

## Chapter 3 Equations of State

The simplest way to derive the Helmholtz function of a fluid is to directly integrate the equation of state with respect to volume (Sadus, 1992a, 1994). An equation of state can be applied to either vapour-liquid or supercritical phenomena without any conceptual difficulties. Therefore, in addition to liquid-liquid and vapour-liquid properties, it is also possible to determine transitions between these phenomena from the same inputs. All of the physical properties of the fluid except ideal gas are also simultaneously calculated. 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), Anderko (1990), Sandler (1994), Economou and Donohue (1996), Wei and Sadus (2000) and Sengers et al. (2000).

The van der Waals equation of state (1873) 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 of the Redlich-Kwong equation to more accurately predict the vapour pressure, liquid density, and equilibria ratios. Guggenheim (1965) and Carnahan and Starling (1969) modified the repulsive term of van der Waals equation of state and obtained more accurate expressions for hard sphere systems. Christoforakos and Franck (1986) modified both the attractive and repulsive terms of van der Waals equation of state. Boublik (1981) extended the Carnahan-Starling hard sphere term to obtain an accurate equation for hard convex geometries.

In addition to modeling small and simple molecules, considerable emphasis has been placed on modeling long and convex molecules. Based on theory of Prigogine (1957) and Flory (1965), an equation for molecules treated as chains of segments, which is called Perturbed-Hard-Chain-Theory (PHCT) was constructed by Beret and Prausnitz (1975) and Donohue and Prausnitz (1978). To reduce the mathematical complexity of Perturbed-Hard-Chain-Theory, Kim et al. (1986) developed a simplified version of the theory by replacing the complex attractive part by a simpler expression. At the almost same time, Vimalchand and Donohue (1985) obtained a fairly accurate multipolar mixture calculation by using the Perturbed Anisotropic Chain theory, and Ikonomou and Donohue (1986) extended the Perturbed Anisotropic Chain Theory to the Associated Perturbed Anisotropic Chain Theory by taking into account the existence of hydrogen bonding.

Wertheim (1987) proposed a thermodynamic perturbation theory (TPT), which accommodates hard-chain molecules. Chapman et al. (1988) generalized the TPT model to obtain the compressibility factor of a hard-chain of segments. Ghonasagi and Chapman (1994) and Chang and Sandler (1994) modified TPT for the hard-sphere chain by incorporating structural information for the diatomic fluid (TPT-D). Sadus (1995) derived the simplified thermodynamic perturbation theory-dimer (STPT-D) equation from TPT-D. Sadus (1999b) later developed STPT-D to the empirical simplified thermodynamic perturbation theory-dimer (ESTPT-D) equation, and tested the accuracy of the equation against simulation data for hard-sphere chains containing up to 201 hard-sphere segments. Sadus (1999 a) also derived an equation of state for hard convex body chains from the TPT of hard sphere chains (Wertheim, 1987; Chapman et al., 1988).

Jin et al. (1993), Povodyrev et al. (1996) and Kiselev (1997) developed theoretical crossover equations of state for pure fluids and binary mixtures which incorporate the scaling laws asymptotically close to the critical point and which are transformed into the regular classical expansion far away from the critical point. Kiselev (1998) used the modified Patel-Teja cubic equation of state (Patel and Teja, 1982) as a starting point to propose a general procedure for transforming any classical equation of state into a crossover equation of state. Wyczalkowska et al. (1999) also developed a global crossover equation of state, and Kiselev et al. (2001) extended the crossover modification of the statistical-associating fluid theory (Chapman et al., 1988, 1990) equation of state. Wyczalkowska et al. (2000) demonstrated that both pure H<sub>2</sub>O and D<sub>2</sub>O obey a universal scaled crossover equation of state in the critical region which satisfies corresponding state for the near-critical behaviour of the thermodynamic properties. Abdulkadirova et al. (2002) extended the pure component to binary mixtures (H<sub>2</sub>O + D<sub>2</sub>O) using a crossover equation of state.

In this chapter we will review equations of state for high pressure with particular emphasis on critical points calculations. A crossover theory for equations of state is also discussed.

## 3.1 Equations of State for High Pressure Equilibria and Critical Phenomena

### 3.1.1 Cubic Equations of State

Cubic equations of state are equations, which when expanded have volume terms raised to the first, second, and third power. Most commonly encountered phase equilibrium calculations, such as vapour-liquid equilibria, involve only two phases for which a cubic equation is suitable. Cubic equations have the advantage that the three values of volume can be obtained analytically without the need for an iterative solution procedure.

The van der Waals equation of state (1873) is the simplest cubic equation of state for fluid phase equilibria. It can be regarded as a “hard sphere term + attractive term” equation of state composed from the contribution of repulsive and attractive intermolecular interactions (Sadus, 1994). The van der Waals equation was the first equation capable of representing vapour-liquid coexistence. The pressure ( $p$ ) is related to the temperature ( $T$ ), ideal gas constant ( $R$ ) and molar volume ( $V$ ) via:

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

It has two pure component parameters  $a$  and  $b$ . The parameter  $a$  is a measure of the attractive forces between the molecules, and  $b$  is related to the size of the molecules. Since the van der Waals equation of state is cubic in volume, three volumes exist for any given temperature and pressure. Usually,  $p_c$ ,  $T_c$  and  $V_c$  are known and Eq. 2.1 (Chapter 2) may be simultaneously solved to provide solutions for the parameters  $a$  and  $b$ :

$$a = \frac{27R^2T_c^2}{64p_c} \quad (3.2)$$

$$b = \frac{RT_c}{8p_c} \quad (3.3)$$

Van Konynenburg and Scott (1980) successfully demonstrated that most of the critical equilibria exhibited by binary mixtures could be qualitatively predicted by the van der Waals equation of state, but it is rarely sufficiently accurate for critical properties and phase equilibria calculations. For example, the critical compressibility factor of all fluids including pure component and binary mixtures predicted by van der Waals equation is 0.375 (Eq. 3.2 and Eq. 3.2 are used in Eq. 2.1 at the critical point), whereas the real value for different hydrocarbons varies from 0.24 to 0.29. Many modifications at the van der Waals equation of state have been proposed to address this deficiency. Five examples of cubic equations of state based on the van der Waals equation are listed in Table 3.1.

Table 3.1 Examples of Improved Cubic Equations of State

Reference	Equations of state	Eq.
Redlich-Kwong (1949)	$p = \frac{RT}{V-b} - \frac{a}{V(V+b)T^{0.5}}$	(3.4)
Soave-Redlich-Kwong (1972)	$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)}$	(3.5)
Peng-Robinson (1976)	$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$	(3.6)
Stryjek-Vera-Peng-Robinson (1986)	$p = \frac{RT}{V-b} - \frac{a(\mathbf{q},T)}{V(V+b)+b(V-b)}$	(3.7)
Patel-Teja (1982)	$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$	(3.8)

Eq. (3.4) was proposed as an empirical modification of the van der Waals equation to make the attractive term temperature-dependent. The parameters  $a$  and  $b$  are usually expressed as

$$a = 0.4278 \frac{R^2 T_c^{2.5}}{p_c} \quad (3.9)$$

$$b = 0.0867 \frac{RT_c}{p_c} \quad (3.10)$$

Spear et al. (1969) demonstrated that the Redlich-Kwong equation of state could be used to reliably calculate the vapour-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. Deiters and Schneider (1976) and Baker and Luks (1980)

have successfully applied the Redlich-Kwong equation to the high pressure phase equilibria of binary mixtures. Deiters and Pegg (1989) used the Redlich-Kwong equation with quadratic mixing rules to calculate phase diagrams for binary fluid mixtures and to classify them according to the global phase diagram. Polishuk et al. (1999) predicted the closed loop critical behaviour between type III and V with the Redlich-Kwong equation of state.

Soave (1972) suggested to replace the term  $\frac{a}{T^{0.5}}$  with a more general temperature-dependent term  $a(T)$  (Eq. (3.5) in the Table 3.1), where

$$a(T) = 0.4274 \left( \frac{R^2 T_c^2}{p_c} \right) \left\{ 1 + m \left[ 1 - \left( \frac{T}{T_c} \right)^{0.5} \right] \right\}^2 \quad (3.11)$$

$$m = 0.480 + 1.57w - 0.176w^2 \quad (3.12)$$

$$b = 0.08664 \frac{RT_c}{p_c} \quad (3.13)$$

and  $w$  is the acentric factor. Soave (1972) calculated the vapour pressures of a number of hydrocarbons and several binary systems with the Soave-Redlich-Kwong equation, and compared the results of the calculations with experimental data. In contrast to the original Redlich-Kwong equation, Soave's modification fitted the experimental (vapour-liquid) curve well and it was able to predict the phase behaviour of mixtures in the critical region. Elliott and Daubert (1987) improved the accuracy of the calculated critical properties of 95 binary

systems containing hydrocarbons. Zheng et al. (1999) also used the Soave-Redlich-Kwong equation to calculate the phase equilibria of systems containing methane, carbon dioxide and nitrogen, and compared the results of calculation with experimental data.

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

$$a(T) = 0.45724 \frac{R^2 T_c^2}{p_c} \left\{ 1 + k \left[ 1 - \left( \frac{T}{T_c} \right)^{0.5} \right] \right\}^2 \quad (3.14)$$

$$k = 0.37464 + 1.5422 w - 0.26922 w^2 \quad (3.15)$$

$$b = 0.07780 \frac{RT_c}{p_c} \quad (3.16)$$

The Peng and Robinson equation of state was proposed as Eq. (3.6), it slightly improves the prediction of liquid volumes and predicts a critical compressibility factor of  $Z_c = 0.307$  (the critical compressibility factor of the Redlich-Kwong equation is 0.333, and that van der Waals is 0.375). Peng and Robinson (1977) gave examples of the use of the Peng-Robinson equation for predicting the vapour pressure and volumetric behaviour of pure component and binary mixtures. In general, Eq. (3.6) performed as well as or better than Eq. (3.5). Han et al. (1988) reported that the Peng-Robinson equation of state was superior for predicting vapour-liquid equilibrium in hydrogen and nitrogen containing mixtures. Harstad et al. (1997) showed that the Peng-Robinson equation of state could be used to obtain a relatively accurate, noniterative and computationally efficient correlation of high-pressure fluid



mixtures used in gas turbines and rocket engines. Zhao and Olesik (1999) used the Peng-Robinson equation of state to calculate methanol and CHF<sub>3</sub> binary mixtures. The results showed that the Peng-Robinson equation of state with two temperature-independent binary parameters was capable of representing the experimental data over the entire temperature range with an average relative deviation within 6%.

Stryjek and Vera (1986) proposed the following modified temperature functionality for the Peng-Robinson equation of state to extend the range of applicability to polar components:

$$a(T) = 0.45724 \frac{R^2 T_c^2}{p_c} \left\{ k + k_1 \left[ 1 + \left( \frac{T}{T_c} \right)^{0.5} \right] \left( 0.7 - \frac{T}{T_c} \right) \right\} \quad (3.17)$$

$$k = 0.378893 + 1.4897153w - 0.17131848w^2 + 0.0196554w^3 \quad (3.18)$$

$$b = 0.0778 \frac{RT_c}{p_c} \quad (3.19)$$

where  $k_1$  is an adjustable parameter characteristic of each pure component. The Stryjek-Vera-Peng-Robinson equation of state (Stryjek and Vera, 1986) was proposed as Eq. (3.7). In addition, it must be noticed that optimization of  $k_1$  values was performed using a particular set of critical constants (Stryjek and Vera, 1986). The correct application of Stryjek-Vera-Peng-Robinson equation of state requires usage of this set.

The Peng-Robinson and Soave-Redlick-Kwong equations are widely used in industry (Sadus, 1994). The advantages of these equations are they are easy to use and that they often accurately represent the relation between temperature, pressure, and phase compositions in binary and multicomponent systems. These equations only require the critical properties and acentric factor for the generalized parameters. Little computer resources are required and those lead to good phase equilibrium correlation. However, the success of these modifications is restricted to the estimation of phase equilibria pressure. The calculated saturated liquid volumes are not improved and they are invariably higher than the measured data.

Patel and Teja (1982) proposed a third constant  $c$  into the van der Waals equation's attraction term, resulting in Eq. (3.8). The equation of state allows for adjustment of the critical compressibility factor  $Z_c$  instead of predicting a fixed value. This added flexibility improves saturation property predictions for polar fluids while maintaining a simple form that doesn't require a large amount of pure component or mixture experimental data for accuracy.

As with the van der Waals equation of state, the parameters  $a$  and  $b$  in the Patel-Teja equation are evaluated using the conditions at the critical point given by Eq. (2.1). The condition for the third parameter  $c$  is:

$$\mathbf{h}_c = \frac{p_c V_c}{RT_c} \tag{3.20}$$

Instead of having a fixed value of the critical compressibility factor fixed by parameters  $a$  and  $b$ , the value is the arbitrary, substance specific, empirical parameter  $h_c$ .  $h_c$  is determined by minimizing the errors between experimental saturated liquid volume and those calculated by the equation of state. Patel and Teja (1982) calculated  $h_c$  for 38 substances. They also correlated  $h_c$  to the acentric factor  $w$ , for non-polar substances yielding the following equation.

$$h_c = 0.329032 - 0.076799 w + 0.0211947 w^2 \quad (3.21)$$

Satisfying the conditions of Eq. (2.1) and Eq. (3.20) yields the following equations for the parameters  $a$ ,  $b$ , and  $c$ :

$$a(T) = \Omega_a \frac{R^2 T_c^2}{P_c} \mathbf{a}(T) \quad (3.22)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (3.23)$$

$$c = \Omega_c \frac{RT_c}{P_c} \quad (3.24)$$

where,

$$\Omega_c = 1 - 3h_c \quad (3.25)$$

$$\Omega_a = 3h_c^2 + 3(1 - 2h_c)\Omega_b + \Omega_b^2 + 1 - 3h_c \quad (3.26)$$

and  $\Omega_b$  is the smallest positive root of the following cubic equation:

$$\Omega_b^3 + (2 - 3z_c)\Omega_b^2 + 3h_c^2\Omega_b - h_c^3 = 0 \quad (3.27)$$

In the Eq. (3.22), the term  $\mathbf{a}(T)$  is given by:

$$\mathbf{a}(T) = \{1 + [1 - (\frac{T}{T_c})^{0.5}]F\} \quad (3.28)$$

$F$  is a substance specific empirical parameter also determined by minimizing errors between experimental saturated vapour pressures and those calculated by the equation of state. Patel and Teja (1982) calculated  $F$  for the same 38 substances and also correlated it to the acentric factor for non-polar substances:

$$F = 0.452413 + 1.30982 w - 0.295937 w^2 \quad (3.29)$$

Smith (1995) gave an expression for the compressibility factor  $Z$ ,

$$Z^3 + (C - 1)Z^2 + (-2BC - B^2 - B - C + A)Z + (B^2C + BC - AB) = 0 \quad (3.30)$$

where

$$A = \frac{ap}{(RT)^2} \quad (3.31)$$

$$B = \frac{bp}{RT} \quad (3.32)$$

$$C = \frac{cp}{RT} \quad (3.33)$$

Eq. (3.30) will yield one to three positive real roots depending upon the number of phases in the system. If a vapour and liquid phase are present, the smallest root represents the liquid's compressibility while the largest root is that of the vapour.

Palenchar et al. (1986) have reported a rare, direct comparison of the quality of prediction of the critical locus using different cubic equations of state. In addition to the Redlich-Kwong, Peng-Robinson and Soave-Redlich-Kwong equations, calculations for equations of state proposed by Teja and Patel (1982) and Adachi et al. (1983) were reported for the carbon dioxide + methane, butane, decane or water; methane + hexane or heptane; and propane + hexane and water + benzene binary mixtures. They concluded that the critical temperatures and pressures of type I systems could be adequately predicted although there was a substantial discrepancy between theory and experiment for the critical volume. The Peng-Robinson and Soave-Redlich-Kwong equations yielded a more accurate representation of mixtures exhibiting a discontinuity in critical equilibria than the Patel and Teja equation.

Polishuk et al. (1999) compared the critical lines predicted by Redlich-Kwong, Peng-Robinson, Soave-Redlich-Kwong, Stryjek-Vera-Peng-Robinson, Patel-Teja and Trebble-Bishnoi (1987) equations of state using classical mixing rules with the experimental data available for the mixtures of methane + alkanes up to and including octane. The results show that different cubic equation of state can yield similar semi-quantitative and even quantitative predictions with the optimised values.

### **3.1.2 Noncubic Equations of State**

The development of cubic equations of state has been focused on obtaining an improved empirical representation of attractive interactions. Improvements to cubic equations emphasize obtaining better agreement with experiment at low temperatures and pressures for phase equilibria. At high pressures and temperatures, repulsive interactions can be expected to be the dominant influence determining the properties of the fluid. There are many accurate representations which have been developed for the repulsive interactions of hard spheres and which were incorporated into equation of state. In general, the effect of using an accurate model of repulsion is to generate a noncubic equation of state.

Normally, noncubic equations of state are of two broad types. One type is obtained by simply modifying the repulsive term of the van der Waals equation (hard sphere term). Another type is obtained by modifying both attractive and repulsive terms or combining an accurate hard sphere model with an empirical temperature dependent attractive contribution.

Many improvements to the simple van der Waals hard sphere repulsive term have been reported (Mulero et al., 2001). Some important hard sphere expressions are summarised in Table 3.2. A comprehensive review of hard sphere terms is given by Mulero et al. (2001).

Table 3.2 Summary of hard sphere expressions of modification of repulsive term of van der Waals equation. Where  $y = b/(4V)$  is a temperature independent packing fraction of spherical molecules.

Reference	Hard sphere expression	Eq.
Reiss-Frisch-Lebowitz (1959)	$\frac{1 + y + y^2}{(1 - y)^3}$	(3.34)
Thiele (1963)	$\frac{1 + 2y + 3y^2}{(1 - y)^2}$	(3.35)
Guggenheim (1965)	$\frac{1}{(1 - y)^4}$	(3.36)
Carnahan-Starling (1969)	$\frac{1 + y + y^2 - y^3}{(1 - y)^3}$	(3.37)
Scott (1971)	$\frac{V + b}{V - b}$	(3.38)
Boublik (1981)	$\frac{1 + (3a - 2)y + (3a^2 - 3a + 1)y^2 - a^2y^3}{(1 - y)^3}$	(3.39)
Kolafa and Nezbeda (1994)	$\frac{1 + y + y^2 - \frac{2}{3}(y^3 + y^4)}{(1 - y)^3}$	(3.40)
Malijevsky-Veverka (1999)	$\frac{1 + 1.056y + 1.6539y^2 + 0.3262y^3}{(1 - y)^3(1 + 0.056y + 0.5979y^2 + 0.3076y^3)}$	(3.41)

The Guggenheim equation of state (1965) is a more accurate hard sphere model which has been extensively used for the calculation of critical equilibria:

$$p = \frac{RT}{V(1-y)^4} - \frac{a}{V^2} \quad (3.42)$$

Both  $a$  and  $b$  can be obtained by using critical properties ( $a = 0.4963 R^2 T_c^2 / p_c$ ,  $b = 0.18727 RT_c / p_c$ ), and at critical point, the compressibility factor  $Z_c = p_c V_c / (RT_c) = 0.3611$ . The Guggenheim equation has been used to predict the critical properties of a diverse range of binary mixtures (Hicks and Young, 1976; Hurle et al., 1977a,b; Hicks et al. 1977, 1978; Toczylkin and Young, 1977, 1980a, b, c; Waterson and Young, 1978; Semmens et al., 1980; Sadus and Young, 1985a, b; Sadus, 1992a, 1994; and Wang et al. 2000). Despite the diversity of the systems studied, good results were consistently reported for the vapour-liquid critical locus. The critical liquid-liquid line of type II binary 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 vapour-liquid and liquid-liquid behaviour.

Carnahan and Starling (1969) obtained an accurate representation of hard sphere interactions. The Carnahan-Starling-van der Waals (CSvdW) equation is formed by coupling this hard sphere term with the van der Waals attractive term (Carnahan and Starling, 1972):



$$p = \frac{RT(1 + y + y^2 - y^3)}{V(1 - y)^3} - \frac{a}{V^2} \quad (3.43)$$

The covolume ( $b = 0.18727 RT / p_c$ ) and attractive ( $a = 0.4963 R^2 T_c^2 / p_c$ ) equation of state parameters are related to the critical properties, and critical compressibility factor  $Z_c = 0.35896$ .

Sadus (1993) has demonstrated the CSvdW equation of state can be used to predict type III equilibria of nonpolar mixtures with considerable accuracy. Yelash and Kraska (1998) found several types of closed loop liquid-liquid immiscibility behaviour in binary mixtures based on CSvdW equation of state.

Boublik (1981) has generalised the Carnahan-Starling hard sphere potential for molecules of arbitrary geometry via the introduction of a nonsphericity parameter ( $\alpha$ ). 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:

$$p = \frac{RT[1 + (3\alpha - 2)y + (3\alpha^2 - 3\alpha + 1)y^2 - \alpha^2 y^3]}{V(1 - y)^3} - \frac{a}{V^2} \quad (3.44)$$

In Eq. (3.44),  $\mathbf{a}$  is the deviation from spherical geometry which is obtained by considering the mean radius  $R^*$ , surface area  $S^*$  and volume  $V^*$  of a convex body:

$$\mathbf{a} = \frac{R^* S^*}{3V^*} \quad (3.45)$$

In the limiting case of a hard sphere,  $\mathbf{a} = 1$ , and Eq. (3.44) becomes identical to the Carnahan-Starling equation Eq. (3.43).

Eq. (3.44) has been used for the calculation of the vapour-liquid critical properties of binary mixtures containing nonspherical molecules (Sadus et al., 1988; Christou et al. 1991). 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. (3.44) 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.

There are many other nonspherical or hard chain equations of state which have not been used for the calculation of critical equilibria. Vimalchand and Donohue (1989) have reviewed several hard chain equations of state. Van Pelt et al. (1992) have applied a simplified version

of the perturbed hard chain theory (SPHCT) equation of state proposed by Beret and Prausnitz (1975) to binary critical equilibria.

The SPHCT equation of state has the following form:

$$p = (1+c) \frac{RT}{V} \left( 4\mathbf{h} - \frac{2\mathbf{h}^2}{(1-\mathbf{h})^3} \right) - \frac{RTzc v^* Y}{V^2 + v^* YV} \quad (3.46)$$

where  $Y = \exp(\mathbf{e} q/2ckT) - 1$  and  $\mathbf{h} = 0.7405 v^*/V$ , where  $v^*$  is the molecular volume parameter,  $\mathbf{e}$  is the intermolecular potential energy per unit area;  $c$  is 1/3 of the total number of external degrees of freedom of a molecule;  $q$  is the number of segments per molecule and  $z$  is the close-packed coordination number. In common with other equations of state, good results were obtained for the critical pressures and temperatures of many binary mixtures. The calculations cannot be expected to yield accurate critical volumes for binary mixtures because the critical volume of the components was used as an adjustable parameter to optimise the agreement of theory and experiment for the critical pressures and temperatures of the pure components. Eq. (3.46) was successfully used (van Pelt et al., 1995) to qualitatively reproduce a variety of binary mixture phenomena including type VI behaviour. Recently, development of shape factor model equations of state were reported by Huber and Ely (1994), and Estela-Urbe and Trusler (1998).

Christoforakos and Franck (1986) and Heilig and Franck (1989) have developed equations specifically for high pressure equilibria which also incorporate the Carnahan-Starling hard sphere term. The Christoforakos-Franck equation of state introduces a temperature dependent covolume term  $4\mathbf{b} = b(T_c/T)^{0.3}$  into the repulsive term:

$$p = \frac{RT}{V} \frac{1 + \mathbf{b}/V + \mathbf{b}^2/V^2 - \mathbf{b}^3/V^3}{(1 - \mathbf{b}/V)^3} - \frac{4RT\mathbf{b}(I^3 - 1)(\exp(\mathbf{e}/kT) - 1)}{V^2} \quad (3.47)$$

The attractive term was obtained by examining the virial coefficient of gases in terms of a square-well potential. The  $\mathbf{e}$  parameter reflects the depth of the potential, whereas  $I$  is the relative width of the well. The equation has been successfully applied to the high pressure phase behaviour of some binary aqueous mixtures (Christoforakos and Franck, 1986; Franck, 1987). In particular, the type III critical locus of binary mixtures of  $\text{H}_2\text{O} + \text{Ar}$ ,  $\text{Xe}$ ,  $\text{N}_2$ ,  $\text{CH}_4$  or carbon dioxide is predicted accurately.

The Heilig-Franck (1989) equation of state uses the same form of repulsive term of Eq. (3.47), but it has a different attractive term which is obtained by applying the Padé approximation of the virial coefficients of a square-well fluid:

$$p = \frac{RT(1 + \mathbf{b}/V + \mathbf{b}^2/V^2 - \mathbf{b}^3/V^3)}{V(1 - \mathbf{b}/V)^3} - \frac{RTB}{V(V + C/B)} \quad (3.48)$$

where  $B$  and  $C$  are the second and third virial coefficients of a square-well fluid respectively. Accurate calculations of the critical properties of binary mixtures have been reported (Heilig and Franck, 1989, 1990). Mather et al. (1993) have demonstrated that Heilig-Franck equation of state can accurately predict type III critical loci of  $\text{H}_2\text{O} + \text{Ne}$  and  $\text{H}_2\text{O} + \text{Kr}$  mixtures.

Deiters (1981a, b) has adopted a semiempirical approach to construct an equation with three adjustable parameters  $a$ ,  $b$  and  $c$ .

$$p = \left\{ 1 + c c_0 \left[ 4\mathbf{h} - 2\mathbf{h}^2 / (1 - \mathbf{h})^3 \right] \right\} \frac{RT}{\mathbf{r}} - aI \left[ \exp(1/T_{eff}) - 1 \right] \frac{R\mathbf{r}^2 T_{eff}}{b} \quad (3.49)$$

where  $\mathbf{r} = b/V$ ,  $\mathbf{h} = 0.7404 \mathbf{r}$ ,  $c_0 = 0.6887$ ,  $I = -0.06911 c$  and  $T_{eff} = (cT/a + I\mathbf{r})/y$ .

Parameter  $I$  is a hard sphere constant, and the values of  $y$  range from 1 for a dilute gas and between 0.34 and 0.46 for dense fluids. In Eq. (3.49), the Carnahan Starling expression for hard spheres has been adjusted to accurately fit the experimental vapour pressure data for Ar via parameter  $c_0$ , and deviations from spherical geometry are reflected in values of  $c > 1$ . The equation can be used to accurately predict the vapour-liquid properties of binary mixtures (Deiters, 1982; Deiters and Swaid, 1984; Calado et al., 1981). Calculations of the vapour-liquid critical locus of binary mixtures (Mainwaring et al., 1988a, b) indicate that good results can only be obtained for mixtures of molecules of similar size. The equation has not

been extensively tested for noncontinuous critical equilibria, but type III critical properties of  $\text{H}_2\text{O} + \text{benzene}$  and  $\text{H}_2\text{O} + \text{He}$  can be adequately predicted (Mainwaring et al., 1988a).

### **3.1.3 Thermodynamic Perturbation Theory Equations of State**

The hard chain equations of state are potentially important for developing accurate equations of state for macromolecules. Historically, attention has been focused on using accurate hard sphere models to represent the repulsive interactions of geometrically simple molecules. Progress has been achieved in depicting the properties of hard nonspherical bodies (Sadus, 1995).

Boublik (1981) used Kihara's (1963) concept of a hard convex body (HCB) as the basis of an equation of state for nonspherical hard bodies. Flory's concept of excluded volume has been incorporated (Dickman and Hall, 1986) in a reasonably accurate hard chain equation of state. Chiew (1990) developed a rigorous theory for representing hard chains, and Song et al. (1994) formulated the theory into a useful equation of state for polymers. Wertheim (1987) proposed a thermodynamic perturbation theory (TPT) which accommodates hard-chain molecules. Chapman et al. (1988) generalised Wertheim's TPT model to obtain the equation of state for the compressibility factor of a hard chain of  $m$  segments. The form of the compressibility factor is

$$Z^{HC} = mZ^{HS} - (m-1) \left( 1 + y \frac{\partial \ln g_{HS}(\mathbf{s})}{\partial y} \right) \quad (3.50)$$

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

$$g_{HS}(\mathbf{s}) = \frac{2-y}{2(1-y)^3} \quad (3.51)$$

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

$$Z^m = mZ^{HS} - \frac{m}{2} \left( 1 + y \frac{\partial \ln g_{HS}(\mathbf{s})}{\partial y} \right) - \left( \frac{m}{2} - 1 \right) \left( 1 + y \frac{\partial \ln g_{HD}(\mathbf{s})}{\partial y} \right) \quad (3.52)$$

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

$$g_{HD}(\mathbf{s}) = \frac{1+2y}{2(1-y)^2} \quad (3.53)$$

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

$$Z^m = m \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) - \frac{m}{2} \left( 1 + \frac{y(5-2y)}{(1-y)(2-y)} \right) - \left( \frac{m}{2} - 1 \right) \left( 1 + \frac{2y(2+y)}{(1-y)(1+2y)} \right) \quad (3.54)$$

TPT-D2 can be represented as

$$Z^m = m \left( \frac{1+y+y^2-y^3}{(1-y)^3} \right) - \frac{m}{2} \left( 1 + \frac{y(5-2y)}{(1-y)(2-y)} \right) - \left( \frac{m}{2} - 1 \right) \left( 1 + \frac{y(3.498 - 0.24y - 0.414y^2)}{(1-y)(2-y)(0.534 + 0.414y)} \right) \quad (3.55)$$

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

$$g_{HD} = g_{HS}(\mathbf{a}y + c) \quad (3.56)$$



where  $a$  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 perturbed theory-dimer (STPT-D) equation of state. The general form of the STPT-D equation of state for pure hard sphere chains is

$$Z^m = 1 + m(Z^{HS} - 1) + (1 - m)y \frac{\partial \ln g_{HS}}{\partial y} + \frac{a(2 - m)y}{2(ay + c)} \quad (3.57)$$

Sadus (1995) applied the STPT-D equation to the prediction of both the compressibility factors 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 factors 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.

Recently, Sadus (1999a) proposed an empirical simplified thermodynamic perturbed theory-dimer (ESTPT-D) equation of state, which is a simplification of STPT-D equation. In the equation of state an empirical relationship (Shah et al., 1994) for  $Z^{HS}$  is used,

$$Z^{HS} = \frac{1 + (k_0 + k_1)y}{(1 - k_0 y)} \quad (3.58)$$

where  $k_0 = 1.2864$  and  $k_1 = 2.8225$  are empirically evaluated constants (Shah et al., 1994). The addition of Eq. (3.58) dimer properties into Eq. (3.57), the resulting ESTPT equation (Sadus, 1999a) is

$$Z^m = 1 + m \left( \frac{(k_0 + k_1)y - k_0^2 y^2}{(1 - k_0 y)^2} \right) + (1 - m) \left( \frac{2k_0 y}{1 - k_0 y} - \frac{k_0^2 y}{k_0 + k_1 - k_0^2 y} \right) + \frac{\mathbf{a}y(2 - m)}{2\mathbf{a}y + c} \quad (3.59)$$

Sadus (1999b) extended the hard sphere chain equation to hard convex body chain equation of state (HCBC). The compressibility factor of a hard-convex-chain of  $m$  segments is obtained as

$$Z_{HCBC} = mZ_{HCB} - (m-1) \left( 1 + y \frac{\partial \ln g_{HCB}(\mathbf{s})}{\partial y} \right) \quad (3.60)$$

where  $g_{HCB}(\mathbf{s})$  is the hard convex body site-site correlation function at contact, the symbol  $\mathbf{s}$  in Eq. (3.60) represents the breadth of the HCB. The compressibility factor of a hard convex body can be accurately determined from the HCB equation. For the HCB equation, the site-site correlation function is

$$g_{HCB} = 1 + S_R \left( \frac{1 - y/2}{(1 - y)^3} - 1 \right) \quad (3.61)$$

where  $S_R$  is the ratio of the actual surface area of the HCB  $S_{HCB}$  to the surface area of hard spheres  $S_{HS}(equiv)$  occupying a diameter equivalent to the HCB diameter:

$$S_R = \frac{S_{HCB}}{S_{HS}(equiv)} \quad (3.62)$$

Sadus (1999b) discussed the details on how to obtain  $S_R$ , and gave the general form of packing fraction for pure component,

$$Z_{HCBC} = \frac{m(1 + (3a - 2)y + (3a^2 - 3a + 1)y^2 - a^2y^3)}{(1 - y)^3} - (m - 1) \left( 1 + \frac{2.5S_R y - S_R y^2}{(1 - y)(1 - (3 - 2.5S_R)y + (3 - 3S_R)y^2 - (1 - S_R)y^3)} \right) \quad (3.63)$$

Sadus (1999b) examined the effect of molecular shape on the compressibility factor and the second virial coefficient for chain molecule consisting of spheres, prolate spherocylinders, oblate spherocylinders and doublecones, and found that these properties are very sensitive to segment shape.

### 3.2 Mixing rules

Most models of the fluid state such as conformal solution theory, perturbation models and equations of state are initially developed for pure substances. Therefore, directly extending an existing pure fluid model to multicomponent equilibria is an important task (Sadus, 1992a). This is most commonly achieved by mixing rules and combining rules which relate the properties of the pure components to the properties of the mixtures. The discussion will be limited to the extension of parameters  $a$  and  $b$ . 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:

$$a = \sum_i x_i a_i \quad (3.64)$$

$$b = \sum_i x_i b_i \quad (3.65)$$

Eq. (3.64) is sometimes employed (Han et al., 1988) because of its simplicity, but Eq. (3.64) is rarely used because it does not account for the important role of unlike interactions in binary fluids. Consequently, employing both Eq. (3.64) and Eq. (3.65) would lead to the poor agreement of theory with experiment.

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

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (3.66)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (3.67)$$

where  $a_{ii}$  and  $b_{ii}$  are the equation of state parameters for pure components and cross parameters  $a_{ij}$  and  $b_{ij}$  ( $i \neq j$ ) are determined by an appropriate combining rule.

Eq. (3.66) and Eq. (3.67) are based on the implicit assumption that the radial distribution function of the component molecules is 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 to obtain parameter  $a$  and a linear mixing rule to obtain parameter  $b$ . The 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. (3.65) and Eq. (3.66) were adequate for 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 mixing rules 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. There is some evidence (Deiters, 1987) that the following mixing rules are more appropriate at high pressure:

$$\mathbf{e}_0 \mathbf{s}_0^g = \sum_i \sum_j x_i x_j \mathbf{e}_{ij} \mathbf{s}_{ij}^g \quad (3.68)$$

$$\mathbf{s}_0^g = \sum_i \sum_j x_i x_j \mathbf{s}_{ij}^g \quad (3.69)$$

where  $a$  and  $b$  are proportional to  $\mathbf{e}_0 \mathbf{s}_0^3$  and  $\mathbf{s}_0^3$ , respectively.  $\mathbf{e}_0$  and  $\mathbf{s}_0$  are the characteristic attractive energy and collision diameter. The parameter  $g$  is obtained from comparison with experimental data, and is typically assigned a value of either 2 or 2.4. Some attempts have been made to estimate it from theoretical considerations. In terms of the conformal parameters (recall  $h_{ij} = g_{ij}^3$ ) the above relationships can be represented as:

$$fg^g = \sum_i \sum_j x_i x_j f_{ij} g_{ij}^g \quad (3.70)$$

$$g^g = \sum_i \sum_j x_i x_j g_{ij}^g \quad (3.71)$$

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 pure component parameter data, the parameter  $a$  for the mixture is calculated directly.

Consequently,  $a$  is a function of composition only via the conformal parameters and the contribution from the combinatorial entropy of mixing. The parameter  $a$  is obtained by taking the positive root of the following quadratic equation:

$$\begin{aligned}
 a^2 \mathbf{q}^6 & [-2f''/f + (f'/f)^2 - 2h''/h - 2f'h'/fh + (h'/h)^2] \\
 & + aRTV[\mathbf{f}_B \mathbf{q}^2 (-h''/h - f''/f)] + 2\mathbf{f}_A \mathbf{q}^3 (h''/h + f'h'/fh - (h'/h)^2) \\
 & + 2\mathbf{q}^6 [-h''/h + (h'/h)^2 + 1/\{x(1-x)\}] - (RTV)^2 [\mathbf{f}_A^2 \{(f'/f)^2 - (h'/h)^2\}] \\
 & + \mathbf{f}_B \mathbf{q}^2 \{h''/h - (h'/h)^2 - 1/[x(1-x)]\} - \mathbf{f}_A \mathbf{f}_B h''/(h\mathbf{q})] = 0
 \end{aligned} \tag{3.72}$$

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. (3.72) is that the parameter  $a$  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 vapour-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.

Huron and Vidal (1979) have developed mixing rules from the excess thermodynamic properties of mixing. For example, in the case of the van der Waals equation and assuming a simple model of the energy of the fluid, the following relationship (Mollerup, 1986) is obtained:



$$a = V \sum_i x_i (a_i / b_i) y_i - G^E V + RTV [\sum_i x_i \ln \{ b_i (y_i - 1) / (y - 1) b \}] \quad (3.73)$$

where  $y = V/b$ ,  $y_i = V_i/b_i$  and  $G^E$  is the excess Gibbs function. The above approach is mainly limited to low pressure equilibria but it may be useful for predicting critical solution temperature phenomena. Another approach, which is discussed elsewhere (Hoheisel and Kohler, 1984), is the concept of local composition.

Many of the above density dependent prescriptions are undoubtedly more accurate than the van der Waals model at high densities. But for high pressure phenomena, there is insufficient data to make an assessment. Some computer simulation of the high pressure behaviour of binary fluids would be useful in this instance. It is clear that the increased complexity is a disadvantage for high pressure calculations, particularly if reliable theoretical estimates of parameters such as  $g$  and  $g_j$  (Eq. 3.71) cannot be obtained and empirical methods must be adopted. High pressure phenomena also occur over a range of densities. The van der Waals prescriptions are certainly appropriate for vapour-liquid phenomena but other rules may be beneficial for dense liquid-liquid critical phenomena. The analysis of type III phenomena, where there is a transition between vapour-liquid and liquid like densities, could also benefit. However it is difficult to isolate the effect of mixing rules on the phase behaviour of fluids because most equation of state calculations rely on additional combining rule parameters for their accuracy. It appears unlikely that any of the above prescription could eliminate this

feature. Thus, the overall effect may be to increase the complexity of the calculations without necessarily improving the accuracy and genuine predictive capability.

A different approach has been adopted by Boublik (1970) and Mansoori et al. (1971). They proposed a direct extension of the Carnahan-Starling hard sphere term,

$$Z = [1 + \{(3DE / F - 2\}y + \{(3E^3 / F^2) - (3DE / F) + 1\}y^2 - (E^3 / F^2)y^3] / (1 - y)^3 \quad (3.74)$$

where

$$y = \rho N_A F / 6V \quad (3.75)$$

$$F = \sum_i x_i \mathbf{s}_i^3 \quad (3.76)$$

$$E = \sum_i x_i \mathbf{s}_i^2 \quad (3.77)$$

and

$$D = \sum_i x_i \mathbf{s}_i \quad (3.78)$$

At low densities, the compressibility factor predicted by Eq. (3.71) is identical to the Carnahan-Starling equation with the one-fluid model. However, at moderate and high densities, there is a significant deviation, particularly if molecules of dissimilar size are involved. Therefore, the analysis of vapour-liquid properties is unlikely to be affected, but in common with other density dependent mixing rules, it may be beneficial for some dense fluid critical phenomena. Dimitrelis and Prausnitz (1986) have concluded that the equation is particularly advantageous for the prediction of vapour-liquid equilibria if the molecular size ratio  $(s_1/s_2)^3$  exceeds 2.

The temperature dependence of the equation of state parameters is typically obtained by scaling the values obtained at the vapour-liquid critical point to lower temperatures and pressures. The critical values are adequate for high pressure equilibria. The exception is liquid-liquid phenomena for which the vapour-liquid values are intuitively inadequate. The following equation (Christoforakos and Franck, 1986) is acceptable:

$$b(T_2) = b(T_1)(T_1/T_2)^{0.3} \quad (3.79)$$

It should be noted that the temperature dependence of the parameter  $a$  is normally reflected in a lower than normal  $\omega$  value (see Eq. 3.84) and that the agreement with experiment is often very good without formally introducing any temperature dependence in the  $b$  term.

Wong and Sandler (1992) used the Helmholtz function to develop mixing rules to satisfy the second virial condition. For the mixture parameters of an equation of state,  $a$  and  $b$  are

$$a = b \left( \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \right) \quad (3.80)$$

$$b = \frac{\sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij}}{1 + \frac{A_\infty^E}{RT} - \sum_i x_i \frac{a_i}{b_i RT}} \quad (3.81)$$

where  $C$  is a constant dependent on the equation of state selected and  $A_\infty^E$  is the excess Helmholtz function at infinite pressure, and

$$(b - \frac{a}{RT})_{ij} = \frac{(1 - k_{ij})}{2} [(b_i - \frac{a_i}{RT}) + (b_j - \frac{a_j}{RT})] \quad (3.82)$$

where  $k_{ij}$  is a binary interaction parameter.

Wong and Sandler (1992) tested the Eq. (3.80) and Eq. (3.81), and reported that they were accurate in describing both simple and complex phase behaviour of binary systems for

diverse systems. Wong et al. (1992) demonstrated that the Wong-Sandler mixing rules can be used for highly nonideal mixtures. Huang and Sandler (1993) compared the Wong-Sandler mixing rules for nine binary systems. They demonstrated that the mixing rules can be used to make high pressure vapour-liquid equilibrium predictions from low pressure data. 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.

To go smoothly from activity coefficient-like behaviour to the van der Waals one fluid mixing rule, Orbey and Sandler (1995) slightly reformulated the Wong-Sandler mixing rules by rewriting the cross second virial term given in Eq. (3.82) as

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j} (1 - k_{ij})}{RT} \quad (3.83)$$

Orbey and Sandler (1995) tested five binary systems, 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. Castier and Sandler (1997a, b) performed critical point calculations in binary systems utilizing cubic equations of state combined with the Wong-Sandler mixing rules, and investigated the

influence of the mixing rules on the shape of the calculated critical phase diagrams. The results showed that the combination can obtain many different types of critical phase diagrams. Rudolph et al. (2000) used the Peng-Robinson equation of state with the Wong-Sandler mixing rule to investigate binary mixtures of water plus surfactant systems containing C<sub>4</sub>E<sub>1</sub>, C<sub>6</sub>E<sub>3</sub>, C<sub>7</sub>E<sub>3</sub> and C<sub>7</sub>E<sub>5</sub>. They found that the model fitted the experimentally found type of phase behaviour quite correctly. Comparison and evaluation for various mixing rules can be found in the works of Knudsen et al. (1996), Michelsen and Heidemann (1996), Wang et al (1996), Orbey and Sandler (1996), Twu et al. (1998), Wei and Sadus (1999b) and Saghafi and Moshfeghian (2000).

### 3.3 Combining Rules

Any realistic mixture prescriptions will invariably contain contributions from interactions between unlike molecules. This means that the cross term  $a_{ij}$  and  $b_{ij}$  ( $i \neq j$ ) must be evaluated. The most widely used combining rule for the  $a_{ij}$  term was first proposed by van der Waals:

$$a_{ij} = \mathbf{x}_{ij} \sqrt{a_{ii} a_{jj}} \quad (3.84)$$

Alternatively, the following combining rule for critical calculations can be used,

$$a_{ij} = \mathbf{x}_{ij} b_{ij} \sqrt{\frac{a_{ii} a_{jj}}{b_{ii} b_{jj}}} \quad (3.85)$$

The  $\mathbf{x}_{ij}$  term (also commonly defined as  $k_{ij}$ ) is frequently introduced into combining rules to optimise the agreement between theory and experiment. The  $\mathbf{x}_{ij}$  parameter is frequently interpreted as reflecting the strength of intermolecular interaction. This interpretation is supported by the fact that values of  $\mathbf{x}_{ij}$  obtained from the analysis of the critical properties of many binary mixtures consistently decline with increasing size difference between the component molecules. Mixtures of molecules of similar size, but different molecular interactions, are associated with different interaction parameters. Nonetheless, the requirement for  $\mathbf{x}_{ij}$  values to optimise agreement between theory and experiment is also testimony to the inadequacy of the combining rule, mixture prescriptions and the equation of state. It has been frequently documented (Mainwaring et al. 1988b; Elliot and Daubert, 1987) that different  $\mathbf{x}_{ij}$  values are required to obtain optimal agreement between theory and experiment for vapour-liquid and liquid-liquid critical equilibria, respectively.

The most widely used combining rules for  $b_{ij}$  are the simple arithmetic rules:

$$b_{ij} = \mathbf{z}_{ij} \frac{b_{ii} + b_{jj}}{2} \quad (3.86)$$

and the Lorentz combining rule (Hicks and Young, 1975; Sadus, 1992a, 1994):

$$b_{ij} = z_{ij} \frac{(b_{ii}^{1/3} + b_{jj}^{1/3})^3}{8} \quad (3.87)$$

Both the simple arithmetic and Lorentz combining rules yield nearly identical results for mixtures of molecules of similar size, but the discrepancy increases substantially for mixtures of molecules of very dissimilar size. The adjustable parameter  $z_{ij}$  is used to optimise the agreement between theory and experiment. It is generally found that the parameter  $z_{ij}$  is not required for the accurate prediction of vapour-liquid critical properties (Sadus, 1994). Similarly, good agreement between theory and experiment for type II liquid-liquid equilibria can usually be obtained by solely adjusting the  $x_{ij}$  term and setting  $z_{ij} = 1$ . However, obtaining an optimal  $z_{ij}$  parameter is essential for the accurate representation of type III behaviour. It is found (Sadus, 1993) that the arithmetic combining rule substantially overestimates the two-phase region, whereas the Lorentz rule is more accurate but it extends the one-phase region. Sadus (1993) has examined type III behaviour of nonpolar mixtures using both arithmetic and Lorentz combining rules. Good agreement between theory and experiment could be obtained by determining both the optimal  $x_{ij}$  and  $z_{ij}$  parameters.

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



$$b_{ij} = \{1/4(2^{1/3})\}(b_{ii}^{1/3} + b_{jj}^{1/3})^2 (b_{ii} + b_{jj})^{1/3} \quad (3.88)$$

Sadus (1993) reported that the new combining rule (Eq. 3.88) is generally more accurate than either the simple arithmetic or Lorentz combining rules.

### 3.4 Crossover Equation of State

Chen et al. (1990) and Jin et al. (1993) introduced a theory that incorporates scaling laws asymptotically close to the critical point and that are transformed into the regular classical expansion far away from the critical point, and this leads to the crossover equations of state. Although the original crossover equation of state gives an accurate representation of the thermodynamic properties of fluids in a wide region around the critical point of pure components, it cannot be extrapolated to low densities (Kiselev, 1998).

Fox (1983) proposed an approach to the incorporation of scaling laws in classical equations of state. The idea of the approach consists in the renormalization of the temperature and the density in the equations of state. The result is that the temperature and the density become non-analytic scaling functions of the dimensionless distance to the critical point. Kiselev (1998) developed a cubic crossover equation of state based on the non-classical critical phenomena for pure fluids which incorporates the scaling laws asymptotically close to the

critical point and which is transformed into the original cubic equation of state far away from the critical point.

### 3.4.1 Classical Expression for the Critical part

In the critical region, the van der Waals equation of state corresponds to the mean-field, or Landau theory of critical phenomena (Landau and Lifshitz, 1980; Patashinskii and Pokrovskii, 1979). The main assumption of the classical theory of critical phenomena is that the critical part of the Helmholtz function,  $\Delta A$  of the system can be represented by a Taylor expansion in the powers of the order parameter (Kiselev, 1998)

$$\Delta A(\mathbf{t}, \Delta \mathbf{h}) = \sum_i \sum_j a_{ij} \mathbf{t}^i \Delta \mathbf{h}^j \quad (3.89)$$

where  $\mathbf{t} = T/T_c - 1$  is the dimensionless deviation of the temperature  $T$  from the critical temperature  $T_c$ ,  $a_{ij}$  are the system-dependent coefficients, and  $\Delta \mathbf{h}$  is an order parameter (Landau and Lifshitz, 1980). In the critical region  $|\mathbf{t}| \ll 1$  and  $|\Delta \mathbf{h}| \ll 1$ , therefore, there are two main terms in Eq. (3.89)

$$\Delta A(\mathbf{t}, \Delta \mathbf{h}) = a_{12} \mathbf{t} \Delta \mathbf{h}^2 + a_{04} \Delta \mathbf{h}^4 \quad (3.90)$$

that correspond to the critical phenomena (Landau and Lifshitz, 1980). Eq. (3.90) is valid only in the temperature region  $G_i \ll |\mathbf{t}| \ll 1$  ( $G_i$  is the Ginzburg number, Landau and Lifshitz, 1980) where the long-scale fluctuations in the order parameter are negligible

(Laudau and Lifshitz, 1980; Patashinskii and Pokrovskii, 1979). If  $|t| \ll Gi$ , the singular part of the thermodynamic potential of a system becomes a non-analytical scaling function of the  $t$  and  $\Delta h$ .

A theoretical approach for constructing a crossover expression for the thermodynamic potential of a system in the critical region based on the renormalization-group calculations of Nicoll and Bhattachajee (1981) and Nicoll and Albright (1986) has been developed by Chen et al. (1990). Using this approach, the critical fluctuations close to the critical point result is:

$$\Delta A(t, \Delta h) = a_{12} t Y^{-\frac{a}{2\Delta_1}} \Delta h^2 Y^{\frac{g-2b}{2\Delta_1}} + a_{04} \Delta h^4 Y^{\frac{g-2b}{\Delta_1}} - K(t^2) \quad (3.91)$$

where,  $a, b$  and  $g$  are critical exponents,  $K(t^2)$  is the kernel term, which provides the correct scaling behaviour of the isochoric specific heat asymptotically close to the critical point (Kiselev, 1998),

$$K(t^2) = \frac{1}{2} a_{20} t^2 (Y^{\frac{a}{\Delta_1}} - 1) \quad (3.92)$$

where,  $Y$  is a crossover function to be determined from the set of coupled algebraic equations by Jin et al. (1993).

Eq. (3.91) is equivalent to Eq. (3.90) with the replacement of the dimensionless temperature  $t$  and the order parameter  $\Delta h$  by the renormalized values (Kiselev, 1998):

$$\tilde{t} = tY^{\frac{a}{2\Delta_1}}, \quad \Delta\tilde{h} = \Delta h Y^{\frac{g-2b}{4\Delta_1}} \quad (3.93)$$

and adding the kernel term  $K(t^2)$ . As one moves further from the critical point,  $|t|$  and  $|\Delta h|$  increase, more terms in Eq. (3.89) and Eq. (3.90) may be considered.

### 3.4.2 Crossover Expression

It is well-known the Helmholtz energy per mole (Sandler, 1999) that can be described as

$$A(T, V) = -\int p dV + A_{ideal} \quad (3.94)$$

where  $A_{ideal}$  corresponds to the temperature dependent function of the ideal-gas part of the Helmholtz energy.

For a classical equation of state  $p(V, T)$ , can be written in the dimensionless form

$$\tilde{p} = \frac{PV_c}{RT} \quad (3.95)$$

The dimensionless Helmholtz energy can be represented in the form

$$\tilde{A}(T, V) = \frac{A(T, V)}{RT} = -\frac{1}{RT} \int \frac{RT}{V_c} \tilde{p} dV + \frac{A_{ideal}}{RT} = \Delta \tilde{A}(\Delta T, \Delta V) - \Delta V \tilde{p}_0(T) + \tilde{u}_0(T) \quad (3.96)$$

where  $\Delta \tilde{A}(\Delta T, \Delta V)$  corresponds to the critical part of the Helmholtz function,  $\Delta T = T_r - 1$  ( $T_r = T/T_c$ ) is the dimensionless deviation of the temperature from the critical temperature  $T_c$ , and  $\Delta V = V/V_c - 1$  is also the dimensionless order parameter,  $\tilde{p}_0(T) = p(V_c, T)V_c / RT$  is the dimensionless pressure at the critical isochore  $V = V_c$  and  $\tilde{u}_0$  is relation to employed equation of state.

$\Delta T$  and  $\Delta V$  are needed to renormalized in the critical part of the classical Helmholtz function  $\Delta \tilde{A}(\Delta T, \Delta V)$  according to Eq. (3.95) by Kiselev (1998). The critical temperature and pressure of the equations of state can be taken from available measurements or predictions, while the critical density is usually found as fitting parameter of the model, chosen to the best description of the vapour-liquid equilibrium surface far away from the critical point. Since any classical equation of state does not reproduce the thermodynamic surface of a fluid in the critical region, the critical density found by this method does not coincide with the real critical density of the system (Kiselev, 1998). The additional terms to take into account the difference between the classical critical temperature  $T_c$  and critical volume  $V_c$ , and the real critical parameters  $T_{Rc}$  and  $V_{Rc}$  were introduced in Eq. (3.94) by Kiselev (1998). The new forms of dimensionless temperature  $\tilde{t}$  and the order parameter  $\Delta h$

$$\tilde{\mathbf{t}} = \mathbf{t} Y^{-\frac{a}{2\Delta_1}} + (1+\mathbf{t})\Delta\mathbf{t}_c Y^{\frac{2(2-a)}{3\Delta_1}} \quad (3.97)$$

$$\Delta\tilde{\mathbf{h}} = \Delta\mathbf{h} Y^{\frac{g-2b}{4\Delta_1}} + (1+\Delta\mathbf{h})\Delta\mathbf{h}_c Y^{\frac{2-a}{2\Delta_1}} \quad (3.98)$$

where the order parameter  $\Delta\mathbf{h} = V/V_c - 1$ , while  $\Delta\mathbf{t}_c = \Delta T_c/T_{Rc}$  and  $\Delta\mathbf{h}_c = \Delta V_c/V_{Rc}$  are the dimensionless shifts of the critical temperature and the critical volume, respectively. Parameters  $T_{Rc}$  and  $V_{Rc}$  are the real critical temperature and volume of fluid. The crossover function  $Y$  in Eqs. (3.97) and (3.98) can be written in the parametric form as

$$Y(q) = \left[ \frac{q(1+q)}{1+q+q^2} \right]^{2\Delta_1} \quad (3.99)$$

and the parametric variable  $q$  can be found from the solution of the equation

$$q^2 = \frac{\mathbf{t}}{Gi} + b_{LM}^2 \left( \frac{\Delta\mathbf{h} + d_1\mathbf{t} + d_2\mathbf{t}^2}{Gi^b} \right)^2 Y^{\frac{1-2b}{\Delta_1}}(q) \quad (3.100)$$

$b_{LM}^2 = (\mathbf{g} - 2\mathbf{b})/\mathbf{g}(1 - 2\mathbf{b}) = 1.359$  is the linear-model parameter (Kiselev and Sengers, 1993). The terms  $\propto \mathbf{t}$  and  $\propto \mathbf{t}^2$  correspond to a projection of the rectilinear diameter of the coexistence curve in the temperature-density variables  $\mathbf{r}_d = (\mathbf{r}_V + \mathbf{r}_L)/2 = \mathbf{r}_c(1 + d\mathbf{t})$  on the temperature-volume projection  $V_d = 1/\mathbf{r}_d \cong V_c(1 + d_1\mathbf{t} + d_2\mathbf{t}^2)$ .

To complete the transformation of the classical Helmholtz function into the crossover form, we must replace the classical dimensionless temperature  $\Delta T$  and the volume  $\Delta V$  in Eq. (3.96) with the renormalized values  $\tilde{t}$  and  $\Delta\tilde{h}$ , and the kernel term  $K(\mathbf{t}^2)$ . The crossover expression for the Helmholtz function is

$$\tilde{A}(T, V) = \Delta \tilde{A}(\tilde{t}, \Delta\tilde{h}) - \Delta V \tilde{p}_0(T) + \tilde{u}_0(T) - K(\mathbf{t}^2) \quad (3.101)$$

### 3.4.3 Crossover Equation of State

A crossover equation of state incorporates the scaling laws asymptotically close to the critical point and is transformed into the original equation of state far away from the critical point. The general form of the crossover equation of state obtained from the crossover expression in Eq. (3.102):

$$p = \frac{RT}{V_c} \left[ -\frac{V_c}{V_{Rc}} \left( \frac{\partial \Delta \tilde{A}}{\partial \Delta \tilde{h}} \right)_T + \tilde{p}_0(T) + \frac{V_c}{V_{Rc}} \left( \frac{\partial K(\mathbf{t}^2)}{\partial \Delta \tilde{h}} \right)_T \right] \quad (3.102)$$

For the Patel-Teja crossover equation of state (Kiselev, 1998), the value of  $\tilde{p}_0$  is:

$$\tilde{p}_0(T) = \frac{1}{b_1} - \frac{T_c}{T} \frac{\Omega_a \mathbf{a}(T)}{Z_c b_2 b_3} \quad (3.103)$$

and the critical part  $\Delta \tilde{A}$  is given by

$$\Delta \tilde{A}(\tilde{t}, \Delta \tilde{h}) = -\ln\left(\frac{\Delta \tilde{h}}{b_1} + 1\right) + \frac{T_c}{T} \frac{\Omega_a \mathbf{a}(\tilde{t})}{\Omega} \ln\left(\frac{\Delta \tilde{h}/b_2 + 1}{\Delta \tilde{h}/b_3 + 1}\right) + \frac{\Delta \tilde{h}}{b_1} - \frac{T_c}{T} \frac{\Omega_a \mathbf{a}(\tilde{t}) \Delta \tilde{h}}{Z_c b_2 b_3} \quad (3.104)$$

where  $\Omega_a$ ,  $\Omega_b$ , and  $\Omega_c$  are functions of the critical compressibility factor  $Z_c$  (Eq. (3.25)-Eq. (3.27)), and  $\Omega$

$$\Omega = \sqrt{\Omega_b^2 + 6\Omega_b \Omega_c + \Omega_c^2} \quad (3.105)$$

The definition of  $\mathbf{a}(T)$  can be found in Eq. (3.28) and Eq. (3.29). Parameters  $b_1$ ,  $b_2$  and  $b_3$  in Eq. (3.104) and Eq. (3.105) are

$$\begin{aligned} b_1 &= 1 - \frac{\Omega_b}{Z_c} \\ b_2 &= 1 + \frac{\Omega_b + \Omega_c - \Omega}{2Z_c} \\ b_3 &= 1 + \frac{\Omega_b + \Omega_c + \Omega}{2Z_c} \end{aligned} \quad (3.106)$$

Remember that  $\tilde{u}_0$  in Eq. (3.101) with Patel-Teja equation of state is



$$\tilde{u}_0(T) = -\ln b_1 + \frac{T_c}{T} \frac{\Omega_a \mathbf{a}(T)}{\Omega} \ln\left(\frac{b_2}{b_3}\right) + \tilde{A}_{ideal} \quad (3.107)$$

and

$$\tilde{A}_{ideal} = \frac{A_{ideal}}{RT} \quad (3.108)$$

Kiselev (1998) used the modified Patel-Teja cubic equation of state (Patel and Teja, 1982) to compare with experimental data for pure CO<sub>2</sub>, water, and refrigerants R32 and R125 in the one- and two-phase regions. He showed that the crossover Patel-Teja equation of state yields a much better representation of the thermodynamic properties of pure fluids, especially in the critical region and for vapour-liquid equilibrium, than the original Patel-Teja equation of state.

Kiselev and Ely (1999) also developed a crossover modification of the statistical associating fluid theory equation of state for macromolecular chain fluids. The crossover statistical associating fluid theory equation of state has the same form as the cubic one of Eq. (3.103),

but  $\tilde{p}_0(T)$  and  $\Delta \tilde{A}$  have the different forms because of different classical equation of state,

$$\tilde{p}_0(T) = \frac{V_c}{RT} p(T, V_c) \quad (3.109)$$

and

$$\Delta \tilde{A}(\tilde{t}, \Delta \tilde{\mathbf{h}}) = \tilde{A}_r(\tilde{t}, \Delta \tilde{\mathbf{h}}) - \tilde{A}_r(\tilde{t}, 0) - \ln(\Delta \tilde{\mathbf{h}} + 1) + \Delta \tilde{\mathbf{h}} \tilde{p}_0(\tilde{t}) \quad (3.110)$$

where  $\tilde{A}_r$  is the dimensionless residual part of the Helmholtz energy.

Kiselev and Ely (1999) compared the crossover statistical associating fluid theory and original equation of state with experimental single-phase data for n-triacontane and n-tetracontane. The results show that the crossover statistical associating fluid theory equation of state reproduces the saturated pressure data in the entire temperature range from the triple point to the critical temperature with an average absolute deviation of about 3.8%, the saturated liquid densities with an average absolute deviation of about 1.5%, the saturated vapour densities with an average absolute deviation of about 3.4%, and gives a much better representation of the experimental values of pressure and the liquid density in the critical region.

Wyczalkowska et al. (1999) also developed a global crossover equation of state to show how the density fluctuations affect all thermodynamic properties more and more significantly when the fluid approaches the critical point.

## References

- Abdulkadirova, K. S., Wyczalkowska, A. K., Anisimov, M. A. and Sengers, J. V. (2002). Thermodynamic Properties of Mixtures of H<sub>2</sub>O and D<sub>2</sub>O in the Critical Region, *J. Chem. Phys.*, **116**, 4597-4610.
- Adachi, Y., Lu, B. C. Y. and Sugie, H. (1983). Three-Parameter Equation of State, *Fluid Phase Equilib.*, **13**, 133-142.
- Anderko, A. (1990). Equation-of-State Methods for the Modelling of Phase Equilibria, *Fluid Phase Equilib.*, **61**, 145-225.

- Baker, L. E. and Luks, K. D. (1980). Critical Point and Saturation Pressure Calculations for Multipoint Systems, *Soc. Pet. Eng. J.*, **20**, 15-24.
- Beret S. and Prausnitz, J. M. (1975). Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules, *AIChE J.*, **26**, 1123-1132.
- Boublik, T. (1970). Hard-Sphere Equation of State, *J. Chem. Phys.*, **53**, 471-473.
- Boublik, T. (1981). Statistical Thermodynamics of Nonspherical Molecule Fluids. *Ber. Bunsenges, Phys. Chem.* **85**, 1038-1041.
- Calado, J. C. G., Deiters, U. and Streett, W. B. (1981). Liquid-Vapour Equilibrium in the Krypton + Methane System, *J. Chem. Soc. Farad I.*, **77**, 2503-2513.
- Carnahan, N. F. and Starling, K. E. (1969). Equation of State for Nonattracting Rigid Spheres, *J. Chem. Phys.*, **51**, 635-636.
- Castier, M. and Sandler, S. I. (1997a). Critical Points with the Wong-Sandler Mixing Rule. I. Calculations with the van der Waals Equation of State, *Chem. Eng. Sci.*, **52**, 3393-3399.
- Castier, M. and Sandler, S. I. (1997b). Critical Points with the Wong-Sandler Mixing Rule. II. Calculations with a Modified Peng-Robinson Equation of State, *Chem. Eng. Sci.*, **52**, 3579-3588.
- Chang, J. and Sandler, S. I. (1994). An Equation of State for the Hard-Sphere Chain Fluid: Theory and Monte Carlo Simulation, *Chem. Eng. Sci.*, **49**, 2777-2791.
- Chapman, W. G., Jackson, G. and Gubbins, K. E. (1988). Phase Equilibria of Associating Fluid: Chain Molecules with Multiple Bonding Sites, *Mol. Phys.*, **65**, 1057-1079.
- Chapman, W. G., Gubbins, Gubbins, K. E., Jackson, G. and Radosz, M. (1990). New Reference Equation of State for Associating Liquids, *Ind. Eng. Chem. Res.*, **29**, 1709-1721.

- Chen, Z. Y., Albright, P. C. and Sengers, J. V. (1990). Crossover from Singular Critical to Regular Classical Thermodynamic Behavior of Fluids, *Phys. Rev. A* **41**, 3161-3177.
- Chiew, Y. C. (1990). Percus-Yevick Integral-Equation Theory for Athermal Hard-Sphere Chains: I. Equations of State, *Mol. Phys.*, **70**, 129-143.
- Chiew, Y. C. (1991). Percus-Yevick Integral-Equation Theory for Athermal Hard-Sphere Chains: II. Average Intermolecular Correlation Functions, *Mol. Phys.*, **73**, 359-373.
- Christoforakos, M. and Franck, E. U. (1986). An Equation of State for Binary Fluid Mixtures to High Temperatures and High Pressures. *Ber. Bunsenges. Phys. Chem.*, **90**, 780-789.
- Christou, G., Morrow, T. Sadus, R. J. and Young, C. L. (1986). Phase Behaviour of Fluorocarbon + Hydrocarbon Mixtures: Interpretation of Type II and Type III Behaviour in Terms of a 'Hard Sphere + Attractive Term' Equation of State, *Fluid Phase Equilib.*, **25**, 263-272.
- Christou, G., Young, C. L. and Svejda, P. (1991). Gas-Liquid Critical Temperatures of Binary Mixtures of Polar Compounds + Hydrocarbons or + Other Polar Compounds. *Ber. Bunsenges. Phys. Chem.*, **95**, 510-514.
- Chueh, P. L. and Prausnitz, J. M. (1967a). Vapour-Liquid Equilibria at High Pressures. Vapour-Phase Fugacity Coefficients in Nonpolar and Quantum-Gas Mixtures, *Ind. Eng. Chem. Fundam.*, **6**, 492-498.
- Chueh, P. L. and Prausnitz, J. M. (1967b). Vapour-Liquid Equilibria at High Pressures. Calculation of Partial Molar Volumes in Nonpolar Liquid Mixtures, *AIChE J.*, **13**, 1099-1107.
- Deiters, U. K. and Schneider, G. M. (1976). Fluid Mixtures at High Pressures. Computer Calculations of the Phase Equilibrium and the Critical Phenomena in Fluid Binary

- Mixtures from the Redlich-Kwong Equation of State, *Ber. Bunsenges. Phys. Chem*, **80**, 1316-1321.
- Deiters, U. (1982). A New Semiempirical Equation of State for Fluid: III. Application to Phase Equilibria in Binary Mixtures, *Chem. Eng. Sci.*, **37**, 855-861.
- Deiters, U. K. and Swaid, I. (1984). Calculation of Fluid-Fluid and Solid-Fluid Phase Equilibria in Binary Mixtures at High Pressures, *Ber. Bunsenges. Phys. Chem*, **88**, 791-796.
- Deiters, U. K. (1987). Density-Dependent Mixing Rules for the Calculation of Fluid Phase Equilibria at High Pressures, *Fluid Phase Equilib.*, **33**, 267-293.
- Deiters, U. K. and Pegg, I. L., (1989). Systematic Investigation of the Phase Behaviour in Binary Fluid Mixtures. I. Calculations Based on the Redlich-Kwong Equation of State, *J. Chem. Phys.* **90**, 6632-6641.
- Dickman, R. and Hall, C. K. (1986). Equation of State for Chain Molecules: Continuous-Space Analog of Flory Theory, *J. Chem. Phys.*, **85**, 4108-4115.
- Dimitrelis, D. and Prausnitz, J. M. (1986). Comparison of two Hard Sphere Reference Systems for Perturbation Theories for Mixtures, *Fluid Phase Equilib.*, **31**, 1-21.
- Donohue, M. D. and Prausnitz J. M. (1978). Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology, *AIChE J.*, **24**, 849-860.
- Economou, I. G. and Donohue, M. D. (1996). Equations of State for Hydrogen Bonding Systems, *Fluid Phase Equilib.*, **116**, 518-529.
- Elliott, J. R. and Daubert, T. E. (1987). Evaluation of an Equation of State Method for Calculating the Critical Properties of Mixtures, *Ind. Eng. Chem. Res.*, **26**, 1686-1691.

- Estela-Uribe, J. F. and Trusler, J. P. M. (1998). Shape Factors for Light Hydrocarbons, *Fluid Phase Equilib.*, **151**, 225-234.
- Flory, P. I. (1965). Statistical Thermodynamics of Liquid Mixtures, *J. Am. Chem. Soc.*, **87**, 1833-1838.
- Fox, J. F. (1983). Method for Construction of Nonclassical Equation of State, *Fluid Phase Equilib.*, **14**, 45-53.
- Franck, E. U. (1987). Fluid at High Pressures and Temperatures, *J. Chem. Thermodyn.*, **19**, 225-244.
- Ghonasgi, D. and Chapman, W. G. (1994). A New Equation of State for Hard Chain Molecules, *J. Chem. Phys.*, **100**, 6633-6639.
- Gubbins, K. E., Shing, K. S. and Streett, W. B. (1983). Fluid Phase Equilibria: Experiment, Computer Simulation, and Theory *J. Phys. Chem.*, **87**, 4573-4585.
- Guggenheim, E. A. (1965). Variations on van der Waals' Equation of State for High Densities, *Mol. Phys.*, **9**, 199-200.
- Han, S. J., Lin, H. M. and Chao, K. C. (1988). Vapour-Liquid Equilibrium of Molecular Fluid Mixtures by Equation of State, *Chem. Eng. Sci.*, **43**, 2327-2367.
- Harismiadis, V. I., Koutras, N. K., Tassios, D. P. and Panagiotopoulos, A. Z. (1991). How Good is Conformal Solutions Theory for Phase Equilibrium Predictions?, *Fluid Phase Equilib.*, **65**, 1-18.
- Harstad, K. G., Miller, R. S. and Bellan, J. (1997). Efficient High-Pressure State Equations, *AIChE J.*, **43**, 1605-1610.
- Heilig, M. and Franck, E. U. (1989). Calculation of Thermodynamic Properties of Binary Fluid Mixtures to High Temperatures and High Pressures, *Ber. Bunsenges. Phys. Chem.*, **93**, 898-905.

- Heilig, M. and Franck, E. U. (1990). Phase Equilibria of Multicomponent Fluid Systems to High Pressures and Temperatures, *Ber. Bunsenges. Phys. Chem.*, **94**, 27-35.
- Hicks, C. P. and Young C. L. (1975). The Gas-Liquid Critical Properties of Binary Mixtures, *Chem. Rev.*, **75**, 119-175.
- Hicks, C. P. and Young, C. L. (1976). Critical Properties of Binary Mixtures, *J. Chem. Soc. Faraday I*, **72**, 122-133.
- Hicks, C. P., Hurle, R. L. and Young, C. L. (1977). Theoretical Prediction of Phase Behaviour at High Temperatures and Pressures for Non-Polar Mixtures: IV. Comparison with Experimental Results for Carbon Dioxide + n-Alkane mixtures, *J. Chem. Soc. Faraday II*, **73**, 1884-1888.
- Hicks, C. P., Hurle, R. L., Toczylkin, L. S. and Young, C. L. (1978). Upper Critical Solution Temperatures of Hydrocarbon + Fluorocarbon Mixtures, *Aust. J. Chem.*, **31**, 19-25.
- Hoheisel, H. and Kohler, F. (1984). Local Composition in Liquid Mixtures, *Fluid Phase Equilib.*, **16**, 13-24.
- Huang, H. and Sandler, S. I. (1993). Prediction of Vapour-Liquid Equilibria at High Pressure Using Activity Coefficient Parameters Obtained from Low Pressure Data: A Comparison of two Equation of State Mixing Rules, *Ind. Eng. Chem. Res.*, **32**, 1498-1503.
- Huber M.L. and Ely, J. F. (1994). A Predictive Extended Corresponding States Model for Pure and Mixed Refrigerants Including an Equation of State for R134a, *Int. J. Refrig.* **17**, 18-31.
- Hurle, R. L., Toczylkin, L. S. and Young, C. L. (1977a). Theoretical Prediction of Phase Behaviour at High Temperatures and Pressures for Non-Polar Mixtures: II. Comparison

- with Upper Critical Solution Temperatures for Perfluoromethylcyclohexane + Hydrocarbons, *J. Chem. Soc. Faraday II*, **73**, 613-617.
- Hurle, R. L., Toczylkin, L. S. and Young, C. L. (1977b). Theoretical Prediction of Phase Behaviour at High Temperatures and Pressures for Non-Polar Mixtures: III. Gas-Gas Immiscibility, *J. Chem. Soc. Faraday II*, **73**, 618-622.
- Huron, M. J. and Vidal, J. (1979). New Mixing Rules in Simple Equations of State for Representing Vapour-Liquid Equilibria of Strongly Non-Ideal Mixtures, *Fluid Phase Equilib.*, **3**, 255-271.
- Ikonomou, G. D. and Donohue, M. D. (1986). Thermodynamics of Hydrogen-Bonded Molecules: The Associated Perturbed Anisotropic Chain Theory, *AIChE J.* **32**, 1716-1725.
- Jin, G. X., Tang, S. and Sengers, J. V. (1993). Global Thermodynamic Behavior of Fluid Mixtures in the Critical Region, *Phys. Rev. E* **47**, 388-402.
- Kihara, T. (1963). Convex Molecules in Gaseous and Crystalline States, *Adv. Chem. Phys.*, **V**, 147-188.
- Kiselev, S. B. (1997). Prediction of the Thermodynamic Properties and the Phase Behavior of Binary Mixtures in the Extended Critical Region, *Fluid Phase Equilib.*, **128**, 1-28.
- Kiselev, S. B. (1998). Cubic Crossover Equation of State, *Fluid Phase Equilib.*, **147**, 7-23.
- Kiselev S. B., Ely, J. F., Adidharma, H. and Radosz, M. (2001). A Crossover Equation of State for Associating Fluids, *Fluid Phase Equilib.*, **183**, 53-64.
- Kim, C. H., Vimalchand, P., Donohue, M. D. and Sandler, S. I. (1986). Local Composition Model for Chainlike Molecules: A New Simplified Version of the Perturbed Hard Chain Theory, *AIChE J.*, **32**, 1726-1733.



- Knudsen, K., Stenby, E. H. and Fredenslund, A. (1996). A Comprehensive Comparison of Mixing Rules for Calculation of Phase Equilibria in Complex Systems, *Fluid Phase Equilib.*, **82**, 361-368.
- Kolafa, J. and Nezbeda, I. (1994), Lennard-Jones Fluid: An Accurate Analytic and Theoretically-Based Equation of State, *Fluid Phase Equilib.*, **100**, 1-34.
- Landau, L. D. and Lifshitz, E. M. (1980). Statistical Physics, 3<sup>rd</sup> Ed., Pergamon, New York.
- Mainwaring, D. E., Sadus, R. J. and Young, C. L. (1988a). Deiters's Equation of State and Critical Phenomena, *Chem. Eng. Sci.*, **43**, 459-466.
- Mainwaring, D. E., Sadus, R. J. and Young, C. L. (1988b). Prediction of Binary and Ternary Critical Properties Using Deiters' Equation, Hard Sphere and Hard Convex Body Equations of State, *Fluid Phase Equilib.*, **42**, 85-103.
- Malijevsky, A. and Veverka, J. (1999). New Equations of State for Pure and Binary Hard-Sphere Fluids, *Phys. Chem. Chem. Phys.*, **1**, 4267-4270.
- Mansoori, G. A., Carnahan, N. F., Starling, K. E. and Leland, T. W. Jr. (1971). Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres, *J. Chem. Phys.*, **54**, 1523-1525.
- Martin, J. J. (1979). Cubic Equations of State-Which?, *Ind. Eng. Chem. Fundam*, **18**, 81-97.
- Mather, A. E., Sadus, R. J., and Franck, E. U. (1993). Phase Equilibria in the Water + Krypton and Water + Neon Systems to 250 MPa and 700K, *J. Chem. Thermodyn.*, **25**, 771-779.
- Michelsen, M. L. and Heidemann, R. A. (1996). Some Properties of Equation of State Mixing Rules Derived from Excess Gibbs Energy Expressions, *Ind. Eng. Chem. Res.*, **35**, 278-287.

- Mollerup, J. (1986). A Note on the Derivation of Mixing Rules from Excess Gibbs Energy Models, *Fluid Phase Equilib.*, **25**, 323-327.
- Mulero, A., Galan, C. and Cuadros, F. (2001). Equations of State for Hard Spheres. A review of Accuracy and Applications, *Phys. Chem. Chem. Phys.*, **3**, 4991-4999.
- Nicoll, J. F. and Bhattachafjee, J. K. (1981). Crossover Functions by Renormalization-Group Matching:  $O(\epsilon^2)$  Results, *Phys. Rev. B*, **23**, 389-401.
- Nicoll, J. F. and Albright, P. C. (1986). Background Fluctuations and Wegner Corrections, *Phys. Rev. B*, **34**, 1991-1996.
- Orbey, N. and Sandler S. I. (1994). Vapour-Liquid Equilibrium of Polymer Solutions Using a Cubic Equation of State, *AIChE J.*, **40**, 1203-1209.
- Orbey, N. and Sandler S. I. (1995). Reformulation of Wong-Sandler Mixing Rule for Cubic Equations of State, *AIChE J.*, **41**, 683-690.
- Orbey, N. and Sandler S. I. (1996). Analysis of Excess Free Energy Based Equations of State Models, *AIChE J.*, **42**, 2327-2334.
- Palenchar, R. M., Erickson, D. D. and Leland, T. W. (1986). Prediction of Binary Critical Loci by Cubic Equations of State, *ACS Symp. Ser.*, **300**, 132-155.
- Patashinskii, A. Z. and Pokrovskii, V. L. (1979). Fluctuation Theory of Phase Transitions, Pergamon, New York.
- Patel, N. C. and Teja, A. S. (1982). A New Cubic Equation of State for Fluids and Fluid Mixtures, *Chem. Eng. Sci.*, **37**, 463-473.
- Peng, D. -Y. and Robinson, D. B. (1976). A New Two-Constant Equation of State, *Ind. Eng. Chem. Fundam.*, **15**, 59-64.

- Peng, D. -Y. and Robinson, D. B. (1977). A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State, *AIChE J.*, **23**, 137-144.
- Polishuk I., Wisniak J. and Segura H., (1999). Prediction of the Critical Locus in Binary Mixtures Using Equation of State. I. Cubic Equation of State, Classical Mixing Rules, Mixtures of Methane-Alkanes, *Fluid Phase Equilib.*, **164**, 13-47.
- Prigogine, I. (1957). *The Molecular Theory of Solutions*, North-Holland, Amsterdam.
- Povodyrev, A. A., Jin, G. X., Kiselev, S. B. and Sengers, J. V. (1996). Crossover Equation of State for the Thermodynamic Properties of Mixtures of Methane and Ethane in the Critical Region, *Int. J. Thermophysics.*, **17**, 909-944.
- Redlich, O. and Kwong, J. N. S. (1949). On the Thermodynamics of Solutions: V. An Equation of State: Fugacities of Gaseous Solutions, *Chem. Rev.*, **44**, 233-244.
- Reiss, N. R. , Frisch, H. L. and Lebowitz, J. L. L. (1959). Statistical Mechanics of Rigid Spheres, *J. Chem. Phys.*, **31**, 369-380.
- Rudolph, E. S. J., Langeveld, J. H., de Loos, Th. W. and de Swaan Arons, J. (2000). Phase Behaviour of Water Plus Nonionic Surfactant Systems: Experiments and Modeling Applying the Peng-Robinson Equation of State with the Wong-Sandler Mixing Rules and the UNIQUAC gE-Model, *Fluid Phase Equilib.*, **173**, 81-96.
- Sadus, R. J. and Young, C. L. (1985a). Phase Behaviour of Carbon Dioxide and Hydrocarbon Mixtures, *Aust. J. Chem.*, **38**, 1739-1743.
- Sadus, R. J. and Young, C. L. (1985b). Phase Behaviour of Binary n-Alkanenitrile and n-Alkanes and Nitromethane and Alkane Mixtures, *Fluid Phase Equilib.*, **22**, 225-229.

- Sadus, R. J., Young, C. L. and Svejda, P. (1988). Application of Hard Convex Body and Hard Sphere Equation of State to the Critical Properties of Binary Mixtures, *Fluid Phase Equilib.*, **39**, 89-99.
- Sadus, R. J. (1989). Attractive Forces in Binary Mixtures: a Priori Prediction of the Gas-Liquid Critical Properties of Binary Mixtures, *J. Phys. Chem.*, **93**, 3787-3790.
- Sadus, R. J. (1992a). High Pressure Phase Behaviour of Multicomponent Fluid Mixtures, Elsevier, Amsterdam.
- Sadus, R. J. (1992b). Novel Critical Transitions in Ternary Fluids Mixtures, *J. Phys. Chem.*, **96**, 5197-5202.
- Sadus, R. J. (1993). Influence of Combining Rules and Molecular Shape on the High Pressure Phase Equilibria of Binary Fluid Mixtures, *J. Phys. Chem.*, **97**, 1985-1992.
- Sadus, R. J. (1994) Calculating Critical Transitions of Fluid Mixtures: Theory Vs. Experiment, *AIChE J.*, **40**, 1376-1403.
- Sadus R. J. (1995). Equations of State for Hard-Sphere Chains, *J. Phys. Chem.*, **99**, 12363-12366.
- Sadus R. J. (1996). A Simplified Thermodynamic Perturbation Theory-Dimer Equation of State for Mixtures of Hard-Sphere Chains, *Macromol.*, **29**, 7212-7216.
- Sadus, R. J. (1999a). Simple Equation of State for Hard-Sphere Chains, *AIChE J.*, **45**, 2454-2457.
- Sadus, R. J. (1999b). An Equation of State for Hard Convex Body Chains, *Mol. Phys.*, **73**, 1279-1284.
- Saghafi, A. and Moshfeghian, M. (2000). Evaluation of Vapor-Liquid Equilibrium of Ethane Binary Systems Using UNIQUAC-Based Mixing Rules and its Extension to Multicomponent System, *Fluid Phase Equilib.*, **169**, 31-47.

- Sandler, S. I. (1994). Models for Thermodynamic and Phase Equilibria Calculations, Marcel Dekker, New York.
- Sandler, S. I. (1999). Chemical and Engineering Thermodynamics, 3<sup>d</sup> Ed., John Wiley & Sons, New York.
- Scott, R. L. (1956). Corresponding State Treatment of Nonelectrolyte Solutions, *J. Chem. Phys.*, **25**, 193.
- Scott, R. L., (1971). Eyring, H., Henderson, D. and Jost, W. (Eds.), In Physical Chemistry, An Advanced Treatise, Vol. 8A: Liquid State, Academic Press, New York.
- Scott, R. L. (1972). The Thermodynamics of Critical Phenomena in Fluid Mixtures, *Ber. Bunsenges, Phys. Chem.*, **76**, 296-308.
- Semmens, J., Waterson, S. D. and Young, C. L. (1980). Upper Critical Solution Temperatures of Perfluoro-n-Hexane + Alkane, Sulfur Hexafluoride + Siloxane and Perfluoropropane + Siloxane Mixtures, *Aust. J. Chem.*, **33**, 1987-1992.
- Sengers, J. V., Kayser, R. F., Peters, C. J. and White Jr, H. J. (Eds.) (2000). Equations of State for Fluids and Fluid Mixtures, Elsevier, Amsterdam.
- Shah, V. M., Bienkowski, P. R. and Cochran, H. D. (1994). Generalized Quartic Equation of State for Pure Nonpolar Fluids, *AIChE J.*, **40**, 152-159.
- Smith, V. S. (1995). Solid-Fluid Equilibria in Natural Gas Systems, Ph.D. Thesis, Georgia Institute of Technology.
- Soave, G. (1972). Equilibrium Constants From a Modified Redlich-Kwong Equation of State, *Chem. Eng. Sci.*, **27**, 1197-1203.
- Song, Y., Lambert, S. M. and Prausnitz, J. M. (1994). Liquid-Liquid Phase Diagrams for Binary Polymer Solutions from a Perturbed Hard-Sphere-Chain Equation of State, *Chem. Eng. Sci.*, **49**, 2765-2775.

- Spear, R. R., Robinson, Jr. R. L. and Chao, K. C. (1969). Critical States of Mixtures and Equations of State, *Ind. Eng. Chem. Fundam.*, **8**, 2-8.
- Stryjek, R. and Vera, J. H. (1986). PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures, *Can. J. Chem. Eng.*, **64**, 323-340.
- Svejda, P. and Kohler, F. (1983). A Generalized van der Waals Equation of State: I. Treatment of Molecular Shape in Terms of the Boublik Nezbeda Equation, *Ber. Bunsenges. Phys. Chem.*, **87**, 672-680.
- Thiele, E. (1963). Equation of State for Hard Spheres, *J. Chem. Phys.*, **39**, 474-479.
- Toczylkin, L. S. and Young, C. L. (1977). Comparison of the Values of Interaction Parameter from Upper Critical Solution Temperatures of Acetone + Alkanes with Values Obtained from Gas-Liquid Critical Temperatures, *Aust. J. Chem.*, **30**, 767-770.
- Toczylkin, L. S. and Young, C. L. (1980a). Gas-liquid Critical Temperatures of Mixtures Containing Electron Donors. Part 1. Ether Mixtures, *J. Chem. Thermodyn.*, **12**, 355-364.
- Toczylkin, L. S. and Young, C. L. (1980b). Gas-Liquid Critical Temperatures of Mixtures Containing Electron Donors. Part 2. Amine Mixtures, *J. Chem. Thermodyn.*, **12**, 365-370.
- Toczylkin, L. S. and Young, C. L. (1980c). Upper Critical Solution Temperatures of Hydrocarbon + Fluorocarbon Mixtures: Mixtures with Specific Interactions, *J. Chem. Thermodyn.*, **33**, 465-469.
- Trebble, M. A. and Bishnoi, P. R. (1987). Development of a New Four-Parameter Cubic Equation of State, *Fluid Phase Equilib.*, **35**, 1-21.
- Twu, C. H., Coon, J. E. and Bluck, D. (1998). A Zero-Pressure Cubic Equation of State Mixing Rule for Predicting High Pressure Phase Equilibria Using Infinite Dilution Activity Coefficients at Low Temperature, *Fluid Phase Equilib.*, **150-151**, 181-189.

- Van Konynenburg, P. H. and Scott, R. L. (1980). Critical Lines and Phase Equilibria in Binary van der Waals Mixtures, *Philos. Trans. Roy. Soc. London A*, **298**, 495-540.
- Van Pelt, A., Peters, C. J. and de Swaan Arons, J. (1992). Application of the Simplified Perturbed-Hard-Chain Theory for Pure Components Near the Critical Point, *Fluid Phase Equilib.*, **74**, 67-83.
- Vimalchand, P. and Donohue, M. D. (1985). Thermodynamics of Quadrupolar Molecules: The Perturbed-Anisotropic-Chain Theory, *Ind. Eng. Chem. Fundam.*, **24**, 246-257.
- Vimalchand, P. and Donohue, M. D. (1989). Comparison of Equations of State for Chain Molecules, *J. Phys. Chem.*, **93**, 4355-4360.
- Voros, N. G. and Tassios, D. P. (1993). Vapour-Liquid Equilibria in Nonpolar/Weakly Polar Systems with Different Types of Mixing Rules, *Fluid Phase Equilib.*, **91**, 1-29.
- Wang, J. L., Wu, G. W. and Sadus, R. J. (2000). Closed-Loop Liquid-Liquid Equilibria and the Global Phase Behaviour of Binary Mixtures Involving Hard-Sphere + van der Waals Interactions, *Mol. Phys.*, **98**, 715-723.
- Wang, W., Qu, Y., Twu, C. H. and Coon, J. E. (1996). Comprehensive Comparison and Evaluation of the Mixing Rules of WS, MHV2, and Twu et al., *Fluid Phase Equilib.*, **116**, 488-494.
- Waterson, S. D. and Young, C. L. (1978). Gas-Liquid Critical Temperatures of Mixtures Containing an Organo-Silicon Compound, *Aust. J. Chem.*, **31**, 957-962.
- Wei, Y. S. and Sadus, R. J. (2000). Equations of State for the Calculation of Fluid-Phase Equilibria, *AIChE J.*, **46**, 169-195.
- Wertheim, M. S. (1987). Thermodynamic Perturbation Theory of Polymerization, *J. Chem. Phys.*, **87**, 7323-7331.

- Wong, D. S. H., Orbey, H. and Sandler, S. I. (1992). Equation of State Mixing Rule for Nonideal Mixtures Using Available Activity Coefficient Model Parameters and that Allows Extrapolation over Large Ranges of Temperature and Pressure, *Ind. Eng. Chem. Res.*, **31**, 2033-2039.
- Wong, D. S. H. and Sandler, S. I. (1992). A Theoretically Correct Mixing Rule for Cubic Equations of State, *AIChE J.*, **38**, 671-680.
- Wyczalkowska, A. K., Anisimov, M. A. and Sengers, J. V. (1999). Global Crossover Equation of State of a van der Waals Fluid, *Fluid Phase Equilib.*, **160**, 523-535.
- Wyczalkowska, A. K., Abdulkadirova, K. S., Anisimov, M. A. and Sengers, J. V. (2000). Thermodynamic Properties of H<sub>2</sub>O and D<sub>2</sub>O in the Critical Region, *J. Chem. Phys.* **113**, 4985-5002.
- Yelash, L. V. and Kraska, T. (1998). Closed-Loops of Liquid-Liquid Immiscibility in Binary Mixtures of Equal Sized Molecules Predicted with a Simple Theoretical Equation of State, *Ber. Bunsenges, Phys. Chem.*, **102**, 213-223.
- Zhao, J. and Olesik, S. V. (1999). Phase Diagram Studies of Methanol-CHF<sub>3</sub> and Methanol-H<sub>2</sub>O-CHF<sub>3</sub> Mixtures, *Fluid Phase Equilib.*, **154**, 261-284.
- Zheng, D. Q. , Ma, W. D., Wei, R. and Gao, T. M. (1999). Solubility Study of Methane, Carbon Dioxide and Nitrogen in Ethylene Glycol at Elevated Temperatures and Pressures, *Fluid Phase Equilib.*, **155**, 277-286.



