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Equations of State for the Calculation of Fluid-Phase Equilibria

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Progress in developing equations of state for the calculation of fluid-phase equilibria is reviewed. There are many alternative equations of state capable of calculating the phase equilibria of a diverse range of fluids. A wide range of equations of state from cubic equations for simple molecules to theoretically-based equations for molecular chains is considered. An overview is also given of work on mixing rules that are used to apply equations of state to mixtures. Historically, the development of equations of state has been largely empirical. However, equations of state are being formulated increasingly with the benefit of greater theoretical insights. It is now quite common to use molecular simulation data to test the theoretical basis of equations of state. Many of these theoretically-based equations are capable of providing reliable calculations, particularly for large molecules.

Introduction

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). Subsequently, equations of state have developed rapidly for the calculation of phase equilibria in nonpolar and polar mixtures. There are many advantages in using equations of state for phase equilibria calculations. Equations of state can be used typically over wide ranges of temperature and pressure, and they can be applied to mixtures of diverse components, ranging from the light gases to heavy liquids. They can be used to calculate vapor-liquid, liquid-liquid, and supercritical fluid-phase equilibria without any conceptual difficulties. The calculation of phase equilibria has been discussed extensively elsewhere (Sadus, 1992a, 1994; Sandler, 1994; Dohrn, 1994; Raal and Mühlbauer, 1998) and earlier reviews of various aspects of equations of state are also available (Martin, 1979; Gubbins, 1983; Tsonopoulos and Heidman, 1985; Han et al., 1988; Anderko, 1990; Sandler, 1994; Economou and Donohue, 1996).

The van der Waals equation of state was the first equation to predict vapor-liquid coexistence. Later, the Redlich-Kwong equation of state (Redlich and Kwong, 1949) improved the accuracy of the van der Waals equation by introducing temperature-dependence for the attractive term. Soave (1972) and Peng and Robinson (1976) proposed additional modifications to more accurately predict the vapor pressure, liquid density, and equilibria ratios. Carnahan and Starling (1969), Guggenheim (1965), and Boublik (1981) modified the repulsive term of the van der Waals equation of state to obtain accurate expressions for hard body repulsion. Other workers (Chen and Kreglewski, 1977; Christoforakos and Franck, 1986; Heilig and Franck, 1989) modified both the attractive and repulsive terms of the van der Waals equation of state.

In addition to modeling small molecules, considerable emphasis has been placed recently on modeling chain-like molecules. Based on the theories of Prigogine (1957) and Flory (1965), other workers (Beret and Prausnitz, 1975; Donohue and Prausnitz, 1978) developed a perturbed hard-chain theory (PHCT) equation of state for chain molecules.

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To overcome the mathematical complexity of the PHCT equation of state, Kim et al. (1986) developed a simplified version (SPHCT) by replacing the complex attractive part of a 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). Ikonomou and Donohue (1986) extended PACT to obtain an equation of state which takes into account the existence of hydrogen bonding, namely, the associated perturbed anisotropic chain theory (APACT) equation of state.

Advances in statistical mechanics and an increase of computer power have allowed the development of equations of state based on molecular principles that are accurate for real fluids and mixtures. Using Wertheim's theory (Wertheim, 1984a,b), 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 (Banaszak et al., 1994; Kraska and Gubbins, 1996a,b) and VR-SAFT (Gil-Villegas et al., 1997) have been developed. A common feature of many newly developed equations of state is the increasing use of insights gained from molecular simulation (Sadus, 1999a) to improve the accuracy of the underlying model.

Our aim is to present a wide-ranging overview of recent progress in the development of equations of state encompassing both simple empirical models and theoretically-based equations. Many useful equations of state can be constructed by combining different models of repulsive and attractive intermolecular interactions. The theoretical backbone of the contribution from intermolecular repulsion is the concept of hard-sphere repulsion, whereas attractive interactions are modeled commonly using empirical or semi-empirical approach. Polymers and large chain-like molecules can be treated successfully by using a hard-sphere chain model and this aspect is discussed. Equations of state for associating molecules are examined in detail and comparisons between different equations of state are considered. Commonly, equations of state are developed initially for pure substances. Mixing rules are required to extend equations of state to mixtures, and this topic is also addressed.

Equations of State for Simple Molecules

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

$$Z = \frac{V}{V-b} - \frac{a}{RTV} \tag{1}$$

where Z is the compressibility factor ($Z = pV/RT$), T is temperature, V is volume, p is the pressure, and R is the molar universal gas constant. The parameter a is a measure of the attractive forces between the molecules, and the parameter b is the covolume occupied by the molecules (if the molecules are represented by hard-spheres of diameter σ, then $b = 2\pi N\sigma^3/3$). The a and b parameters 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 vapor 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 factor predicted by Eq. 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. Many of these equations can be categorized in terms of modifications to the basic van der Waals model.

Table 1. Modifications to the Attractive Term of van der Waals Equation

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

Modification of the attractive term

Many modifications of the attractive term have been proposed. Some of these are summarized in Table 1.

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

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

where A_0, B_0, C_0, a, b, c, α, γ 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 the reduction of plentiful, accurate pressure-volume-temperature (PVT) and vapor-liquid-equilibrium (VLE) data. Secondly, the large number of adjustable parameters makes it difficult to extend to mixtures. Thirdly, its analytical complexity results in a relatively long computing time. Today, because of advances in computing capabilities, the latter disadvantage has lost much of its significance but the other disadvantages remain.

Perhaps, the most important model for the modification of the van der Waals equation of state is the Redlich-Kwong equation (Redlich and Kwong, 1949). It retains the original van der Waals hard-sphere term with the addition of a temperature-dependent attractive term

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

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

$$\left. \begin{aligned} a &= 0.4278 R^2 T_c^{2.5}/p_c \\ b &= 0.0867 RT_c/p_c \end{aligned} \right\} \quad (4)$$

Carnahan and Starling (1972) used the Redlich-Kwong equation of state to calculate 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. Joffe and Zudkevitch (1966) showed that a substantial improvement in the representation of fugacity of gas mixtures could be obtained by treating interaction parameters as empirical parameters. Calculations of the critical properties of binary mixtures indicated that, for most binary mixtures, the accuracy of the predicted critical properties could be improved substantially by adjusting the value of the interaction parameter in the mixing rule for the a term. Spear et al. (1969) also demonstrated that the Redlich-Kwong equation of state could be used to calculate the vapor-liquid critical properties of binary mixtures. Chueh and Prausnitz (1967a,b) showed that the Redlich-Kwong equation can be adapted to predict both vapor 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 vapor-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 $a/T^{1.5}$ with a more general temperature-dependent term $a(T)$, that is

$$Z = \frac{V}{V - b} - \frac{a(T)}{RT(V + b)} \quad (5)$$

where

$$\left. \begin{aligned} a(T) &= 0.4274 \left(\frac{R^2 T^{c2}}{p^c} \right) \left\{ 1 + m \left[1 - \left(\frac{T}{T^c} \right)^{0.5} \right] \right\}^2 \\ m &= 0.480 + 1.57\omega - 0.176\omega^2 \\ b &= 0.08664 \frac{RT^c}{p^c} \end{aligned} \right\} \quad (6)$$

and ω is the acentric factor. To test the accuracy of Soave-Redlich-Kwong (SRK) equation, the vapor 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 behavior of mixtures in the critical region. Elliott and Daubert (1985) reported accurate correlations of vapor-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 vapor-liquid equilibrium of symmetric mixtures and methane-containing mixtures.

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

$$\left. \begin{aligned} a(T) &= 0.45724 \left(\frac{R^2 T^{c2}}{p^c} \right) \left\{ 1 + k \left[1 - \left(\frac{T}{T^c} \right)^{0.5} \right] \right\}^2 \\ k &= 0.37464 + 1.5422\,\omega - 0.26922\,\omega^2 \\ b &= 0.07780 \frac{RT^c}{p^c} \end{aligned} \right\} \quad (7)$$

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

$$Z = \frac{V}{V-b} - \frac{a(T)V}{RT\left[V(V+b)+b(V-b)\right]} \tag{8}$$

The Peng-Robinson (PR) equation of state slightly improves the prediction of liquid volumes and predicts a critical compressibility factor of $Z_c = 0.307$. Peng and Robinson (1976) gave examples of the use of their equation for predicting the vapor pressure and volumetric behavior of single-component systems, and the phase behavior and volumetric behavior of the binary, ternary, and multicomponent system and concluded that Eq. 8 can be used to accurately predict the vapor 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 vapor-liquid equilibrium in hydrogen and nitrogen containing mixtures.

The Peng-Robinson and Soave-Redlich-Kwong equations are used widely 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 generalized parameters. Little computer time is required and good phase equilibrium correlations can be obtained. However, the success of these modifications is restricted to the estimation of vapor pressure. The calculated saturated liquid volumes are not improved and are invariably higher than experimental measurements.

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

$$Z = \frac{V}{V-b} - \frac{a(T)}{RT(V+cb)} \tag{9}$$

The c parameter in Eq. 9 is defined in terms of the ratio of the covolume to the volume ($\beta = b/V$)

$$c(\beta) = \frac{1}{\beta}\left(\sqrt{\frac{1}{\beta} - \frac{3}{4}} - \frac{3}{2}\right) \tag{10}$$

The other equation of state parameters are calculated from

$$\left.\begin{aligned}
&b = \Omega_b(\beta)\frac{RT_c}{p_c}\\
&\Omega_b(\beta) = \beta\frac{(1-\beta)(2+c\beta)-(1+c\beta)}{(2+c\beta)(1-\beta)^2}\\
&a(T) = \frac{\Omega_a(\beta)R^2T_c\alpha(T)}{p_c}\\
&\Omega_a(\beta) = \frac{(1+c\beta)^2\Omega_b(\beta)}{\beta(1-\beta)^2(2+c\beta)}\\
&\alpha^{1/2}(T) = 1 + q(\beta)\left(1-T_r^{1/2}\right)\\
&q(\beta) = (\beta/0.26)^{1/4}m\\
&m = 0.480 + 1.5740\omega - 0.176\omega^2
\end{aligned}\right\} \tag{11}$$

The compressibility factor at the critical point is

$$Z_c(\beta) = \frac{(1-\beta c)(2+c_c\beta_c)-(1+c_c\beta_c)}{(2+c_c\beta_c)(1-\beta_c)^2} \tag{12}$$

Fuller's modification contains two useful features. First, the equation of state leads to a variable critical compressibility factor, and secondly, 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 $\beta_c = 0.259921$, 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 β_c has a value of 1/3, then $c = 0$, $\Omega_a = 0.421875$, $\Omega_b = 0.125$, $Z_c = 0.375$, and the van der Waals equation is obtained.

Fuller (1976) reported that Eq. 9 could be used to correlate saturated liquid volumes to a root-mean-square deviation of less than 5%. In the majority of cases it also improved the vapor-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.

In common with Fuller's equation, Table 1 shows that a feature of many of the empirical improvements is the addition of adjustable parameters. A disadvantage of three or more parameter equations 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 fulfill the requirements of both simplicity and accuracy since they require little input information, except for the critical properties and acentric factor for the generalized 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. The application of cubic equations of state to the calculation of vapor-liquid equilibria has been discussed recently by Orbey and Sandler (1998).

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 an equation of state. Some alternative hard-sphere terms are summarized in Table 2. Perhaps the most widely used alternative to the van der Waals hard-sphere term is the equation proposed by Carnahan and Starling (1969) who obtained an expression for the compressibility factor of hard-sphere fluids that compares very well (Figure 1) with molecular-dynamics data (Alder and Wainwright, 1960). The form of the Carnahan-Starling equation is

$$Z^{hs} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{13}$$

Table 2. Modifications to the Repulsive Term of the van der Waals Equation

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

where $\eta = b/4V$ is the packing fraction defined in terms of the molecular covolume (b).

To improve the accuracy of the van der Waals equation, Carnahan and Starling (1972) substituted Eq. 13 for the traditional term $V/(V-b)$ in Eq. 1, resulting in the following equation of state (CSvdW)

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{a}{RTV} \tag{14}$$

Both a and b can be obtained by using critical properties ($a = 0.4963 R^2 T^{c2}/p^c$, $b = 0.18727 RT^c/p^c$). Sadus (1993) has demonstrated that Eq. 14 can be used to predict the Type III equilibria of nonpolar mixtures with considerable accuracy.

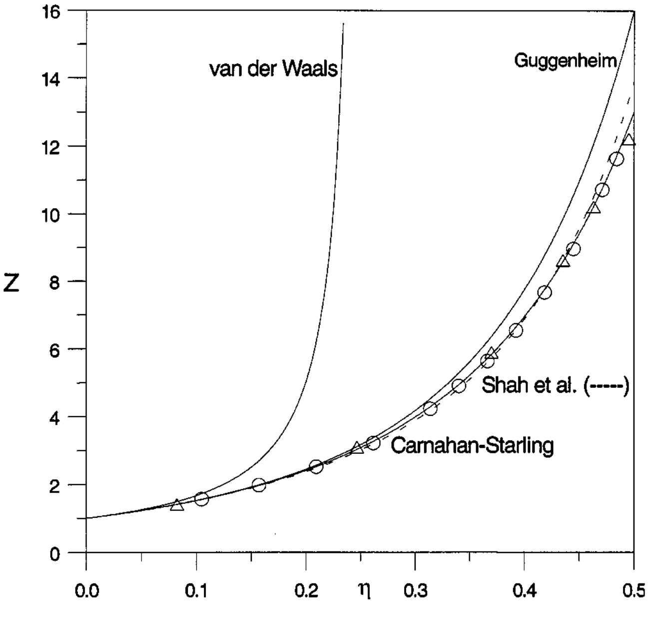

Figure 1. Hard-sphere compressibility factors from different equations of state with molecular simulation data.

△, Alder and Wainwright (1960); ○, Barker and Henderson (1971) for hard spheres.

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

$$Z = \frac{1}{(1-\eta)^4} - \frac{a}{RTV} \tag{15}$$

The covolume ($b = 0.18284 RT^c/p^c$) and attractive ($a = 0.49002 R^2 T^{c2}/p^c$) equation of state parameters are related to the critical properties.

The Guggenheim equation of state 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; Semmens et al., 1980; Sadus and Young, 1985a,b; Waterson and Young, 1978; Toczylkin and Young, 1977, 1980a,b,c; Sadus, 1992a, 1994; Wei and Sadus, 1994a, 1999). Despite the diversity of the systems studied, good results were reported consistently for the vapor-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 semiquantitative (Christou et al., 1986) because of the added difficulty of predicting the transition between vapor-liquid and liquid-liquid behavior. The Guggenheim equation has also proved valuable in calculating both the vapor-liquid critical properties (Sadus and Young, 1988) and general critical transitions of ternary mixtures (Sadus, 1992a; Wei and Sadus, 1994b). Good results have also been reported for the vapor-liquid and liquid-liquid equilibria of binary mixtures containing either helium (Wei and Sadus, 1996) or water (Wei et al., 1996) as one component.

Boublik (1981) generalized the Carnahan-Starling hard-sphere term 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 generalized van der Waals equation of state (HCBvdW)

$$Z = \frac{1+(3\alpha-2)\eta+(3\alpha^2-3\alpha+1)\eta^2-\alpha^2\eta^3}{(1-\eta)^3} - \frac{a}{RTV} \tag{16}$$

Sadus et al. (1988) and Christou et al. (1991) have used Eq. 16 for the calculation of the vapor-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. Equation 16 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 a one-component hard-sphere fluid (Figure 1). The comparison demonstrates that the Guggenheim and Carnahan-Starling hard-sphere terms are of similar accuracy at low to moderately high densities. It is at these densities that most fluid-fluid transitions occur.

The failure of the van der Waals hard-sphere term at moderate to high densities has important consequences for the prediction of phase equilibria at high pressure. For example, it has been demonstrated (Sadus, 1992a) that equations of state such as the Redlich-Kwong and Peng-Robinson equations do not describe correctly the liquid-liquid critical behavior of mixtures that can be classified as exhibiting Type III behavior in the classification scheme of van Konynenburg and Scott (1980). In contrast, equations of state with more accurate hard-sphere terms, such as the Carnahan-Starling or Guggenheim terms, can be often used to reproduce quantitatively the features of Type III behavior (Sadus, 1992a, 1993; Wei et al., 1996).

Combining 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 (CSRK)

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \frac{a}{RT^{1.5}(V+b)} \tag{17}$$

Their results demonstrated that this combination improved the prediction of hydrocarbon densities and supercritical phase equilibria. De Santis et al. (1976) also tested Eq. 17 and concluded that it yielded good results for the case of pure components spanning ideal gases to saturated liquids. When applied to mixtures for predicting vapor-liquid equilibria, good accuracy in wide ranges of temperature and pressure can be obtained.

Chen and Kreglewski (1977) demonstrated that a good representation of the phase behavior of simple fluids could be obtained using an equation of state formed by substituting the a term in Eq. 17 with the power series fit of simulation data reported by Alder et al. (1972) for square-well fluids. The functional form of this equation dubbed 'BACK' is

$$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} - \sum_i \sum_j jD_{ij}\left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j \tag{18}$$

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 molecules and $\tau = 0.7405$. Historically, the complicated nature of the attractive term has precluded it from routine phase equilibria calculations. However, as discussed below, the BACK equation has been the inspiration for further development.

Christoforakos and Franck (1986) proposed an equation (CF) of state which used the Carnahan-Starling (1969) expression for the repulsive term and a square-well intermolecular potential for attractive intermolecular interactions.

$$Z = \frac{V^3+V^2\beta+V\beta^2-\beta^3}{(V-\beta)^3} - \frac{4\beta}{V}(\lambda^3-1)\left[\exp\left(\frac{\epsilon}{RT}\right)-1\right] \tag{19}$$

where $\beta = b(T^c/T)^{3/m}$, 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

$$\left.\begin{aligned} b &= 0.04682\,RT^c/p^c \\ \frac{\epsilon}{R} &= T^c \ln\left[1+2.65025/(\lambda^3-1)\right] \end{aligned}\right\} \tag{20}$$

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

Heilig and Franck (1989, 1990) modified the Christoforakos-Franck equation of state. They used a temperature-dependent Carnahan-Starling (1969) representation of repulsive forces between hard spheres and an alternative square-well representation for attractive forces. The functional form of the Heilig-Franck (HF) equation of state is

$$Z = \frac{V^3+\beta V^2+\beta^2 V-\beta^3}{(V-\beta)^3} + \frac{B}{V+(C/B)} \tag{21}$$

The B and C terms in Eq. 21 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 characterized 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, $\lambda = 1.26684$, $N_A\sigma^3/V^c = 0.24912$ (where N_A denotes Avogadro's constant) and $\epsilon/RT^c = 1.51147$. 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. 21 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.

Deiters (1981) reported a further example of an equation of state, based on the Carnahan-Starling hard-sphere term plus an improved attractive term. A feature of Deiters' equation of state is that the Carnahan-Starling term is adjusted to more accurately reflect the repulsion of real fluids and the attractive term is obtained from an approximate formulation of square-well fluid interactions. The equation works well at low pressures, but the critical properties at high pressures are not predicted accurately (Mainwaring et al., 1988).

Shah et al. (1994) developed an equation of state by defining empirical relationships for the repulsive (Z^{hs}) and the attractive (Z^{att}) contribution to the compressibility factor

$$\left.\begin{aligned} Z^{hs} &= \frac{V}{(V-k_0\alpha)} + \frac{\alpha k_1 V}{(V-k_0\alpha)^2} \\ Z^{\text{att}} &= -\frac{aV^2 + k_0\alpha c V}{V(V+e)(V-k_0\alpha)RT} \\ \alpha &= 0.165V_c\left\{\exp\left[-0.03125\ln\left(\frac{T}{T_c}\right)\right.\right. \\ &\qquad\qquad \left.\left.-0.0054\left\{\ln\left(\frac{T}{T_c}\right)\right\}^2\right]\right\}^3 \end{aligned}\right\} \tag{22}$$

In Eq. 22, α 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, quartic equation of state equation is formed by combining the above relationships

$$Z = \frac{V}{(V-k_0\alpha)} + \frac{\alpha k_1 V}{(V-k_0\alpha)^2} - \frac{aV + k_0\alpha c}{RT(V+e)(V-k_0\alpha)} \tag{23}$$

Equation 23 only needs three properties of a fluid, namely, the critical temperature, the critical volume, and acentric factor 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; therefore, it behaves like a cubic 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 generalized quartic equation of state (Eq. 23) to polar fluids. When applied to polar fluids, the equation requires four characteristic properties of the pure component, namely: 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 generalized 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 generalized quartic equation of state improves the accuracy of calculations of enthalpy, second virial coefficients, and the pressure-volume-temperature properties.

In Figure 1, we compare the compressibility factor predicted by the Shah et al. (1994) hard-sphere term ($k_0 = 1.2864$, $k_1 = 2.8225$, and $y = \alpha/V$) with molecular simulation data (Alder and Wainwright, 1960; Barker and Henderson, 1971) for one-component hard-sphere fluid. Figure 1 shows that the accuracy of hard-sphere term of Shah et al. equation is close to the accuracy of the Carnahan-Starling hard-sphere term.

Equations of State for Chain Molecules

Perturbed hard chain theory

Prigogine (1957) introduced a theory to explain the properties of chain molecules which 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 behavior. Flory's work 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 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 the perturbed hard-chain theory (PHCT) equation of state for fluids containing very large molecules, as well as simple molecules. The PHCT equation of state is valid for 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 wider range of density and temperature, more accurate expressions in the PHCT equation are used for the repulsive and attractive partition functions. Secondly, the PHCT equation corrects the major deficiency in the theories of Prigogine and Flory by meeting the ideal gas limit at low densities.

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

$$Q = \frac{V^N}{N!\Lambda^{3N}}\left(\frac{V_f}{V}\right)^N\left[\exp\left(\frac{-\phi}{2kT}\right)\right]^N (q_{r,v})^N \tag{24}$$

where $q_{r,v}$ is the contribution of rotational and vibrational motion of a molecule, N is the number of molecules, Λ is the thermal de Broglie wavelength and ϕ is the mean potential. The V_f term is the free-volume, which is defined as the volume available to the center 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-spheres

$$V_f = V\exp\left[\frac{(\tau/\tilde{v})(3\tau/\tilde{v}-4)}{(1-\tau/\tilde{v})^2}\right] \tag{25}$$

where $\tilde{v}$ is a reduced volume defined as $\tilde{v} = V/nrv^0$ (where v^0 is the close-packed volume per mole and r is the number of segments per molecule).

In general, the PHCT equation can be written as

$$Z = Z(\text{hard chain}) - \frac{a}{RTV} \tag{26}$$

When Eq. 25 is used to determine the hard chain compressibility factor, and a is calculated from Alder's polynomial relationship (Alder et al., 1972) for square-well molecular dynamics data, the functional form of the PHCT equation of state is

$$Z = 1 + c\frac{4(\tau/\tilde{v}) - 2(\tau/\tilde{v})^2}{(1-\tau/\tilde{v})^3} + \left(\frac{\epsilon q}{kTV}\right)(rv^0)\sum_{n=1}^{4}\sum_{m=1}^{M}\left(\frac{mA_{nm}}{\tilde{v}^{m-1}}\right)\left(\frac{1}{\tilde{T}^{n-1}}\right) \tag{27}$$

where c is 1/3 the number of external degrees of freedom, ϵq is characteristic energy per molecule, and k is Boltzmann's constant. The A_{nm} terms 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 a reciprocal reduced volume. In effect, the PHCT equation of state extends the BACK equation of state (Eq. 18) for chain molecules.

The adjustable parameters $[rv^0, (\epsilon q/k)$ and $c]$ of the PHCT equation of state can be obtained from pressure-volume-temperature data for gases and liquids and from vapor-pressure data. Beret and Prausnitz (1975) gave values for these parameters for 22 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

$$Q = \frac{V^N}{N!\Lambda^{3N}}\left(\frac{V_v}{V}\exp\frac{-\phi}{2ckT}\right)^{N_c} \tag{28}$$

Equation 28 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. Donohue and Prausnitz (1978) reported that the PHCT equation of state 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.

Subsequently, many workers (Kaul et al., 1980; Liu and Prausnitz, 1979a,b, 1980; Ohzone 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 the 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. Ohzone 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). Chien et al. (1983) proposed a useful chain-of-rotators (COR) equation in the spirit of the BACK and PHCT equations.

The PHCT equation is successful in calculating the properties of fluids, but a practical limitation is its mathematical complexity, as a result of the use of the Carnahan-Starling free-volume term and the Alder power series. Consequently, calculations, especially for mixtures, are time consuming. Inspired by the proven ability of the PHCT equation in calculating the properties, modifications of the theory have been proposed with the aim of simplifying the equation of state.

Simplified perturbed hard chain theory

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)

$$Z = 1 + c\left(Z^{\text{rep}} - Z_m\frac{V^*Y}{V + V^*Y}\right) \tag{29}$$

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 $N_A(s\sigma^3/\sqrt{2})$, where N_A is Avogadro's number, s is the number of segments per molecule, and σ is the hard-core diameter of a segment. The remaining terms are calculated from

$$\left.\begin{aligned} Z^{\text{rep}} &= \frac{4\eta - 2\eta^2}{(1-\eta)^3} \\ Y &= \exp\left(\frac{T^*}{2T}\right) - 1 \\ \eta &= \tau V^*/V \\ T^* &= \epsilon q/ck \end{aligned}\right\} \tag{30}$$

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

$$Z = 1 + c\frac{4\eta - 2\eta^2}{(1-\eta)^3} - \frac{Z_m cV^*Y}{V + V^*Y} \tag{31}$$

The SPHCT equation of state has three parameters (c, T^*, and V^*) and these parameters can be evaluated by fitting simultaneously both vapor pressure and liquid density data. Kim et al. (1986) obtained these three parameters for several *n*-alkanes and multipolar fluids, and van Pelt et al. (1992) and Plackov et al. (1995) reported values for more than one hundred fluids.

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

$$\left.\begin{aligned}
\langle V^* \rangle &= \sum_i x_i V_i^* = \sum x_i \frac{s_i \sigma_{ii}^3}{\sqrt{2}} \\
\langle c \rangle &= \sum_i x_i c_i \\
\langle c v^* Y \rangle &= \sum_{ij} x_i x_j c_i v_{ij}^* \left(\exp \frac{\epsilon_{ij} q_i}{2 c_i kT} - 1 \right) \\
\sigma_{ij} &= \frac{\sigma_{ii} + \sigma_{jj}}{2} \\
\epsilon_{ij} &= \sqrt{\epsilon_{ii} \epsilon_{jj}}
\end{aligned}\right\} \qquad (32)$$

The terms in angular brackets ($\langle \cdots \rangle$) represent mixture properties. For mixtures, the SPHCT equation of state becomes

$$Z = 1 + \langle c \rangle \frac{4\eta - 2\eta^2}{(1-\eta)^3} - \frac{Z_m \langle c V^* Y \rangle}{V + \langle c V^* Y \rangle / \langle c \rangle} \qquad (33)$$

The SPHCT equation of state 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 predicts pure-component molar volumes and vapor 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. (1991, 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 vapor pressures of "chain-like" molecules over the entire range of vapor-liquid coexistence. Van Pelt et al. (1991) 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).

Hard-sphere chain equations of state

The concept of a "hard-sphere chain" is the backbone of many systematic attempts to improve equations of state for real fluids. Wertheim (1987) proposed a thermodynamic perturbation theory (TPT) which accommodates hard-chain molecules. As described below, TPT is the basis of many equations of state. The TPT concept has been extended to include dimer properties (Ghonasgi and Chapman, 1994) and application to star-like molecules (Phan et al., 1993) and hard disks (Zhou and Hall, 1995) have been reported. Work on TPT models continues to be an active research area (Stell et al., 1999a,b).

Chapman et al. (1988) generalized Wertheim's TPT model to obtain the following equation of state for the compressibility factor of a hard-chain of m segments

$$Z^{hc} = m Z^{hs} - (m-1) \left(1 + \eta \frac{\partial \ln g^{hs}(\sigma)}{\partial \eta} \right) \qquad (34)$$

where $g^{hs}(\sigma)$ is the hard-sphere site-site correlation function at contact, σ is the hard-sphere diameter, $\eta = \pi m \rho \sigma^3/6$ is the packing fraction, and ρ is the number density. The compressibility factor of hard sphere can be accurately determined from the Carnahan-Starling equation (Eq. 13). For the Carnahan-Starling equation, the site-site correlation function is

$$g^{hs}(\sigma) = \frac{2-\eta}{2(1-\eta)^3} \qquad (35)$$

Dimer properties have also been incorporated successfully into the generalized Flory-type (GF-D) equations of state (Honnell and Hall, 1989; Yethiraj and Hall, 1991; Gulati and Hall, 1998).

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})

$$Z = m Z^{hs} - \frac{m}{2} \left(1 + \eta \frac{\partial \ln g^{hs}(\sigma)}{\partial \eta} \right) - \left(\frac{m}{2} - 1 \right) \left(1 + \eta \frac{\partial \ln g^{hs}(\sigma)}{\partial \eta} \right) \qquad (36)$$

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

$$g^{hd}(\sigma) = \frac{1+2\eta}{2(1-\eta)^2} \qquad (37)$$

The addition of dimer properties into the hard-sphere chain equation of state is also a feature of the Generalized Flory-Dimer (GF-D) equation of state (Honnell and Hall, 1989).

Chang and Sandler (1994) proposed two variants of a thermodynamic perturbation-dimer (TPT-D) equation. The TPT-D1 equation can be expressed as

$$Z = m\left(\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right) - \frac{m}{2}\left(1+\frac{\eta(5-2\eta)}{(1-\eta)(2-\eta)}\right) - \left(\frac{m}{2}-1\right)\left(1+\frac{2\eta(2+\eta)}{(1-\eta)(1+2\eta)}\right) \quad (38)$$

whereas the TPT-D2 can be represented as

$$Z = m\left(\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right) - \frac{m}{2}\left(1+\frac{\eta(5-2\eta)}{(1-\eta)(2-\eta)}\right) - \left(\frac{m}{2}-1\right)\left(1+\frac{\eta(3.498-0.24\eta-0.414\eta^2)}{(1-\eta)(2-\eta)(0.534+0.414\eta)}\right) \quad (39)$$

Using the TPT-D approach (Eq. 36), Sadus (1995) proposed that, in general

$$g^{hd} = g^{hs}(\alpha\eta + c) \quad (40)$$

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}. Equation 40 can be used in conjunction with Eq. 36 to obtain 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

$$Z = 1 + m(Z^{hs}-1) + (1-m)\eta\frac{\partial \ln g^{hs}}{\partial \eta} + \frac{\alpha(2-m)\eta}{2(\alpha\eta+c)} \quad (41)$$

Sadus (1995) applied the STPT-D equation to the prediction of both the compressibility factor 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 factor 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 without requiring additional equation of state parameters. 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 favorably with the results obtained for other hard-sphere chain equations of state. Recently, a simplification of the STPT-D equation has been proposed (Sadus, 1999b). The word-sphere chain approach has also been extended (Sadus, 2000) to include HCB chains.

Perturbed anisotropic chain theory

By including the effects of anisotropic multipolar forces explicitly into the PHCT equation of state, Vimalchand et al. (Vimalchand and Donohue, 1985; 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 of state accounts for the effects of differences in molecular size, shape, and intermolecular forces including anisotropic dipolar and quadrupolar forces. In terms of the compressibility factor, the PACT equation of state can be represented as

$$Z = 1 + Z^{\text{rep}} + Z^{\text{iso}} + Z^{\text{ani}} \quad (42)$$

The $1+Z^{\text{rep}}$ term is evaluated in an identical way to the corresponding of the PHCT equation of state (see Eq. 27).

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

$$Z^{\text{iso}} = \left[Z_1^{LJ} + Z_2^{LJ} - 2Z_1^{LJ}\left(\frac{A_2^{LJ}}{A_1^{LJ}}\right)\right] \Bigg/ \left(1-\frac{A_2^{LJ}}{A_1^{LJ}}\right)^2 \quad (43)$$

where A is the Helmholtz function, *LJ* stands for Lennard-Jones, and *iso* denotes isotropic interactions. The contributions to Eq. 43 are evaluated from

$$\left.\begin{aligned}
\frac{A_1^{LJ}}{NkT} &= \frac{c}{\tilde{T}}\sum_m \frac{A_{1m}}{\tilde{v}^m} \\
\frac{A_2^{LJ}}{NkT} &= \frac{c}{\tilde{T}^2}\sum_m \frac{C_{1m}}{2\tilde{v}^m} + \frac{C_{2m}}{\tilde{v}^{m+1}} + \frac{C_{3m}}{2\tilde{v}^{m+2}} \\
Z_1^{LJ} &= \frac{c}{\tilde{T}}\sum_m \frac{mA_{1m}}{\tilde{v}^m} \\
Z_2^{LJ} &= \frac{c}{\tilde{T}^2}\sum_m \frac{mC_{1m}}{2\tilde{v}^m} + \frac{(m+1)C_{2m}}{\tilde{v}^{m+1}} + \frac{(m+2)C_{3m}}{2\tilde{v}^{m+2}} \\
\tilde{T} &= \frac{T}{T^*} = \frac{ckT}{\epsilon q} \\
\tilde{v} &= \frac{v}{v^*} = \frac{v\sqrt{2}}{N_A r\sigma^3}
\end{aligned}\right\} \quad (44)$$

with the constants $A_{11} = -8.538$, $A_{12} = -5.276$, $A_{13} = 3.73$, $A_{14} = -7.54$, $A_{15} = 23.307$, and $A_{16} = -11.2$, $C_{11} = -3.938$, $C_{12} = -3.193$, $C_{13} = -4.93$, $C_{14} = 10.03$, $C_{21} = 11.703$, $C_{22} = -3.092$, $C_{23} = 4.01$, $C_{24} = -20.025$, $C_{31} = -37.02$, $C_{32} = 26.93$ and $C_{33} = 26.673$.

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

$$Z^{\text{ani}} = \left(Z_2^{\text{ani}} + Z_3^{\text{ani}} - 2Z_2^{\text{ani}}\frac{A_3^{\text{ani}}}{A_2^{\text{ani}}}\right) \Bigg/ \left(1-\frac{A_3^{\text{ani}}}{A_2^{\text{ani}}}\right)^2 \quad (45)$$

where the superscript ani denotes the anisotropic interactions and

$$\left.\begin{aligned}
\frac{A_2^{\text{ani}}}{NkT} &= -12.44\frac{cJ^{(10)}}{\tilde{T}_Q^2\tilde{v}}\\
\frac{A_3^{\text{ani}}}{NkT} &= 2.611\frac{cJ^{(15)}}{\tilde{T}_Q^3\tilde{v}} + 77.716\frac{cK}{\tilde{T}_Q^3\tilde{v}^2}\\
Z_2^{\text{ani}} &= -12.44\frac{cJ^{(10)}}{\tilde{T}_Q^2\tilde{v}}\left[1+\tilde{\rho}\frac{\partial \ln J^{(10)}}{\partial\tilde{\rho}}\right]\\
Z_3^{\text{ani}} &= 2.611\frac{cJ^{(15)}}{\tilde{T}_Q^3\tilde{v}}\left[1+\tilde{\rho}\frac{\partial \ln J^{(15)}}{\partial\tilde{\rho}}\right]\\
&\qquad + 77.716\frac{cK}{\tilde{T}_Q^3\tilde{v}^2}\left[2+\tilde{\rho}\frac{\partial \ln K}{\partial\tilde{\rho}}\right]\\
\tilde{v} &= \frac{v}{v^*} = \frac{v\sqrt{2}}{N_A r\sigma^3}\\
\tilde{T}_Q &= \frac{T}{T_Q^*} = \frac{ckT}{\epsilon_Q q}\\
\epsilon_Q &= \left[\frac{N_A}{\sqrt{2}}\right]^{5/3}\frac{Q_s^2}{a_s}
\end{aligned}\right\}\qquad(46)$$

where a_s is the surface area of a segment, σ is the soft-core diameter of a segment and the quadrupole moment, Q is related to the quadrupolar interaction energy per segment, $Q_s^2 = Q^2/r(v^*)^{5/3}$. In Eq. 46, the J terms are the integrals given by Gubbins and Twu (1978).

The PACT equation is valid for large and small molecules, for nonpolar and polar molecules, and at all fluid densities. The calculations of Vimalchand et al. (1986) show that the explicit inclusion of multipolar forces allows the properties of highly nonideal mixtures to be predicted with reasonable accuracy without the use of a binary interaction parameter. However, for pure fluids, the predictive behavior of the PACT equation of state is similar to other comparable equations of state.

Equations of State for Associating Fluids

Associated perturbed anisotropic chain theory

Ikonomou and Donohue (1986) incorporated the infinite equilibrium model and monomer-dimer model into the PACT equation to derive the associated perturbed anisotropic chain theory (APACT) equation of state. The APACT equation of state 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, as a sum of the contributions from these particular interactions

$$Z = 1 + Z^{\text{rep}} + Z^{\text{att}} + Z^{\text{assoc}}\qquad(47)$$

The Z^{assoc} term for one and two bonding sites per molecule is evaluated from the material balance and expressions for the chemical equilibria. The Z^{assoc} is given by (Ikonomou and Donohue, 1986; Economou and Donohue, 1991, 1992)

$$Z^{\text{assoc}} = \frac{n_T}{n_0} - 1\qquad(48)$$

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 the 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. The Z^{rep} and Z^{attr} are given by Vimalchand et al. (1985, 1986) and Economou et al. (1995)

$$\left.\begin{aligned}
Z^{\text{rep}} &= c\frac{4\eta-2\eta^2}{(1-\eta)^3}\\
Z^{\text{attr}} &= Z_1^{LJ} + Z_2^{LJ} + \cdots + Z_2^{\text{ani}} + Z_3^{\text{ani}} + \cdots
\end{aligned}\right\}\qquad(49)$$

Economou and Donohue (1992) extended the APACT equation of state to compounds with three associating sites per molecule. The three-site APACT equation of state was developed to allow calculation of vapor-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 requires a binary interaction parameter for the 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 that included the near-critical region, the agreement between calculations and experimental data was good. 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 vapor pressure and the saturated liquid and saturated vapor densities of pure hydrogen fluoride from the triple point up to the critical point with good accuracy. Economou et al. (1995) applied the APACT equation to water-salt phase equilibria and showed that the APACT equation accounted explicitly for the strong dipole-dipole interactions between water and salt molecules. Other theoretically based models of association are discussed elsewhere (Stell and Zhou, 1992; Zhou and Stell, 1992).

Statistical associating fluid theory

By extending Wertheim's (1984a,b, 1986a,b,c, 1987) theory, Chapman et al. (1988, 1990) proposed a general statistical associating fluid theory (SAFT) approach. Huang and Radosz (1990) developed the SAFT equation of state. The SAFT equation of state accounts for hard-sphere repulsive forces, dispersion forces, chain formation (for nonspherical molecules) and association, and it is presented as a sum of four Helmholtz function terms

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{seg}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT} \tag{50}$$

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

$$\frac{A^{\text{seg}}}{NkT} = m\frac{A_0^{\text{seg}}}{NkT} \tag{51}$$

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

$$\frac{A_0^{\text{seg}}}{NkT} = \frac{A_0^{hs}}{NkT} + \frac{A_0^{\text{disp}}}{NkT} \tag{52}$$

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

$$\frac{A_0^{hs}}{NkT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{53}$$

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

$$\frac{A_0^{\text{disp}}}{NkT} = \sum_i \sum_j D_{ij}\left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j \tag{54}$$

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

$$\frac{A^{\text{chain}}}{NkT} = (1-m)\ln\frac{1-\eta/2}{(1-\eta)^3} \tag{55}$$

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

$$\frac{A^{\text{assoc}}}{NkT} = \sum_\alpha \left[\ln X_\alpha - \frac{X_\alpha}{2}\right] + \frac{1}{2}M \tag{56}$$

where M is the number of association sites on each molecule, X_α is the mole fraction of molecules that are *not* bonded at site α, and the summation is over all associating sites on the molecule.

Huang and Radosz (1990) also gave the SAFT equation in terms of the compressibility factor

$$Z = 1 + Z^{hs} + Z^{\text{disp}} + Z^{\text{chain}} + Z^{\text{assoc}} \tag{57}$$

where

$$\left.\begin{aligned} Z^{hs} &= m\frac{4\eta - 2\eta^2}{(1-\eta)^3} \\ Z^{\text{disp}} &= m\sum_i \sum_j jD_{ij}\left[\frac{u}{kT}\right]^i \left[\frac{\eta}{\tau}\right]^j \\ Z^{\text{chain}} &= (1-m)\frac{(5/2)\eta - \eta^2}{(1-\eta)[1-(1/2)\eta]} \\ Z^{\text{assoc}} &= \rho\sum_A \left[\frac{1}{X^A} - \frac{1}{2}\right]\frac{\partial X^A}{\partial\rho} \end{aligned}\right\} \tag{58}$$

Chapman et al. (1990) reported that the agreement with molecular simulation data was 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) applied their SAFT equation to correlate vapor-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. 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 associating 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. Yu and Chen (1994) also used the 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.

Simplified statistical associating fluid theory

Fu and Sandler (1995) developed a simplified statistical associating fluid theory (SSAFT) equation by modifying the dispersion term of the equation. The SSAFT equation is of the same form as Eq. 57. It retains the original hard-sphere (Z^{hs}), chain (Z^{chain}), and association (Z^{assoc}) terms (see Eq. 58) but the contribution of dispersion interactions is given by

$$Z^{\text{disp}} = -mZ_M\left(\frac{V^*Y}{V_s + V^*Y}\right) \tag{59}$$

Equation 59 is the attraction term for a square-well fluid (Lee et al., 1985) and was used in the SPHCT equation of state.

For pure components, the parameters of the SSAFT equation of state were obtained by fitting vapor 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.

Hard-sphere statistical associating fluid theory (HS-SAFT)

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

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{hs}}{NkT} + \frac{A^{mf}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{ssoc}}}{NkT} \tag{60}$$

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

$$\frac{A^{\text{mono}}}{NkT} = \frac{A^{hs}}{NkT} + \frac{A^{mf}}{NkT} \tag{61}$$

that is, 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

$$\frac{A^{hs}}{NkT} = \frac{6}{\pi\rho}\left[\left(\frac{\zeta_s^{\,3}}{\zeta_3^{\,2}} - \zeta_0\right)\ln(1-\zeta_3) + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^{\,3}}{\zeta_3(1-\zeta_3)^2}\right] \tag{62}$$

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

$$\zeta_l = \frac{\pi\rho}{6}\sum_{i=1}^{n} x_i m_i \sigma_i^{\,l} = \frac{\pi\rho}{6}\left(x_1 m_1 \sigma_1^{\,l} + x_2 m_2 \sigma_2^{\,l}\right) \tag{63}$$

ζ_3 is the overall packing fraction of the mixture, m_i is the number, and σ_i is 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 binary mixtures

$$\frac{A^{mf}}{NkT} = -\frac{\rho}{kT}\left(\alpha_{11}x_1^2m_1^2 + 2\alpha_{12}x_1x_2m_1m_2 + \alpha_{22}x_2^2m_2^2\right) \tag{64}$$

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

By using the HS-SAFT 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 + hydro fluoride (Galindo et al., 1997). Garcia-Lisbona et al. (1998) used HS-SAFT to describe the phase equilibria of aqueous solutions of alkyl polyoxyethylene mixtures and reported that the HS-SAFT equation was able to describe the phase behavior of these systems. The results showed the reasonable agreement between the theoretical prediction and experimental results.

Lennard-Jones statistical associating fluid theory (LJ-SAFT)

Banaszak et al. (1994) incorporated Lennard-Jones interactions in the context of thermodynamic perturbation theory to formulate an equation of state for Lennard-Jones chains. They demonstrated the feasibility of the LJ-SAFT formulation, however, comparison of the calculated compressibility factor for 8-mer, 16-mer, and 32-mer chains did not match simulation data.

Later, Kraska and Gubbins (1996a,b) also developed an equation of state for Lennard-Jones chains by modifying the SAFT equation of state in two major ways. First, a Lennard-Jones equation of state was used for the segment contribution; secondly, a term was added that accounts for the dipole-dipole interaction in substances like the 1-alkanols and water. In terms of the Helmholtz function the general expression for the LJ-SAFT equation of state is

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{seg}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT} + \frac{A^{\text{dipole}}}{NkT} \tag{65}$$

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

$$\frac{A^{hs}}{NkT} = \frac{5}{3}\ln(1-\eta) + \frac{\eta(34-33\eta+4\eta^2)}{6(1-\eta)^2} \tag{66}$$

For the Lennard-Jones segment term, Kraska and Gubbins (1996a,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

$$\frac{A^{\text{seg}}}{NkT} = \frac{m}{NkT}\left(A^{hs} + \exp\left(-\gamma\rho^{*2}\right)\rho T\Delta B_{2,hBH} + \sum_{ij}\left(C_{ij}T^{i/2}\rho^{*j}\right)\right) \tag{67}$$

where

$$\left.\begin{aligned} \Delta B_{2,hBH} &= \sum_{i=-7}^{0} C_i T^{i/2} \\ \rho^* &= mb/V_m \\ \eta &= \frac{\pi}{6}\rho^*\sigma_{BH}^3 \\ \sigma_{BH} &= \sum_{i=-2}^{1} D_i T^{i/2} + D_{\ln}\ln T \end{aligned}\right\} \tag{68}$$

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

$$\frac{A^{\text{dipole}}}{NkT} = \frac{A_2}{T}\left(\frac{1}{1-(A_3/A_2)}\right) \tag{69}$$

where

$$\left.\begin{aligned} A_2 &= -\frac{2\pi}{3}\frac{\rho^*\mu^{*4}}{T^*}J^{(6)} \\ A_3 &= \frac{32\pi^3}{135}\sqrt{\frac{14\pi}{5}}\frac{\rho^{*2}\mu^{*6}}{T^{*2}}K_{222}^{333} \\ T^* &= \frac{T}{\tilde{T}} = \frac{Tk_B}{\epsilon} \\ \mu^* &= \mu/\sqrt{\epsilon m\sigma^3} \\ \rho^* &= \rho b \\ b &= N_L\sigma^3 \end{aligned}\right\} \tag{70}$$

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 (1978a,b).

Kraska and Gubbins (1996a,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 than the original SAFT equation. Recently, Chen et al. (1998) reported an alternative LJ-SAFT equation. They reported that the vapor pressures calculated from their equation can be fitted to experiment more accurately than the original SAFT equation.

Square-well statistical associating fluid theory (SW-SAFT)

The thermodynamic perturbation formalism was extended by Banaszak et al. (1993) to obtain an equation for chains of square-well statistical associating fluid theory (SW-SAFT) molecules

$$Z^{\text{swc}} = mZ_{\text{ref}}^{\text{sws}} + (1-m)\left(1+\eta\frac{\partial \ln g^{\text{sws}}(\sigma,\eta)}{\partial\eta}\right) \tag{71}$$

where g^{sws} is the site-site correlation function at contact of square-well spheres, and $Z_{\text{ref}}^{\text{sws}}$ is the compressibility factor of square-well spheres which can be calculated from Barker-Henderson perturbation theory. Tavares et al. (1995) also proposed equation of states for square-well chains using the SAFT approach. In addition to properties of monomer segments, they included dimer properties in the spirit of the TPT-D1 equation (Eq. 38). The concepts have been extended to hetero-segmented molecules (Adidharma and Radosz, 1998). Recently, six different SW-SAFT models have been reviewed (Adidharma and Radosz, 1999). According to the comparison reported by Adidharma and Radosz (1999), the addition of dimer structure does not improve the usefulness of SW-SAFT equations for representing real fluids significantly. Originally, the validity of SW-SAFT equations were limited to a square well with a width of 1.5σ. This limitation has been addressed by subsequent work (Chang and Sandler, 1994; Gil-Villegas et al., 1997).

By providing an additional parameter which characterized 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 discussed above, the general form of the SAFT equation of state can be written as

$$\frac{A}{NkT} = \frac{A^{\text{ideal}}}{NkT} + \frac{A^{\text{mono}}}{NkT} + \frac{A^{\text{chain}}}{NkT} + \frac{A^{\text{assoc}}}{NkT} \tag{72}$$

In VR-SAFT (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 in Eq. 50. The contribution due to the monomer segments A^{mono} is given by

$$\frac{A^{\text{mono}}}{NkT} = m\frac{A^m}{NkT} = m\left(\frac{A^{hs}}{NkT} + \beta A_1 + \beta^2 A_2\right) \tag{73}$$

where A^m is the Helmholtz function per monomer, m is the number of monomers per chain, $\beta = 1/kT$, and 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

$$\frac{A^{\text{chain}}}{NkT} = -(1-m)\ln y^M(\sigma) \tag{74}$$

where $y^M(\sigma)$ 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 $1.1 \le \lambda \le 1.8$

$$A_1^{sw} = A_1^{vdW} g^{hs}(1 : \eta_{\text{eff}}) \tag{75}$$

$$A_2^{sw} = \frac{1}{2} \epsilon K^{hs} \eta \frac{\partial A_1^{sw}}{\partial \eta} \tag{76}$$

where ϵ and λ are the depth and the range parameter of the attractive well, respectively, and

$$\left.\begin{aligned} A_1^{vdW} &= -4\eta\epsilon(\lambda^3 - 1) \\ g^{hs}(1; \eta_{\text{eff}}) &= \frac{1 - \eta_{\text{eff}}/2}{(1 - \eta_{\text{eff}})^3} \\ \eta_{\text{eff}} &= c_1\eta + c_2\eta^2 + c_3\eta^3 \end{aligned}\right\} \tag{77}$$

The coefficients c_n were given by the matrix

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda \\ \lambda^2 \end{pmatrix} \tag{78}$$

In the second-order term (Eq. 76), K^{hs} is the isothermal compressibility of the hard-sphere fluid and was given by

$$K^{hs} = \frac{(1-\eta)^4}{1 + 4\eta + 4\eta^2} \tag{79}$$

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 VR-SAFT equation 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 HS-SAFT treatment. Gil-Villegas et al. (1997) demonstrated the adequacy of the VR-SAFT equation in describing the phase equilibria of chain molecules such as the *n*-alkanes and *n*-perfluoroalkanes. Davies et al. (1998) showed the VR-SAFT 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 VR-SAFT 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 VR-SAFT approach for mixtures of fluids with nonconformal intermolecular potentials, that is, 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 VR-SAFT equation of state represented well the vapor-liquid and liquid-liquid phase equilibria of mixtures containing square-well molecules.

Tavares et al. (1997) reported a completely analytical equation of state for square-well chains. Their equation is valid for a range of well widths ($1 \le \lambda \le 2$), and it leads to good predictions of the compressibility factor of 4-mer, 8-mer, and 16-mer square-well chains. A completely analytical equation is desirable for phase equilibria calculations, but it comes at the cost of a considerable increase in mathematical complexity.

Cubic plus association equation of state

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

$$Z = \frac{V}{V-b} - \frac{a}{RT(V-b)} + \rho \sum_{\alpha} \left(\frac{1}{X_\alpha} - \frac{1}{2} \right) \frac{\partial X_\alpha}{\partial \rho} \tag{80}$$

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). Kontogeorgis et al. (1996) applied this new equation of state to pure components and obtained good correlations of both vapor 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 equation of state.

Heteronuclear chains

The preceeding equations of state can only be applied to homogeneous chains, that is, chains composed of identical segments. Instead, many real chain-like fluids are heterogeneous being composed of different alternating segments. Furthermore, we are often interested in studying mixtures of different types of chains. Several equations of state have been proposed relatively recently that tackle the problem of heteronuclear chains.

Amos and Jackson (1992) used a bonded hard-sphere approach to devise an equation of state for the compressibility factor of hard spheres of different size. The compressibility factor for a fluid mixture of heteronuclear hard chain molecules is

$$\begin{aligned} Z = (Z^{hs} - 1) \sum_{i=1}^{r} x_i m_i + 1 \\ - \sum_{i=1}^{r} x_i \sum_{j=1}^{m_i - 1} \eta \left(\frac{\partial \ln g_{j,j+1}^{hs}(\sigma j, j+1)}{\partial \eta} \right) \end{aligned} \tag{81}$$

where x_i is the mole fraction of chains of component i, m_i is the number of segments in a chain of component i, σ_j is the diameter of segment j on a chain of component i, and $\sigma_{j,j+1} = (\sigma_j + \sigma_{j+1})/2$ is the bond length between adjacent segments. Amos and Jackson (1992) reported good agreement between simulation data and the compressibility factor predicted by Eq. 81 for mixtures containing diatomic and triatomic entities. Malakhov and Brun (1992) also generalized thermodynamic perturbation theory in a similar way to formulate an equation of state for heteronuclear chains.

Song et al. (1994a) developed a perturbed hard-sphere chain (PHSC) equation of state that can be applied to heterogeneous mixtures. In general terms, the PHSC equation of state for m-component mixtures containing r segments can be represented as (Song et al., 1994b)

$$Z = 1 + \frac{2\pi\rho}{3}\sum_{ij}^{m} x_i x_j r_i r_j \sigma_{ij} g_{ij}(\sigma_{ij}) - \sum_{i}^{m} x_i (r_i - 1)\left[g_{ij}(\sigma_{ij}) - 1\right] - \frac{\rho}{kT}\sum_{ij}^{m} x_i x_j r_i r_j a_{ij} \quad (82)$$

This equation has been used successfully to predict the liquid-liquid equilibria for binary polymer solutions (Song et al., 1994b). Comparison (Sadus, 1995) of the hard-sphere contributions of Eq. 82 with molecular simulation data indicates that this part of the equation is less accurate than other hard-sphere chain alternatives. However, an advantage of Eq. 82 is that it can be applied easily to mixtures of heterogeneous chains by simply using a different value of r for the different chains. An equation for heteronuclear chains has also been reported (Hu et al., 1996) using a cavity-correlation function approach.

Banaszak et al. (1996) extended the SAFT equation of state to apply to copolymers. The copolymer-SAFT equation includes contributions from chain heterogeneity and microstructure. Banaszak et al. (1996) demonstrated that the copolymer-SAFT equation of state reproduces the qualitative cloud point behavior of propane + poly(ethylene-co-butene). More recently, Han et al. (1998) reported that the copolymer-SAFT equation of state can be used to correlate the soft chain branching effect on the cloud point pressures of copolymers of ethylene with propylene, butene, hexene, and octene in propane. The copolymer-SAFT equation can also be used to predict phase transitions in hydrocarbon + chain solutions (Pan and Radosz, 1998) and solid-liquid equilibria (Pan and Radosz, 1999).

Shukla and Chapman (1997) extended the SAFT equation of state for fluid mixtures consisting of heteronuclear hard chain molecules, and they formulated expressions for the compressibility factor of pure block, alternate, and random copolymer systems. For the relatively simple case of pure alternate copolymers consisting of m_a-mers of type a and m_b-mers of type b, the compressibility factor is

$$Z = (Z^{hs} - 1)m + 1 - (m-1)\eta \frac{\partial \ln g_{ab}^{hs}(\sigma_{ab})}{\partial \eta} \quad (83)$$

where $m = m_a + m_b$ and $m_a = m_b$.

Recently, Blas and Vega (1998) applied their modified version of the SAFT equation of state (Blas and Vega, 1997) to predict thermodynamic properties, as well as liquid-vapor equilibria, of binary and ternary mixtures of hydrocarbons. Adidharma and Radosz (1998) have introduced heterobonding into the SW-SAFT equation of state. The resulting equation can provide reasonable predictions of the phase behavior of mixtures of large homo- and heterosegmented molecules. Kalyuzhnyi et al. (1988) and Lin et al. (1988) have also used the concept of heteronuclear chains to model polymers.

Comparing Equations of State

Interrelationships between different equations of state

It is evident from the preceding descriptions that there is a substantial inter-relationship between various different equations of state. It is very rare for an equation of state to be developed entirely from scratch. Typically, new equations of state are proposed as modifications of existing ones, or successful components of one or more equations of state are reused to form a new equation. This component reuse is common to both empirical and theoretical equations of state.

Invariably, equations of state are formed by combining separate contributions from repulsive and attractive interactions. If we consider the repulsion term as forming the underlying basis of the equation of state, the interrelationships between various equations of state can be summarized conveniently by an equation of state tree, as illustrated in Figure 2. In Figure 2, the tree grows from our knowledge of intermolecular interactions. The main branches of the tree represent different ways of representing intermolecular repulsion. We can identify branches representing the van der Waals, Carnahan-Starling, HCB, PHCT, and TPT terms. The addition of a different attraction term to these branches results in a different equation of state capable of predicting phase equilibria. Figure 2 illustrates the dichotomy between empirical and theoretical equations of state. The empirical equations of state stem almost exclusively from the van der Waals repulsive branch. In contrast, theoretical equations of state are formed from different branches that represent alternative ways of accounting for the repulsion of nonspherical bodies. These different repulsion branches converge to a common point, which represents the limiting case of hard-sphere repulsion as described by the Carnahan-Starling equation.

The tree diagram illustrates the importance of the Redlich-Kwong equation as the precursor for the development of empirical attraction terms. In contrast, the PHCT and SAFT equations of state are the precursors of many theoretical attraction terms.

Comparison with experiment

Experimental data provides the ultimate test of the accuracy of an equation of state. However, there are several factors that make it difficult to make absolute quantitative judgments about the relative merits of competing equations of state from a comparison with experimental data. The distinction must also be made between correlation and genuine prediction. Nevertheless, we can make some useful general comments about the accuracy of different categories of equations of state. However, before doing so, it is instructive to

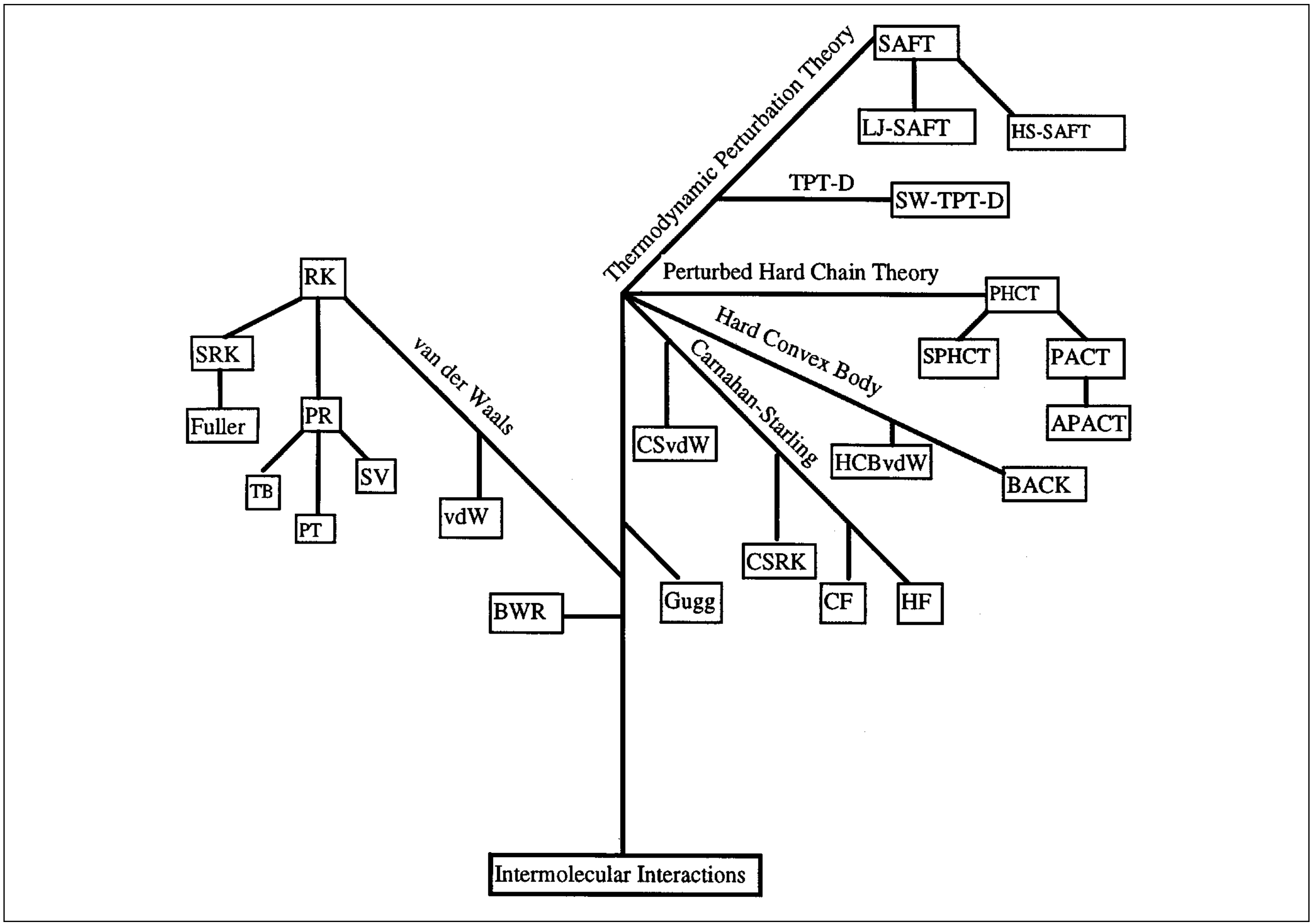

Figure 2. Equation-of-state tree showing the interrelationship between various equations of state.

identify some of the reasons why an absolute quantitative judgment is difficult:

(1) The very large number of equations of state (Sandler, 1994) is an obvious factor that makes the assessment of different equations of state difficult. In this context, it should be noted that the problem is compounded by the practice of equation of state developers testing their equation of state against experimental data, but not offering an identical comparison with other equations of state. Nonetheless, the close inter-relationship between the different equations of state allows some scope for a category by category evaluation.

(2) The accuracy of equations of state is often dependent on highly optimized equation of state parameters. These equations of state parameters are typically tuned to a particular region of interest and breakdown outside this region. For example, an equation of state tuned for atmospheric pressures is unlikely to predict high-pressure phenomena with equal accuracy (Sadus, 1992a).

(3) Comparison of the effectiveness of the equation of state for mixtures is hampered by the additional uncertainties introduced by different mixture prescriptions, combining rules and unlike interaction parameters. These topics are discussed in detail in the section discussing mixing rules.

(4) Users of equations of states often adopt a favorite equation of state with which they become expert in using. This can result in considerable inertia to change that hinders the evaluation of alternatives, particularly if the alternatives are more complicated.

Partly because of the above factors, there are relatively few reports in the literature (Spear et al., 1971; Soave, 1972; Carnahan and Starling, 1972; Beret and Prausnitz, 1975; Peng and Robinson, 1976; Abbott, 1979; Martin, 1979; Elliott and Daubert, 1985; Kim et al., 1986; Han et al., 1988; Mainwaring et al., 1988; Sadus, 1992; Plackov et al., 1995; Plohl et al., 1998) comparing the predictive properties of two or more equations of state over the same range of physical conditions and experimental data.

Equations of state are used frequently to correlate experimental data rather than to provide genuine predictions. It is well known that the van der Waals equation cannot be used to correlate accurately the vapor-liquid coexistence of pure fluids. In contrast, the addition of further adjustable parameters and temperature dependence to the attractive term used in the Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson equations of state result in accurate correlations (Abbott, 1979; Han et al., 1988) of the vapor pressure. However, a large improvement in the prediction of vapor pressures can be obtained (Plackov et al., 1995) by using either the Guggenheim or Carnahan-Starling van der Waals (CSvdW) equations of state. The predictions of the Guggenheim and CSvdW equations cannot compete with the accuracy obtained from empirical correlations with cubic equations of state. However, their improved accuracy alone demonstrates clearly that the success of the cubic equations of state is due largely to the ability of the empirical improvements to compensate for the inadequacy of the van der Waals repulsion term.

Theoretical equations of state can also be used to correlate experimental data. For example, van Pelt et al. (1992) correlated the SPHCT equation of state with experimental data for the vapor-liquid coexistence of polyatomic molecules and *n*-alkanes. The results indicate that the SPHCT provided better correlations than cubic equations of state. This is a common finding for other multiparameter theoretical equations of state. However, the benefit of using a theoretical equation for correlation is moot because they are considerably more complicated than cubic equations. The true value in using a theoretical equation is their improved ability to predict phase equilibria rather than merely correlate data.

At low pressures, either empirical or theoretical equations of state can be used to at least qualitatively predict phase equilibria. In this region, the highly optimized parameters of empirical parameters generally enable empirical equations to provide superior accuracy than otherwise can be obtained from theoretical equations of state. However, empirical equations will almost invariably fail to predict the high-pressure phase behavior of multicomponent mixtures (Sadus, 1992a). For example, the results obtained (Sadus, 1992a, 1994) for the high-pressure equilibria of binary mixtures predicted by either the Redlich-Kwong and Peng-Robinson equations of state are not even qualitatively reliable. This failure can be attributed unequivocally to the breakdown of the van der Waals repulsion term (Figure 1) at the moderate to high densities encountered at high pressures. In contrast, theoretical equations using either the Carnahan-Starling or Guggenheim model of repulsion can be used to obtain quantitatively accurate predictions at high pressures. A curious exception to this rule is the high-pressure phase behavior of the helium + water binary mixture which can be represented accurately (Sretenskaja et al., 1995) by the simple van der Waals equation of state.

Another weakness of empirical equations of state, which is also related to the inadequacy of the van der Waals repulsion term, is that they cannot be used to calculate full range of phase equilibria of mixtures. Van Konynenburg and Scott (1980) classified the phase behavior of binary mixtures into five main types based on different critical behavior. The van der Waals, and other empirical equations, can be used to at least qualitatively predict these five types. However, since the work of van Konynenburg and Scott, many more phase types have been documented experimentally including a sixth type of behavior (Schneider, 1978) associated commonly with aqueous mixtures involving liquid-liquid immiscibility at high pressures. This so-called Type VI behavior can be predicted by the SPHCT equation of state (Van Pelt et al., 1991). More recently, the existence of Type VI behavior has been predicted using the CSvdW (Yelash and Kraska, 1998) and Guggenheim (Wang et al., 2000) equations of state. In contrast, Type VI behavior cannot be calculated by using an empirical equation of state.

Historically, both the empirical and theoretical ''hard-sphere + attractive term'' have been applied successfully beyond the natural range of validity of the hard-sphere concept. This success can be attributed in part to clever correlation rather than the capabilities of the equation of state. However, it is evident that the quest to genuinely predict the phase equilibria of large molecules will rely increasing on theoretically-based models that account for the complexity of molecular interaction. Currently, either the SAFT or PHCT approaches appear to be promising approaches towards this goal. Some improvements have been reported recently (Chiew et al., 1999; Kiselev and Ely, 1999; Feng and Wang, 1999).

Comparison with molecular simulation data

Molecular simulation (Sadus, 1999) is playing an increasingly valuable role in validating the accuracy of the underlying theoretical basis of equations of state. Molecular simulation provides exact data to test the accuracy of theory. For example, an equation of state for the compressibility factor of Lennard-Jones atoms must reproduce the compressibility factors for Lennard-Jones atoms obtained from molecular simulation. Discrepancies between theory and simulation can be attributed unambiguously to the failure of theory to represent adequately the underlying model. In contrast, direct comparison of a theoretical model with experiment does not provide useful information regarding the validity of the theory, because experimental data does not represent the idealized behavior of the theoretical model. However, comparison of the results of a simulation-verified model with experiment does indicate the strength or weakness of theory to represent experiment adequately.

Probably, the best known example of the role of molecular simulation is the testing of hard-sphere repulsion terms against simulation data for hard spheres (Figure 1). The result of this comparison indicates that the Carnahan-Starling and Guggenheim terms are accurate theoretical models, whereas the van der Waals term fails at moderate to high densities.

More recently, molecular simulation data have proved useful in determining the accuracy of theoretical models for hard-sphere chains. A comparison with simulation data for the compressibility factor predicted by several hard-sphere chain equations of state is summarized in Table 3. Generally, the data in Table 3 indicate that the STPT-D equation is considerably more accurate than the GF-D, TPT-D1, TPT-D2, and PROSA equations. The comparison of theory with simulation does not guarantee that using any of these equa-

Table 3. Average Absolute Deviation of the Calculated Compressibility Factor of *m*-Hard-Sphere Chains Compared with Molecular Simulation Data

	AAD (%)				
m	GF-D*	TPT-D1*	TPT-D2*	Virial-PROSA**	STPT-D*
4	1.72	1.04	0.76		0.85
8	3.58	1.88	1.78		1.28
16	6.64	2.63	3.74		1.67
32	10.44	4.27	5.75		1.08
51	5.37	2.72	3.26	6.25	3.97
201	9.35	5.89	6.51	8.98	3.92

*From Sadus (1995).
**From Stell et al. (1999b).

tions will result in an accurate description of real chain molecules. However, using a simulation-verified model does mean that any discrepancies of theory with experiment are not merely due to the failure of theory to represent adequately the underlying model. Instead, the discrepancies can be attributed unambiguously to the limitations of theory per se to model real molecules.

Mixing Rules

The great utility of equations of state is for phase equilibria calculations involving mixtures. The assumption inherent in such a 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 achieved commonly 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

$$a = \sum_i x_i a_i \tag{84}$$

$$b = \sum_i x_i b_i \tag{85}$$

Equation 85 is sometimes employed (Han et al., 1988) because of its simplicity, but Eq. 84 is rarely used because it does not account for the important role of unlike interaction in binary fluids. Consequently, employing both Eqs. 84 and 85 would lead to the poor agreement of theory with experiment.

The van der Waals mixing rules

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

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{86}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{87}$$

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.

Equations 86 and 87 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 tested thoroughly for several equations of state by Han et al. (1988). They used the van der Waals mixing rule (Eq. 86) to obtain parameter a and the linear mixing rule (Eq. 85) to obtain parameter b. Their results showed that most of equations of state with the van der Waals mixing rules were capable of representing vapor-liquid equilibria with only one binary adjustable parameter for obtaining a_{ij}.

Equations 86 and 87 are also adequate for calculating the phase behavior of 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 that contained strongly polar substances such as alcohols, water and acetone, the van der Waals mixing rule did not yield reasonable vapor-liquid equilibrium results. Anderko (1990) gave some examples of the failure of the van der Waals mixing rules for strongly nonideal mixtures.

Improved van der Waals mixing rules

Many workers (Adachi and Sugie, 1986; Panagiotopoulos and Reid, 1986; Stryjec and Vera, 1986a,b; Schwartzentruber et al., 1987; Sandoval et al., 1989) have proposed modifications for the van der Waals prescriptions. A common approach 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 summarized in Table 4.

Table 4. Composition-Dependent Mixing Rules

Reference	a_{ij} Term in Eq. 86
Adachi and Sugie (1986)	$(a_{ii}a_{jj})^{1/2}[1 - l_{ij} + m_{ij}(x_i - x_j)]$
Panagiotopoulos and Reid (1986)	$(a_{ii}a_{jj})^{1/2}[1 - k_{ij} + (k_{ij} - k_{ji})x_i]$
Stryjek and Vera (1986b) (Margules-type)	$(a_{ii}a_{jj})^{1/2}(1 - x_i k_{ij} - x_j k_{ji})$
Stryjek and Vera (1986b) (Van Laar-type)	$(a_{ii}a_{jj})^{1/2}\left[1 - \dfrac{k_{ij}k_{ji}}{x_i k_{ij} + x_j k_{ji}}\right]$
Schwartzentruber et al. (1987)	$(a_{ii}a_{jj})^{1/2}\left[1 - k_{ij} - l_{ij}\dfrac{m_{ij}x_i - m_{ji}x_j}{m_{ij}x_i + m_{ji}x_j}(x_i + x_j)\right]$ $k_{ji} = k_{ij};\quad l_{ji} = -l_{ij};\quad m_{ji} = 1 - m_{ij};\quad k_{11} = l_{11} = 0$
Sandoval et al. (1989)	$(a_{ii}a_{jj})^{1/2}[1 - (k_{ij}x_i + k_{ji}x_j) - 0.5(k_{ij} + k_{ji})(1 - x_i - x_j)]$

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

$$a = \sum \sum x_i x_j a_{ij} \tag{88}$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2} \left[1 - l_{ij} - m_{ij}(x_i - x_j) \right] \tag{89}$$

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

Sadus (1989) used conformal solution theory (Sadus, 1992a, 1994) 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

$$\begin{aligned}
a^2\theta^6 \Big[-2f''/f + (f'/f)^2 + 2h''/h - 2f'h'/fh + (h'/h)^2 \Big] \\
+ aRTV \Big[\phi_B \theta^2 \{ -h''/h - f''/f \} \\
+ 2\phi_A \theta^3 \{ h''/h + f'h'/fh - (h'/h)^2 \} \\
+ 2\theta^6 \{ -h''/h + (h'/h)^2 + 1/x(1-x) \} \Big] \\
- (RTV)^2 \Big[\phi_A^2 \{ (f'/f)^2 - (h'/h)^2 \} \\
+ \phi_B \theta^2 \{ h''/h - (h'/h)^2 - 1/x(1-x) \} - \phi_A \phi_B h''/h\theta \Big] = 0
\end{aligned} \tag{90}$$

where superscripts $'$ and $''$ denote successive differentiation of the conformal parameters, and θ and ϕ are characteristic of the equation of state. The main advantage of Eq. 90 is that the 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 vapor-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 optimize the agreement between theory and experiment.

Mixing rules from excess Gibbs energy models

Huron and Vidal (1979) suggested a method for deriving mixing rules for equations of state from excess Gibbs energy models. Their method relies on three assumptions. First, the 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. Secondly, 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. 5) and applying the common linear mixing rule (Eq. 85) for the volume parameter b, the resulting expression for parameter a is

$$a = b \left[\sum_{i=1}^{n} x_i \frac{a_{ii}}{b_{ii}} - \frac{g_\infty^E}{\ln 2} \right] \tag{91}$$

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

$$g_\infty^E = \sum_{i=1}^{n} x_i \left(\frac{\sum_{j=1}^{n} x_j G_{ji} C_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} \right) \tag{92}$$

with

$$\left. \begin{aligned} C_{ji} &= g_{ji} - g_{ii} \\ G_{ji} &= b_j \exp\left(-\alpha_{ji} \frac{C_{ji}}{RT} \right) \end{aligned} \right\} \tag{93}$$

where g_{ji} and g_{ii} are the interaction energies between unlike (g_{ji}) and like (g_{ii}) molecules; α_{ji} is a nonrandomness parameter. The Huron-Vidal mixing rule for a is deduced by applying Eq. 91

$$a = b \sum_{i=1}^{n} x_i \left[\frac{a_{ii}}{b_{ii}} - \frac{1}{\ln 2} \frac{\sum_{j=1}^{n} x_j G_{ji} C_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} \right] \tag{94}$$

with α_{ji}, C_{ij} and C_{ji} as the three adjustable parameters. When $\alpha_{ji} = 0$, the Huron-Vidal mixing rule reduces to the van der Waals mixing rule. Huron and Vidal (1979) showed that their mixing rule yields 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 vapor-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).

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

Mollerup (1986) modified Eq. 94 by retaining that 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

$$\frac{a}{b} = \sum_i x_i \left(\frac{a_i}{b_i} \right) \left(\frac{f_i}{f} \right) - \frac{G^E}{f} + \left(\frac{RT}{f} \right) \left(\sum_i x_i \ln \left[f_c \frac{b_i}{b} \right] \right) \tag{95}$$

where

$$\left.\begin{aligned} f_i &= \frac{b_i}{v_i} \\ f &= \frac{b}{v} \\ f_c &= \left(\frac{v_i}{b_i} - 1\right) \Big/ \left(\frac{v}{b} - 1\right) \end{aligned}\right\} \tag{96}$$

The mixing rule (Eq. 95) depends on the liquid-phase volume of the mixture and individual components, and is a less restrictive assumption than the Huran-Vidal mixing rule.

This basic concept (Mollerup, 1986) was implemented by Michelsen (1990). Using a reference pressure of zero and the Soave-Redlich-Kwong equation of state (Eq. 5), Michelsen (Michelsen, 1990; Dahl and Michelsen, 1990) repeated the matching procedure of Huron and Vidal resulting in the following mixing rule called the modified Huron-Vidal first order (MHV1)

$$\alpha = \sum_{i=1}^{n} x_i \alpha_{ii} + \frac{1}{q_1}\left[\frac{G^E}{RT} + \sum_{i=1}^{n} x_i \ln\left(\frac{b}{b_{ii}}\right)\right] \tag{97}$$

where

$$\left.\begin{aligned} \alpha &= a/bRT \\ b &= \sum_{i=1}^{n} x_i b_{ii} \\ \alpha_{ii} &= a_{ii}/b_{ii}RT \end{aligned}\right\} \tag{98}$$

with the recommended value of $q_1 = -0.593$. In addition, Dahl and Michelsen (1990) derived an alternative mixing rule referred to as the modified Huron-Vidal second-order (MHV2)

$$q_1\left(\alpha - \sum_{i=1}^{n} x_i \alpha_{ii}\right) + q_2\left(\alpha^2 - \sum_{i=1}^{n} x_i \alpha_{ii}^2\right) = \frac{G^E}{RT} + \sum_{i=1}^{n} x_i \ln\left(\frac{b}{b_{ii}}\right) \tag{99}$$

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 vapor-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 vapor-liquid equilibria of gas-solvent binary systems and to predict vapor-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 mixing rules to satisfy the second virial condition. For the mixture parameters of an equation of state, a and b are

$$a = b\left[\sum x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C}\right] \tag{100}$$

$$b = \frac{\sum\sum x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 + \frac{A_\infty^E}{RT} - \sum x_i \left(\frac{a_i}{b_i RT}\right)} \tag{101}$$

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

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(1 - k_{ij})}{2}\left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)\right] \tag{102}$$

where k_{ij} is a binary interaction parameter.

Wong and Sandler (1992) tested the mixing rules (Eq. 100 and Eq. 101), and concluded that they were reasonably accurate in describing both simple and complex phase behavior of binary and ternary systems for the diverse systems they considered. Wong et al. (1992) demonstrated that the Wong-Sandler mixing rules can be used for highly nonideal mixtures. The mixing rules can be applied at temperatures and pressures that greatly exceed the experimental data used to obtain the parameters. Huang and Sandler (1993) compared the Wong-Sandler and MHV2 mixing rules 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 vapor-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 of those obtained when using the MHV2 mixing rule. Orbey and Sandler (1994) used the Wong-Sandler mixing rule to correlate the vapor-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 behavior to the classical 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. 102 as

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{(b_i + b_j)}{2} - \frac{\sqrt{a_i a_j}\,(1 - k_{ij})}{RT} \tag{103}$$

while retaining the basic equations, Eq. 100 and Eq. 101. 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 vapor-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 vapor-liquid equilibria.

Castier and Sandler (1997a,b) performed critical point calculations in binary systems utilizing cubic equations of state combined with the Wong-Sandler mixing rules. To investigate the influence of the mixing rules on the shape of the calculated critical phase diagrams, the van der Waals equation of state was combined with the Wong-Sandler mixing rules (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 rules are combined with the Stryjek and Vera (1986a) version of the Peng-Robinson (1976) equation of state (Castier and Sandler, 1997b), it was able to predict quantitatively the critical behavior of some highly nonideal systems involving compounds such as water, acetone, and alkanols. For some highly asymmetric and nonideal mixtures, such as water + n-dodecane, only qualitatively correct critical behavior could be predicted.

Several other mixing rules have been proposed (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. (1996), 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).

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 contribution from unlike interaction to the intermolecular parameters representing energy (ϵ) and hard-sphere diameter (σ) can be obtained from

$$\left.\begin{aligned} \epsilon_{ij} &= \xi_{ij}\sqrt{\epsilon_{ii}\epsilon_{jj}} \\ \sigma_{ij} &= \zeta_{ij}\frac{(\sigma_{ii}+\sigma_{jj})}{2} \end{aligned}\right\} \qquad (104)$$

In Eq. 104, the ξ_{ij} (also commonly defined as $1-k_{ij}$) and ζ_{ij} (also commonly defined as $1-l_{ij}$) terms are adjustable parameters which are used to optimize agreement between theory and experiment. The ζ_{ij} term does not significantly improve the analysis of high-pressure equilibria, and it can be usually omitted ($\zeta_{ij}=1$). The ξ_{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 ξ_{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).

In terms of the equation of state parameters, the equivalent combining rules to Eq. 104 are

$$\left.\begin{aligned} a_{ij} &= \xi_{ij} b_{ij}\sqrt{\frac{a_{ii}a_{jj}}{b_{ii}b_{jj}}} \\ b_{ij} &= \zeta_{ij}\frac{\left(b_{ii}^{1/3}+b_{jj}^{1/3}\right)^3}{8} \end{aligned}\right\} \qquad (105)$$

where the rule for b_{ij} is referred to as the Lorentz rule (Hicks and Young, 1975; Sadus, 1992a). More commonly, the equation of state parameters are obtained from

$$\left.\begin{aligned} a_{ij} &= \xi_{ij}\sqrt{a_{ii}a_{jj}} \\ b_{ij} &= \zeta_{ij}\frac{(b_{ii}+b_{jj})}{2} \end{aligned}\right\} \qquad (106)$$

where the combining rule for a_{ij} is referred to as the van der Waals combining rule. At this point, it should be noted that there is a common misconception in the literature that Eq. 106 and not Eq. 105 is the equivalent of Eq. 104. This error is understandable in view of the functional similarity of Eqs. 106 and 104. However, it should also be observed that the a and b parameters have dimensions of energy × volume and volume, respectively, compared with a dimension of energy for ϵ and a dimension of distance for σ. Another combining rule for b_{ij} is the geometric mean rule proposed by Good and Hope (1970)

$$b_{ij} = \zeta_{ij}\sqrt{b_{ii}b_{jj}} \qquad (107)$$

Sadus (1993) compared the accuracy of the Lorentz (Eq. 105), arithmetic (Eq. 106), and geometric (Eq. 107) rules for b_{ij} when used in the prediction of Type III phenomena. For molecules of similar size, all three combining rules give almost identical results, but the discrepancy increases substantially for mixtures of molecules of very dissimilar size. Sadus (1993) proposed an alternative combining rule by taking a 2:1 geometric average of the Lorentz and arithmetic rules without the ζ_{ij} parameter, that is,

$$b_{ij} = \left\{1/4\left(2^{1/3}\right)\right\}\left(b_{ii}^{1/3}+b_{jj}^{1/3}\right)^2\left(b_{ii}+b_{jj}\right)^{1/3} \qquad (108)$$

Sadus (1993) reported that the new combining rule (Eq. 108) is generally more accurate that either the Lorentz, arithmetic, or geometric combining rules.

Conclusions

Considerable progress has been achieved in the development of equations of state. Many highly successful empirical equations of state have been proposed that can be used to calculate the phase behavior of simple fluids. However, a more sophisticated approach is required for complicated molecules. To meet the challenge posed by large and complicated molecules, equations of state are being developed increasingly with an improved theoretical basis. These new equations are playing an expanding role in the accurate calculation of fluid-phase equilibria. Equation of state development has been aided greatly by new insights into the nature of intermolecular interaction and molecular simulation data. In particular, molecular simulation is likely to have an ongoing and crucial role in the improvement of the accuracy of equations of state. A continuing challenge is to improve the prediction of the phase behavior of mixtures. The main impediment to the prediction of mixture phenomena is our understanding of interactions between dissimilar molecules. This is also an area that is likely to benefit from the input of molecular simulation data.

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Notation

BWR = Benedict-Webb-Rubin
CPA = cubic plus association
CF = Christoforakos-Franck
GF-D = generalized Flory-dimer
HCB = hard convex body
HCBvdW = hard convex body van der Waals
HF = Heilig-Franck
HS-SAFT = hard sphere statistical associating fluid theory
LJ-SAFT = Lennard-Jones statistical associating fluid theory
MHV1 = modified Huron-Vidal first order
MHV2 = modified Huron-Vidal second order
PROSA = product-reactant Ornstein-Zernike approach
RK = Redlich-Kwong
SRK = Soave-Redlich-Kwong
SSAFT = simplified statistical Associating fluid theory
SW-TPT-D = square-well thermodynamic perturbation theory-dimer
TB = Trebble and Bishnoi
TPT-D1 = thermodynamic perturbation theory-dimer 1
TPT-D2 = thermodynamic perturbation theory-dimer 2
TPT1 = first-order thermodynamic perturbation theory
TPT2 = second-order thermodynamic perturbation theory
VR-SAFT = variable range statistical associating fluid theory

B = second virial coefficient
c = equation of state parameter
C = third virial coefficient
D_{ij} = universal constants in BACK equation
e = equation of state constant
f = conformal parameter, free energy
g = conformal parameter; interaction energy between molecules
$g(\sigma)$ = site-site correlation function at contact
G = Gibbs function
h = conformal parameter
k = equation of state constant
m = number of monomers; equation of state parameter
$\tilde{p}$ = reduced pressure
q = number of external segments per molecule; equation of state parameter
T^* = characteristic temperature in the SPHCT equation of state
$\tilde{T}$ = reduced temperature
u = intermolecular potential term
Y = parameter of SPHCT equation of state
z = temperature-dependence constant
α = nonsphericity parameter
β = equation of state parameter, 1/kT
ϵ = energy of interaction; attractive depth of square-well
ζ = interaction parameter; reduced density
λ = equation of state parameter, width of square-well
μ = chemical potential
ξ = unlike interaction parameter
π = 3.14159
τ = numerical constant
ω = acentric factor; orientation of molecule
Σ = summation

Subscripts and superscripts

0 = denotes component; reference system
1 = denotes component; first-order term of perturbation theory
2 = denotes component; second-order term of perturbation theory
$*$ = configurational property; perfect gas contribution
assoc = association
att = attractive
BH = Barker-Henderson
c = critical property
chain = chain term
dipole = dipole-dipole term
disp = dispersion
D_{ij} = universal constants
hc = hard chain
hcb = hard convex body
hBH = hybrid Barker-Henderson
hd = hard-dimer
i = ith component
j = jth component
LJ = Lennard-Jones
m = mixture
mf = mean field
mono = monomer-monomer term
p = perturbation
r = rotational motion of a molecule; number of segment per molecule
rep = repulsive
res = residual
sw = square well
v = vibrational motion of a molecule

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