

## **4 CUBIC AND GENERALIZED VAN DER WAALS EQUATIONS**

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Cubic and generalized van der Waals equations of state have been a subject of active research since van der Waals (1) proposed his famous equation in 1873. During the intervening years, they played a major role in the development of fluid state theories as well as in modeling fluid behavior for practical purposes. Currently, their development is motivated primarily by industrial needs for accurate process-design calculations and supported by steadily advancing computational techniques.

The cubic and generalized van der Waals equations are not the most appropriate models for the accurate representation of pure-fluid properties, because they usually lack the necessary flexibility in some regions of the phase diagram. Also, they are not the most useful methods for understanding the properties of fluids from a microscopic perspective. For such purposes, their theoretical background is usually insufficiently rigorous. However, cubic and, to a lesser extent, generalized van der Waals equations are the most frequently used equations of state for practical applications. This is due to the fact that they offer the best balance between accuracy, reliability, simplicity and speed of computation. Additionally, their success stems from the importance of multicomponent mixtures for many industrial applications. Cubic equations of state are usually the models of choice for phase-equilibrium computations for multicomponent mixtures.

The purpose of this chapter is to review cubic and generalized van der Waals equations of state as convenient practical tools for modeling the properties of multicomponent fluids. The subject is extremely broad and it is virtually impossible to enumerate all significant approaches that appeared in the literature during the last 130 years. However, an attempt will be made to identify the most useful equations of state as well as those that appear to be most promising for future research.

## 4.1 CUBIC EQUATIONS OF STATE FOR PURE COMPONENTS

### 4.1.1 Historical Perspective

The first equation of state that was capable of reasonably representing both gas and liquid phases was proposed by van der Waals in 1873 (1). Although van der Waals derived his equation in an intuitive manner, he was able to create a model of fluid behavior that was later proven to be qualitatively correct. According to van der Waals' assumptions, molecules have a finite diameter, thus making a part of the volume  $v$  not available to molecular motion. This increases the number of collisions with the walls of the vessel and, subsequently, increases the pressure. Therefore, the actual volume available to molecular motion is  $v-b$ , where  $b$  is a characteristic constant for each fluid. On the other hand, intermolecular attraction decreases the pressure. It is reasonable to assume that the pressure decrease due to intermolecular attraction is proportional to the number of molecules in a volume unit and inversely proportional to volume. Therefore, the correction for intermolecular attraction becomes  $(-a/v^2)$ . It can be further assumed that the available volume  $(v-b)$  and the corrected pressure  $(P+a/v^2)$  should obey the ideal gas law, so that

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (4.1)$$

This gives rise to a two-term equation for pressure, namely

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (4.2)$$

where the two terms correspond to repulsive and attractive contributions to pressure. Although the original van der Waals terms do not quantitatively represent the true repulsive and attractive forces, the concept of separating the repulsive and attractive terms in equations of state has proven to be extremely valuable for the representation of fluid properties. In fact, it is the cornerstone of the generalized van der Waals theory.

The original van der Waals equation has two features that make it very convenient for calculations. First, it can be rewritten as a cubic polynomial with respect to volume. Therefore, it can be solved analytically for volume or density. This feature has been retained by contemporary cubic equations of state. Second, the two van der Waals parameters  $a$  and  $b$  can be determined from critical-point coordinates by applying the critical-point conditions:

$$\frac{\partial P}{\partial v} = \frac{\partial^2 P}{\partial v^2} = 0 \quad (4.3)$$

After simple algebraic manipulations, the values of the van der Waals parameters  $a$  and  $b$  at the critical point can be found as functions of the critical temperature  $T_c$  and pressure  $P_c$ :

$$a_c = \frac{27}{64} \frac{R^2 T_c^2}{P_c^2} \quad (4.4)$$

$$b_c = \frac{1}{8} \frac{RT_c}{P_c} \quad (4.5)$$

These values remain reasonable, although not accurate, in other regions of the P-V-T space.

The van der Waals equation inspired a huge number of researchers to work on improved equations of state. Partington (2) summarized the modifications proposed through the late 1940's. Here, we mention only two of the earlier researchers, whose equations can be regarded as precursors of modern cubic equations of state. In 1881, Clausius (3) replaced the volume in the van der Waals attractive term by  $(v+c)$ , thus creating a three-parameter equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{(v+c)^2} \quad (4.6)$$

This approach resembles the volume-translation technique, which became popular roughly a century later. In 1899, Berthelot (4) introduced an equation with a temperature-dependent attractive parameter, *i.e.*,  $a_T = a/T$ . Several decades later, the concept of temperature-dependent attractive parameters proved to be essential for the practical success of cubic equations of state for phase-equilibrium calculations.

In the first half of the 20th century, the van der Waals equation and its modifications became gradually superseded by the virial equation and its empirical modifications. From the theoretical viewpoint, the statistical-mechanical foundations of the virial equation seemed superior. At the same time, empirical virial-type equations like the Benedict-Webb-Rubin EOS

(5) were shown to be empirically effective for pure fluids and promising for mixtures. However, the need for simple analytical tools for the calculation of fugacities for process design spurred a revival of interest in cubic equations of state. Redlich and Kwong (6) proposed the first cubic EOS that became widely accepted as a tool for routine engineering calculations of the fugacity. The Redlich-Kwong equation was constructed by postulating two reasonable boundary conditions in the low- and high-density limit. In the low-density limit, the equation was constrained to give a reasonable second virial coefficient:

$$B = b - \frac{\text{constant}}{T^{1/2}} \quad (4.7)$$

At high densities, it was noted that the reduced volume at infinite pressure could be approximated by 0.26. This condition, together with the usual critical-point conditions, provided guidance for the functional form of the attractive term in which the  $v^2$  term was replaced by  $v(v+b)$ :

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \quad (4.8)$$

In analogy to the van der Waals equation, the parameters  $a$  and  $b$  were calculated from critical point conditions:

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \quad (4.9)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (4.10)$$

where  $\Omega_a$  and  $\Omega_b$  are numerical constants equal to 0.42747 and 0.0867, respectively. The Redlich-Kwong equation proved to be very successful for the calculation of the properties of gas mixtures. However, it was still not adequate for the modeling of *both* gas and liquid phases. The simple temperature dependence of the attractive parameter was insufficient for the representation of vapor pressures. Also, liquid volumes were not predicted with acceptable accuracy.

The success of the Redlich-Kwong EOS stimulated many investigators to introduce a number of improvements. The early modifications of the Redlich-Kwong EOS were reviewed by Horvath (7), Tsonopoulos and Prausnitz (8), Wichterle (9) and Abbott (10). Here, we mention the modification due to Zudkevitch and Joffe (11) because of its general character. In 1970, Zudkevitch and Joffe introduced temperature-dependent parameters  $a$  and  $b$  by constraining the quantities  $\Omega_a$  and  $\Omega_b$  to match vapor pressures and liquid densities along the vapor-liquid saturation line. In this way, the quantities  $\Omega_a$  and  $\Omega_b$  became temperature-dependent at subcritical conditions, whereas they remained fixed at  $T > T_c$ . Although an EOS constructed in this way exactly reproduces the vapor pressure and liquid density, it is inconvenient because of the lack of analytical expressions for  $\Omega_a$  and  $\Omega_b$  and the need for extensive pure-component data.

Therefore, further research in this area focused on the development of fully analytical cubic equations of state. The developments concentrated in two areas:

- (1) Improving the temperature dependence of the attractive parameter to control the vapor-pressure predictions and
- (2) Improving the  $P(v)$  functional form to optimize the prediction of volumetric properties.

#### 4.1.1 Temperature Dependence of Parameters

For the prediction of vapor pressures, it is entirely sufficient to introduce a temperature-dependent attractive parameter. Thus, it is perfectly possible (and, in fact, common) that an equation of state can correctly reproduce the vapor pressure even when it gives inaccurate  $PVT$  predictions. It is convenient to express the parameter  $a$  as a product of its value at the critical point (*i.e.*,  $a_c$ ) and a dimensionless function of temperature  $\alpha(T)$ :

$$a = a_c \alpha(T) \quad (4.11)$$

In 1964, the first generalized  $\alpha$  function was introduced by Wilson (12):

$$\alpha = T_r [1 + (1.57 + 1.62\omega)T_r^{-1}] \quad (4.12)$$

where  $T_r$  is the reduced temperature and  $\omega$  is the acentric factor. This equation was established by forcing the EOS to give reasonable values of the terminal slope of the vapor pressure curve. However, this did not guarantee good predictions far away from the critical point and, therefore, the Wilson form turned out to be insufficiently accurate.

The first  $\alpha$  function that gained widespread popularity was introduced by Soave in 1972 (13):

$$\alpha = [1 + m(1 - T_r^{1/2})]^2 \quad (4.13)$$

where  $m$  is a function of the acentric factor:

$$m = 0.480 + 1.574\omega - 0.175\omega^2 \quad (4.14)$$

Soave developed his function by forcing the EOS to reproduce the vapor pressures at  $T_r=0.7$ . Therefore, the Redlich-Kwong EOS with Soave's  $\alpha$  form (frequently referred to as RKS or SRK) accurately predicts the vapor pressures at reduced temperatures ranging from about 0.6 to 1.0. Since the  $\alpha$  form is generalized in terms of the acentric factor, it is fully predictive for nonpolar compounds with acentric factors not exceeding about 0.6 (thus excluding heavy hydrocarbons).

The Soave function played a pivotal role in the development of cubic equations of state and greatly contributed to their acceptance as tools for vapor-liquid equilibrium calculations. It was used in conjunction with other equations of state such as those developed by Peng and Robinson (14), Schmidt and Wenzel (15), Patel and Teja (16), Adachi *et al.* (17) and Watson *et al.* (18). Only the dependence of  $m$  on  $\omega$  had to be changed to accommodate other equations of state. Further improvements of the  $\alpha$  form focused on three problems:

1. Introduction of adjustable parameters to correlate the vapor pressure of any fluids, without the restriction to nonpolar fluids;
2. Improvement of the behavior of the  $\alpha$  form in the supercritical region;
3. Development of generalized forms that overcome the limitations of Soave's function at low reduced temperatures and for large acentric factors.

The introduction of substance-specific parameters is necessary to obtain a satisfactory correlation of vapor pressures of polar or associating compounds. Several empirical extensions of the Soave function have been proposed for this purpose. Among the most significant modifications, Mathias and Copeman (19) proposed a three-parameter form:

$$\alpha = \left[ 1 + c_1(1 - T_r^{1/2}) + c_2(1 - T_r^{1/2})^2 + c_3(1 - T_r^{1/2})^3 \right]^2 \quad (4.15)$$

Soave (20) proposed a two-parameter equation:

$$\alpha = 1 + m(1 + T_r) + n(T_r^{-1}) \quad (4.16)$$

Stryjek and Vera (21) developed an equation with one generalized ( $k_0$ ) and one adjustable ( $k_1$ ) parameter:

$$\alpha = \left\{ 1 + \left[ k_0(\omega) + k_1(1 + T_r^{1/2})(0.7 - T_r) \right] (1 - T_r^{1/2}) \right\}^2 \quad (4.17)$$

Androulakis *et al.* (22) analyzed several two- and three-parameter forms of the  $\alpha$  function and recommended a three-parameter form:

$$\alpha = 1 + d_1(1 - T_r^{2/3}) + d_2(1 - T_r^{2/3})^2 + d_3(1 - T_r^{2/3})^3 \quad (4.18)$$

and its simplified version with  $d_2=0$ .

An optimum  $\alpha$  function should be positive at all temperatures to prevent the attractive parameter from switching from positive to negative values. It should decrease continuously with temperature and reach zero at infinite temperature. The original function of Soave does not satisfy these requirements because it becomes negative at some temperatures in the supercritical region and then increases. The above modifications of the Soave function may also share this deficiency for some parameter sets. The simplest way to obtain a qualitatively correct  $\alpha$  function is to use an exponential form. Early exponential forms were proposed by Graboski and Daubert (23):

$$\alpha = c_1 \exp(-c_2 T_r) \quad (4.19)$$

and Heyen (24):

$$\alpha = \exp[c(1 - T_r^n)] \quad (4.20)$$

Melhem (25) analyzed several forms and recommended an exponential version of the Soave (20) equation:

$$\alpha = \exp\left[m(1 - T_r) + n(1 - T_r^{-1})\right]^2 \quad (4.21)$$

which has a similar accuracy, but extrapolates better above the critical temperature. Yu and Lu (26) developed a generalized exponential  $\alpha$  form:

$$\log_{10} \alpha = M(\omega)(A_0 + A_1 T_r + A_2 T_r^2)(1 - T_r) \quad (4.22)$$

Twu *et al.* (27) derived a modified exponential  $\alpha$  form and found that it is superior to other functions:

$$\ln \alpha = N(M - 1) \ln T_r + L(1 - T_r^{NM}) \quad (4.23)$$

Although the additional adjustable parameters provide the necessary flexibility, they do not guarantee the accurate simultaneous representation of vapor pressure and derivative properties. Therefore, it is advisable to obtain the  $\alpha$  form parameters by multiproperty regression. It is especially convenient to use vapor pressures and heat capacity departures simultaneously because  $C_p$  can be related to the second derivative of the vapor pressure, *cf.* Mathias and Klotz (28).

Another important area of research to improve the  $\alpha$  functions is the development of their extensions to heavy hydrocarbons, which are characterized by low reduced temperatures and high acentric factors. Carrier *et al.* (29) and Rogalski *et al.* (30,31) developed such a method in conjunction with the Peng-Robinson EOS (14). They divided hydrocarbons into thirteen groups and calculated the parameter  $b$  from additive contributions. The attractive parameter of a heavy hydrocarbon was expressed as

$$a = a(T_b) \left[ 1 + m_1 \left( 1 - (T / T_b)^{1/2} \right) + m_2 \left( 1 - T / T_b \right) \right] \quad (4.24)$$

where

$$\begin{aligned} m_1 &= Am + B \\ m_2 &= Cm + D \end{aligned} \quad (4.25)$$

The constants  $A$ ,  $B$ ,  $C$ , and  $D$  have universal values and, therefore, the only characteristic parameters are  $a(T_b)$  and  $m$ . The value of  $a$  at the normal boiling point  $T_b$  is determined from one vapor-pressure datum and  $m$  is calculated from group contributions. This fairly complicated technique gives very good results for vapor pressures of heavy hydrocarbons at low reduced temperatures.

A particularly simple and elegant approach has been proposed by Twu *et al.* (32), who observed that the  $\alpha$  function should be linear with respect to the acentric factor, *i.e.*,

$$\alpha = \alpha^{(0)} + \omega(\alpha^{(1)} - \alpha^{(0)}) \quad (4.26)$$

This is in sharp contrast with the original Soave form, which is equivalent to a fourth-order equation with respect to the acentric factor. The linearity of the  $\alpha$  form is remarkably good and makes it possible to make extrapolations for compounds with high acentric factors. Both terms  $\alpha^{(0)}$  and  $\alpha^{(1)}$  are expressed by the same function of reduced temperature, see Equation (4.23). The method is applicable to any cubic equation of state.

A different approach has been proposed by Dohrn (33), who developed a correlation for two-parameter cubic equations by using the liquid density at 20°C and the normal boiling point as characteristic parameters instead of  $T_c$ ,  $P_c$  and  $\omega$ . While this approach may be advantageous for large molecules, it does not address the issue of diminished accuracy at low reduced temperatures.

Besides the generalizations for hydrocarbons and other nonpolar fluids, several attempts have been made to generalize the  $\alpha$  form for polar fluids. Such attempts are hampered by the lack of a truly effective characterization parameter for polar fluids that would be comparable to the acentric factor for nonpolar fluids. For example, Guo *et al.* (34) utilized the dipole moment and Valderrama *et al.* (35) used the product  $\omega z_c$  where  $z_c$  is the critical compressibility factor. Although such correlations are adequate for selected groups of polar compounds, they cannot be generally valid in the whole universe of polar, associating and nonpolar compounds. Therefore, the use of individual parameters for polar and associating fluids should be regarded as the only safe approach.

In contrast to the attractive parameter, the repulsive parameter  $b$  of cubic equations of state is usually kept independent of temperature. A temperature-dependent parameter  $b$  usually does not lead to any significant improvement of the equation's accuracy. As shown by Salim and Trebble (36), a temperature-dependent  $b$  is even dangerous because it results in the prediction of negative heat capacities at constant volume when the pressure exceeds a certain value.

#### 4.1.2 Functional Form of the Pressure-Volume Relationship

While an appropriate temperature dependence of the attractive parameter is sufficient for the accurate representation of vapor pressures, the functional form of the pressure-volume relationship is important for the prediction of volumetric properties. To keep the cubic form of the equation of state, at most five parameters can be used on an isothermal basis. Since the two-parameter Redlich-Kwong EOS gives a reasonable representation of fluid properties, it might appear that a five-parameter EOS would be vastly superior. Unfortunately, this intuitive reasoning is not true. In fact, the additional parameters can bring only a limited incremental improvement of the accuracy because of the fundamental limitations of the cubic form.

The most popular modification of the pressure-volume relationship, due to Peng and Robinson (14), does not involve any additional parameters beyond the original two. Peng and Robinson recognized that the critical compressibility factor of the Redlich-Kwong EOS, which is equal to 0.333, is greater than the compressibility factors of practically all fluids. Therefore, they postulated a function that reduces  $z_c$  to 0.307:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (4.27)$$



The Peng-Robinson EOS predicts better liquid volumes for medium-size hydrocarbons and other compounds with intermediate values of the acentric factor. However, it is worse than the Soave-Redlich-Kwong EOS for compounds with small acentric factors.

When a third parameter is introduced into a cubic EOS, the critical compressibility factor becomes substance dependent. Although a three-parameter equation can be forced to predict the correct critical compressibility factor, the isotherms at low and high pressures are then distorted much more than can be tolerated for the purposes of modeling PVT relations. Better overall results are usually obtained when the apparent (calculated) compressibility factor  $\zeta$  is greater than the real one  $z_c$ . Early three-parameter cubic equations of state were proposed by Fuller (37) and Heyen (24). These two equations involve temperature-dependent co-volumes  $b$ , which adversely affects their accuracy for derivative properties.

A well-known three-parameter cubic EOS was proposed by Schmidt and Wenzel (15), who designed their equation as a form of interpolation between the Soave-Redlich-Kwong and Peng-Robinson equations. This interpolation ensures a better representation of liquid volumes over a reasonable range of acentric factors. Schmidt and Wenzel analyzed a general form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ubv + wb^2} \quad (4.28)$$

and constrained the parameters  $u$  and  $w$  by

$$u = 1 - w \quad (4.29)$$

Additionally, they related  $w$  to the acentric factor by  $w = -3\omega$ . The apparent critical compressibility factor was found to be a linear function of the acentric factor.

Other three-parameter cubic equations were proposed by Harmens and Knapp (38):

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + vcb - (c-1)b^2} \quad (4.30)$$

and Patel and Teja (16):

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + c(v-b)} \quad (4.31)$$

Patel and Teja treated the apparent compressibility factor as an adjustable parameter, which is temperature dependent for  $0.9 < T_r < 1.0$ .

Yu and Lu (26) considered the four-parameter form proposed originally by Schmidt and Wenzel (Equation (4.28)) and arrived at a different constraint for the parameters  $u$  and  $w$ , *i.e.*,  $u-w = 3$ . Their final equation takes the form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+c) + b(3v+c)} \quad (4.32)$$

where  $c = wb$ . Twu *et al.* (39) systematically analyzed the cubic equations of state on a  $u-w$  diagram with respect to the representation of volumetric properties. They checked 21 possible

combinations of  $u$  and  $w$  for a number of alkanes, alcohols and glycols. The optimum constraint was found to be  $u-w=4$ , which is closer to the result of Yu and Lu than to that of Schmidt and Wenzel. This gives the form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+4b)+c(v+b)} \quad (4.33)$$

with the apparent critical compressibility factor optimized as a third parameter.

In the development of these three-parameter equations, use was made of the fact that acceptable representation of both low- and high-density regions requires that the apparent critical compressibility factor be treated as an empirical parameter. A simple, yet useful method to achieve this is the so-called volume translation. This concept, proposed by Martin (40) and refined by Peneloux *et al.* (41), is based on a translation along the volume axis, *i.e.*,

$$v_i^{\text{translated}} = v_i^{\text{original}} - c_i \quad (4.34)$$

If the translation parameter  $c$  for a mixture is related to composition by a linear mixing rule, the partial molar volumes are also translated and the fugacities are multiplied by a composition-independent coefficient so that the phase-equilibrium conditions (*i.e.*, the isofugacity criteria) are not affected by the volume translation. Peneloux *et al.* (41) showed that this method markedly improves the prediction of liquid volumes except in the vicinity of the critical point. It should be noted that the original van der Waals EOS becomes, after volume translation, identical to the Clausius EOS (3). Martin (40) found the Clausius EOS to be the best cubic equation with respect to the representation of gas-phase properties. Joffe (42) and Kubic (43) used the Clausius EOS in a modified form. Salerno *et al.* (44), Czerwinski *et al.* (45) and Androulakis *et al.* (22) presented a translated van der Waals EOS, called vdW-711, that contains a temperature-dependent volume translation. The translating function was fitted to experimental liquid volumes including the critical volume and generalized in terms of the acentric factor.

A somewhat different volume translation was presented by Mathias *et al.* (46), namely

$$v^{\text{translated}} = v^{\text{original}} + s + f_c \left( \frac{0.41}{0.41 + \delta} \right) \quad (4.35)$$

where  $\delta$  is the bulk modulus,

$$\delta = -\frac{v^2}{RT} \left( \frac{\partial P}{\partial v} \right)_T \quad (4.36)$$

and the correction function  $f_c$  is chosen so that the actual critical volume is obtained:

$$f_c = v_c - (v_c^{\text{original}} + s) \quad (4.37)$$

Although a volume translation, defined in such a way, is very accurate, it introduces a thermodynamic inconsistency into the calculations because the bulk modulus is a function of

the equation of state and, therefore, the fugacity and volume calculations are not decoupled as in Peneloux's method. It is interesting to note that the concept of volume translation has even been used to develop an equation of state that reproduces the solid phase (47).

It should be noted that the invariance of the isofugacity condition with respect to the (original) volume translation is only one example of the useful mathematical properties of the cubic equations. In particular, Leibovici (48) showed that the properties calculated from the generic Schmidt-Wenzel EOS (see Equation (4.28)) can be divided into two classes, called variant and invariant properties. The variant properties depend on the individual parameters whereas the invariant properties depend only on the combined quantity

$$K = \frac{1 + u + w}{(u + 2)^2} \quad (4.38)$$

The difference of fugacities is an example of an invariant property. Other invariant properties include entropy, heat capacity at constant  $P$  or  $V$ , enthalpy of vaporization, internal energy and Helmholtz energy. On the other hand, volume is an example of the variant properties, which also include enthalpy, sound velocity, Joule-Thomson coefficient, Gibbs energy, isothermal compressibility and adiabatic compressibility. Thus, the volume translation can be applied to improve the representation of any variant property while keeping the invariant properties constant.

In addition to the three-parameter cubic EOS discussed above, several authors tried to improve the flexibility of cubic equations by using four or five parameters. A four-parameter form was used by Trebble and Bishnoi (49) and Salim and Trebble (50):

$$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + (b + c)v - (bc + d^2)} \quad (4.39)$$

Five-parameter cubic equations were analyzed by Adachi *et al.* (51) in the traditional two-term form, *i.e.*,

$$P = \frac{RT}{v - b} - \frac{a(T)[v - c(T)]}{[v - b][v - d(T)][v + e(T)]} \quad (4.40)$$

and by Kumar and Starling (52) in a generic form, *i.e.*,

$$z = \frac{1 + d_1(T)\rho + d_2(T)\rho^2}{1 + d_3(T)\rho + d_4(T)\rho^2 + d_5(T)\rho^3} \quad (4.41)$$

The Kumar-Starling EOS was more recently modified by Chu *et al.* (53), who added additional temperature-dependent functions in the near-critical region and attempted to generalize the parameters for polar fluids.

The results obtained from the four- and five-parameter equations are only slightly better than those obtained from the three-parameter EOS. In most cases, the differences resulting from a more flexible  $P$ - $V$  dependence are masked by the temperature dependence of parameters. It should be noted that, in contrast to other cubic equations, the original Kumar-

Starling EOS was not constrained at the critical point, which automatically improves the results in the far-from-critical regions.

The results of several authors indicate that cubic equations of state require at least three parameters for a reasonable representation of both vapor and liquid volumes. More than three parameters lead to only small incremental improvements. The attractive parameter has to be temperature-dependent. However, the temperature dependence of other parameters, such as the co-volume, may lead to spurious results. It appears that the property that can be most easily correlated using cubic equations of state is the vapor pressure. It is customary that cubic equations can predict vapor pressure within 1 - 2 % when their parameters are generalized in terms of  $T_c$ ,  $P_c$  and  $\omega$ . With parameters fitted to an individual fluid's properties, the deviations can drop to a fraction of a percent. The liquid and vapor volumes can be predicted within 3 - 4 % by the more advanced equations with at least three parameters. All cubic equations give a very poor performance in a relatively wide "near-critical" region. This is not only due to the fact that every cubic equation shows classical critical behavior. Another reason for this deficiency is the relative rigidity of the cubic form, which imposes limits on the quality of the representation of derivative properties such as residual enthalpy, entropy and heat capacity. Not surprisingly, the enthalpy of vaporization is usually the derivative property that is most accurately reproduced by cubic equations. This results from the fact that the enthalpy of vaporization is related to the slope of the vapor pressure curve by the Clausius-Clapeyron equation. Therefore, the relative error of the predicted enthalpy of vaporization is usually very similar to the relative error of vapor pressure. However, the residual enthalpies of the liquid and the vapor phases are usually predicted with a significantly lower accuracy. Second-order derivative properties such as the specific heat capacities  $C_p$  and  $C_v$  as well as the Joule-Thomson coefficient are predicted with a still lower accuracy, but the results are usually reasonable (*i.e.*, deviations of the order of 10 - 15 % are typical). The equations that are correctly constructed (*i.e.*, with carefully introduced temperature-dependent parameters) produce consistent results and anomalies are usually not detected. One of the few anomalies that is commonly detected in cubic equations of state is their failure to qualitatively reproduce  $C_v$  in the critical region, *cf.* Salim and Trebble (50). In fact, all cubic equations of state give physically incorrect  $C_v$  versus density relationships within *ca.* 20-30 K from the critical point. Numerical values of deviations between experimentally determined properties (*i.e.*, residual thermodynamic functions and  $PVT$  properties) and those predicted from selected cubic equations of state can be found in the papers of Trebble and Bishnoi (49), Salim and Trebble (50), Lielmezs and Mak (54), Mak and Lielmezs (55) and Solimando *et al.* (56) and in chapter 4 of Malanowski and Anderko (57).

For practical purposes, cubic equations can be easily tailor-made to fit specific properties in a specified range, *e.g.*, by adjusting the parameters of the temperature-dependent attractive term or by making a volume translation. However, it should be noted that such fine-tuning may result in inaccurate extrapolations, *e.g.*, in the supercritical region.

## 4.2 EQUATIONS BASED ON THE GENERALIZED VAN DER WAALS THEORY

Although the original van der Waals equation was developed on the basis of simple molecular concepts, cubic equations of state can be regarded as nothing more than comprehensive empirical correlations of fluid properties. Although a cubic EOS can work very well as a whole, neither its repulsive nor its attractive terms reflect the physical reality.

Therefore, numerous researchers focused their efforts on the development of equations of state with clear physical foundations.

The basic premise of the generalized van der Waals theory is the separation of the repulsive and attractive contributions to pressure. Originally postulated by van der Waals in 1873, it was theoretically established several decades later by Zwanzig (58), Hemmer *et al.* (59) and Barker and Henderson (60) for some model intermolecular potentials. Subsequently, more practically-oriented approaches were presented by Vera and Prausnitz (61), Sandler (62), Lee *et al.* (63), Lee and Sandler (64) and Abbott and Prausnitz (65). The development of equations of state based on the generalized van der Waals theory was strongly influenced by the progress in the theory of hard-body fluids, which are commonly used to model the effects of repulsive interactions. Since the structure of fluids has been shown to be determined primarily by repulsive forces, the equations of state for hard-body fluids can be conveniently used as reference terms for equations of state for real fluids.

Carnahan and Starling (66) developed an accurate equation of state for hard spheres, *i.e.*,

$$z_{\text{rep}} = \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} \quad (4.42)$$

where  $\xi = \pi\rho\sigma^3/6$  is the reduced density with  $\sigma$  being the hard-sphere diameter. This equation has been extended to hard convex bodies by Boublik and Nezbeda (67):

$$z_{\text{rep}} = \frac{1 + (3\alpha - 2)\xi + (3\alpha^2 - 3\alpha + 1)\xi^2 - \alpha^2\xi^3}{(1 - \xi)^3} \quad (4.43)$$

where  $\alpha$  is the nonsphericity parameter defined as  $\alpha = R_0S_0/V_0$ , where  $R_0$ ,  $S_0$  and  $V_0$  are the mean curvature, mean surface and volume of the hard convex body, respectively. A different expression for the effect of hard-core geometry on molecular repulsions was formulated by Naumann *et al.* (68). Tildesley and Streett (69) obtained an accurate expression for dimers (or dumbbells). More recently, several authors (70-72) obtained equations of state for hard-sphere-chain fluids.

Several authors combined the rigorous hard-body repulsive terms with empirical attractive terms that had been used earlier in cubic equations of state. In early attempts to utilize the hard-core repulsive terms to construct equations for real fluids, the simple van der Waals or Redlich-Kwong attractive terms were employed as perturbations by Carnahan and Starling (73). The Carnahan-Starling - van der Waals EOS was further studied by Anderson and Prausnitz (74) and Dimitrelis and Prausnitz (75). More recently, the Carnahan-Starling EOS was combined with the Schmidt-Wenzel attractive term (76) and the Patel-Teja attractive term (77). The Carnahan-Starling EOS was also used with attractive terms expressed by truncated virial expressions (78-81). For example, Dohrn and Prausnitz (81) formulated an attractive term that optimizes the representation of the critical isotherm for several fluids:

$$z = z_{\text{rep}}(CS) - \frac{4a}{RTb} \eta(1 - 1.41\eta + 5.07\eta^2) \quad (4.44)$$

where  $\eta = b / 4v$ .

The combinations of the Carnahan-Starling repulsive term and various empirical attractive terms are not more accurate than comparable cubic equations with respect to the representation of pure fluid properties. They are usually reported to give better predictions of volumes in the high-density region, but this is mostly due to the fact that they are not constrained at the critical point, which facilitates the fitting of volumes. Thus, they are mostly useful for testing and developing mixing rules, for which a correct separation of repulsive and attractive terms may be advisable.

Further progress in the area of generalized van der Waals equations of state resulted from the use of molecular-simulation data, which made it possible to establish accurate attractive terms for selected intermolecular potentials. For example, Alder *et al.* (82) obtained an expression for the attractive term of a square-well fluid:

$$z_{\text{attr}} = \sum_{n,m} m D_{nm} (u / kT)^n (v^0 / v)^m \quad (4.45)$$

where  $u$  is the characteristic energy,  $v^0$  is the hard-core volume and  $D_{nm}$  are numerical coefficients. An alternative expression for the attractive term of a square-well fluid was proposed by Heilig and Franck (83), who constructed a Padé approximant from the second and third virial coefficients:

$$z_{\text{attr}} = \frac{Bv}{(v^2 - vC / B)} \quad (4.46)$$

where both  $B$  and  $C$  are expressed in terms of the square-well parameters.

The theoretically based repulsive and attractive terms have been used by several authors to construct generalized van der Waals - type equations of state. Chen and Kreglewski (84) and Kreglewski and Chen (85) combined Equations (4.43) and (4.45) into the BACK (Boublik-Alder-Chen-Kreglewski) equations of state. They determined the parameters  $D_{nm}$  from the residual energy and volumetric data of argon and treated them as universal constants. Both hard-core volume and characteristic energy were assumed to be temperature-dependent:

$$v^0 = v^{00} [1 - C \exp(-3u^0 / kT)]^3 \quad (4.47)$$

$$u / k = (u^0 / k) (1 + \eta / kT) \quad (4.48)$$

The BACK equation contains three parameters that have to be determined from experimental data, *i.e.*,  $v^{00}$ ,  $\alpha$  and  $u^0/k$ . The remaining parameters are assigned fixed values.

Beret and Prausnitz (86) and Donohue and Prausnitz (87) created the first generalized van der Waals-type equation of state that was designed for chains of segments. They utilized Prigogine's (88) arguments that the rotational and vibrational contributions to the canonical partition function can be factorized as

$$q_{r,v} = (q_{r,v})_{\text{ext}} (q_{r,v})_{\text{int}} \quad (4.49)$$

where  $(q_{r,v})_{\text{ext}}$  and  $(q_{r,v})_{\text{int}}$  are the external (density-dependent) and internal (density-independent) contributions to the partition function, respectively. The essential assumption was that the external contributions could be calculated in essentially the same way as the contributions of translational motion. Since the contribution of each translational degree of freedom is  $(q_{\text{rep}}q_{\text{attr}})$  and the total number of external degrees of freedom is assumed to be equal to a substance-specific parameter  $3c$ , the canonical partition function is postulated to be

$$Q = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N (q_{\text{rep}}q_{\text{attr}})^{Nc} (q_{r,v})_{\text{int}} \quad (4.50)$$

where  $\Lambda$  is the thermal de Broglie wave length. This partition function has two characteristic features. First, the ideal-gas term  $(V/\Lambda^3)^N$  is factorized so that the ideal-gas limit can be recovered (which is not the case in the original work of Prigogine). Second, the substance-specific number of external degrees of freedom in a system of  $N$  molecules, equal to  $Nc$ , replaces the number of molecules in the part of the partition function that accounts for nonideality (*i.e.*,  $(q_{\text{rep}}q_{\text{attr}})^{Nc}$ ). The partition function factorized in this way gives rise, according to elementary statistical thermodynamics, to a general expression for the compressibility factor:

$$z = 1 + c(z_{\text{rep}} + z_{\text{attr}}) \quad (4.51)$$

where  $z_{\text{rep}}$  is calculated from the Carnahan-Starling equation corrected for the ideal-gas term and  $z_{\text{attr}}$  is obtained from the equation of Alder *et al.* (82). The complete equation was called PHCT (Perturbed-Hard-Chain Theory). Similarly to the BACK EOS, the PHCT equation contains three parameters for each substance: the characteristic temperature  $T^*$  related to the depth of the potential well, characteristic volume  $v^*$  related to the size of the segments and one-third of the external degrees of freedom  $c$ . These parameters were found to correlate smoothly within homologous series of hydrocarbons.

The PHCT EOS was further refined by Morris *et al.* (89), who replaced the attractive term based on the square-well potential by one based on the Lennard-Jones potential. Jin *et al.* (90) recast this equation in terms of group contributions. Cotterman *et al.* (91) improved the performance of PHCT at low densities by separating the attractive Helmholtz energy into high- and low-density contributions and applying a switching function to interpolate between them. Kim *et al.* (92) developed a simplified version of PHCT (SPHCT = Simplified Perturbed-Hard-Chain Theory) by replacing the complex attractive part of PHCT by a simpler expression that combines ingredients of the radial distribution function theory for square-well molecules with the lattice statistics for chain molecules:

$$z_{\text{attr}} = -z_M \frac{cv^*Y}{v + v^*Y} \quad (4.52)$$

with

$$Y = \exp(\epsilon q / 2ckT) - 1 \quad (4.53)$$

where  $z_M$  is the maximum coordination number,  $\varepsilon$  is the characteristic energy per unit surface area and  $q$  is the normalized surface area.

Chien *et al.* (93) developed their COR (Chain of Rotators) EOS by adopting a different approximation for the chain-like structure of molecules than that used in PHCT and related models. They suggested treating the first segment of a chain-like species like a free molecule. The subsequent segments are assumed to rotate about their neighbors. Therefore, the configurational (*i.e.*, excluding the internal degrees of freedom) canonical partition function is given by

$$Q_{\text{conf}} = Q_t q_r^{N_c} Q_{\text{attr}} \quad (4.54)$$

where  $Q_t$  is the translational partition function calculated in analogy to that of a spherical molecule,  $q_r$  is the partition function of an elementary rotator and  $c$  is the number of rotational degrees of freedom of the chain.  $Q_t$  is calculated from the Carnahan-Starling expression whereas  $q_r$  is evaluated by forcing Equation (4.54) to represent the partition function of a hard dumbbell, *i.e.*,  $Q_{\text{db}} = Q_t q_r^{2N}$ . The obtained expression is arbitrarily assumed to be valid for chains containing more than one segment. The  $Q_{\text{attr}}$  contribution is calculated from the expression of Alder *et al.* given by Equation (4.45). The main difference between COR and PHCT is in the term that is not affected by the  $c$  parameter. In the case of PHCT, it is the ideal-gas term. In COR, it is the single-segment translation term.

Deiters (94) developed a different generalized van der Waals EOS by deriving a semi-empirical approximation for the radial distribution function for square-well fluids, involving corrections for nonspherical molecular shape, "soft" repulsive potential and three-body effects. The equation was shown to reproduce the *PVT* behavior in a large pressure range using only three characteristic parameters.

An important equation for fluids with chain-like molecules was proposed by Chapman *et al.* (95) and Huang and Radosz (96). This equation, called SAFT (Statistical Associating Fluid Theory), is a combination of Wertheim's (97) perturbation theory for intermolecular association and chain formation with the usual expressions of Carnahan and Starling and Alder *et al.* In the SAFT equation, the Helmholtz energy (and all thermodynamic functions that can be derived from it) is expressed as

$$A = A^{\text{ig}} + A^{\text{seg}} + A^{\text{chain}} + A^{\text{assoc}} \quad (4.55)$$

where the four terms on the right hand side represent contributions from the ideal gas, intermolecular interactions between segments, the formation of chains from segments and association. The segment Helmholtz energy is

$$A^{\text{seg}} = r(A^{\text{hs}} + A^{\text{disp}}) \quad (4.56)$$

where  $r$  is the number of segments and  $A^{\text{hs}}$  and  $A^{\text{disp}}$  are the hard-sphere and dispersive contributions for a single segment, respectively. The  $A^{\text{hs}}$  and  $A^{\text{disp}}$  terms are calculated from the Carnahan-Starling and modified Alder *et al.* expressions, respectively. The  $A^{\text{chain}}$  and  $A^{\text{assoc}}$  terms are obtained from Wertheim's perturbation theory of association. For more information about this theory, the reader is referred to the chapter of this book that deals with associated fluids (Chapter 12).



More recently, Song *et al.* (98) presented a different equation, called PHSC (Perturbed Hard-Sphere Chain). It is based on Chiew's (72) Percus-Yevick integral-equation theory for chain molecules. The methods for treating chain molecules in both SAFT and PHSC are firmly based on statistical mechanics and are superior to those used in PHCT or COR. Both SAFT and PHSC have been shown to be very useful primarily for systems containing polymers even though they can also be applied to other systems (*e.g.*, SAFT was used for heavy hydrocarbons). A more complete discussion of PHSC and SAFT can be found in the chapter on equations of state for polymer systems (Chapter 14).

Several authors attempted to improve the performance of generalized van der Waals-type equations for polar fluids by adding an additive term that explicitly accounts for anisotropic interactions that result from the presence of dipoles and quadrupoles. A perturbation theory for mixtures of multipolar fluids was developed by Gubbins and Twu (99) following an earlier work of Stell *et al.* (100). Vimalchand and Donohue (101) incorporated the perturbation expansion of Gubbins and Twu into the PHCT EOS. The resulting equation, called PACT (Perturbed-Anisotropic-Chain Theory) contains an additional  $z^{\text{ani}}$  term:

$$z = 1 + c(z^{\text{rep}} + z^{\text{iso}} + z^{\text{ani}}) \quad (4.57)$$

Similarly, Saager and Fischer (102) added dipolar and quadrupolar terms to the BACK equation. For the dipolar and quadrupolar terms, they used expressions fitted to molecular simulation data. Since the anisotropic term from the perturbation theory is quite complex, several simplified expressions have been developed. A particularly simple formula was proposed by Bryan and Prausnitz (103), who incorporated dipolar effects into a single term whose density dependence is identical to that of the Carnahan-Starling term:

$$z^{\text{rep+dipolar}} = \frac{1 + f^{[1]}\eta + f^{[2]}\eta^2 - f^{[3]}\eta^3}{(1 - \eta)^3} \quad (4.58)$$

where  $f^{[1]}$ ,  $f^{[2]}$  and  $f^{[3]}$  are functions of the reduced dipole moment. Brandani *et al.* (104) developed an equation of state on the basis of this term. Another simplification of the multipolar term was proposed by Sheng and Lu (105).

The main reason for introducing the multipolar terms into generalized van der Waals - type equations of state is to improve the predictions for mixtures. It has been found that smaller values of binary parameters are needed when the multipolar terms are taken into account and, in favorable cases, phase equilibria can be predicted without any binary parameters. The multipolar terms are, in general, not needed for improving the representation of pure fluid properties. It should be noted that the improvement for mixed fluids is usually limited to mixtures that contain multipolar and nonpolar, but not hydrogen-bonding fluids. However, the usefulness of the dipolar term has also been demonstrated for systems such as NaCl + H<sub>2</sub>O or KCl + H<sub>2</sub>O at very high temperatures (106).

A different, more empirical approach to decoupling the effect of polar interactions from the rest of the equation of state has been proposed by Lee and Chao (107). They postulated that the properties of hydrogen-bonding fluids could be treated using the dipolar-fluid formalism and separated the nonpolar and polar contributions to the pressure of water:

$$P = P_{\text{rep}} + P_{\text{att,np}} + P_{\text{att,p}} \quad (4.59)$$

where the subscripts np and p stand for the nonpolar and polar contributions, respectively. The nonpolar contribution was evaluated from the BACK EOS with parameters determined from the Lennard-Jones constants that represent the nonpolar interactions in water. The polar contribution was obtained by forcing the complete equation of state to be identical with the accurate multiparameter EOS developed by Keenan *et al.* (108). Later, Lee and Chao (109) and Peng and Chao (110) developed closed-form empirical expressions for  $P_{\text{att,p}}$ . The model was also extended to other polar fluids using a corresponding-states transformation. For mixtures, the model requires two binary parameters in the BACK EOS. The polar pressure is extended to mixtures using a corresponding-states-based technique. In this approach, the effects of hydrogen bonding are not treated explicitly and the polar term effectively describes both dipole-dipole and hydrogen-bonding interactions. The equation was shown to give good accuracy for correlating phase equilibria in aqueous hydrocarbon systems. It should be noted, however, that equations of state that explicitly take into account hydrogen bonding (described here in Section 4.5) can give similar results for aqueous hydrocarbon systems with only one binary parameter and have a simpler form.

The main virtue of the equations based on the generalized van der Waals theory is their ability to represent the saturated properties and *PVT* data outside of the saturation region using only a few (typically three) substance-dependent parameters. However, they contain a large number of universal parameters and their functional form is much more complex than that of cubic equations of state. Although the characteristic parameters of these equations are not correlated with the critical temperature, pressure and acentric factor, they usually follow well-established patterns. For example, the parameters of the SAFT EOS follow regular linear correlations within some homologous series of hydrocarbons (96). This makes it possible to apply the equation to heavy hydrocarbons, for which very little experimental information is available. It is becoming increasingly evident, however, that this family of equations is most useful for systems containing polymers as well as small molecules. For such systems, cubic equations of state appear to be not very well suited whereas models like SAFT and PHSC are at their best.

### 4.3 SIMPLE EQUATIONS INSPIRED BY THE GENERALIZED VAN DER WAALS THEORY

Several researchers have presented methods that attempt to combine the simplicity of cubic equations of state with the theoretical background of equations based on the augmented van der Waals theory. This approach has resulted in the development of models that include reformulated cubic equations, quartic equations (which still can be solved analytically) and higher-order polynomials. In the majority of models of this type, the Carnahan-Starling hard-sphere term is replaced by a simple approximation, *i.e.*,

$$z_{\text{rep}} = \frac{v + c}{v - b} \quad (4.60)$$

This term can be used to approximate the Carnahan-Starling expression by appropriately adjusting the parameter  $c$  or by expressing it as a function of  $b$  and other parameters.

An early example of such an approximation is the expression of Scott (111), in which the parameter  $c$  is related to the co-volume  $b$ , *i.e.*,

$$z_{\text{rep}} = \frac{2v + b}{2v - b} \quad (4.61)$$

This equation was later combined with the Redlich-Kwong attractive term by Ishikawa *et al.* (112) to yield a cubic EOS. A more complex cubic EOS was developed by Guo *et al.* (113) and Kim *et al.* (114), who simplified the COR EOS. The simplified equation, called CCOR (Cubic Chain of Rotators), contains analytical approximations for the hard-core and rotational-pressure contributions in COR:

$$P = \frac{RT(1 + 0.77b/v)}{v - 0.42b} - \frac{c^R(0.055RTb/v)}{v - 0.42b} - \frac{a(T)}{v(v + c(T))} - \frac{bd}{v(v + c(T))(v - 0.42b)} \quad (4.62)$$

Unlike in most modern cubic equations of state, the critical compressibility factor in the CCOR EOS is constrained to match the experimental value. This appears to impair the equation's performance in some regions of  $PVT$  space.

Several authors developed quartic equations of state in the attempt to improve the prediction of  $PVT$  properties. Among them, Kubic (115) developed a quartic equation of state by simplifying the Beret-Prausnitz generalized van der Waals partition function:

$$P = \frac{RT}{v} - \frac{1.19cbRT}{v(v - 0.42b)} - \frac{a}{(v + d)^2} \quad (4.63)$$

Soave (116) developed a quartic EOS by combining a modified form of Equation (4.60) with a generic attractive term, *i.e.*,

$$P = \frac{RT}{v} \left( 1 + c \frac{b}{v - b} - \frac{av}{(v + d)(v + e)} \right) \quad (4.64)$$

Soave further reduced the number of independent adjustable parameters to three and found that the quartic equation was superior to cubic equations in the supercritical-fluid region. Another quartic EOS was developed by Shah *et al.* (117), who obtained a repulsive term by fitting molecular-simulation results for hard spheres:

$$P = \frac{RT}{(v - k_0b)} + \frac{\beta k_1 RT}{(v - k_0\beta)^2} - \frac{av + k_0\beta c}{v(v + e)(v - k_0\beta)} \quad (4.65)$$

where  $k_0$ ,  $k_1$ ,  $e$  and  $\beta$  are coefficients regressed from simulation data. In the above equation, the first two terms on the right-hand side form the repulsive contribution and the third term is an attractive contribution, obtained by fitting experimental data for argon.

An equation of a higher order was proposed by Anderko and Pitzer (118), *i.e.*,

$$P = \frac{RT}{v} \left( \frac{1 + c\rho_r}{1 - b\rho_r} \right) + \alpha\rho_r + \beta\rho_r^2 + \gamma\rho_r^3 \quad (4.66)$$

where  $\rho_r$  is the reduced density and the parameters  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$  are functions of reduced temperatures. Anderko and Pitzer found this equation to be very effective over large ranges of pressure and temperature.

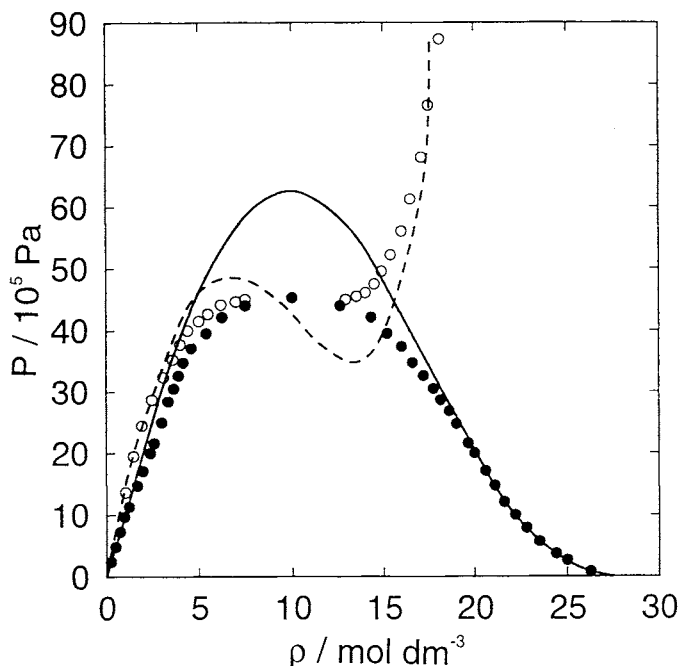
From the practical point of view, one of the main reasons for using the equations based on the generalized van der Waals theory (whether simplified or not) is their superiority over cubic equations of state with respect to the representation of  $PVT$  properties, especially in the supercritical region and for dense liquids. This is usually achieved with a reasonable number of parameters. However, it should be kept in mind that most of the equations based on the generalized van der Waals theory are not constrained to reproduce the critical point (Deiters' equation (94), Soave's quartic equation (116) and the implementation of the SPHCT EOS by van Pelt et al. (231) are notable exceptions). This is due to the fact that their form is usually too complex to derive analytical relations for the critical point. As a result, the equations overshoot the critical temperature and pressure by considerable amounts. Such behavior is unavoidable when no near-critical corrections are introduced and is very similar for practically all equations that are not constrained at the critical point. This is illustrated in Figure 4.1 for methane. It should be noted that, if the equations were constrained at the critical point, the overall numerical deviations between experimental data and predicted values would be worse. Thus, an equation that is not constrained at the critical point will usually perform better when compared with a large set of experimental data points. Therefore, the frequently published comparisons between generalized van der Waals-type equations that are not constrained at the critical point and cubic equations (which are usually constrained) should be taken with a grain of salt. Additionally, it should be noted that the overprediction of the critical point coordinates is a serious disadvantage for process simulation because it may result in qualitatively incorrect phase equilibrium calculations. Such a disadvantage is usually not compensated by a better prediction of  $PVT$  properties in most regions of the  $PVT$  phase diagram. This is one of several reasons why cubic equations are, by far, the most popular equations of state for industrial process design.

## 4.4 METHODS FOR EXTENDING EQUATIONS OF STATE TO MIXTURES

Representation of mixed-fluid properties is the main, if not the only, purpose of using cubic and generalized van der Waals equations of state. Whenever only pure fluids are of interest, equations of this kind are not the method of choice. Here, we outline the various methods for extending the equations discussed above to mixtures.

### 4.4.1 Classical Quadratic Mixing Rules

The classical quadratic mixing rules can be easily deduced from the composition dependence of virial coefficients, which is known from basic statistical thermodynamics. If we



**Figure 4.1** Vapor-liquid coexistence curve for methane calculated from a typical van der Waals-type equation of state by fitting its parameters to vapor-pressure and liquid-density data without imposing critical-point constraints (solid line). Experimental data are shown as solid circles. Also, the calculated critical isotherm is shown as a dashed line and compared with experimental data (hollow circles).

expand the original van der Waals EOS in a power series around zero density, we get

$$z = 1 + \sum_{i=1}^{\infty} \left( \frac{b}{v} \right)^i - \frac{a}{RTv} \quad (4.67)$$

This allows us to identify the second, third, and higher virial coefficients:

$$\begin{aligned} B &= b - a / RT \\ C &= b^2, D = b^3, \text{ etc.} \end{aligned} \quad (4.68)$$

To maintain consistency with the quadratic composition dependence of the second virial coefficient, the parameters  $a$  and  $b$  can be, at most, quadratic functions of composition. However, the cubic composition dependence of the third virial coefficient imposes a more stringent restriction that the parameter  $b$  should be only a linear function of composition. Very

similar conclusions can be reached for other equations of state. Thus, the simplest (although not the only possible) function for the attractive parameter is given by

$$a = \sum \sum x_i x_j a_{ij} \quad (4.69)$$

where the cross-term  $a_{ij}$  is related to the pure-fluid terms  $a_{ii}$  and  $a_{jj}$  by the geometric-mean rule with one adjustable binary parameter  $k_{ij}$ :

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) \quad (4.70)$$

The co-volume  $b$  is usually expressed by a linear mixing rule:

$$b = \sum x_i b_i \quad (4.71)$$

However, many authors use a quadratic mixing rule for  $b$  in analogy with the mixing rule for  $a$  even though it violates the composition dependence of the third and higher virial coefficients. In addition to the results obtained from the virial equation, the classical mixing rules are supported by the results of Leland *et al.* (119,120), who derived them from the theory of radial distribution functions.

In the case of the generalized van der Waals equations, the mixing rules are either analogous to the quadratic mixing rules described above, or are derived from more sophisticated theories. For the ubiquitous Carnahan-Starling term, an extension to mixtures has been derived by Boublik (121) and Mansoori *et al.* (122):

$$z = \frac{1 + (3DE / F - 2)\xi + (3E^3 / F^2 - 3DE / F + 1)\xi^2 - (E^3 / F^2)\xi^3}{(1 - \xi)^3} \quad (4.72)$$

with  $F = \sum x_i \sigma_i^3$ ,  $E = \sum x_i \sigma_i^2$  and  $D = \sum x_i \sigma_i$ . Dimitrelis and Prausnitz (75) found that this equation is superior to the one-fluid approximation (essentially given by Equation (4.71)) when applied to the correlation of VLE in mixtures of nonpolar molecules that appreciably differ in size. The mixing rules for the attractive terms are equation-specific, but they generally follow the form of Equations (4.69) and (4.71).

The classical quadratic mixing rules are, in general, suitable for the representation of phase equilibria in multicomponent systems containing nonpolar and weakly polar components. Their performance has been extensively tested by Han *et al.* (123) for seven van der Waals-type equations including five cubic ones. It should be noted that very similar results are obtained from vapor-liquid equilibrium calculations using various equations of state. This indicates that the form of the mixing rules is more important than the particular  $P$ - $V$ - $T$  relationship embodied in an EOS.

There are very few examples that would indicate the superiority of generalized van der Waals-type equations over cubic equations when it comes to the correlation of phase equilibria in typical nonpolar systems. Peters *et al.* (124) obtained better results from the SPHCT EOS (92) than from the Soave-Redlich-Kwong EOS for the correlation of the phase behavior of mixtures containing short and long n-alkanes. Ashour and Aly (125) found that the correlation of VLE for mixtures containing CO<sub>2</sub> and fatty-acid esters could be somewhat improved when

the Carnahan-Starling-Boublik-Mansoori expression was used as a repulsive term. Such findings are corroborated, to a certain extent, by the study of the topology of phase diagrams obtained from the Carnahan-Starling-Redlich-Kwong EOS by Kraska and Deiters (126) and the SPHCT EOS by van Pelt *et al.* (232). Although the global phase diagrams obtained from these equations are similar to those obtained from the van der Waals EOS when the components have equal sizes, significant differences appear when the sizes are different (*e.g.*, a new tricritical line).

In most practical applications, a linear mixing rule is used for the co-volume  $b$ . However, several authors used a quadratic form for  $b$  even though it violates the cubic composition dependence of the third virial coefficient. In this way, a second binary parameter can be introduced. This parameter is usually found to be useful for correlating VLE in mixtures with components of very different sizes, such as hydrogen and hydrocarbons (127). Similarly, it usually improves results for solid - supercritical-fluid equilibria because of the large size differences in such systems. This was demonstrated by Caballero *et al.* (128) for a large number of solid + supercritical fluid systems.

An important application of cubic equations of state with classical quadratic mixing rules is the modeling of reservoir-fluid phase behavior and volumetric properties. Research in this field was initiated by Katz and Firoozabadi (129), who showed that the Peng-Robinson EOS can be used to compute high-pressure reservoir crude VLE by characterizing the heptane-plus fraction and using a methane - last fraction adjustable binary parameter. This subject was reviewed by Firoozabadi (130), who concluded that the prediction of VLE in reservoir fluids is influenced mainly by the binary parameters between  $C_1$ ,  $CO_2$ ,  $N_2$  and the last fraction. Cubic equations are, however, deficient in the critical region, where they have a tendency to fail to predict sharp changes of saturation pressures and liquid-dropout curves. In general, the use of equations of state for modeling reservoir fluids requires judicious tuning of both pure-component and binary parameters because both phase equilibria and volumetric properties are of interest. For example, Aasberg-Petersen and Stenby (131) obtained accurate volumes and liquid-dropout curves by using a volume-translated cubic EOS and proposing a characterization procedure for the  $C_{7+}$  fraction. The performance of various equations of state for modeling reservoir fluids was analyzed by Danesh *et al.* (132) and Anastasiades *et al.* (133).

Methods for improving the performance of cubic equations of state in the near-critical region will not be discussed here because they are described in Chapter 11 of this book. However, it should be mentioned that some techniques have been proposed specifically for near-critical hydrocarbon mixtures and may be applicable to reservoir-fluid simulation (134-136).

In addition to phase equilibria, the van der Waals-type equations of state with classical mixing rules can be used to correlate thermodynamic functions such as excess enthalpy and excess volume. Several authors analyzed the prediction of excess enthalpies in mixtures containing nonpolar and weakly polar components (137-139). As shown by Casielles *et al.* (137) and Zebolsky and Renuncio (138), even complex shapes of  $H^E$  vs.  $x$  curves can be reproduced (*e.g.* curves in which  $H^E$  changes from positive to negative values depending on composition). Also, excess enthalpies in ternary systems can be reasonably predicted from binary data. A simultaneous representation of VLE and heats of mixing is possible, although it has not been investigated extensively. A particularly accurate simultaneous representation of VLE and  $H^E$  has been obtained by Abdoul *et al.* (218) using their group contribution method.

Van der Waals-type equations of state are also capable of representing excess molar volumes of fluid mixtures. For example, Serbanovic *et al.* (140) examined the application of cubic equations of state for the calculation of excess volumes in hydrocarbon mixtures and obtained satisfactory results. However, there is very little chance that excess volumes can be calculated simultaneously with vapor-liquid equilibria. The theoretical basis of the equations is too weak to predict consistently the different phenomena that manifest themselves in  $G^E$  and  $V^E$ . A successful simultaneous correlation can be obtained only in individual cases.

The classical quadratic mixing rules become inappropriate when applied to mixtures containing strongly polar and, in particular, associating components. A typical example of the failure of classical mixing rules for such systems is provided by mixtures of water and hydrocarbons. Fairly accurate results can be obtained only when different values of binary parameters are used for the water-rich and hydrocarbon-rich phases. This is, however, unacceptable because it leads to a thermodynamic inconsistency (141). A very convincing example of the failure of classical mixing rules for alcohol + hydrocarbon systems was presented by Trebble (142). Trebble used the Trebble-Bishnoi EOS, which makes it possible to use as many as four binary parameters by applying the quadratic mixing rules to its four constants. Even with four binary parameters, a satisfactory correlation of VLE for alcohol + hydrocarbon systems was not obtained. In the next three sections, we will discuss various techniques that have been used to create models that are applicable to strongly nonideal systems.

#### 4.4.2 Composition-Dependent Combining Rules

Since the classical quadratic mixing rules are not sufficiently flexible to correlate the phase behavior of mixtures containing strongly polar and associating components, several authors introduced empirical modifications to enhance their flexibility. These modifications effectively replace the composition-independent combining rule in Equation (4.70) with composition-dependent expressions.

Panagiotopoulos and Reid (143), Stryjek and Vera (21) and Adachi and Sugie (144) proposed three mathematically equivalent combining rules with two binary parameters. In the notation of Panagiotopoulos and Reid (143), the final mixing rule takes the form:

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} (1 - k_{ij} + (k_{ij} - k_{ji}) x_i) \quad (4.73)$$

Stryjek and Vera (21) also proposed another form, which they called a van Laar-type mixing rule because of a similarity with the van Laar equation for the excess Gibbs energy:

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} (1 - k_{ij} k_{ji} / (x_i k_{ij} + x_j k_{ji})) \quad (4.74)$$

Kabadi and Danner (145) proposed a two-parameter equation designed specifically for water + hydrocarbon mixtures:

$$a = x_1^2 a_{11} + x_2^2 a_{22} + 2x_1 x_2 [(a_{11} a_{22})^{1/2} (1 - k_{12}) + x_1 G(1 - T_{r1}^{0.8})] \quad (4.75)$$



where the subscript 1 denotes water. Correlations were established for the parameters  $k_{12}$  and  $G$  within homologous series of hydrocarbons. Michel *et al.* (146) and Daridon *et al.* (147) developed alternative correlations for mixtures containing water and hydrocarbons.

Schwartzentruber *et al.* (148) proposed a three-parameter expression to further enhance the flexibility of the Panagiotopoulos - Reid mixing rule:

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} \left[ 1 - k_{ij} - l_{ij} \frac{m_{ij} x_i - m_{ji} x_j}{m_{ij} x_i + m_{ji} x_j} \right] \quad (4.76)$$

where  $k_{ji} = k_{ij}$ ,  $l_{ji} = -l_{ij}$ ,  $m_{ji} = 1 - m_{ij}$  and  $k_{ii} = l_{ii} = 0$ . This expression reduces to the Panagiotopoulos-Reid mixing rule when  $m_{ij} = 0$ .

In general, the composition-dependent combining rules constitute the simplest method for applying equations of state to complex systems. Their accuracy for binary systems is usually very satisfactory as shown by Sandoval *et al.* (149), Margerum and Lu (150) and others. However, the mixing rules described above suffer from a very serious deficiency, which was discovered for the first time by Michelsen and Kistenmacher (151). They are not invariant to dividing a component into a number of identical subcomponents. If a binary mixture with composition  $(x_1, x_2)$  is treated as a ternary system with composition  $(x_1, x_2, x_3)$ , where the ternary is formed by dividing component 2 into two pseudocomponents with identical properties, a different value for the parameter  $a$  will result. Therefore, the calculated properties of a mixture will depend on the number of pseudocomponents, which is in contrast to experimental evidence.

Several attempts have been made to eliminate this inconsistency while retaining the flexibility of the composition-dependent combining rules for mixtures. Mathias *et al.* (152) proposed a mixing rule that overcomes the problem of invariance:

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) + \sum_i x_i \left( \sum_j x_j [(a_{ii} a_{jj})^{1/2}]^{1/3} l_{ji}^{1/3} \right)^3 \quad (4.77)$$

The first term is the classical quadratic mixing rule. The second term introduces a cubic composition dependence, when  $l_{ji} = -l_{ij}$  or a quartic one, when  $l_{ji} \neq -l_{ij}$ . It can be shown that Equation (4.77) reduces to the Panagiotopoulos-Reid mixing rule when  $l_{ji} = -l_{ij}$ . Twu *et al.* (27) proposed a somewhat similar mixing rule:

$$a = \sum_i \sum_j x_i x_j (a_{ii} a_{jj})^{1/2} (1 - k_{ij}) + \sum_i x_i \frac{\left[ \sum_j H_{ij}^{1/3} G_{ij}^{1/3} (a_{ii} a_{jj})^{1/6} x_j \right]^3}{\sum_j G_{ij} x_j} \quad (4.78)$$

where

$$H_{ij} = (k_{ji} - k_{ij}) / T \quad (4.79)$$

$$G_{ij} = \exp(-\beta_{ij}H_{ij}) \quad (4.80)$$

This mixing rule can be used either in a two-parameter version (*i.e.*, with only  $k_{ij}$  and  $k_{ji}$  adjusted) or in a four-parameter version (*i.e.*, with  $\beta_{ij}$  and  $\beta_{ji}$  adjusted in addition to  $k_{ij}$  and  $k_{ji}$ ). In both Equations (4.77) and (4.78), an improvement for multicomponent mixtures was obtained by introducing more symmetry into the non-quadratic part of the mixing rule, which bears resemblance to the composition dependence of the third virial coefficient. Another method for overcoming the Michelsen-Kistenmacher consistency problems was proposed by Schwartzentruber and Renon (153), who also introduced more symmetry into the cubic composition dependence of the mixing rule.

Figure 4.2 illustrates the performance of several composition-dependent combining rules for the strongly nonideal ternary system methanol + cyclohexane + hexane. It should be noted that all combining rules are capable of correlating vapor-liquid equilibria for the binary subsystems with reasonable accuracy. However, a much more stringent test is provided by the prediction of VLE in the ternary system using the parameters obtained from binary data. In this case, the three mixing rules that suffer from the Michelsen-Kistenmacher inconsistency (*i.e.*, Panagiotopoulos-Reid, Stryjek-Vera and Schwartzentruber *et al.*) show a large loss of accuracy for the ternary system. Similar conclusions were also reached for other systems in the more comprehensive studies by Knudsen *et al.* (154) and Malanowski and Anderko (57). However, the mixing rule of Twu *et al.* (27) shows a more satisfactory behavior. Although it loses accuracy for the ternary system when only two binary parameters (*i.e.*,  $k_{ij}$  and  $k_{ji}$ ) are regressed from binary data, it becomes more accurate in its four-parameter form. The parameters of all the mixing rules discussed above usually show appreciable temperature dependence. The temperature dependence of these mixing rules cannot be established *a priori* and has to be determined from experimental data at several temperatures.

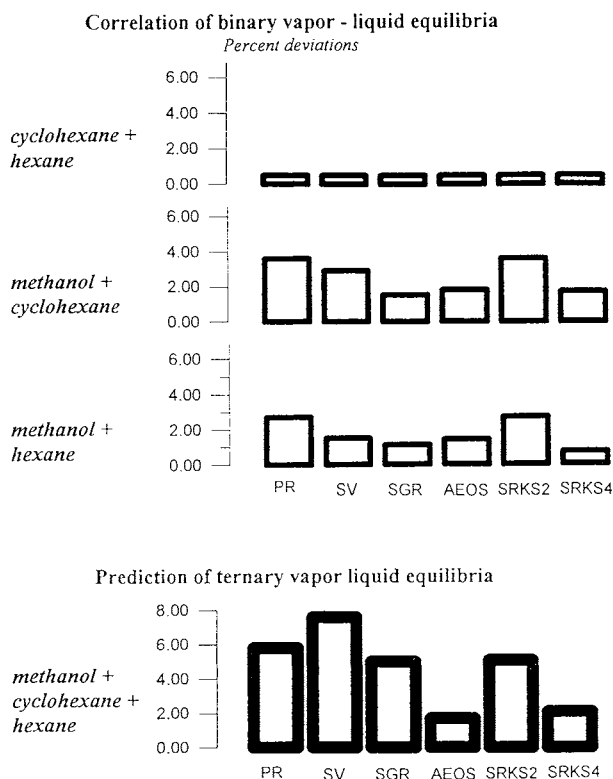
#### 4.4.3 Density-Dependent Mixing Rules

It is evident from the functional form of the composition-dependent combining rules that they do not reproduce the quadratic composition dependence of the second virial coefficient and, thus, violate basic statistical thermodynamics. This is indicative of their weak theoretical background. Therefore, several authors came up with a theoretically appealing concept that better results could be obtained if the constants of a selected equation of state were allowed to depend not only on composition and, sometimes, temperature, but also on density. To illustrate this concept, we consider the mixing rule of Luedecke and Prausnitz (155), who postulated that the attractive parameter can be written as

$$a = \sum_i \sum_j x_i x_j a_{ij} + a^{\text{nc}} \quad (4.81)$$

where the first term is identical to the classical quadratic mixing rule,  $a_{ij}$  is equal to  $(a_{ii}a_{jj})^{1/2}(1-k_{ij})$  and  $a^{\text{nc}}$  is a contribution of noncentral forces which are due to differences in polarity, size and shape of molecules. An expression for this term is constructed by analyzing boundary conditions. First, since  $a^{\text{nc}}$  refers only to contributions from unlike pairs, then:

$$\lim_{x_i \rightarrow 0} a^{\text{nc}} = 0 \quad (4.82)$$



**Figure 4.2** Application of several composition-dependent combining rules to the correlation and prediction of VLE in the ternary system methanol + cyclohexane + hexane. Vapor-liquid equilibria in the three binary subsystems are correlated and the parameters are used to predict VLE in the ternary system. The following models are used in conjunction with the Peng-Robinson or Soave-Redlich-Kwong EOS: PR - Panagiotopoulos and Reid's mixing rule; SV - Stryjek and Vera's van Laar-type mixing rule; AEOS - Anderko's EOS incorporating association; SRKS2 - Twu, Bluck, Coon and Cunningham's mixing rule with two binary parameters; SRKS4 - the same model with four binary parameters.

Second, it can be assumed that, as temperature rises or as density falls, the importance of noncentral forces declines:

$$\lim_{\rho/RT \rightarrow 0} a^{nc} = 0 \quad (4.83)$$

The simplest non-quadratic approximation that is consistent with these boundary conditions introduces cubic composition dependence and linear density dependence:

$$a^{\text{nc}} = (\rho / RT) \sum \sum x_i x_j (x_i c_{i(j)} + x_j c_{j(i)}) \quad (4.84)$$

where  $c_{i(j)}$  is a binary parameter that reflects noncentral forces when molecule  $j$  is infinitely dilute. The resulting mixing rule is

$$a = \sum \sum x_i x_j (a_{ij} a_{ji})^{1/2} (1 - k_{ij}) + (\rho / RT) \sum \sum x_i x_j (x_i c_{i(j)} + x_j c_{j(i)}) \quad (4.85)$$

and contains three binary parameters. In the low-density limit, it correctly reproduces the quadratic composition dependence of the second virial coefficient. While this mixing rule accurately correlates binary VLE and LLE, it was found to be inaccurate for ternary systems.

Following the early studies of Whiting and Prausnitz (156) and Mollerup (157), most density-dependent mixing rules were derived using the local composition concept to represent mixture nonideality. These methods have been reviewed by Danner and Gupte (158) and, later, by Anderko (159). We will not discuss them here because they have not been proven advantageous for practical calculations. The density-dependent mixing rules do not improve the results of phase-equilibrium computations over the density-independent, composition-dependent combining rules. The loss of accuracy for ternary and multicomponent systems, which has been discussed in Section 4.4.2, is also shared by the density-dependent mixing rules (25). At the same time, the density-dependent mixing rules eliminate the third-order density dependence of cubic equations of state and impose a higher-order dependence. Also, there are alternative techniques for satisfying the second-order composition dependence of the second virial coefficient, which will be discussed in Section 4.4.4.

#### 4.4.4 Combining Equations of State with Excess-Gibbs-Energy Models

Excess Gibbs energy ( $g^E$ ) models based on the local composition concept have proven very useful for the correlation of low-pressure phase equilibria. Therefore, much effort has been focused on combining them with equations of state. A detailed discussion of the combined  $g^E$ -EOS models is provided in Chapter 9 of this book. However, it is worthwhile to mention them here in order to provide an appropriate perspective for other methods discussed in this chapter.

Standard thermodynamics defines a simple relationship between the excess Gibbs energy and fugacity coefficients, which are calculated from an equation of state:

$$g^E(T, P, x) = RT(\ln \phi_{\text{mix}} - \sum x_i \ln \phi_i) \quad (4.86)$$

where  $\phi_{\text{mix}}$  and  $\phi_i$  are the fugacity coefficients of the mixture and the  $i$ -th pure component, respectively. This relationship was employed by several authors to combine excess-Gibbs-energy models and equations of state so that the desirable features of both classes of models can be utilized.

Vidal (160) derived the infinite-pressure limit of the excess Gibbs energy calculated from the Redlich-Kwong EOS with quadratic mixing rules. To arrive at an explicit expression, Vidal assumed that  $v = b$  and  $v^E = 0$  at infinite pressure.

$$g^E(P = \infty) = \ln 2 \left( -a/b + \sum x_i a_i / b_i \right) \quad (4.87)$$

It is interesting to write this equation specifically for a binary system when the binary parameter  $k_{ij}$  is equal to zero:

$$g^E(P = \infty) = \ln 2 \left( \frac{x_1 b_{11}}{b} \right) \left( \frac{x_2 b_{22}}{b} \right) \left[ \left( \frac{a_{11}/b_{11}}{b_{11}} \right)^{1/2} - \left( \frac{a_{22}/b_{22}}{b_{22}} \right)^{1/2} \right]^2 \quad (4.88)$$

In this equation,  $x_i b_{ii}/b$  are the infinite-pressure volume fractions and the terms  $[(a_{ii}/b_{ii}) \ln 2 / b_{ii}]^{1/2}$  can be identified with solubility parameters. Therefore, Equation (4.88) becomes essentially identical to the well-known Hildebrand-Scatchard regular solution theory:

$$g^E(P = \infty) = b \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 \quad (4.89)$$

where  $\Phi_i$  and  $\delta_i$  are the volume fractions and solubility parameters, respectively. This explains the inherent limitations of quadratic mixing rules because it becomes evident that they are applicable only to mixtures whose excess properties can be approximated by the regular-solution theory. While this is a good approximation for hydrocarbon mixtures, it cannot be applied to systems containing strongly polar or associating components.

Vidal's (160) derivation can be generalized to other equations of state as shown by Huron and Vidal (161):

$$g^E(P = \infty) = \Lambda \left( -a/b + \sum x_i a_i / b_i \right) \quad (4.90)$$

where  $\Lambda$  is a characteristic parameter for each cubic EOS used. This equation suggests a mixing rule for the attractive parameter in cubic equations of state:

$$a = b \left( \sum x_i a_{ii} / b_{ii} - g^E(P = \infty) / \Lambda \right) \quad (4.91)$$

Any excess-Gibbs-energy model can be selected to represent the infinite-pressure excess Gibbs energy. Huron and Vidal (161) suggested using the NRTL equation. It should be noted, however, that the excess Gibbs energies at finite and infinite pressure are not identical and cannot be used interchangeably. Therefore, the parameters of the Huron - Vidal mixing rule have to be determined by fitting the complete equation of state to phase-equilibrium data. Parameters of the original NRTL model cannot be used for that purpose. The Huron - Vidal mixing rule was shown by several authors to give results similar to those from the NRTL model. In particular, it makes it possible to predict multicomponent phase equilibria from binary data with satisfactory accuracy (162,163). It was also shown to compare favorably with several composition-dependent combining rules by Knudsen *et al.* (154).

Kurihara *et al.* (164) proposed a modification of the Huron-Vidal mixing rule that separates the classical quadratic term from a “residual” term, which is calculated from the Wilson equation:

$$a = \sum_i \sum_j x_i x_j (a_{ij} a_{ji})^{1/2} - (b / \ln 2) g^{\text{E(residual)}} (P = \infty) \quad (4.92)$$

Tochigi *et al.* (165) used this equation to predict ternary vapor-liquid equilibria from binary data and obtained satisfactory results.

More recently, the focus of research in this area shifted to developing mixing rules that not only share the numerical properties of equations for the excess Gibbs energy, but also can be used with exactly the same parameters as the original excess-Gibbs-energy models. For this purpose, the infinite-pressure limit was abandoned in favor of a more realistic zero-pressure limit. An early method for accomplishing this was proposed by Mollerup (166). It should be noted that the zero-pressure limit creates problems whenever the equation of state does not predict a liquid root, which is needed to calculate the liquid-phase fugacity coefficients and, subsequently, the excess Gibbs energy. For example, the zero-pressure liquid root of the van der Waals EOS exists when  $a/RTb \geq 4$ . In other cases, it has to be determined by suitable extrapolation. For this purpose, two techniques have been proposed by Michelsen (167) and Heidemann and Kokal (168).

Michelsen (167) applied the Huron-Vidal technique of matching the excess Gibbs energy using the reference pressure of zero. In contrast to the Huron-Vidal mixing rule, the expression obtained is not explicit:

$$q(\alpha) = \sum_i z_i q(\alpha_{ii}) + \frac{g^E}{RT} + \sum_i z_i \ln \left( \frac{b}{b_{ii}} \right) \quad (4.93)$$

In this equation,  $\alpha$  is a shortcut notation for  $a/bRT$  and the function  $q(\alpha)$  is given, for the Redlich-Kwong EOS, by:

$$q(\alpha) = -1 - \ln(u - 1) - \alpha \ln \left( \frac{u + 1}{u} \right) \quad (4.94)$$

with

$$u = (v / b)_{P=0} = \frac{1}{2} \left( \alpha - 1 - \sqrt{\alpha^2 - 6\alpha + 1} \right) \quad (4.95)$$

These equations cannot be used to evaluate the mixing rule under all conditions because the function  $q(\alpha)$  is defined only for  $\alpha > 3 + 2^{3/2}$ . To maintain continuity for all values of  $\alpha$ , Michelsen suggested two approximations. In the first approximation, a linear relation was used:

$$q(\alpha) = q_0 + q_1 \alpha \quad (4.96)$$

This leads to an explicit mixing rule:

$$a_{\text{mix}} = \sum_i z_i \alpha_{ii} + \frac{1}{q_1} \left[ \frac{g^E}{RT} + \sum_i z_i \ln \frac{b}{b_{ii}} \right] \quad (4.97)$$

where  $q_1$  has a universal recommended value. Due to its similarity to the Huron-Vidal mixing rule, this equation was called the Modified Huron-Vidal First-Order mixing rule (MHV1). In the second approximation, Michelsen employed a quadratic approximation  $q(\alpha) = q_0 + q_1\alpha + q_2\alpha^2$ , which yields the Modified Huron-Vidal Second-Order (MHV2) mixing rule:

$$q_1 \left( a_{\text{mix}} - \sum_i z_i \alpha_{ii} \right) + q_2 \left( \alpha_{\text{mix}}^2 - \sum_i z_i \alpha_{ii}^2 \right) = \frac{g^E}{RT} + \sum_i z_i \ln \frac{b}{b_{ii}} \quad (4.98)$$

where  $q_1$  and  $q_2$  are universal parameters. Dahl and Michelsen (169) demonstrated that the MHV2 mixing rule gives very good predictions of high-pressure VLE using parameters obtained from low-pressure VLE regressions. In spite of its success, it should be noted that MHV2 requires a relatively arbitrary quadratic extension for the calculation of volumes. Also, similarly to the Huron-Vidal mixing rule, it fails to satisfy the quadratic composition dependence of the second virial coefficient.

Heidemann and Kokal's procedure (168) is, in spirit, similar to Michelsen's because it also involves the use of an auxiliary function  $q(\alpha)$ . Since this function is cubic, the  $a_{\text{mix}}$  parameter has to be found in an iterative way. However, it has similar properties. More recently, Boukouvalas *et al.* (170) proposed a linear combination of the algebraically similar MHV1 and Huron-Vidal mixing rules and obtained an improvement for mixtures containing components with appreciably different sizes. This combination is purely empirical because the MHV1 and Huron-Vidal mixing rules have been derived at different reference pressures and the reason for the improvement is unclear.

A different approach has been proposed by Wong and Sandler (171). Instead of trying to match the zero-pressure excess Gibbs energy, Wong and Sandler observed that the excess Helmholtz energy is practically independent of pressure, which makes it almost the same at low and infinite pressure. At the same time, the zero-pressure Helmholtz energy is equal to the zero-pressure Gibbs energy. This makes it possible to identify the low-pressure excess Gibbs energy calculated from an activity-coefficient model with the infinite-pressure excess Helmholtz energy calculated from an equation of state:

$$A_{\text{EOS}}^E(T, P = \infty, x) = G(T, P(\text{low}), x) \quad (4.99)$$

Additionally, Wong and Sandler utilized the quadratic composition dependence of the second virial coefficient to relate the mixed-fluid  $a$  and  $b$  parameters to their pure-fluid counterparts:

$$B(T, x) = b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left( b_{ij} - \frac{a_{ij}}{RT} \right) \quad (4.100)$$

where the cross-term for  $i \neq j$  is related to the pure-fluid terms by a combining rule, *i.e.*,

$$b_{ij} - \frac{a_{ij}}{RT} = \frac{1}{2} \left[ \left( b_{ii} - \frac{a_{ii}}{RT} \right) + \left( b_{jj} - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij}) \quad (4.101)$$

with an additional binary parameter  $k_{ij}$ . The two conditions given by Equations (4.99) and (4.100) give the following mixing rules:

$$\frac{a_{\text{mix}}}{RT} = Q \frac{D}{1 - D} \quad (4.102)$$

$$b_m = \frac{Q}{1 - D} \quad (4.103)$$

where

$$Q = \sum \sum x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (4.104)$$

$$D = \sum x_i \frac{a_i}{b_i RT} + \frac{G^E(x)}{\sigma RT} \quad (4.105)$$

and  $\sigma$  is an EOS-specific constant.

The Wong-Sandler mixing rule contains one additional binary parameter  $k_{ij}$  (*cf.* Equation (4.101)), which has to be regressed, preferably using low-pressure data. Alternatively, it can be obtained from the same excess Gibbs energy model that was used to formulate the mixing rule. Therefore, the application of this mixing rule is not automatic even though the parameters of the excess Gibbs energy model can be used unchanged. Wong *et al.* (172) showed that the Wong-Sandler mixing rule remains accurate even when it is used at pressures and temperatures that are very remote from the conditions of the low-pressure VLE data that were used to regress the parameters. Huang and Sandler (173) compared the MHV2 and Wong-Sandler mixing rules and found that the Wong-Sandler formulation is more accurate, especially at high pressures and temperatures. Also, Escobedo-Alvarado and Sandler (236) studied the application of the MHV1 and Wong-Sandler mixing rules to liquid-liquid equilibrium computations and concluded that the Wong-Sandler rule is better for predicting high-pressure LLE from low-pressure data although both mixing rules are appropriate for correlating the data.

An extension of the Wong-Sandler mixing rule was proposed by Chou and Wong (174), who imposed the correct composition dependence on the third virial coefficient. Since the mixing rule for the third virial coefficient contains triplet interaction parameters, Chou and Wong utilized them to introduce ternary parameters for fitting ternary phase equilibrium data. It should be noted that this kind of additional flexibility limits the predictive character of the model.



In their original forms, the combined  $G^E$ -EOS models do not reduce to the classical quadratic mixing rules, which makes it difficult to use them in a unified computational environment for both hydrocarbons and polar and associated chemicals. This is important in the context of process and reservoir simulation, where users have a tendency to rely on the well-established quadratic mixing rules for hydrocarbon systems. Therefore, Orbey and Sandler (237) and Twu *et al.* (238,239) developed modifications of the Wong-Sandler mixing rule so that the classical quadratic mixing rule can be recovered. The modification of Orbey and Sandler (237) is based on a reformulation of the excess Gibbs energy model so that it can reduce to the classical mixing rule. The approach of Twu *et al.* (238,239) relies on a different concept. It is based on equating the difference between the excess Helmholtz energies for the complex fluid and a classical van der Waals fluid with an analogous difference for the Helmholtz energy departure, i.e.,

$$A^E - A_{vdW}^E = \Delta A - \Delta A_{vdW} \quad (4-105a)$$

where the subscript vdW denotes a van der Waals fluid for which the classical quadratic mixing rule is used. This expression makes it possible to define a mixing rule that combines the quadratic mixing rule with an excess Gibbs energy model.

The mixing rules based on excess Gibbs energy models have gained considerable popularity for practical calculations. This is due to the fact that they share their features with the activity coefficient models such as NRTL or UNIQUAC, which have been commonly used for engineering calculations for almost three decades, especially in the context of process simulation.

## 4.5 EXPLICIT TREATMENT OF ASSOCIATION IN EMPIRICAL EQUATIONS OF STATE

Molecular association and solvation strongly affect the thermophysical properties of pure and mixed fluids. In the case of pure-fluid *PVT* properties, association significantly increases the critical temperature, makes the second virial coefficient more negative and affects the shape of the vapor-pressure curve. For a number of compounds, such as carboxylic acids or hydrogen fluoride, association drastically reduces the gas-phase compressibility factor even at low densities. Derivative properties such as enthalpies are also strongly influenced. While the behavior of vapor-pressure curves can be adequately modelled up to the critical temperature using the empirical techniques described in Section 4.1, the effect of strong association on the gas-phase *PVT* properties makes it necessary to account for association in the equation of state. In addition to *PVT* properties, association profoundly influences the nonideality of mixtures, which affects phase equilibria. In principle, the multiparameter mixing rules discussed in Section 4.4 are sufficiently flexible to correlate the phase behavior of strongly nonideal, associated systems. However, these methods require a substantial number of binary parameters (typically 2-4 per binary) and are, therefore, only correlative. It is usually difficult to extrapolate their parameters beyond the range of experimental data and the prediction of phase equilibria in multicomponent systems from binary data is frequently unreliable. Therefore, several methods have been devised to incorporate association explicitly into the framework of equations of state.

The possibility of representing phase equilibria by postulating that molecules associate or solvate to form new species has been recognized for a long time (175). The chemical theory has been shown by many authors to be particularly useful when applied to mixtures containing one associating compound and some inert solvents. In this case, the chemical approach made it possible to obtain an accurate representation of phase equilibria with a limited number of physically meaningful parameters. However, the application of the chemical theory to systems containing any number of associating species encountered substantial difficulties. The major drawback of the chemical theory has been its specific character, restricted to particular classes of mixtures, and the difficulty of extending the models that are valid for binaries to multicomponent mixtures. In this section we will show how these and other problems were treated by various investigators. Our discussion will be limited to the application of the chemical theory to the modeling of associated fluids. Statistical-mechanical methods for treating association will not be discussed because they are described in Chapter 12 of this book.

In general, there are two methods for incorporating association equilibria into an equation of state. The first one is conceptually simpler, but it is more difficult to use, as we will show later. It consists in simultaneously solving chemical equilibria between associated species and physical (phase) equilibria for all species in the mixture. A pure associated compound is assumed to be a mixture of a few associated species  $A_i$ , each of them containing  $i$  monomeric units in a multimer. Once the associates are selected, they are treated as pseudocomponents and the system of equations to be solved is as follows:

Chemical equilibria for the reaction  $iA_1 = A_i$  in each phase:

$$K_i = \frac{x_i}{x_1^i} \frac{\varphi_1^i}{\varphi_i} \quad (4.106)$$

Phase equilibria:

$$f_i^{\text{phase1}}(T, P, \underline{x}) = f_i^{\text{phase2}}(T, P, \underline{x}) \quad (4.107)$$

where the superscripts stand for any two phases in equilibrium. The association constant  $K_i$  depends only on temperature because the standard state for the  $A_i$  species in both the gas and liquid phases is pure  $A_i$  in the ideal-gas state. These equations can be solved numerically provided that the fugacity coefficients of each species are calculated from an equation of state that is suitable for multicomponent mixtures. For this purpose, Wenzel *et al.* (176) used the Schmidt-Wenzel (15) cubic EOS whereas Grenzheuser and Gmehling (177) employed the PHCT EOS (87). In general, the most difficult problem in this approach is the assignment of associated species, the number of which has to be minimized. For example, if we assumed the continuous linear association model, the number of equations would be infinite. Therefore, Grenzheuser and Gmehling (177) restricted their calculations to dimers, which makes their method applicable primarily to carboxylic acids. On the other hand, Wenzel *et al.* (176) allow for the existence of higher multimers. For example, methanol is assumed to be a mixture of monomers, tetramers and dodecamers. The selection of multimers is arbitrary and results from a compromise between the requirements of reproducing the data and minimizing the number of adjustable parameters. Nevertheless, the number of adjustable pure-component parameters is very large (three parameters for each mono- or multimer and two or three for each reaction)

and their determination is by no means simple. To determine pure-component parameters, Wenzel *et al.* (176) utilize not only pure-component data (*i.e.*, vapor pressure, liquid and vapor volumes and critical properties), but also binary VLE data.

Extension of this scheme to mixtures is straightforward, provided that the mixture contains only one associating component. In this case the chemical equilibria are not changed and the number of phase-equilibrium equations only increases by the number of inert components that are present in the mixture. However, in the case of mixtures containing two or more associating components, a problem of cross-associates appears. Since it is impossible to deduce all parameters for cross-associates from binary data, only arbitrarily selected cross-associates (usually cross-dimers) are allowed for.

The computational scheme outlined above makes it possible to represent VLE and LLE with good accuracy using only one binary parameter as shown by Wenzel *et al.* (176) and Kolasinska *et al.*, (178). Lang and Wenzel (179) were even able to simulate a third phase for a pure component by assuming the existence of a large oligomer (*e.g.*, a 25-40 mer). The parameters of that oligomer were adjusted to match the properties of the solid phase. This approach can be used as an alternative to introducing an additional physical term to simulate a solid phase in an equation of state as done by Schmidt and Wenzel (230).

However, the good features of this method for introducing association equilibria have been achieved at a considerable cost. First, the determination of pure-component parameters is cumbersome and no clear-cut algorithm exists for guessing which associates should be assumed to provide a good representation of phase equilibria. This can be done only by trial and error. Second, this approach cannot overcome the traditional deficiency of association models, *i.e.*, the difficulty of formulating a consistent model for systems containing any number of associating and inert components.

A successful attempt to solve these problems has been made in the development of the second method for incorporating association into an equation of state. This method is based on solving the chemical-equilibrium expressions for an assumed association model analytically in order to derive an explicit equation of state with association built-in. The first model of this type was proposed by Heidemann and Prausnitz (180), who combined an EOS with the continuous linear-association model. According to this model, the equilibrium constants for the consecutive association reactions  $A_i + A_1 = A_{i+1}$  ( $i = 1, \dots, \infty$ ) are equal to each other (*i.e.*,  $K_{i,i+1} = K$ ). Heidemann and Prausnitz used a generalized van der Waals EOS:

$$P = \frac{RT}{v} z_{\text{rep}}(\xi) - \frac{a}{b^2} \Pi_{\text{att}}(\xi) \quad (4.108)$$

where  $a$  and  $b$  are the generalized van der Waals parameters and  $z_{\text{rep}}$  and  $\Pi_{\text{att}}$  are functions of the reduced density  $\xi$ . For associated species, the classical quadratic mixing rules have been used:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} \quad (4.109)$$

$$b = \sum_i x_i b_i \quad (4.110)$$

with the following combining rules for the multimers' parameters:

$$a_i = i^2 a_1 \quad (4.111)$$

$$b_i = i b_1 \quad (4.112)$$

Heidemann and Prausnitz obtained the remarkable result that, with these combining rules, the reduced density and, subsequently, the  $z_{\text{rep}}$  and  $\Pi_{\text{att}}$  functions are independent of association. The effects of association enter the equation of state only through the factor  $n_T/n_0$ , where  $n_T$  is the total number of moles of the associated species and  $n_0$  is the number of moles of the compound in the absence of association. Then, the van der Waals parameters take the form:

$$a = (n_0 / n_T)^2 a_1 \quad (4.113)$$

$$b = (n_0 / n_T) b_1 \quad (4.114)$$

and the equation of state becomes

$$P = \frac{n_T}{n_0} \frac{RT\xi}{b} z_{\text{rep}}(\xi) - \frac{a}{b^2} \Pi_{\text{att}}(\xi) \quad (4.115)$$

After evaluating the material-balance and chemical-equilibrium equations, the factor  $n_T/n_0$  becomes

$$\frac{n_T}{n_0} = \frac{2}{1 + (1 + 4RTKe^g / \nu)^{1/2}} \quad (4.116)$$

where

$$g = \int_0^\xi [(z_{\text{rep}} - 1) / \xi] d\xi \quad (4.117)$$

The expression for  $n_T/n_0$  can be easily generalized for mixtures containing one associating component  $A$  and any number of inert ones:

$$\frac{n_T}{n_0} = \frac{2x_A}{1 + (1 + 4RTKe^g x_A / \nu)^{1/2}} + 1 - x_A \quad (4.118)$$

It should be noted that the final equation of state is strongly dependent on the combining rules for the parameters  $a$  and  $b$  of the multimers. These combining rules were tested by Wenzel and Krop (181), who analyzed the  $a$  and  $b$  parameters calculated for a series of hydrocarbons using the Peng-Robinson EOS (14). They found that the multipliers  $i^2$  and  $i$  in Equations (4.111) and (4.112) are reasonable, but not very accurate. A closer inspection of the  $a$  and  $b$  values would suggest the multipliers  $i^e$  where the exponent  $e$  lies between 1 and 2 (closer to 2 for  $a$  and closer to 1 for  $b$ ). However, it is not worthwhile to establish a more accurate approximation for the parameters  $a$  and  $b$  of hydrocarbons for two reasons. First,

hydrocarbons provide only a very rough approximation of the properties of multimers and, second, any fractional exponent would preclude any further analytical derivations. It should be realized that the combining rules for the associates are purely hypothetical and serve merely as a tool for deriving a convenient closed-form equation of state.

The original Heidemann-Prausnitz (180) technique yields equations of state that can be very accurate for the calculation of PVT properties of pure fluids. This has been demonstrated by Twu *et al.* (182,183), who applied this technique in conjunction with the Redlich-Kwong EOS to carboxylic acids and hydrogen fluoride. They achieved a very good representation of gas-phase PVT properties, which are extremely nonideal for these fluids. However, Twu *et al.* did not obtain any simplification for mixtures and continued to use a multiparameter mixing rule with composition-dependent combining rules for mixtures containing HF and acids. Thus, the original Heidemann-Prausnitz method is fully successful for PVT properties, but still requires multiparameter mixing rules for mixtures. Therefore, several authors introduced modifications to develop a more convenient equation for mixtures.

Ikonomou and Donohue (184,185) used the concept of Heidemann and Prausnitz in conjunction with the PACT equation of state given by Equation (4.57). They assumed that the mixing rules for the associated species are analogous to those used for nonassociating components. As with the Heidemann-Prausnitz EOS, the key step was to assign appropriate combining rules for the associated species:

$$\begin{aligned}\varepsilon_{ij} &= \varepsilon_{11} \\ \sigma_{ij}^3 &= \sigma_{11}^3 \\ r_j &= jr_1 \\ q_j &= jq_1\end{aligned}\tag{4.119}$$

The form of the resulting equation of state, called APACT (Associated Perturbed-Anisotropic-Chain Theory) is significantly different from that obtained by Heidemann and Prausnitz in that it contains the ratio  $(n_T/n_0)$  as a separate term:

$$z = \frac{n_T}{n_0} + z_{\text{rep}}^{\text{PACT}} + z_{\text{attr}}^{\text{PACT}}\tag{4.120}$$

This is a consequence of a different equation of state. In particular, it can be shown that the presence of the Prigogine parameter  $c$ , which multiplies the nonideal part of the equation, gives rise to the separation of the  $(n_T/n_0)$  term from the rest of Equation (187). The factor  $(n_T/n_0)$  is similar to that obtained by Heidemann and Prausnitz except for the term  $g(\xi)$ , which is equal to zero in APACT. Thus, for a mixture containing one associating component and any number of inert ones, the factor  $(n_T/n_0)$  becomes:

$$\frac{n_T}{n_0} = \frac{2x_A}{1 + (1 + 4RTKx_A / \nu)^{1/2}} + 1 - x_A\tag{4.121}$$

This equation was later extended to systems with multiple associating components (186). It should be noted that an analytical solution for  $(n_T/n_0)$  cannot be found when more than one

associating component is present. Therefore, Ikononou and Donohue (186) and Economou *et al.* (189) solved the chemical equilibria and material balances numerically and, subsequently, devised an analytical approximation. Economou and Peters (233) also developed a specialized version of AFACT for systems containing hydrogen fluoride. The method of Ikononou and Donohue was also used by Elliott *et al.* (188) in conjunction with a much simpler equation of state that approximates the Perturbed-Hard-Chain Theory. A somewhat similar model has also been proposed by Deiters (190).

Anderko (191-195) developed an equation for associated mixtures that combines a cubic EOS with a chemical term that accounts for association. Initially, Anderko (191) added a chemical term  $z^{(ch)}$  to the usual (or physical) compressibility factor, *i.e.*,

$$z = z^{(ph)} + z^{(ch)} - 1 \quad (4.122)$$

by generalizing the observation that the second and higher virial coefficients could be separated into physical and chemical contributions (196,197). Later, Anderko (195) rederived Equation (4.122) by applying the Heidemann-Prausnitz technique with different combining rules. The term  $z^{(ch)}$  is equivalent to the ratio  $n_T/n_0$ , *i.e.*,

$$z^{(ch)} = \frac{n_T}{n_0} \quad (4.123)$$

whereas the term  $z^{(ph)}$  is an equation of state for the hypothetical monomeric fluid and can be expressed by any cubic equation of state. Most calculations were performed, however, using the Yu-Lu (26) EOS because of its accuracy for liquid-density calculations. The combined model was called AEOS (Association + Equation of State).

For the continuous linear association model, the expression for  $z^{(ch)}$  is identical to Equation (4.121) obtained by Ikononou and Donohue. To extend the applicability of the equation to systems containing any number of associating components, Anderko (193) developed a multicomponent analog of the continuous linear association model. The model is based on the assumption that,

1. Only linear multimers containing any possible combinations of monomeric units occur in the mixture. There is no upper limit on the size of the multimer and
2. The multimers are formed in consecutive association reactions. For each of the elementary reactions the equilibrium constant depends on the chemical identity of the monomers that form the bond but not on the number of monomers that constitute the multimer. In this scheme a system containing  $n$  associating components is characterized by  $n$  self-association constants  $K_{ii}$  and  $n(n-1)/2$  cross-association (solvation) constants  $K_{ij}$  ( $i \neq j$ ).

The derivation requires certain approximations because the system of chemical equilibrium and mass-balance equations cannot be solved analytically. The final result is:

$$z^{(ch)} = \frac{n_T}{n_0} = \sum_{i=1}^n \frac{2x_{A^{(i)}}}{1 + [1 + 4RT(\sum_{j=1}^n K_{ij}x_{A^{(j)}})/v]^{1/2}} + \sum_{k=1}^r x_{B^{(k)}} \quad (4.124)$$

where  $A^{(i)}$  and  $B^{(k)}$  denote the  $i$ -th associating and  $k$ -th inert components, respectively. This equation satisfies three important boundary conditions:

1. If the number of associating components is equal to one, Equation (4.124) reduces to Equation (4.121) for a mixture with one self-associating component.
2. When all self- and cross-association constants are equal to each other, the associated species become indistinguishable. Then, the expression for  $z^{(ch)}$  reduces to the pure-component case.
3. In the low-density limit, the correct composition dependence of the chemical contribution to the second virial coefficient is recovered, *i.e.*,

$$B^{(ch)} = \sum_i^n \sum_j^n x_{A^{(i)}} x_{A^{(j)}} (-RTK_{ij}) \quad (4.125)$$

Although the continuous linear-association model is successful for a variety of associating compounds (*e.g.*, alcohols, phenols, amines, *etc.*), some compounds require different association models. An important example is water because the structures of water clusters are three-dimensional rather than linear. Another example is hydrogen fluoride, which preferentially forms associates of some intermediate sizes (such as 5, 6, 7,... mers) rather than long chains. At the same time, the analytical solution of the chemical-equilibrium and mass-balance expressions is very difficult, if not impossible, for more complex association models. To overcome this difficulty, Anderko (195) noted that the  $n_T/n_0$  term is always an algebraic function of the product  $RTKx_A/v$  for any one-equilibrium-constant association model. In the simple case of a mixture containing one associating component, the term  $n_T/n_0$  is

$$\frac{n_T}{n_0} = x_A F\left(\frac{RTKx_A}{v}\right) + 1 - x_A \quad (4.126)$$

where  $F$  is an algebraic (even though unknown *a priori*) function of the product  $RTKx_A/v$ . This equation is valid irrespective of the characteristics of the association model. If, for brevity, we use the symbol  $q$  to denote the product  $RTKx_A/v$ , then the function  $F(q)=2/[1+(1+4q)^{1/2}]$  will give us the expression for the continuous linear-association model.

Lencka and Anderko (198) and Anderko and Prausnitz (199) utilized this result to arrive at a closed-form expression for hydrogen fluoride. The preferential formation of intermediate-size associated HF species can be expressed using a Poisson-type distribution function (199):

$$K_{j,j+1} = K \frac{\kappa^{j-1}}{j!} \quad (4.127)$$

which can be compared with the simple relationship  $K_{j,j+1}=K$  for the continuous linear model. For this model, the values of  $n_T/n_0$  were found numerically and closely approximated using the function

$$F(q) = \frac{1 + \sum_{k=1}^8 a_k q^k}{(1+q)^8} \quad (4.128)$$

where  $a_k$  are numerical coefficients and  $q$  denotes, again, the product  $RTKx_A/v$ .

For water, Anderko (195) developed a simple function:

$$F(q) = \frac{1}{1 + q + \alpha q^2} \quad (4.129)$$

where  $\alpha$  is a numerical constant. This function was later empirically improved by Shinta and Firoozabadi (200):

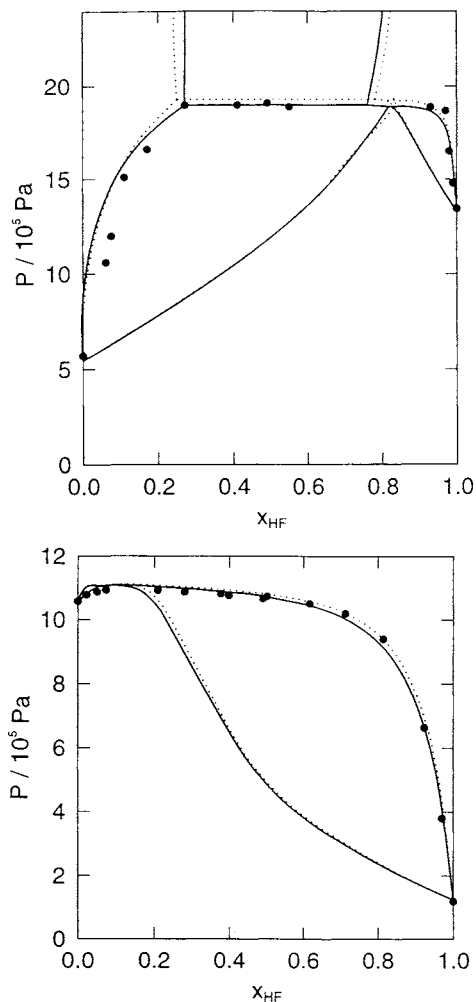
$$F(q) = \frac{\zeta}{\sqrt{\zeta} + q + \beta q^2} \quad (4.130)$$

where  $\zeta$  and  $\beta$  are, again, numerical constants.

For any association model, the final AEOS equation of state contains five parameters for each associating compound, *i.e.*, the enthalpy and entropy of association to evaluate the temperature dependence of the association constant and the apparent critical temperature, critical pressure and acentric factor of a hypothetical monomer. The latter three parameters are used to calculate the physical contribution to the compressibility factor ( $z^{(ph)}$ ), which is expressed by a generalized cubic EOS. All of these parameters are fitted to match pure-component vapor pressure, liquid density and (optionally) critical coordinates. Alternatively, the equation-of-state parameters can be evaluated locally for each temperature of interest using vapor-pressure and liquid-density data generated from another equation of state as discussed by Anderko (201).

When applied to mixture calculations, the AEOS model is capable of reproducing VLE and LLE in strongly nonideal systems using only one binary parameter. This parameter is introduced in the most traditional way, *i.e.*, by applying the classical quadratic mixing rule to the  $a$  parameter in the cubic equation of state that represents the physical contribution to the compressibility factor  $z^{(ph)}$ . For example, Shinta and Firoozabadi (200) demonstrated that AEOS is very effective for the simultaneous correlation of VLE and LLE in aqueous hydrocarbon systems. Similar results were obtained by Lencka and Anderko (198) and Anderko and Prausnitz (199) for mixtures containing hydrogen fluoride and various chlorinated and fluorinated hydrocarbons. Anderko and Malanowski (194) showed very good results for mixtures containing alcohols and phenols. Since only one binary parameter is needed, there are no problems with the intercorrelation of binary parameters. This enhances the accuracy of the model for multicomponent systems. As shown in Figure 4.2, AEOS predicts the VLE in the ternary system methanol + cyclohexane + hexane with a very good accuracy, which is similar to the accuracy of VLE correlation for the binary subsystems. Shinta and Firoozabadi (200,202) showed that AEOS accurately predicts the phase behavior of multicomponent systems encountered in reservoir engineering (*i.e.*, water + H<sub>2</sub>S + CO<sub>2</sub> + hydrocarbons). Also, they demonstrated that the behavior of water + reservoir-crude systems (*e.g.*, in high-pressure steam distillation) can be modeled with the same degree of simplicity as for dry reservoir-crude systems (202). In many cases, AEOS is purely predictive, *i.e.*, good estimates can be obtained with the binary interaction parameters set equal to zero. This has been demonstrated for the industrially important systems containing HF and halocarbons (198, 199). For example, Figure 4.3 shows the representation of VLE and VLLE for the HF +





**Figure 4.3** Vapor-liquid-liquid equilibria calculated for the systems HF +  $\text{CF}_3\text{CCl}_3$  (upper graph) and HF +  $\text{CHF}_2\text{Cl}$  (lower graph) using the AEOS equation (198) without any binary parameters (dotted lines) and with one regressed binary parameter (solid lines). Experimental data (solid circles) are from Knapp *et al.* (234) and Wilson *et al.* (235).

$\text{CHF}_2\text{Cl}$  and HF +  $\text{CF}_3\text{CCl}_3$  systems without any binary parameters (dotted lines) and with one regressed binary parameter (solid line).

The main difficulty associated with the use of equations of state based on the chemical theory is the determination of pure-component parameters because five parameters have to be fitted to vapor-pressure and liquid-density data and, most importantly, their values have to be physically meaningful. However, this difficulty is compensated by the simplicity of calculations for mixtures.

## 4.6 EQUATIONS OF STATE AS FULLY PREDICTIVE MODELS

Most equations of state contain some binary parameters that have to be determined from experimental data. Therefore, numerous methods have been developed to enhance the predictive capability of equations of state so that they can be used without having to regress experimental data. The simplest way to achieve this is to develop correlations for the binary parameter  $k_{ij}$  for separate families of mixtures that contain one common component. A more general approach is to create equations of state with parameters calculated from group contributions. A third possible approach is to combine equations of state with existing predictive group-contribution methods such as UNIFAC.

### 4.6.1 Correlations for Binary Parameters

Correlations for binary parameters in equations of state can be developed for homologous series of mixtures, *i.e.*, mixtures containing one common component and a number of components that belong to a certain family. Not surprisingly, most such correlations have been developed for mixtures of hydrocarbons and a few selected nonhydrocarbons such as carbon dioxide or nitrogen. To develop such correlations, it is necessary to determine the binary parameters for individual binary pairs and find appropriate independent variables for the correlation.

For example, Valderrama *et al.* developed correlations for binary pairs containing hydrogen sulfide (203), carbon dioxide (204), hydrogen (205), nitrogen (206) and nonpolar compounds. They used a temperature-dependent function for the  $k_{ij}$  parameter:

$$k_{ij} = A - B/T_{Rj} \quad (4.131)$$

with the parameters  $A$  and  $B$  correlated with the acentric factor:

$$A = A_0 + A_1\omega_j + A_2\omega_j^2 \quad (4.132)$$

$$B = B_0 + B_1\omega_j + B_2\omega_j^2 \quad (4.133)$$

In this correlation, the subscript  $j$  denotes the nonpolar component that forms a binary system with either H<sub>2</sub>S or CO<sub>2</sub> or H<sub>2</sub> or N<sub>2</sub>.

Kordas *et al.* (207) and Avlonitis *et al.* (208) developed similar, but somewhat more elaborate correlations for systems containing carbon dioxide and nitrogen, respectively. Correlations for CO<sub>2</sub> - containing mixtures were also developed by Kato *et al.* (209) and Moysan *et al.* (210). Nishiumi and Gotoh (211) obtained a correlation for systems containing hydrogen and Schulze (212) generalized the parameters for helium-containing mixtures. Another correlation was proposed by Gao *et al.* (213) for light hydrocarbon systems. More recently, Coutinho *et al.* (214) proposed a correlation for binary parameters on the basis of the theory of dispersion forces and applied it to systems containing CO<sub>2</sub> and hydrocarbons.

It should be noted that such correlations can be obtained only when a single binary parameter is used for each binary pair. If two or more parameters are used, they usually become strongly correlated with each other which makes it practically impossible to correlate

them with parameters such as  $T_c$  and  $\omega$ . Therefore, correlations of this kind are used only in conjunction with the classical quadratic mixing rule with one binary parameter. In particular, they can be established when the one-parameter quadratic mixing rule is used for equations of state based on the chemical theory. This has been demonstrated by Anderko and Malanowski (194), who obtained correlations for homologous series of mixtures containing methanol and phenol.

#### 4.6.2 Group-Contribution Equations of State

A much more general approach is the development of equations of state in which all parameters are calculated from group contributions. Generalization of the classical quadratic mixing rules in terms of groups rather than components is relatively straightforward even though it requires large-scale parameter regressions. For example, Pults *et al.* (215,216) presented a generalization of the classical quadratic mixing rule in terms of group contributions:

$$a = \sum_i^{N_C} \sum_j^{N_C} x_i x_j \sum_m^{N_G} \sum_n^{N_G} v_{im} v_{jn} q_m q_n a_{mn} \quad (4.134)$$

$$b = \sum_i^{N_C} x_i \sum_m^{N_G} v_{im} b_m \quad (4.135)$$

where the number of groups  $m$  in molecule  $i$  is given by  $v_{im}$  and the quantities  $N_C$  and  $N_G$  represent the number of components and the number of groups, respectively. The quantity  $q_m$  is a reduced area for group  $m$ , normalized to a value of 10 for methane. Pults *et al.* applied these mixing rules to a simplified version of the COR EOS (93) obtained by combining the COR repulsive term with a Redlich-Kwong attractive term. Since the mixing rule is a group-contribution version of the classical quadratic mixing rule, the equation is limited to nonpolar components. Another equation of state for nonpolar fluids was proposed by Georgeton and Teja (217), who rewrote the Patel-Teja EOS (16) in terms of group contributions.

A more elaborate group-contribution EOS for hydrocarbons and nonpolar fluids was proposed by Abdoul *et al.* (218). Their model is based on the combination of a cubic equation of state with an excess-Gibbs-energy model. The excess Gibbs energy is defined at a constant packing fraction  $\eta = b/v$ . The same packing fraction is used for pure components and mixtures so that the excess functions can be unambiguously calculated. Apart from the constant-packing-fraction assumption, the method of Abdoul *et al.* (218) is similar to the Huron-Vidal technique (161). To calculate the properties of mixtures, an excess Helmholtz energy is added to pure-component Helmholtz energies calculated from an equation of state. The excess function is given by

$$A^E(T, \eta, x) = NRT \sum_i x_i \ln \frac{b_i}{b} + E(T, x) \xi(\eta) \quad (4.136)$$

The first term results from mixing at the constant packing fraction and corresponds to a combinatorial contribution to the excess functions. The term  $\xi(\eta)$  is chosen in such a way that

the same P-V relationship applies to mixtures and pure components. Since Abdoul *et al.* use a translated Peng-Robinson EOS, the term  $\xi(\eta)$  is equal to  $[\ln(1+\gamma\eta)]/\gamma$ . The term  $E(T,x)$  introduces the actual excess function and is calculated from

$$E(T,x) = E_1(T,x) + E_2(T,x) \quad (4.137)$$

where  $E_1$  follows from Guggenheim's quasi-lattice model and  $E_2$  is an empirical correction for chain-length differences.  $E_1$  is given by

$$E_1 = -\frac{b}{2} \sum_{i=1}^p \sum_{j=1}^p \frac{x_i b_i}{b} \frac{x_j b_j}{b} E_{ij}(T) \quad (4.138)$$

with

$$E_{ij}(T) = -\frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl}(T) \quad (4.139)$$

where  $\alpha_{ik}$  is the relative amount of group  $k$  in molecule  $i$  and  $A_{kl}$  is the interaction parameter between groups  $k$  and  $l$ . The parameters  $A_{kl}$  are calculated from temperature-dependent group contributions. In view of the composition dependence of  $E_1$ , this method is suitable only for mixtures containing nonpolar or weakly polar compounds. For these classes of compounds, this method is very accurate because it predicts not only phase equilibria, but also heats of mixing and volumetric properties. Following the original work of Abdoul *et al.*, Le Roy *et al.* (219) expanded the group contribution table to improve the prediction for systems containing heavy hydrocarbons. Also, Fransson *et al.* (220) extended the method to chlorinated and fluorinated hydrocarbons.

A group contribution method that is not limited to mixtures of nonpolar and weakly polar components has been developed by Skjold-Jorgensen (221,222). In this equation, the residual Helmholtz energy is calculated as a sum of a free-volume term and an attractive term. The free-volume term is obtained from the Carnahan-Starling EOS with the Boublik-Mansoori mixing rules whereas the attractive term is a group-contribution version of a density-dependent mixing rule with the NRTL equation used as the excess-Gibbs-energy model. The Skjold-Jorgensen model was specifically designed for the calculation of gas solubilities in solvents of different chemical character. The original group contribution tables were later extended by Wolff *et al.* (223) and Pusch and Schmelzer (224).

The existing group-contribution equations of state gained only limited popularity for two reasons. First, their group contribution tables are not as extensive as those of the existing excess-Gibbs-energy group contribution methods (*i.e.*, UNIFAC and ASOG). Second, end users in industry tend to prefer to use the well-known and extensively tested UNIFAC method. Since UNIFAC can be coupled with cubic equations of state in an essentially unchanged form, the resulting UNIFAC-based equations tend to be more appealing. However, equations of state with independent group contributions may be advantageous for mixtures containing components with strongly differing volatilities, for which the UNIFAC parameters may be missing or less reliable.

### 4.6.3 Utilization of Predictive Excess-Gibbs-Energy Models

Because of the great popularity of the UNIFAC group-contribution model for chemical-engineering calculations, several authors developed methods for combining UNIFAC with cubic equations of state so that the group-contribution tables can be used unchanged. An early method for achieving this, called UNIWAALS, was proposed by Gupte *et al.* (225), who developed a technique for matching the excess Gibbs energy at zero pressure obtained from the van der Waals EOS with that from UNIFAC. The technique of Gupte *et al.* suffered from a problem that precluded it from generating the critical point. UNIWAALS was later improved by Gani *et al.* (226) to remove this deficiency. However, the resulting EOS was difficult to use because the pressure and volume were related through a differential equation rather than the customary cubic equation.

More recent procedures developed by Heidemann and Kokal (168), Michelsen (167) and Wong and Sandler (171) made it possible to incorporate UNIFAC into equations of state in a fully consistent way. These procedures have been described in Section 4.4.4. Their usefulness has been extensively demonstrated. In particular, Dahl and Michelsen (169) and Dahl *et al.* (227) used Michelsen's MHV2 mixing rule (167) and obtained good prediction of high-pressure VLE. Holderbaum and Gmehling (228) applied a slightly modified MHV2. Orbey *et al.* (229) used the Wong-Sandler mixing rule and obtained good predictions of both VLE and LLE. In all cases, the UNIFAC group-contribution parameters were used unchanged.

Although these methods make it possible to use the existing UNIFAC parameters, it should be noted that new parameters have to be regressed for numerous systems of interest. This is due to the simple fact that components that occur in high-pressure VLE do not necessarily occur in low-pressure VLE. For example, Holderbaum and Gmehling (228) had to regress additional group-contribution parameters that were necessary for calculating gas-gas and gas-alkane phase equilibria. Another problem associated with this approach is the temperature range for which the UNIFAC parameters are valid. Since the UNIFAC parameters were determined from low-pressure VLE, this temperature range is usually very limited. As we go to high-pressure VLE, the high pressures are frequently accompanied by high temperatures. Therefore, an extrapolation of the parameters is necessary. This extrapolation may be particularly doubtful if temperature-dependent UNIFAC parameters are used (*i.e.*, the so-called Dortmund and Lyngby modifications of UNIFAC).

## 4.7 CLOSING REMARKS

Cubic equations of state are currently the most widely used models for a variety of practical applications, including chemical-process and reservoir simulation. Cubic equations for pure components have reached maturity and no substantial progress can be expected in this area. Reliable techniques have been established to represent vapor pressures of both nonpolar and polar or associating compounds. The representation of volumetric properties has been improved within the limits imposed by the cubic form. The only exception is the representation of properties of heavy hydrocarbons and ill-defined compounds, which is still an area of active research.

In contrast to pure components, the representation of mixed-fluid properties by using cubic equations of state is still in a state of flux. While the classical quadratic mixing rules are the method of choice for mixtures containing nonpolar or weakly polar components, several alternative methods are available for mixtures containing strongly polar or associating

components. The composition - dependent combining rules provide the simplest successful method. They are capable of satisfactorily representing the properties of binary mixtures, but may lose accuracy for multicomponent mixtures. This may be due either to their internal consistency problems (*i.e.*, the Michelsen-Kistenmacher syndrome) or the simple fact that empirical parameters regressed for a multiparameter model may be strongly correlated with each other and, therefore, not always suitable for extrapolations to systems with a larger number of components. An alternative method is based on the combination of excess-Gibbs-energy models with equations of state. Such combined models have essentially the same properties for multicomponent mixtures as the excess-Gibbs-energy models. Thus, they are usually fairly reliable for the prediction of multicomponent phase equilibria from binary data, except for the most strongly nonideal systems. An important advantage of the more recent models of this type (such as the MHV2 or Wong-Sandler mixing rules) is the possibility of using the existing parameters of excess-Gibbs-energy models without having to regress them specifically for the combined EOS+ $G^E$  model. This feature has been extensively utilized to extend the applicability of the UNIFAC group-contribution method to high pressures and temperatures.

Substantial progress has been achieved in the generalized van der Waals equations of state. Their development has been influenced, in particular, by the progress in the statistical mechanics of chain-like molecules. It is becoming apparent that the more recent equations of this kind (such as SAFT or PHSC) are particularly suitable for polymer systems. Another area in which the generalized van der Waals equations may be somewhat superior to cubic equations is the modeling of ill-defined mixtures, for which special parameterization techniques are necessary. However, cubic equations of state are well entrenched in the modeling of phase equilibria and thermodynamic properties for hydrocarbon processing and the manufacture of commodity chemicals. It is extremely unlikely that they will be superseded in these areas by models with a better theoretical background.

A lot of attention has been devoted in this review to methods that combine simple equations of state with chemical association models. This is justified by the fact that these methods significantly improve the performance of equations of state for associated mixtures without resorting to multiparameter, empirical mixing rules. Also, they are only moderately more computer-time consuming than regular cubic equations of state. The only major shortcoming of the equations of state based on the chemical theory is the relatively cumbersome procedure for evaluating both the chemical and physical pure-component parameters from the same experimental data (*i.e.* vapor pressures and densities). It should be noted that the equations of state based on the chemical theory face a strong competition from associated-mixture models based on the thermodynamic perturbation theory, which are reviewed in Chapter 12 of this book. The statistical mechanics-based equations of state (such as the SAFT equation) have been proven to be very valuable for systems, in which the strength of association varies from weak hydrogen bonding to covalently-bound polymers. However, the models based on the chemical theory give very good results for several important systems, such as mixtures containing hydrogen fluoride or hydrocarbon-water reservoir systems.

At present, most researchers in this area believe that further progress will result from developments of statistical thermodynamics. At the same time, almost all calculations in industrial practice are performed using empirical, mostly cubic, equations. For practical applications, equations of state with a better theoretical background have been shown to be superior to the cubic equations only in a few niche areas such as polymer systems and electrolyte mixtures at high pressures and temperatures. It can be expected that the slow

process of merging theoretical concepts with empirical techniques will lead to improvements in the future.

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