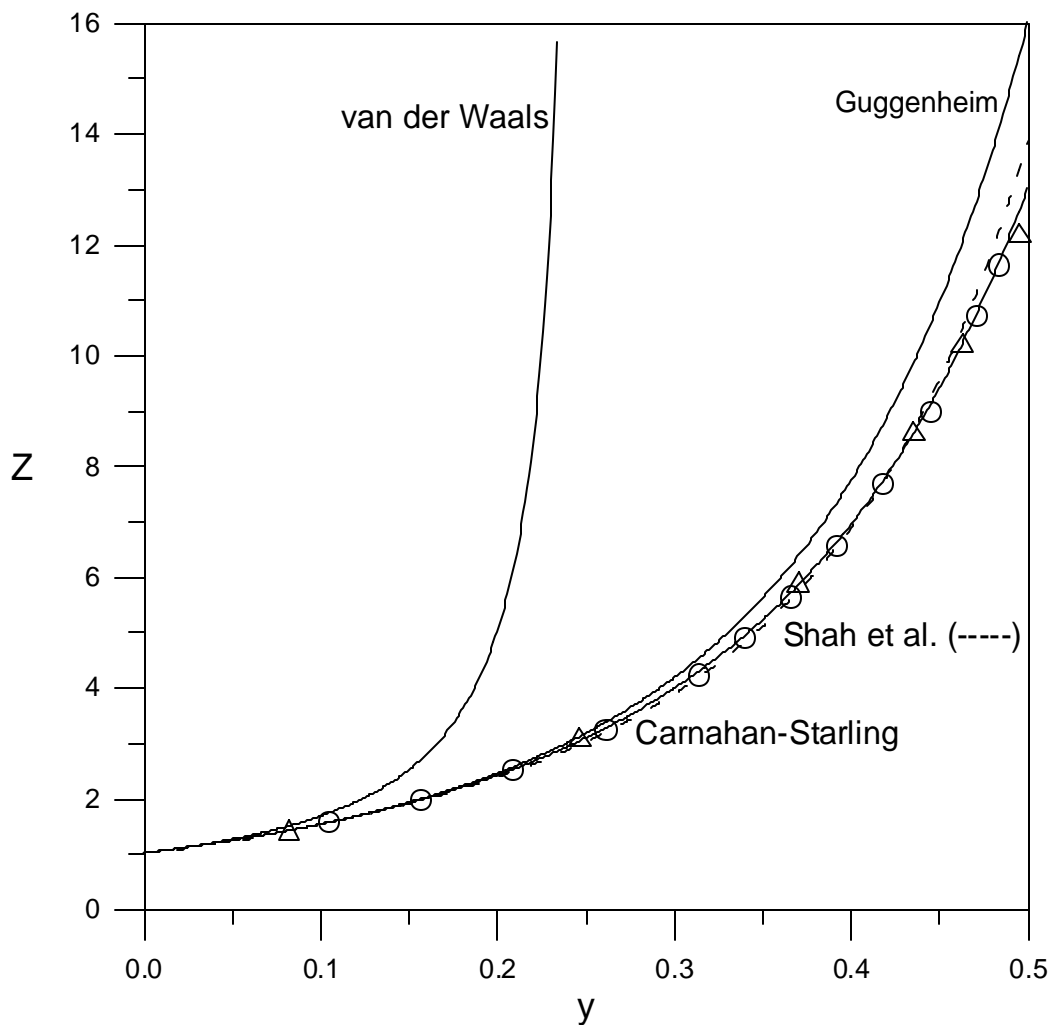


Figure 3.1. Comparison of the hard-sphere compressibility obtained from different equations of state with molecular simulation data (Δ , Alder and Wainwright, 1960, O , Barker and Henderson, 1971) for hard spheres.

3.1.4 Modification of both Attractive and Repulsive Terms

Other equations of state have been formed by modifying both attractive and repulsive terms, or by combining an accurate hard sphere model with an empirical temperature dependent attractive contribution.

Carnahan and Starling (1972) combined the Redlich-Kwong attractive term with their repulsive term

$$p = \frac{RT(1 + y + y^2 - y^3)}{V(1 - y)^3} - \frac{a}{T^{0.5}V(V + b)} \quad (3.29)$$

Their results (Carnahan and Starling, 1972) demonstrated that this combination improved the predication of hydrocarbon densities and supercritical phase equilibria. De Santis et al. (1976) also tested Eq.(3.29) and concluded that Eq.(3.29) yielded good results for the case of pure components in the range spanning ideal gas to saturated liquids. When applied to mixtures for predicting vapour-liquid equilibria, good accuracy in wide ranges of temperature and pressure can be obtained.

McElroy (1983) has combined the Guggenheim hard sphere model with the attractive term of the Redlich-Kwong equation.

$$p = \frac{RT}{V(1 - y)^4} - \frac{a}{T^{0.5}V(V + b)} \quad (3.30)$$

The accuracy of this equation has not been widely tested.

Christoforakos and Franck (1986) proposed an equation of state which used the Carnahan-Starling (1969) expression for the construction of repulsive term and a square well intermolecular potential to obtain the contribution of attractive intermolecular interaction to address deficiencies in the representation of both attractive and repulsive interactions:

$$p = \frac{RT}{V} \frac{V^3 + V^2 \mathbf{b} + V \mathbf{b}^2 - \mathbf{b}^3}{(V - \mathbf{b})^3} - \frac{4 \mathbf{b} RT}{V^2} (\mathbf{I}^3 - 1) \left[\exp\left(\frac{\mathbf{e}}{RT}\right) - 1 \right] \quad (3.31)$$

where $\mathbf{b} = b(T^c / T)^{3/m}$, m is typically assigned a value of 10, and V denotes molar volume.

The other equation of state parameters can be derived from the critical properties:

$$b = 0.04682 RT^c / p^c \quad (3.32)$$

$$\frac{\mathbf{e}}{R} = T^c \ln[1 + 2.65025 / (\mathbf{I}^3 - 1)] \quad (3.33)$$

The ε parameter reflects the depth of the square well intermolecular potential and λ is the relative width of the well. This equation was successfully applied to the high temperature and high pressure phase behaviour of some binary aqueous mixtures (Christoforakos and Franck, 1986).

Heilig and Franck (1989 & 1990) modified the Christoforakos-Franck equation of state and they also employ a temperature-dependent Carnahan-Starling (1969) representation of repulsive forces between hard-spheres and a square-well representation for attractive forces,

$$p = \frac{RT(V^3 + bV^2 + b^2V - b^3)}{V(V-b)^3} + \frac{RTB}{V^2 + (C/B)V} \quad (3.34)$$

where $b = b^c(T^c/T)^z$, b^c is the critical molecular volume and $z = 0$. The B and C terms in Eq.(3.34) represent the contributions from the second and third virial coefficients, respectively, of a hard-sphere fluid interacting via a square-well potential. This potential is characterised by three parameters reflecting intermolecular separation (σ), intermolecular attraction (ε/RT) and the relative width of the well (λ). The following universal values (Mather et al., 1993) were obtained by solving the critical conditions of a one-component fluid, for example, $\lambda = 1.26684$, $N_A s^3 / V^c = 0.24912$ (where N_A denotes Avogadro's constant) and $\varepsilon/RT^c = 1.51147$. Accurate calculations of the critical properties of both binary and ternary mixtures (Heilig and Franck, 1989 & 1990) have been reported. Shmonov et al. (1993) used Eq.(3.34) to predict high-pressure phase equilibria for the water + methane mixture and reported that the Heilig-Franck equation of state was likely to be more accurate than other "hard sphere + attractive term" equations of state for the calculation of phase equilibria involving a polar molecule.

Shah et al. (1994) developed a new equation of state. They used Z_{hs} and Z_{att} as the repulsive and the attractive contribution to the compressibility, respectively,

$$Z_{hs} = \frac{V}{(V - k_0 a)} + \frac{ak_1 V}{(V - k_0 a)^2} \quad (3.35)$$

$$Z_{att} = -\frac{aV^2 + k_0 \mathbf{a}cV}{V(V+e)(V-k_0 \mathbf{a})RT} \quad (3.36)$$

where $\mathbf{a} = 0.165V_c \left\{ \exp \left[-0.03125 \ln \left(\frac{T}{T_c} \right) - 0.0054 \left\{ \ln \left(\frac{T}{T_c} \right) \right\}^2 \right] \right\}^3$ represents the molar

hard-sphere volume of the fluid, $k_0 = 1.2864$, $k_1 = 2.8225$ and e is a constant, and a and c are temperature-dependent parameters. A new equation, called the quartic equation of state, was formed as

$$p = \frac{RT}{(V-k_0 \mathbf{a})} + \frac{\mathbf{a}k_1 RT}{(V-k_0 \mathbf{a})^2} - \frac{aV + k_0 \mathbf{a}c}{V(V+e)(V-k_0 \mathbf{a})} \quad (3.37)$$

It only needs three properties of a fluid, critical temperature, critical volume, and acentric factor, to be specified to reproduce pressure-volume-temperature and thermodynamic properties accurately. Although it is a quartic equation and yields four roots, one root is always negative and hence physically meaningless, and three roots behave like three roots of an equation. Shah et al. (1994) compared their quartic equation with the Peng-Robinson (1976) and Kubic (1982) equations of state and concluded that it was more accurate than either the Peng-Robinson or the Kubic equation of state.

Lin et al. (1996) extended the generalised quartic equation of state, Eq.(3.37) to polar fluids. When applied to polar fluids, the equation requires four characteristic properties of the pure component, critical temperature, critical volume, acentric factor and dipole moment. They calculated thermodynamic properties of 30 polar compounds, and also compared with experimental literature values and the Peng-Robinson equation for seven polar compounds. Their results showed that various thermodynamic properties predicted from the generalised quartic equation of state were in satisfactory agreement with the experimental data over a wide range of states and for a variety of thermodynamic properties. The generalised quartic equation of state made good improvement in calculating the enthalpy departure, second virial coefficients, and the pressure-volume-temperature properties.

In Figure 3.1, we also compare the compressibility factor predicted by the Shah et al. (1994) hard-sphere contributions ($k_0=1.2864$, $k_1=2.8225$ and $y=\mathbf{a}/V$) with molecular simulation data (Alder and Wainwright, 1960, Barker and Henderson, 1971) for one-component hard-sphere fluid. Figure 3.1 shows that the accuracy of hard-sphere term of Shah et al. equation (----) is the same with Carnahan-Starling hard-sphere term.

3.2 Equations of State for Chain Molecules

3.2.1 Perturbed Hard Chain Theory (PHCT)

Prigogine (1957) introduced a theory to explain the properties of chain molecules. This theory is based on the premise that some rotational and vibrational motions depend on density and hence affect the equation of state and other configurational properties. Based on Prigogine's ideas, Flory (1965) proposed a simple theory for polymer behaviour. It is similar to Prigogine's theory except the expressions used to account for intermolecular interactions are taken from free-volume concepts instead of lattice theory. Limitations of both Prigogine's and Flory's theories are that they can only be used at high densities and they are limited to calculations of liquid phase properties. They give qualitatively incorrect results at low densities because they do not approach the ideal gas law at zero density.

Based on perturbed-hard-sphere theory for small molecules (valid at all densities) and Prigogine's theory for chain molecules (valid only at liquid-like densities), Beret and Prausnitz (1975) developed a new equation of state, called the Perturbed-Hard-Chain-Theory (PHCT) equation of state that is applicable to fluids containing very large molecules as well as simple molecules and to calculations of both gas and liquid phase properties. The PHCT equation differs from Prigogine's and Flory's equations in two important aspects (Vimalchand and Donohue, 1989). First, to increase the applicability of the PHCT equation to a wide range of density and temperature, more accurate expressions in PHCT equation are used for the repulsive and attractive partition functions. Second, to overcome the limitations of the Prigogine's and Flory's theories, the PHCT equation corrects the major deficiency in the Prigogine's and Flory's theories by meeting the ideal gas limit at low densities.

The PHCT equation of state is derived from the following partition function (Q)

$$Q = \frac{V^N}{N! \Lambda^{3N}} \left(\frac{V_f}{V} \right)^N \left[\exp \left(\frac{-\mathbf{f}}{2kT} \right) \right]^N (q_{r,v})^N \quad (3.38)$$

where $q_{r,v}$ is the contribution of rotational and vibrational motion of a molecule, N is the number of molecules, Λ is the length of the thermal de Broglie wave (a constant depending on temperature), ϕ is the mean potential, V_f is called the free-volume which is the volume available to the centre of mass of one molecule as it moves around the system holding the positions of all other molecules fixed. The value of V_f can be calculated from the Carnahan and Starling (1972) expression for hard-sphere molecules.

$$V_f = V \exp \left[\frac{(\mathbf{t} / \tilde{v})(3\mathbf{t} / \tilde{v} - 4)}{(1 - \mathbf{t} / \tilde{v})^2} \right] \quad (3.39)$$

where τ is a numerical constant ($\mathbf{t} = \mathbf{p}\sqrt{2} / 6 = 0.7405$), and \tilde{v} is a reduced volume defined as $\tilde{v} = \frac{V}{Nr v^0}$ (where v^0 is the close-packed volume per mole and r is the number of segments per molecule).

The PHCT equation can be written as

$$Z = Z(\text{hard chain}) - \frac{a}{RTV} \quad (3.40)$$

where compressibility factor Z is defined as $Z = \frac{pV}{RT}$ and

$$Z(\text{hard chain}) = 1 + c \frac{4(\mathbf{t} / \tilde{v}) - 2(\mathbf{t} / \tilde{v})^2}{(1 - \mathbf{t} / \tilde{v})^3} \quad (3.41)$$

where c is 1/3 the number of external degrees of freedom. By using Alder's square-well molecular dynamics results (Alder et al., 1972), the value of a in Eq.(3.40) can be defined as

$$a = -R \left(\frac{e q}{k} \right) (r v^0) \sum_{n=1}^4 \sum_{m=1}^M \left(\frac{m A_{nm}}{\tilde{v}^{m-1}} \right) \left(\frac{1}{\tilde{T}^{n-1}} \right) \quad (3.42)$$

where $e q$ is characteristic energy per molecule, k is Boltzmann's constant, Coefficients A_{nm} are dimensionless constants and are independent of the nature of the molecules and n, m are the index for the exponent in a Taylor series in reciprocal reduced volume.

The PHCT equation has three adjustable parameters: $r v^0$, $(e q/k)$ and c . They can be obtained from pressure-volume-temperature data for gases and liquids and from the vapour-pressure data. In the same paper, Beret and Prausnitz (1975) gave these parameters for twenty-two pure fluids and compared theory with experiment for several fluids. The results indicated that the PHCT equation was applicable to a wide variety of fluids, from hydrogen to eicosane to polyethylene. However, they also reported that the PHCT equation was not good in the critical region in common with other analytical equations of state.

In re-deriving the PHCT equation to allow calculation of mixture properties, Donohue and Prausnitz (1978) slightly modified the perturbed hard chain theory to yield better pure component results and, more importantly, extended the PHCT equation to multicomponent mixtures. The partition function was given by

$$Q = \frac{V^N}{N! \Lambda^{3N}} \left(\frac{V_v}{V} \exp \frac{-\mathbf{f}}{2ckT} \right)^{N_c} \quad (3.43)$$

Eq.(3.43) accounts for the effect of rotational and vibrational degrees of freedom on both the repulsive and attractive forces. The pure component and binary parameters can be obtained by fitting experimental data. For systems where experimental data are not available, correlation allows prediction of parameters. By using these methods they concluded that the PHCT equation can represent the properties of most mixtures commonly encountered in petroleum refining and natural-gas processing even when the components differ greatly in size, shape, or potential energy.

Since then, many workers (Kaul et al., 1980; Liu and Prausnitz, 1979a,b, 1980; Ohzono et al., 1984) have applied the PHCT equation to predict thermodynamic properties of

numerous and varied types of systems of industrial interest. Kaul et al. (1980) predicted Henry's constants using the PHCT equation with low values of binary interaction parameter and they extended the PHCT equation to predict the second virial coefficient of both pure fluids and mixtures. Liu and Prausnitz (1979a) showed that the PHCT equation can be used to accurately predict the solubilities of gases in liquid polymers, where the light component is supercritical, whereas the usual approach using excess functions is not useful in treating such supercritical gas-polymer systems. Liu and Prausnitz (1979b, 1980) also applied the PHCT equation for phase equilibrium calculations in polymeric systems (polymer-solvent, polymer-polymer, polymer-polymer-solvent), taking into account the molecular weight distribution of polymeric molecules. Ohzono et al. (1984) correlated the pure component parameters reported by Donohue and Prausnitz (1978) and Kaul et al. (1980), with the group volumes of Bondi (1968).

The PHCT equation is successful but a practical limitation of the PHCT equation is its mathematical complexity, as a result of the use of the Carnahan-Starling free-volume term and the Alder power series. Consequently, computer calculations, especially for mixtures, are time consuming. Because the PHCT equation has already proved to be valuable in calculating properties of various types of systems, it is useful to consider modifications of the theory which simplify the equation of state. Such simplifications would make the PHCT equation of state more useful to the engineering community.

3.2.2 Simplified Perturbed Hard Chain Theory (SPHCT)

Kim et al. (1986) developed a simplified version of PHCT equation by replacing the attractive term of the PHCT equation with a theoretical but simple expression based on the local composition model of Lee et al. (1985), the equation is called the simplified perturbed hard chain theory (SPHCT)

$$Z = 1 + c \left(Z^{rep} - Z_m \frac{V^* Y}{V + V^* Y} \right) \quad (3.44)$$

where, c is 1/3 the number of external degrees of freedom per molecule; Z_m is the maximum coordination number; V^* represents the closed-packed molar volume given by $N_A \frac{s\mathbf{S}^3}{\sqrt{2}}$, where N_A is Avogadro's number, s is the number of segments per molecule, σ is the hard-core diameter of a segment; Z^{rep} is calculated from the hard-sphere equation of Carnahan and Starling (1972)

$$Z^{rep} = \frac{4\mathbf{h} - 2\mathbf{h}^2}{(1 - \mathbf{h})^3} \quad (3.45)$$

and

$$Y = \exp\left(\frac{T^*}{2T}\right) - 1 \quad (3.46)$$

where $\mathbf{h} = tV^* / V$ and $T^* = \frac{eq}{ck}$.

For pure components, the SPHCT equation of state can be written as

$$p = \frac{RT}{V} + \frac{cRT}{V} \frac{4\mathbf{h} - 2\mathbf{h}^2}{(1 - \mathbf{h})^3} - \frac{RT}{V} \frac{Z_m c V^* Y}{V + V^* Y} \quad (3.47)$$

The SPHCT equation of state has three parameters (c , T^* and V^*) and these parameters can be evaluated by fitting simultaneously both vapour pressure and liquid density data. Kim et al. (1986) obtained these three parameters for several n-alkanes and multipolar fluids and van Pelt (1992) obtained them for more than 100 fluids.

To extend the SPHCT equation to mixtures, Kim et al. (1986) proposed the following mixing rules

$$\langle V^* \rangle = \sum_i x_i V_i^* = \sum_i x_i \frac{s_i \mathbf{S}_{ii}^3}{\sqrt{2}} \quad (3.48)$$

$$\langle c \rangle = \sum_i x_i c_i \quad (3.49)$$

$$\langle cV^*Y \rangle = \sum_{ij} x_i x_j c_i v_{ji}^* \left(\exp \frac{\mathbf{e}_{ij} q_i}{2c_i kT} - 1 \right) \quad (3.50)$$

with the cross terms given by

$$\mathbf{s}_{ij} = \frac{\mathbf{s}_{ii} + \mathbf{s}_{jj}}{2} \quad (3.51)$$

$$\mathbf{e}_{ij} = \sqrt{\mathbf{e}_{ii} \mathbf{e}_{jj}} \quad (3.52)$$

The term in angular brackets, $\langle \dots \rangle$, represents a mixture property. For mixtures, the equations of state given by Eq.(3.44) and Eq.(3.47) become:

$$Z = 1 + \langle c \rangle Z^{rep} - \frac{Z_m \langle cV^*Y \rangle}{v + \langle cV^*Y \rangle / \langle c \rangle} \quad (3.53)$$

$$p = \frac{RT}{V} + \frac{\langle c \rangle RT}{V} \frac{4\mathbf{h} - 2\mathbf{h}^2}{(1 - \mathbf{h})^3} - \frac{RT}{V} \left[\frac{Z_m \langle cV^*Y \rangle}{V + \langle cV^*Y \rangle / \langle c \rangle} \right] \quad (3.54)$$

where $\mathbf{h} = \tau (\langle V^* \rangle / V)$ and τ is a constant equal to 0.7405.

The SPHCT equation retains the advantages of the PHCT equation and it also can be used to predict the properties, at all densities, of fluids covering the range from argon and methane to polymer molecules. The SPHCT equation predicted pure-component molar volumes and vapour pressures almost as accurately as the original PHCT equation (Beret and Prausnitz, 1975). It can also predict mixture properties with reasonable accuracy using only pure-component properties. This simpler equation has been used in a number of applications, including for mixtures of molecules which differ greatly in size (Peters et al., 1988). Van Pelt et al. (van Pelt et al., 1991, van Pelt, 1992) applied this simplified version to binary critical

equilibria. Ponce-Ramirez et al. (1991) reported that the SPHCT equation of state was capable of providing adequate phase equilibrium predictions in binary carbon dioxide-hydrocarbon systems over a range of temperature of interest to the oil industry. Plackov et al. (1995) showed that the SPHCT equation of state can be used to improve the quality of predicted vapour pressures of “chain-like” molecules over the entire range of vapour-liquid coexistence. Van Pelt et al. (1995) used the SPHCT equation to calculate phase diagrams for binary mixtures and to classify these phase diagrams in accordance with the system of van Konynenburg and Scott (1980).

3.2.3 Hard Sphere Chain Equation of State

Wertheim (1987) proposed a thermodynamic perturbation theory (TPT) which accommodates hard-chain molecules (Chapter 2). Chapman et al. (1988) generalised Wertheim's TPT model to obtain the following equation of state for the compressibility of a hard-chain of m segments:

$$Z_{HC} = mZ_{HS} - (m-1) \left(1 + \mathbf{h} \frac{\partial \ln g_{HS}(\mathbf{s})}{\partial \mathbf{h}} \right) \quad (3.55)$$

where $g_{HS}(\mathbf{s})$ is the hard-sphere site-site correlation function at contact, σ is the hard-sphere diameter, $\mathbf{h} = \rho m r \sigma^3 / 6$ is the packing fraction, and ρ is the number density. The compressibility of hard sphere can be accurately determined from the Carnahan-Starling equation, Eq.(3.25). For the Carnahan-Starling equation, the site-site correlation function is

$$g_{HS}(\mathbf{s}) = \frac{2 - \mathbf{h}}{2(1 - \mathbf{h})^3} \quad (3.56)$$

Ghonasgi and Chapman (1994) modified TPT for the hard-sphere chain by incorporating structural information for the diatomic fluid. The compressibility of a hard chain can be determined from the hard-sphere compressibility and the site-site correlation function at contact of both hard spheres (g_{HS}) and hard dimers(g_{HD})

$$Z_m = mZ_{HS} - \frac{m}{2} \left(1 + \mathbf{h} \frac{\partial \ln g_{HS}(\mathbf{s})}{\partial \mathbf{h}} \right) - \left(\frac{m}{2} - 1 \right) \left(1 + \mathbf{h} \frac{\partial \ln g_{HD}(\mathbf{s})}{\partial \mathbf{h}} \right) \quad (3.57)$$

Chiew (1991) obtained the site-site correlation results for hard dimers:

$$g_{HD}(\mathbf{s}) = \frac{1 + 2\mathbf{h}}{2(1 - \mathbf{h})^2} \quad (3.58)$$

Chang and Sandler (1994) proposed TPT-D1 and TPT-D2. TPT-D1 can be expressed as

$$Z_m = m \left(\frac{1 + \mathbf{h} + \mathbf{h}^2 - \mathbf{h}^3}{(1 - \mathbf{h})^3} \right) - \frac{m}{2} \left(1 + \frac{\mathbf{h}(5 - 2\mathbf{h})}{(1 - \mathbf{h})(2 - \mathbf{h})} \right) - \left(\frac{m}{2} - 1 \right) \left(1 + \frac{2\mathbf{h}(2 + \mathbf{h})}{(1 - \mathbf{h})(1 + 2\mathbf{h})} \right) \quad (3.59)$$

TPT-D2 can be represented as

$$Z_m = m \left(\frac{1 + \mathbf{h} + \mathbf{h}^2 - \mathbf{h}^3}{(1 - \mathbf{h})^3} \right) - \frac{m}{2} \left(1 + \frac{\mathbf{h}(5 - 2\mathbf{h})}{(1 - \mathbf{h})(2 - \mathbf{h})} \right) - \left(\frac{m}{2} - 1 \right) \left(1 + \frac{\mathbf{h}(3.498 - 0.24\mathbf{h} - 0.414\mathbf{h}^2)}{(1 - \mathbf{h})(2 - \mathbf{h})(0.534 + 0.414\mathbf{h})} \right) \quad (3.60)$$

Starting from the points of Ghonasgi and Chapman (1994) and Chang and Sandler (1994) above, Sadus (1995) proposed that, in general,

$$g_{HD} = g_{HS}(\alpha \mathbf{h} + c) \quad (3.61)$$

where α and c are the constants for a straight line and the values can be obtained by fitting the molecular simulation data for g_{HS} and g_{HD} , and obtained a new equation of state, called the simplified Thermodynamic Perturbation Theory-Dimer (STPT-D) equation of state. The general form of the STPT-D equation of state for pure hard-sphere chains is

$$Z_m = 1 + m(Z_{HS} - 1) + (1 - m)\mathbf{h} \frac{\partial \ln g_{HS}}{\partial \mathbf{h}} + \frac{\mathbf{a}(2 - m)\mathbf{h}}{2(\mathbf{a}\mathbf{h} + c)} \quad (3.62)$$

Sadus (1995) applied the STPT-D equation to the prediction of both the compressibility of 4-, 8-, 16-, 51- and 201-mer hard-chains and the second virial coefficients of up to 128-mer chains. Comparison with molecular simulation data indicated that the STPT-D equation generally predicts both the compressibility and the second virial coefficient more accurately than other equations of state (Chiew equation, GF-D, TPT-D1, TPT-D2).

By using some elements of the one-fluid theory, Sadus (1996) extended the STPT-D equation to hard-sphere chain mixtures with no additional equation of state parameters required. The compressibility factor predicted by the STPT-D equation of state was compared with molecular simulation data for several hard-sphere chain mixtures containing components with either identical or dissimilar hard-sphere segments. Good agreement with simulation data was obtained when the ratio of hard-sphere segment diameters for the component chains is less than 2. The accuracy of the STPT-D equation compared favourably with the results obtained for other hard-sphere chain equations of state.

3.2.4 Perturbed Anisotropic Chain Theory (PACT)

By including the effects of anisotropic multipolar forces explicitly into the PHCT equation of state, Vimalchand and Donohue (1985) and Vimalchand et al. (1986) developed the perturbed anisotropic chain theory (PACT) which is applicable to simple as well as large polymeric molecules with or without anisotropic interactions. The PACT equation takes into account the effects of differences in molecular size, shape and intermolecular forces including anisotropic dipolar and quadrupolar forces. In terms of the compressibility factor Z , the PACT equation of state can be represented as

$$Z = \frac{pV}{RT} = 1 + Z^{rep} + Z^{iso} + Z^{ani} \quad (3.63)$$

The repulsion term due to hard chains is calculated using the parameter c and the equation of Carnahan-Starling (1972) for hard-sphere molecules defined as

$$Z^{rep} = c \left[\frac{4(\mathbf{t}/\tilde{v}_d) - 2(\mathbf{t}/\tilde{v}_d)^2}{(1 - \mathbf{t}/\tilde{v}_d)^3} \right] \quad (3.64)$$

where, similar to the perturbed hard chain theory, τ is a numerical constant (0.7405) and \tilde{v}_d is a reduced volume.

By extending the perturbation expansion of Barker and Henderson (1967 and Chapter 2) for spherical molecules to chainlike molecules, the attractive Lennard-Jones isotropic interactions are calculated as

$$Z^{iso} = \left[Z_1^{LJ} + Z_2^{LJ} - 2Z_1^{LJ} \left(\frac{A_2^{LJ}}{A_1^{LJ}} \right) \right] / \left(1 - \frac{A_2^{LJ}}{A_1^{LJ}} \right)^2 \quad (3.65)$$

where Z is the compressibility factor, A is the Helmholtz function, LJ stands for Lennard-Jones, iso denotes isotropic interactions,

$$\frac{A_1^{LJ}}{NkT} = \frac{c}{\tilde{T}} \sum_m \frac{A_{1m}}{\tilde{v}_d^m} \quad (3.66)$$

$$Z_1^{LJ} = \frac{c}{\tilde{T}} \sum_m \frac{mA_{1m}}{\tilde{v}_d^m} \quad (3.67)$$

with the constants $A_{11} = -8.538$, $A_{12} = -5.276$, $A_{13} = 3.73$, $A_{14} = -7.54$, $A_{15} = 23.307$, and $A_{16} = -11.2$.

$$\frac{A_2^{LJ}}{NkT} = \frac{c}{\tilde{T}^2} \sum_m \frac{C_{1m}}{2\tilde{v}_d^m} + \frac{C_{2m}}{\tilde{v}_d^{m+1}} + \frac{C_{3m}}{2\tilde{v}_d^{m+2}} \quad (3.68)$$

$$Z_2^{LJ} = \frac{c}{\tilde{T}^2} \sum_m \frac{mC_{1m}}{2\tilde{v}_d^m} + \frac{(m+1)C_{2m}}{\tilde{v}_d^{m+1}} + \frac{(m+2)C_{3m}}{2\tilde{v}_d^{m+2}} \quad (3.69)$$

with the constants $C_{11} = -3.938$, $C_{12} = -3.193$, $C_{13} = -4.93$, $C_{14} = 10.03$, $C_{21} = 11.703$, $C_{22} = -3.092$, $C_{23} = 4.01$, $C_{24} = -20.025$, $C_{31} = -37.02$, $C_{32} = 26.93$, $C_{33} = 26.673$ and the parameter c and two reduced quantities:

$$\tilde{T} = \frac{T}{T^*} = \frac{ckT}{\epsilon q} \quad \text{and} \quad \tilde{v}_d = \frac{v}{v_d^*} = \frac{v\sqrt{2}}{N_A r \sigma^3}$$

where r is the number of segments in a molecule, σ is the segment's hard-core diameter.

The anisotropic multipolar interactions are calculated using the perturbation expansion of Gubbins and Twu (1978) assuming the molecules to be effectively linear,

$$Z^{ani} = \left(Z_2^{ani} + Z_3^{ani} - 2Z_2^{ani} \frac{A_3^{ani}}{A_2^{ani}} \right) \left/ \left(1 - \frac{A_3^{ani}}{A_2^{ani}} \right)^2 \right. \quad (3.70)$$

where the superscript *ani* denotes the anisotropic interactions

$$\frac{A_2^{ani}}{NkT} = -12.44 \frac{cJ^{(10)}}{\tilde{T}_Q^2 \tilde{v}} \quad (3.71)$$

$$Z_2^{ani} = -12.44 \frac{cJ^{(10)}}{\tilde{T}_Q^2 \tilde{v}} \left[1 + \tilde{r} \frac{\partial \ln J^{(10)}}{\partial \tilde{r}} \right] \quad (3.72)$$

$$\frac{A_3^{ani}}{NkT} = 2.611 \frac{cJ^{(15)}}{\tilde{T}_Q^3 \tilde{v}} + 77.716 \frac{cK}{\tilde{T}_Q^3 \tilde{v}^2} \quad (3.73)$$

$$Z_3^{ani} = 2.611 \frac{cJ^{(15)}}{\tilde{T}_Q^3 \tilde{v}} \left[1 + \tilde{r} \frac{\partial \ln J^{(15)}}{\partial \tilde{r}} \right] + 77.716 \frac{cK}{\tilde{T}_Q^3 \tilde{v}^2} \left[2 + \tilde{r} \frac{\partial \ln K}{\partial \tilde{r}} \right] \quad (3.74)$$

where $\tilde{v} = \frac{v}{v^*} = \frac{v\sqrt{2}}{N_A r \mathbf{S}^3}$ and $\tilde{T}_Q = \frac{T}{T_Q^*} = \frac{ckT}{\mathbf{e}_Q q}$ with $\mathbf{e}_Q = \left[\frac{N_A}{\sqrt{2}} \right]^{5/3} \frac{Q_s^2}{a_s}$, a_s is the surface area of a segment and σ is the soft-core diameter of a segment. The quadrupole moment, Q is related to the quadrupolar interaction energy per segment, $Q_s^2 = Q^2 / r(v^*)^{5/3}$.

The PACT equation is valid for large and small molecules, for nonpolar and polar molecules, and at all fluid densities. Vimalchand et al. (1986)'s calculations showed that explicit inclusion of multipolar forces allowed the properties of highly nonideal mixtures to be predicted with reasonable accuracy without the use of a binary interaction parameter. For pure fluids, although prediction of properties for the PACT equation was not better than many other equations of state, the pure-component parameters obtained with the PACT equation were fairly reasonable and could be correlated smoothly.

3.3 Equations of State for Associating Fluids

3.3.1 Associated Perturbed Anisotropic Chain Theory (APACT)

Ikonomou and Donohue (1986) incorporated the infinite equilibrium model and monomer-dimer model into the PACT equation and derived a new equation of state, the associated perturbed anisotropic chain theory (APACT). APACT accounts for isotropic repulsive and attractive interactions, anisotropic interactions due to the dipole and quadrupole moments of the molecules and hydrogen bonding and is capable of predicting thermodynamic properties of pure associating components as well as mixtures of more than one associating component (Ikonomou and Donohue, 1988). The APACT equation of state is written in terms of the compressibility factor, Z , as a sum of the contributions from these particular interactions:

$$Z = 1 + Z^{assoc} + Z^{rep} + Z^{att} \quad (3.75)$$

where Z^{assoc} , Z^{rep} and Z^{att} are the contributions from association, repulsion and attraction, respectively. The Z^{assoc} term for one and two bonding sites per molecule is evaluated from the material balances and expressions for the chemical equilibria. Z^{assoc} is given by Ikonomou and Donohue (1986) and Economou and Donohue (1991, 1992)

$$Z^{assoc} = \frac{n_T}{n_0} - 1 \quad (3.76)$$

where n_T is the true number of moles, and n_0 is the number of moles that would exist in the absence of association. The repulsive and the attractive terms in APACT equation are association independent because of the assumptions made about the variation of the parameters of the associating species with the extent of association. Z^{rep} and Z^{attr} are given by Vimalchand et al. (1985, 1986) and Economou et al. (1995).

$$Z^{rep} = c \frac{4h - 2h^2}{(1-h)^3} \quad (3.77)$$

$$Z^{attr} = Z_1^{LJ} + Z_2^{LJ} + \dots + Z_2^{ani} + Z_3^{ani} + \dots \quad (3.78)$$

Economou and Donohue (1992) extended the APACT equation to compounds with three associating sites per molecule. The three-site APACT equation of state was developed to allow calculation of vapour-liquid equilibria and liquid-liquid equilibria of systems of water and hydrocarbons. Economou and Donohue (1992) tested the accuracy of the three-site APACT equation over a large range of temperatures and pressures for aqueous mixtures with polar and nonpolar hydrocarbons. They concluded that the three-site APACT equation was accurate in predicting phase equilibria of different types for aqueous mixtures of nonpolar hydrocarbons with no adjustable parameters. For aqueous mixtures with polar hydrocarbons, the three-site APACT equation needed a binary parameter for accurate estimation of the phase equilibria. The comparison (Economou and Donohue, 1992) of the two-site and three-site APACT equations of state was also investigated for the prediction of the thermodynamic properties of pure water from the triple point to the critical point. For most of the systems examined, the three-site APACT equation was in better agreement with the experimental data than the two-site APACT equation.

Smits et al. (1994) applied the APACT equation to the supercritical region of pure water and showed that over a large pressure and temperature range the agreement between

the experimental data and the calculated results with APACT equation was good, including the near-critical region. They also reported that, although the difference between the APACT two-site and the APACT three-site model appeared to be small, the accuracy of the three-site APACT equation of state for volumetric properties was higher than that of the two-site model. Economou and Peters (1995) demonstrated that the APACT equation can be applied to correlate the vapour pressure and the saturated liquid and saturated vapour densities of pure hydrogen fluoride from the triple point up to the critical point with good accuracy. In the same year, Economou et al. (1995) applied the APACT equation to water-salt phase equilibria and showed that APACT equation accounted explicitly for the strong dipole-dipole interactions between water and salt molecules.

3.3.2 Statistical Associating Fluid Theory (SAFT)

By extending Wertheim's (1984a & b; 1986a, b & c) theory, Chapman et al. (1988, 1990) and Huang and Radosz (1990) developed the Statistical Associating Fluid Theory (SAFT) equation of state. SAFT equation accounts for hard sphere repulsive forces, dispersion forces, chain formation (for non-spherical molecules) and association and it is presented as a sum of three Helmholtz function terms:

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{seg}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \quad (3.79)$$

where A and A^{ideal} are the total Helmholtz function and the ideal gas Helmholtz function at the same temperature and density.

The term A^{seg} represents segment-segment interactions and can be calculated from

$$\frac{A^{seg}}{NkT} = m \frac{A_0^{seg}}{NkT} \quad (3.80)$$

where m is the number of segments per chain, and A_0^{seg} (per mole of segments) is the residual Helmholtz function of nonassociated spherical segments and it has two contributions: the hard sphere and dispersion:

$$\frac{A_0^{seg}}{NkT} = \frac{A_0^{hs}}{NkT} + \frac{A_0^{disp}}{NkT} \quad (3.81)$$

the hard sphere term can be calculated as proposed by Carnahan and Starling (1969)

$$\frac{A_0^{hs}}{NkT} = \frac{4\mathbf{h} - 3\mathbf{h}^2}{(1 - \mathbf{h})^2} \quad (3.82)$$

where \mathbf{h} is a reduced density and for pure component it defined as

$$\mathbf{h} = \frac{\rho N_{AV}}{6} \mathbf{r} \mathbf{s}^3 m \quad (3.83)$$

where N_{AV} is Avogadro's number, \mathbf{s} is the temperature-dependent segment diameter and \mathbf{r} is the molar density of molecules.

For the dispersion term, Huang and Radosz (1990) used a power series which was initially fitted by Alder et al. (1972) to molecular dynamics data for a square-well fluids,

$$\frac{A_0^{disp}}{NkT} = \sum_i \sum_j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\mathbf{h}}{\mathbf{t}} \right]^j \quad (3.84)$$

where D_{ij} are universal constants which have been fitted to accurate pressure-volume-temperature, internal energy, and second virial coefficient data for argon by Chen and Kreglewski (1977), and u/k is the temperature-dependent dispersion energy of interaction between segments.

The term A^{chain} is due to the presence of covalent chain-forming bonds among the segments and can be determined from

$$\frac{A^{chain}}{NkT} = (1-m) \ln \frac{1-h/2}{(1-h)^3} \quad (3.85)$$

The term A^{assoc} is the Helmholtz function change due to association and for pure components it can be calculated from

$$\frac{A^{assoc}}{NkT} = \sum_{\mathbf{a}} \left[\ln X_{\mathbf{a}} - \frac{X_{\mathbf{a}}}{2} \right] + \frac{1}{2}M \quad (3.86)$$

where M is the number of association sites on each molecule, $X_{\mathbf{a}}$ is the mole fraction of molecules which are *not* bonded at site \mathbf{a} , and the summation is over all associating sites on the molecule.

The SAFT equation was also given by Huang and Radosz (1990) in terms of the compressibility factor Z

$$Z = 1 + Z^{hs} + Z^{disp} + Z^{chain} + Z^{assoc} \quad (3.87)$$

where

$$Z^{hs} = m \frac{4h - 2h^2}{(1-h)^3} \quad (3.88)$$

$$Z^{seg} = m \sum_i \sum_j j D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{h}{t} \right]^j \quad (3.89)$$

$$Z^{chain} = (1-m) \frac{(5/2)h - h^2}{(1-h)[1 - (1/2)h]} \quad (3.90)$$

$$Z^{assoc} = r \sum_A \left[\frac{1}{X^A} - \frac{1}{2} \right] \frac{\mathcal{I}X^A}{\mathcal{I}r} \quad (3.91)$$

Chapman et al. (1990) reported that the agreement with molecular simulation data has been found to be good, at all the stages of model development, for associating spheres, mixtures of associating spheres, and nonassociating chains up to $m=8$. Huang and Radosz (1990, 1991) used the SAFT equation to correlate vapour-liquid equilibria of over 100 real fluids and they also demonstrated that the SAFT equation was applicable to small, large, polydisperse, and associating molecules over the whole density range. When extended to mixtures, Huang and Radosz (1991) tested 60 phase equilibrium data sets for asymmetric (small + large) and associating binary systems. They concluded that the mixing rules for the hard sphere, chain and association terms were not required when using rigorous statistical mechanical expressions. Only the dispersion term required mixing rules, and only one binary temperature-independent parameter was required to represent the experimental data that usually were difficult to predict from the equation of state. The calculation details were given by Huang and Radosz (1991). Yu and Chen (1994) also used SAFT equation to examine the liquid-liquid phase equilibria for 41 binary mixtures and 8 ternary mixtures using many of the parameters of Huang and Radosz (1990, 1991).

Economou and Tsonopoulos (1997) applied APACT and SAFT equations of state to predict the phase equilibrium of water/hydrocarbon mixtures. Shukla and Chapman (1997) presented the form of the SAFT equation of state for fluid mixtures consisting of heteronuclear hard chain molecules and compared well with simulation results for the compressibility factor of pure block, alternate and random copolymer systems. Blas and Vega (1998) applied their modified version of SAFT equation of state (Blas and Vega, 1997) to predict thermodynamic properties, as well as liquid -vapour equilibria, of binary and ternary mixtures of hydrocarbons.

3.3.3 Simplified Statistical Associating Fluid Theory (SSAFT)

Fu and Sandler (1995) developed a simplified statistical associating fluid theory (SSAFT) equation by modifying the dispersion term of the equation. The SSAFT is of the same form as Eq.(3.87)

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

The original hard-sphere, chain, and association terms were kept and the single attraction term of Lee et al. (1985) for the square-well fluid was used to replace the multiterm double series dispersion term which created a much simpler equation of state.

$$Z^{disp} = -mZ_M \left(\frac{V^*Y}{V_s + V^*Y} \right) \quad (3.92)$$

where, similar to the simplified perturbed hard chain theory (SPHCT), Z_M is the maximum coordination number, V_s is the molar volume of a segment, V^* is the closed-packed molar volume of a segment, and

$$Y = \exp\left(\frac{u}{2kT}\right) - 1 \quad (3.93)$$

For pure components, the parameters of the SSAFT equation of state were obtained by fitting vapour pressure and liquid density data and the results (Fu and Sandler, 1995) showed that the SSAFT equation was generally similar to, or slightly more accurate than the original SAFT equation. When the SSAFT equation applied to both self-associating and cross-associating binary mixtures, only one binary adjustable parameter was needed. The comparison (Fu and Sandler, 1995) with the original SAFT equation for binary mixtures demonstrated that the simplified SAFT equation of state usually led to better correlated results than the original SAFT equation, and was simpler and easier to use.

3.3.4 Lennard-Jones Statistical Associating Fluid Theory (LJ-SAFT)

Kraska and Gubbins (1996a & b) modified SAFT equation of state in two major ways. First, a Lennard-Jones equation of state was used for the segment contribution; second, a term was added that accounts for the dipole-dipole interaction in substances like the 1-alkanols and water. This modification was called the LJ-SAFT equation of state and the general expression for the Helmholtz function is given by

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{seg}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} + \frac{A^{dipole}}{NkT} \quad (3.94)$$

where A^{dipole} is a term for the effect of long-range dipolar interaction.

For the Lennard-Jones segment term, Kraska and Gubbins (1996 a&b) used the Kolafa and Nezbeda (1994) equation which covers a larger range of temperature and density and is more reliable outside the region of fit. It can be expressed as

$$\frac{A^{seg}}{NkT} = m \left(A^{hs} + \exp(-\mathbf{g}\mathbf{r}^{*2}) \mathbf{r}T\Delta B_{2,hBH} + \sum_{ij} (C_{ij}T^{i/2} \mathbf{r}^{*j}) \right) \quad (3.95)$$

$$\frac{A^{hs}}{NkT} = T \left(\frac{5}{3} \ln(1-\mathbf{h}) + \frac{\mathbf{h}(34 - 33\mathbf{h} + 4\mathbf{h}^2)}{6(1-\mathbf{h})^2} \right) \quad (3.96)$$

$$\Delta B_{2,hBH} = \sum_{i=-7}^0 C_i T^{i/2} \quad (3.97)$$

$$\mathbf{r}^* = mb/V_m \quad (3.98)$$

$$\mathbf{h} = \frac{\mathbf{p}}{6} \mathbf{r}^* \mathbf{s}_{BH}^3 \quad (3.99)$$

$$\mathbf{s}_{BH} = \sum_{i=-2}^1 D_i T^{i/2} + D_{\ln} \ln T \quad (3.100)$$

where C_i and D_i , C_{ij} and D_{\ln} are numerical constants and adjustable parameters, hBH stands for hybrid Barker-Henderson and details were given by Kolafa and Nezbeda(1994).

For the dipole-dipole term, the resulting Helmholtz function is

$$\frac{A^{dipole}}{NkT} = R\tilde{T}B_2 \left(\frac{1}{1 - (B_3/B_2)} \right) \quad (3.101)$$

$$B_2 = -\frac{2\mathbf{p}}{3} \frac{\mathbf{r}^* \mathbf{m}^{*4}}{T^*} J^{(6)} \quad (3.102)$$

$$B_3 = \frac{32\mathbf{p}^3}{135} \sqrt{\frac{14\mathbf{p}}{5}} \frac{\mathbf{r}^{*2} \mathbf{m}^{*6}}{T^{*2}} K_{222}^{333} \quad (3.103)$$

$$\tilde{T} = \mathbf{e} / k_B \quad (3.104)$$

$$T^* = \frac{T}{\tilde{T}} = \frac{Tk_B}{\mathbf{e}} \quad (3.105)$$

$$\mathbf{m}^* = \mathbf{m} / \sqrt{em\mathbf{s}^3} \quad (3.106)$$

$$\mathbf{r}^* = \mathbf{r}b \quad (3.107)$$

$$b = N_L \mathbf{s}^3 \quad (3.108)$$

The coefficients $J^{(6)}$ and K_{222}^{333} are integrals over two-body and three-body correlation function for the Lennard-Jones fluid and have been calculated by Twu and Gubbins (1978 a&b).

Kraska and Gubbins (1996 a&b) applied the LJ-SAFT equation of state to pure fluids and binary mixtures. The results for pure fluids showed substantially better agreement with experiment than the original SAFT equation for the phase diagram the n-alkanes, 1-alkanols and water. The LJ-SAFT equation of state was also found (Kraska and Gubbins, 1996b) to be more accurate in describing binary mixtures of n-alkane/n-alkane, 1-alkanol/n-alkane, and water/n-alkane mixtures than the original SAFT equation.

3.3.5 Statistical Associating Fluid Theory - Hard Sphere (SAFT-HS)

Another simplified version of SAFT is SAFT-HS equation which treats molecules as chains of hard-sphere segments with van der Waals interactions. In the SAFT-HS (Chapman et al., 1988) equation, the Helmholtz function A is separated into different contributions as

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{hs}}{NkT} + \frac{A^{mf}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{ssoc}}{NkT} \quad (3.109)$$

where A^{hs} is the contribution from hard spheres (HS) to the Helmholtz function and A^{mf} is the contributions from the long-range dispersion forces (MF) to the Helmholtz function. The sum of A^{hs} and A^{mf} is called A^{mono}

$$\frac{A^{mono}}{NkT} = \frac{A^{hs}}{NkT} + \frac{A^{mf}}{NkT} \quad (3.110)$$

the monomer-monomer contribution to the Helmholtz function which refers to the term A^{seg} in the original SAFT equation (Chapman et al., 1990, Huang and Radosz, 1990).

Galindo et al. (1996, 1997) and Garcia -Lisbona et al. (1998) used the expression of Boublik (1970) for the hard sphere contribution,

$$\frac{A^{hs}}{NkT} = \frac{6}{\rho r} \left[\left(\frac{z_2^3}{z_3^2} - z_0 \right) \ln(1 - z_3) + \frac{3z_1 z_2}{(1 - z_3)} + \frac{z_2^3}{z_3(1 - z_3)^2} \right] \quad (3.111)$$

where $\rho = N/V$ is the total number density of the mixture. The reduced densities z_i for a binary mixture are defined as

$$z_i = \frac{\rho r}{6} \left(\sum_{l=1}^n x_l m_l s_{2^l} \right) = \frac{\rho r}{6} (x_1 s_1^l + x_2 m_2 s_2^l) \quad (3.112)$$

z_3 is the overall packing fraction of the mixture, and m_i is the number and s_i the diameter of spherical segments of chain i .

The contribution due to the dispersive attractive interactions is given at the mean-field level in terms of the van der Waals one-fluid theory, for example, for binary mixtures

$$\frac{A^{mf}}{NkT} = -\frac{\mathbf{r}}{kT} (\mathbf{a}_{11}x_1^2 + 2\mathbf{a}_{12}x_1x_2m_2 + \mathbf{a}_{22}x_2^2m_2^2) \quad (3.113)$$

where α represents the integrated strength of segment-segment mean-field attraction, m_2 is the number of spherical segments of chain 2.

By using SAFT-HS equation, Galindo et al. (1996, 1997) performed the phase equilibria predictions with good agreement with experimental results for binary mixtures of water + n-alkanes (Galindo et al., 1996) and water + containing hydro fluoride (Galindo et al., 1997). Garcia-Lisbona et al. (1998) used SAFT-HS to describe the phase equilibria of aqueous solutions of alkyl polyoxyethylene mixtures and reported that the SAFT-HS equation was able to describe the phase behaviour of these systems and the results showed the reasonable agreement between the theoretical prediction and experimental results.

3.3.6 Statistical Associating Fluid Theory - Variable Range (SAFT-VR)

The SAFT expressions are continually being improved. By providing an additional parameter which characterised the range of the attractive part of the monomer-monomer potential, Gil-Villegas et al. (1997) proposed a general version of SAFT for chain molecules formed from hard-core monomers with an arbitrary potential of variable range (VR). As we discussed above, the general form of the SAFT equation of state can be written as

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \quad (3.114)$$

In SAFT-VR (Gil-Villegas et al., 1997), the ideal Helmholtz function A^{ideal} and the contribution to the Helmholtz function due to interaction association A^{assoc} are the same as Eq. (3.79). The contribution due to the monomer segments A^{mono} is given by

$$\frac{A^{mono}}{NkT} = m \frac{A^m}{NkT} = m \left(\frac{A^{hs}}{NkT} + \mathbf{b} \frac{A_1}{NkT} + \mathbf{b}^2 \frac{A_2}{NkT} \right) \quad (3.115)$$

where A^m is the Helmholtz function per monomer, m is the number of monomers per chain,

$\mathbf{b} = \frac{1}{kT}$, A_1 and A_2 are the first two perturbation terms associated with the attractive well.

The contribution to the Helmholtz function due to the formation of a chain of m monomers A^{chain} is

$$\frac{A^{chain}}{NkT} = (1-m) \ln y^M(\mathbf{s}) \quad (3.116)$$

where $y^M(\mathbf{s})$ is the monomer-monomer background correlation function evaluated at hard-core contact.

Gil-Villegas et al. (1997) gave the analytical expressions of the A_1 and A_2 for square-well fluids ranges $1.1 \leq I \leq 1.8$,

$$A_1^{SW} = A_1^{VDW} g^{HS}(1; \mathbf{h}_{eff}) \quad (3.117)$$

$$A_2^{SW} = \frac{1}{2} \epsilon K^{HS} \mathbf{h} \frac{\partial A_1^{SW}}{\partial \mathbf{h}} \quad (3.118)$$

where $\mathbf{h} = \mathbf{r}b$ is the packing fraction, ϵ and λ are the depth and the range parameter of the attractive well, respectively.

$$A_1^{VDW} = -4\mathbf{h}\epsilon(I^3 - 1) \quad (3.119)$$

$$g^{HS}(1; \mathbf{h}_{eff}) = \frac{1 - \mathbf{h}_{eff} / 2}{(1 - \mathbf{h}_{eff})^3} \quad (3.120)$$

with

$$\mathbf{h}_{eff} = c_1 \mathbf{h} + c_2 \mathbf{h}^2 + c_3 \mathbf{h}^3 \quad (3.121)$$

the coefficients c_n were given by the matrix

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix} \begin{pmatrix} 1 \\ \mathbf{I} \\ \mathbf{I}^2 \end{pmatrix} \quad (3.122)$$

In the second-order term (Eq. (3.118)), K^{HS} is the isothermal compressibility of the hard-sphere fluid and was given by

$$K^{HS} = \frac{(1-\mathbf{h})^4}{1+4\mathbf{h}+4\mathbf{h}^2} \quad (3.123)$$

The analytical expressions of the A_1 and A_2 for Sutherland fluids and Yukawa fluids over variable range were also given by Gil-Villegas et al. (1997).

The SAFT-VR theory broadens the scope of the original SAFT equation (Huang and Radosz, 1990) and improves the chain contribution and the mean-field van der Waals description for the dispersion forces of the SAFT-HS treatment. Gil-Villegas et al. (1997) demonstrated the adequacy of the SAFT-VR equation in describing the phase equilibria of chain molecules such as the n -alkanes and n -perfluoroalkanes. Davies et al. (1998) showed that SAFT-VR provided a simple and compact equation of state for Lennard-Jones chains and it is valid for ranges of density and temperature of practical interest. McCabe et al. (1998) used the SAFT-VR equation to predict the high pressure fluid phase equilibrium of binary mixtures of n -alkanes and obtained good agreement with experiment. Galindo et al. (1998) provided a detailed analysis of the SAFT-VR approach for mixtures of fluids with non-conformal intermolecular potentials, i.e., which have attractive interactions of variable range. They examined the adequacy of the monomer contribution to the Helmholtz function by comparing with computer simulation data. The results showed that the SAFT-VR equation of

state provide good representation well for the vapour-liquid and liquid-liquid phase equilibria of mixtures containing square-well molecules.

3.3.7 Cubic Plus Association (CPA) Equation of State

Finally, one interesting equation of state should be mentioned. Kontogeorgis et al. (1996) presented an equation of state suitable for describing associating fluids. The equation combines the simplicity of a cubic equation of state (the Soave-Redlich-Kwong) and the theoretical background of the perturbation theory employed for the association part. The resulting equation, called Cubic Plus Association (CPA) equation of state, was given by

$$p = \frac{RT}{V-b} - \frac{a}{V(V-b)} + \frac{RT}{V} \mathbf{r} \sum_a \left[\frac{1}{X_a} - \frac{1}{2} \right] \mathcal{J} X_a \quad (3.124)$$

where the physical term is that of the Soave-Redlich-Kwong equation of state and the associating term is taken from SAFT equation (Huang and Radosz, 1990). They applied this new equation of state to pure components and obtained good correlations of both vapour pressures and saturated liquid volumes for primary-alcohols, phenol, tert-butyl alcohol, triethylene glycol, and water.

Voutsas et al. (1997) applied the CPA equation of state to liquid-liquid equilibrium calculations in alcohol + hydrocarbon mixtures. They used the conventional van der Waals one-fluid mixing rules for the attractive parameter a and the co-volume parameter b . Satisfactory results were obtained in all cases using only a single temperature-independent binary interaction parameter. They also compared the performance of CPA equation of state with that of the SRK and SAFT equations of state and concluded that the CPA equation provided an improvement over the SRK equation and performed similar to the SAFT model, but it was much simpler, which is of great important for engineering purposes.

3.4 Mixing Rules

The great utility of equation of state is for phase equilibrium calculations involving mixtures. The assumption inherent in such calculation is that the same equation of state used for pure fluids can be used for mixtures if we have a satisfactory way to obtain the mixture parameters. This is commonly achieved by using mixing rules and combining rules which related the properties of the pure components to that of the mixture. The discussion will be limited to the extension of a and b parameters. These two parameters have a real physical significance and are common to many realistic equations of state.

The simplest possible mixing rule is a linear average of the equation of state parameters:

$$a = \sum_i x_i a_i \quad (3.125)$$

$$b = \sum_i x_i b_i \quad (3.126)$$

Eq.(3.126) is sometimes employed (Han et al., 1988) because of its simplicity, but Eq.(3.125) is rarely used because it does not account for the important role of unlike interaction in binary fluids. Consequently, employing both Eq.(3.125) and Eq.(3.126) would lead to the poor agreement of theory with experiment.

3.4.1 The van der Waals Mixing rules

The most widely used mixing rules are the van der Waals one-fluid prescriptions:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (3.127)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (3.128)$$

where a_{ii} and b_{ii} are the constants of the equation for pure component i and cross parameters a_{ij} and b_{ij} ($i \neq j$) are determined by an appropriate combining rule with or without binary parameters.

Eq.(3.127) and Eq.(3.128) are based on the implicit assumption that the radial distribution function of the component molecules are identical, and they both explicitly contain a contribution from interactions between dissimilar molecules. A comparison (Harismiadis et al., 1991) with computer simulation has concluded that the van der Waals mixing rules are reliable for mixtures exhibiting up to an eight-fold difference in the size of the component molecules. The performance of the van der Waals mixing rules has also been thoroughly tested for several equations of state by Han et al. (1988). They used the van der Waals mixing rule Eq.(3.127) to obtain parameter a and the linear mixing rule Eq.(3.126) to obtain parameter b . Their results showed that most of equations of state with the van der Waals mixing rules were capable of representing vapour-liquid equilibria with only one binary adjustable parameter for obtaining a_{ij} .

Eq.(3.127) and Eq.(3.128) were quite adequate with mixtures of nonpolar and slightly polar compounds (Peng and Robinson, 1976; Han et al., 1988). Voros and Tassios (1993) compared six mixing rules (the one- and two parameters van der Waals mixing rules; the pressure- and density-dependent mixing rules; two based on excess Gibbs energy models: MHV2 and Wong-Sandler) and concluded that the van der Waals mixing rules give the best results for nonpolar systems. For the systems which contained strongly polar substances such as alcohol, water and acetone, the van der Waals mixing rule did not yield reasonable vapour-liquid equilibrium results. Anderko (1990) gave some examples of the failure of the van der Waals mixing rules for strongly nonideal mixtures.

3.4.2 *The Improved van der Waals Mixing Rules*

Many workers (Adachi and Sugie, 1986, Panagiotopoulos and Reid, 1986, Stryjek and Vera, 1986 a&b, Schwartzendruber et al, 1987, Sandoval et al., 1989) have proposed modifications for the van der Waals prescriptions. They used similar ideas, that is to include composition-dependent binary interaction parameters to the a parameter in the van der Waals

mixing rule and leave the b parameter rule unchanged. Some of examples are summarised in Table 3.3.

Adachi and Sugie (1986) kept the functional form of the van der Waals mixing rule, left the b parameter unchanged and added an additional composition dependence and parameters to the a parameter in the van der Waals one-fluid mixing rules.

$$a = \sum \sum x_i x_j a_{ij} \quad (3.129)$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} [1 - l_{ij} - m_{ij}(x_i - x_j)] \quad (3.130)$$

Adachi and Sugie (1986) showed that their new mixing rule can be applied to the binary and ternary systems containing strongly polar substances.

Table 3.3 Summary of Composition-dependent

Authors	Term a_{ij}	Reference
Adachi and Sugie	$(a_{ii} a_{jj})^{1/2} [1 - l_{ij} + m_{ij}(x_i - x_j)]$	1986
Panagiotopoulos and Reid	$(a_{ii} a_{jj})^{1/2} [1 - k_{ij} + (k_{ij} - k_{ji})x_i]$	1986
Stryjek and Vera (Margules-type)	$(a_{ii} a_{jj})^{1/2} (1 - x_i k_{ij} - x_j k_{ji})$	1986b
Stryjek and Vera (Van Laar-type)	$(a_{ii} a_{jj})^{1/2} \left[1 - \frac{k_{ij} k_{ji}}{x_i k_{ij} + x_j k_{ji}} \right]$	1986b
Schwartzentruber et al.	$(a_{ii} a_{jj})^{1/2} \left[1 - k_{ij} - l_{ij} \frac{m_{ij} x_i - m_{ji} x_j}{m_{ij} x_i + m_{ji} x_j} (x_i + x_j) \right]$ $k_{ji} = k_{ij}; l_{ji} = -l_{ij}; m_{ji} = 1 - m_{ij}; k_{11} = l_{11} = 0$	1987
Sandoval et al.	$(a_{ii} a_{jj})^{1/2} [1 - (k_{ij} x_i + k_{ji} x_j) - 0.5(k_{ij} + k_{ji})(1 - x_i - x_j)]$	1989

Sadus (1989) used conformal solution theory to derive an alternative to the conventional procedure for obtaining parameter a of equation of state. Instead of proposing an

average of the pure component parameter data, the a parameter for the mixture is calculated directly. Consequently, a is a function of composition only via the conformal parameters (f, h) and the contribution from the combinatorial entropy of mixing. The a parameter is obtained by taking the positive root of the following quadratic equation:

$$\begin{aligned}
 a^2 \mathbf{q}^6 [-2f''/f + (f'/f)^2 - 2h''/h - 2f'h'/fh + (h'/h)^2] \\
 + aRTV[\mathbf{f}_B \mathbf{q}^2 \{-h''/h - f''/f\}] + 2\mathbf{f}_A \mathbf{q}^3 \{h''/h + f'h'/fh - (h'/h)^2\} \\
 + 2\mathbf{q}^6 \{-h''/h + (h'/h)^2 + 1/x(1-x)\}] - (RTV)^2 [\mathbf{f}_A^2 \{(f'/f)^2 - (h'/h)^2\} \\
 + \mathbf{f}_B \mathbf{q}^2 \{h''/h - (h'/h)^2 - 1/x(1-x)\} - \mathbf{f}_A \mathbf{f}_B h''/hq] = 0
 \end{aligned} \quad (3.131)$$

where superscripts ' and '' denote successive differentiation of the conformal parameters, and \mathbf{q} and \mathbf{f} are characteristic of the equation of state. The main advantage of Eq.(3.131) is that a parameter can be calculated directly from the critical properties of pure components without using combining rules for the contribution of unlike interactions. Sadus (1992a & b) has applied the above equation to the calculation of the gas-liquid critical properties of a wide range of binary mixtures. The agreement was generally very good in view of the fact that no adjustable parameters were used to arbitrarily optimise the agreement between theory and experiment.

3.4.3 Mixing Rules from Excess Gibbs Energy Models

Huron and Vidal (1979) suggested a new method for deriving mixing rules for equations of state from excess Gibbs energy models. The method relies on three assumptions. First, an excess Gibbs energy calculated from an equation of state at infinite pressure equals an excess Gibbs energy calculated from a liquid phase activity coefficient model. Second, the covolume parameter b equals the volume V at infinite pressure. Third, the excess volume is zero. By using the Soave-Redlich-Kwong equation, Eq.(3.6) and applying the common linear mixing rule Eq.(3.126) for volume parameter b , the resulting expression for parameter a is

$$a = b \left[\sum_{i=1}^n x_i \frac{a_{ii}}{b_{ii}} - \frac{g_\infty^E}{\ln 2} \right] \quad (3.132)$$

where g_{∞}^E is the value of the excess Gibbs energy at infinite pressure and can be calculated from (Renon and Prausnitz, 1968)

$$g_{\infty}^E = \sum_{i=1}^n x_i \left(\frac{\sum_{j=1}^n x_j G_{ji} C_{ji}}{\sum_{k=1}^n x_k G_{ki}} \right) \quad (3.133)$$

with

$$C_{ji} = g_{ji} - g_{ii} \quad (3.134)$$

and

$$G_{ji} = b_j \exp\left(-a_{ji} \frac{C_{ji}}{RT}\right) \quad (3.135)$$

where g_{ji} and g_{ii} are the interaction energies between unlike (g_{ji}) and like (g_{ii}) molecules; a_{ji} is a non-randomness parameter. Finally, the Huron-Vidal mixing rule for a is deduced by applying Eq.(3.132):

$$a = b \sum_{i=1}^n x_i \left[\frac{a_{ii}}{b_{ii}} - \frac{1}{\ln 2} \frac{\sum_{j=1}^n x_j G_{ji} C_{ji}}{\sum_{k=1}^n x_k G_{ki}} \right] \quad (3.136)$$

with a_{ji} , C_{ij} and C_{ji} as the three adjustable parameters. With $a_{ji} = 0$, the Huron-Vidal mixing rule reduces to the van der Waals mixing rules. Huron and Vidal (1979) showed that their mixing rule yielded good results for nonideal mixtures. Soave (1984) found that the Huron-Vidal mixing rule represented an improvement over the classical quadratic mixing rules

and made it possible to correlate vapour-liquid equilibria for highly nonideal systems with good accuracy. The Huron-Vidal mixing rule has also been applied to a variety of polar and asymmetric systems (Adachi and Sugie, 1985; Gupte and Daubert, 1986; Heidemann and Rizvi, 1986).

However, the equation of state excess Gibbs energy at near atmospheric pressure differs from that at infinite pressure. Therefore, the Huron-Vidal mixing rule has the difficulty to deal with low pressure data. Several proposals (Lermite and Vidal, 1992; Soave et al., 1994) has been given to overcome this difficulty.

Mollerup (1986) modified Eq.(3.132) by retaining the excess volume is zero but evaluating the mixture parameter a directly from the zero pressure excess free energy expression. The modified mixing rule has the form

$$\frac{a}{b} = \sum_i x_i \left(\frac{a_i}{b_i} \right) \left(\frac{f_i}{f} \right) - \frac{G^E}{f} + \left(\frac{RT}{f} \right) \left(\sum_i x_i \ln \left[f_c \frac{b_i}{b} \right] \right) \quad (3.137)$$

where $f_i = \frac{b_i}{v_i}$, $f = \frac{b}{v}$ and $f_c = (\frac{v_i}{b_i} - 1) / (\frac{v}{b} - 1)$. The mixing rule Eq.(3.137) depends on

the liquid phase volume of the mixture and individual components and is less restrictive assumption than the Huron-Vidal mixing rule.

This proposal (Mollerup, 1986) was implemented by Michelsen (1990). Based on a reference pressure of zero and Soave-Redlich-Kwong equation of state, Eq.(3.5), Michelsen (1990) and Dahl and Michelsen (1990) repeated the matching procedure of Huron and Vidal and lead to the following mixing rule

$$q(\mathbf{a}) = \sum_{i=1}^n x_i q(\mathbf{a}_{ii}) + \frac{G^E}{RT} + \sum_{i=1}^n x_i \ln \left(\frac{b}{b_{ii}} \right) \quad (3.138)$$

where $\mathbf{a} = a/bRT$, $b = \sum_{i=1}^n x_i b_{ii}$, $\mathbf{a}_{ii} = a_{ii}/b_{ii}RT$ and for the function $q(\mathbf{a})$, a variety of

approximations can be used. Dahl and Michelsen (1990) suggested various $q(\mathbf{a})$ functions.

The simplest is the linear relation

$$q(\mathbf{a}) \cong q_0 + q_1 \mathbf{a} \quad (3.139)$$

This yields a new mixing rule, called the modified Huron-Vidal first order (MHV1),

$$\mathbf{a} = \sum_{i=1}^n x_i \mathbf{a}_{ii} + \frac{1}{q_1} \left[\frac{G^E}{RT} + \sum_{i=1}^n x_i \ln \left(\frac{b}{b_{ii}} \right) \right] \quad (3.140)$$

with the recommended value of $q_1 = -0.593$.

Dahl and Michelsen (1990) also found that better result can be obtained with employing a second order polynomial,

$$q(\mathbf{a}) \cong q_0 + q_1 \mathbf{a} + q_2 \mathbf{a}^2 \quad (3.141)$$

Consequently, a new mixing rule, called the modified Huron-Vidal second-order (MHV2), is of the form

$$q_1 \left(\mathbf{a} - \sum_{i=1}^n x_i \mathbf{a}_{ii} \right) + q_2 \left(\mathbf{a}^2 - \sum_{i=1}^n x_i \mathbf{a}_{ii}^2 \right) = \frac{G^E}{RT} + \sum_{i=1}^n x_i \ln \left(\frac{b}{b_{ii}} \right) \quad (3.142)$$

with suggested values of $q_1 = -0.478$ and $q_2 = -0.0047$.

Dahl and Michelsen (1990) investigated the ability of MHV2 to predict high-pressure vapour-liquid equilibrium when used in combination with the parameter table of modified UNIFAC (Larsen et al., 1987). They concluded that satisfactory results were obtained for the mixtures investigated. Dahl et al. (1991) demonstrated that MHV2 was also able to correlate and predict vapour-liquid equilibria of gas-solvent binary systems and to predict vapour-liquid equilibria for multicomponent mixtures using the new parameters for gas-solvent interactions together with the modified UNIFAC parameter table of Larsen et al. (1987).

Generally, the use of the infinite pressure or zero pressure standard states for mixing in the equation of state will lead to inconsistencies with the statistical mechanical result that the

second virial coefficient must be a quadratic function of composition. Wong and Sandler (1992) used the Helmholtz function to develop a mixing rule to satisfy the second virial condition. For the mixture parameters of an equation of state, a and b , are

$$b = \frac{\sum \sum x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \frac{A_\infty^E}{RT} - \sum x_i \left(\frac{a_i}{b_i RT} \right)} \quad (3.143)$$

$$a = b \left[\sum x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \right] \quad (3.144)$$

where C is a constant dependent on the equation of state selected (e. g., C is equal to $\frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1)$ for the Peng-Robinson equation of state) and A_∞^E is the excess Helmholtz function at infinite pressure, and

$$\left(b - \frac{a}{RT} \right)_{ij} = \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] \frac{(1 - k_{ij})}{2} \quad (3.145)$$

where k_{ij} is a binary interaction parameter for the second virial coefficient.

Wong and Sandler (1992) tested the new mixing rule, Eq.(3.143) and Eq.(3.144), and concluded that the Wong-Sandler mixing rule was reasonably accurate in describing both simple and complex phase behaviour of binary and ternary systems for the diverse systems they considered. Wong et al. (1992) demonstrated that the Wong-Sandler mixing rule can be used for highly nonideal mixtures with six examples. The new mixing rule can also make predictions at conditions which were hundreds of degrees and hundreds of bars above the experimental data used to obtain parameters. Huang and Sandler (1993) compared the Wong-Sandler with MHV2 mixing rule for nine binary and two ternary systems. They showed that either the MHV2 or Wong-Sandler mixing rules can be used to make reasonable high pressure vapour-liquid equilibrium predictions from low-pressure data. They used the Peng-

Robinson and Soave-Redlich-Kwong equations of state and found that the errors in the predicted pressure with the Wong-Sandler mixing rule were, on the average, about half or less those obtained when using the MHV2 mixing rule. Orbey and Sandler (1994) used the Wong-Sandler mixing rule to correlate the vapour-liquid equilibria of various polymer + solvent and solvent + long chain hydrocarbon mixtures. They concluded that the Wong-Sandler mixing rule can correlate the solvent partial pressure in concentrated polymer solutions with high accuracy over a range of temperatures and pressures with temperature-independent parameters. For solvent + long chain hydrocarbon and polymer + solvent systems, the Wong-Sandler mixing was best used as a three-parameter correlation. Huang et al. (1994) extended the Wong-Sandler mixing rule to hydrogen-hydrocarbon equilibria with good results as well.

To go smoothly from activity coefficient-like behaviour to the classical van der Waals one fluid mixing rule, Orbey and Sandler (1995) slightly reformulated the Wong-Sandler mixing rule by rewriting the cross second virial term given in Eq.(3.145) as

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(b_i + b_j)}{2} - \frac{\sqrt{a_i a_j} (1 - k_{ij})}{RT} \quad (3.146)$$

and retained the basic equations, Eq.(3.143) and Eq.(3.144). Orbey and Sandler (1995) tested five binary systems and one ternary mixture and showed that this new mixing rule was capable of both correlating and predicting the vapour-liquid equilibrium of various complex binary mixtures accurately over wide ranges of temperature and pressure and that it can be useful for accurate predictions of multicomponent vapour-liquid equilibria.

Castier and Sandler (1997a & b) performed critical point calculations in binary systems utilising cubic equations of state combined with the Wong-Sandler mixing rule (Eq. (3.146)). In order to investigate the influence of the Wong-Sandler mixing rule on the shapes of the calculated critical phase diagrams, the van der Waals equation of state was combined with the Wong-Sandler mixing rule (Castier and Sandler, 1997a). The results showed that many different types of critical phase diagrams can be obtained from this combination. When the Wong-Sandler mixing rule combined with Stryjek and Vera (1986a) version of the Peng-Robinson (1976) equation of state (Castier and Sandler, 1997b), it was able to quantitatively predict the critical behaviour of some highly non-ideal systems involving compounds such as

water, acetone and alkanols. For some highly asymmetric and non-ideal mixtures, such as water + n-dodecane, only qualitatively correct critical behaviour could be predicted.

There are also some other proposals (Heidemann and Kokal, 1990; Soave, 1992; Holderbaum and Gmehling, 1991; Boukouvalas et al., 1994; Tochigi, 1995; Novenario et al., 1996; Twu and Coon, 1996; Twu et al., 1998) based on excess free energy expressions. Comparison and evaluation for various mixing rules can be found in the works of Knudsen et al. (1993), Voros and Tassios (1993), Michelsen and Heidemann (1996), Wang et al. (1996), Abdel-Ghani and Heidemann (1996), Orbey and Sandler (1996), Heidemann (1996) and Twu et al. (1998).

3.5 Combining Rules

As noted above, any mixing rule will invariably contain a contribution from interactions between unlike molecules. In other words, the cross terms a_{ij} and b_{ij} ($i \neq j$) must be evaluated. They can be determined by an appropriate combining rule. The usual used combining rule for the a_{ij} term was first proposed by van der Waals

$$a_{ij} = \mathbf{x}_{ij} (a_{ii} a_{jj})^{0.5} \quad (3.147)$$

The widely used combining rule for the b_{ij} is the simple arithmetic rule

$$b_{ij} = \mathbf{z}_{ij} (b_{ii} + b_{jj}) / 2 \quad (3.148)$$

Alternatively, some workers prefer to use the following combining rule for critical calculations:

$$a_{ij} = \mathbf{x}_{ij} b_{ij} (a_{ii} a_{jj} / b_{ii} b_{jj})^{0.5} \quad (3.149)$$

The \mathbf{x}_{ij} (also commonly defined as $1 - k_{ij}$) and \mathbf{z}_{ij} (also commonly defined as $1 - l_{ij}$) terms are adjustable parameters which are used to optimise agreement between theory and experiment. The \mathbf{z}_{ij} term does not significantly improve the analysis of high pressure equilibria

and it can be usually omitted ($z_{ij} = 1$). The x_{ij} term is required because it can be interpreted as reflecting the strength of unlike interaction except the simple mixtures of molecules of similar size. This interpretation is supported by the fact that values of x_{ij} obtained from the analysis of the critical properties of many binary mixtures consistently decline with increasing size difference between the component molecules as detailed elsewhere (Sadus, 1992a & 1994).

The Lorentz rule (Hicks and Young, 1975; Sadus, 1992a) is a widely used alternative to the arithmetic rule

$$b_{ij} = 0.125 z_{ij} (b_i^{1/3} + b_j^{1/3})^3 \quad (3.150)$$

Good and Hope (1970) also proposed a geometric mean rule

$$b_{ij} = z_{ij} (b_i b_j)^{0.5} \quad (3.151)$$

Sadus (1993) compared the accuracy of the arithmetic Eq.(3.148), Lorentz Eq.(3.150) and geometric Eq.(3.151) rules for type III phenomena and concluded that they give almost identical results for molecules of similar size, but the discrepancy increases substantially for mixtures of molecules of very dissimilar size, see Figure 3.2.

Sadus (1993) proposed an alternative combining rule by taking a 2:1 geometric average of the Lorentz and arithmetic rules without the z_{ij} parameter, i.e.

$$b_{ij} = \{1/4(2^{1/3})\} (b_i^{1/3} + b_j^{1/3})^2 (b_i + b_j)^{1/3} \quad (3.152)$$

Sadus (1993) reported that the new combining rule Eq.(3.152) is generally more accurate than either the Lorentz, arithmetic, or geometric combining rules.

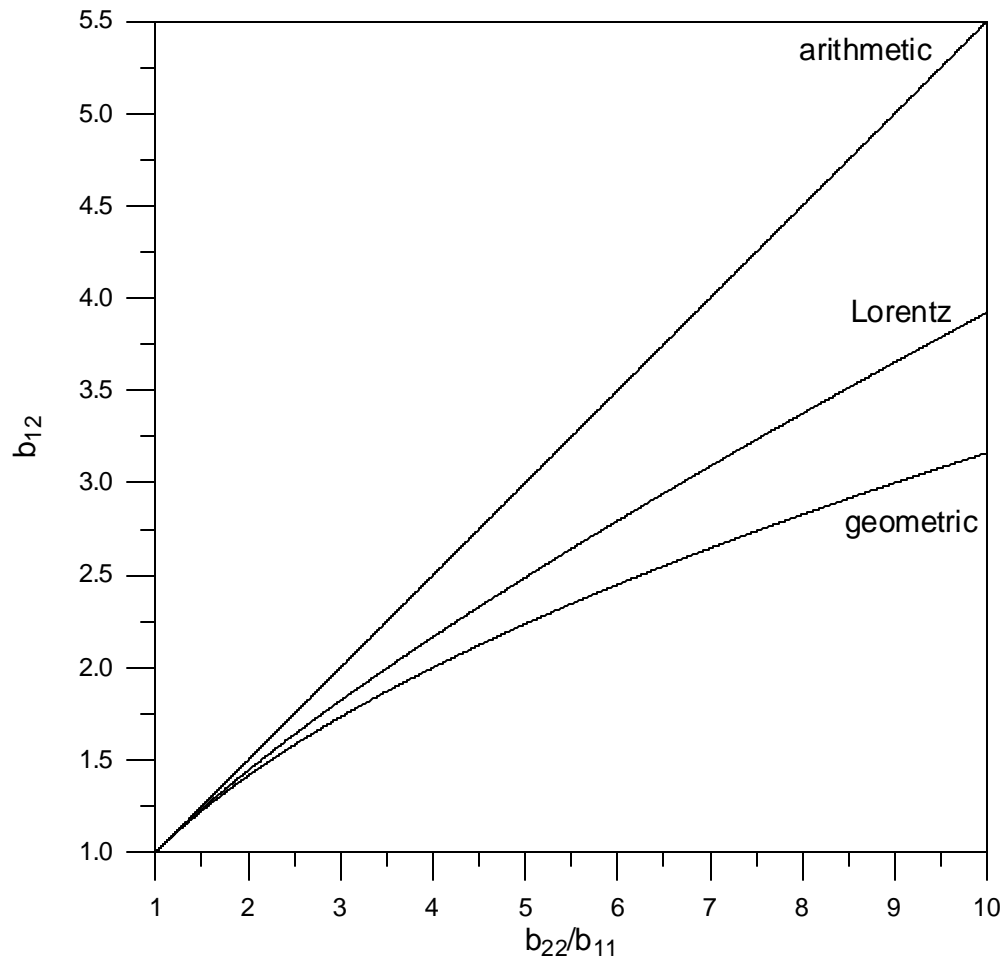


Figure 3.2 Variation of b_{12} with respect to the ratio of b_{22} relative to b_{11} predicted by the arithmetic, Lorentz, and geometric combining rules for the prediction of Type III phase behaviour.

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