3 Thermodynamics of Polymer Solutions

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3.1 INTRODUCTION

Knowledge of phase behavior (thermodynamics) of polymer solutions is important for the design of many processes and products, including many specific applications in colloid and surface chemistry. Among the many applications, we can mention the following:

1. The design of separations for the removal of unreacted monomers, colorants, by-products, and additives after solution or emulsion polymerizations
2. Selection of appropriate mixed solvents for paints and coatings, which can meet strict production and environmental criteria (fewer VOCs, water-based products)\textsuperscript{3,4}

3. Numerous applications in the coatings industry, for example, in the control of emissions during production and application, the effect of temperature, and swelling of film or sorption of gases and chemicals from the atmosphere\textsuperscript{3–6}

4. Novel recycling methods for polymer waste based on physicochemical methods, the so-called selective dissolution\textsuperscript{7,8}

5. Design of advanced materials based on compatible polymer blends\textsuperscript{9} or novel structures, for example, star or hyperbranched polymers\textsuperscript{10,11}

6. Permeabilities of gases in the flexible polymeric pipelines used, for example, in the North Sea for transporting hydrocarbons from the seabed to the surface\textsuperscript{12,13}

7. Use of CO\textsubscript{2} as user-friendly solvent for many polymer-related applications including those involving paints and coatings\textsuperscript{14–16}

8. Simultaneous representation of bulk and surface thermodynamic properties\textsuperscript{17}

9. Migration of plasticizers from PVC\textsuperscript{18–21}

10. Separation of proteins based on the so-called aqueous two-phase systems using polymers like PEG or dextran\textsuperscript{1,22,23}

11. Choice of suitable solvents for polymers and especially copolymers used as stabilizers in colloidal dispersions

The aforementioned list shows some of the many applications where polymer thermodynamics plays a key role. Polymer solutions and blends are complex systems: frequent existence of liquid–liquid equilibria (LLE) (UCST, LCST, closed loop, etc.), the significant effect of temperature and polymer molecular weight including polydispersity in phase equilibria, free-volume (FV) effects, and other factors may cause difficulties. For this reason, many different models have been developed for polymer systems and often the situation may seem rather confusing to the practicing engineer.

The choice of a suitable model will depend on the actual problem and depends, specifically, on

- Type of mixture (solution or blend, binary or multicomponent, etc.)
- Type of phase equilibria (VLE, LLE, SLLE, gas solubility, etc.)
- Conditions (temperature, pressure, concentration)
- Type of calculations (accuracy, speed, yes/no answer or complete design, etc.)

This chapter will present key tools in polymer thermodynamics at three different levels from the “simpler” but also “more easy-to-use” methods up to the “more advanced” but also “more complex” and potentially more accurate approaches:

1. Rules of thumb for choosing solvents including a discussion of the Flory–Huggins (FH) approach (Section 3.2)
2. FV activity coefficient models based on UNIFAC (Section 3.3), which are often predictive, and have found widespread applications at low pressures
3. The advanced statistical-associating fluid theory (SAFT) (Section 3.4), which is a theoretically based equation of state, which can be rigorously applied, unlike the activity coefficient models, at both low and high pressures

### 3.2 CHOICE OF SOLVENTS

A summary of some rules of thumb for predicting polymer–solvent miscibility, with focus on the screening of solvents for polymers, is presented here. These rules are based on well-known concepts of thermodynamics (activity coefficients, solubility parameters) and some specific ones for polymers
(the FH parameter). It can be roughly stated that a chemical (1) will be a good solvent for a specific polymer (2), or in other words, the two compounds will be miscible if one (or more) of the following “rules of thumb” are valid:

1. If the polymer and the solvent have similar hydrogen bonding degrees:
   \[ |\delta_1 - \delta_2| \leq 1.8 \text{ (cal/cm}^3\text{)}^{1/2} \]  
   where \( \delta \) is the solubility parameter.

2. If the polymer and the solvent have very different hydrogen bonding degrees:
   \[ \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2} \leq R \]  
   where \( R \) is the Hansen-solubility parameter sphere radius and the subscripts \( d, p, h \) in the solubility parameter denote the dispersion, polar, and hydrogen bonding contributions, respectively.

3. \( \Omega \leq 6 \) (the lower the infinite dilution activity coefficient of the solvent, the greater is the miscibility of a chemical). Values of the infinite dilution activity coefficient above 10 indicate nonmiscibility. In the intermediate region, it is difficult to conclude if the specific chemical is a solvent or a nonsolvent.

4. \( \chi_{12} \leq 0.5 \) (the lower the FH parameter value, the greater is the miscibility). Values much above 0.5 indicate nonmiscibility.

### 3.2.1 Rules of Thumb Based on Solubility Parameters

They are widely used. The starting point (in their derivation and understanding) is the equation for the Gibbs free energy of mixing:

\[ \Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}} \]  

A negative value implies that a solvent–polymer system forms a homogeneous solution, that is, the two components are miscible. Since the contribution of the entropic term \((-T\Delta S)\) is always negative, it is the heat of mixing term that determines the sign of the Gibbs energy. The heat of mixing can be estimated from various theories, for example, the Hildebrand regular solution theory for nonpolar systems, which is based on the concept of the solubility parameter. For a binary solvent (1)–polymer (2) system, according to the regular solution theory,

\[ \Delta H^{\text{mix}} = \varphi_1 \varphi_2 V(\delta_1 - \delta_2)^2 \]  

where \( \varphi_i \) is the so-called volume fraction of component \( i \). This is defined via the mole fractions \( x_i \) and the molar volumes \( V_i \) as (for binary systems):

\[ \varphi_i = \frac{x_i V_i}{x_i V_i + x_j V_j} \]  

According to Equation 3.4, the heat of mixing is always positive. For some systems with specific interactions (hydrogen bonding), the heat of mixing can be negative and Equation 3.4 does not hold.
Thus, the regular solution theory is strictly valid for nonpolar–slightly polar systems, without any specific interactions.

According to Equations 3.3 and 3.4, if solvent and polymer have the same solubility parameters, the heat of mixing is zero and they are therefore miscible at all proportions. The lower the solubility parameter difference, the larger the tendency for miscibility. Many empirical rules of thumb have been proposed based on this observation. Seymour\(^{24}\) suggests that if the difference of solubility parameters is below 1.8 (cal/cm\(^3\))\(^{1/2}\), then polymer and solvent are miscible (Equation 3.1).

Similar rules can be applied for mixed solvent–polymer systems, which are very important in many practical applications, for example, in the paints and coatings industry and for the separation of biomolecules using aqueous two-phase systems.

The solubility parameter of a mixed solvent is given by the equation:

\[ \delta = \sum q_i \delta_i \]  

(3.6)

Barton\(^{25,26}\) provides empirical methods based on solubility parameters for ternary solvent systems.

Charles Hansen introduced the concept of 3D solubility parameters, which offers an extension of the regular solution theory to polar and hydrogen bonding systems. Hansen observed that when the solubility parameter increments of the solvents and polymers are plotted in 3D plots, then the “good” solvents lie approximately within a sphere of radius \(R\) (with the polymer being in the center). This can be mathematically expressed as shown in Equation 3.2. The quantity under the square root is the distance between the solvent and the polymer. Hansen found empirically that a universal value 4 should be added as a factor in the dispersion term to approximately attain the shape of a sphere. This universal factor has been confirmed by many experiments. Hansen\(^{27}\) in his book provides a review of the method together with extensive tables of parameters.

The Hansen method is very valuable. It has found widespread use particularly in the paints and coatings industry, where the choice of solvents to meet economical, ecological, and safety constraints is of critical importance. It can explain some cases in which polymer and solvent solubility parameters are almost perfectly matched and yet the polymer will not dissolve. The Hansen method can also predict cases where two nonsolvents can be mixed to form a solvent. Still, the method is approximate; it lacks the generality of a full thermodynamic model for assessing miscibility and requires some experimental measurements. The determination of \(R\) is typically based on visual observation of solubility (or not) of 0.5 g polymer in 5 cm\(^3\) solvent at room temperature. Given the concentration and the temperature dependence of phase boundaries, such determination may seem a bit arbitrary. Still, the method works out pretty well in practice, probably because the liquid–liquid boundaries for most polymer–solvent systems are fairly “flat.”

### 3.2.2 Rule of Thumb Based on the Infinite Dilution Activity Coefficient

Since in several practical cases concerning polymer–solvent systems, the “solvent” is only present in very small (trace) amounts, the so-called infinite dilution activity coefficients are important. On a molar and weight basis, they are defined as follows:

\[ \gamma_i^\infty = \lim_{x_i \to 0} \gamma_i \]

\[ \Omega_i^\infty = \lim_{w_i \to 0} \left( \frac{x_i \gamma_i}{w_i} \right) = \gamma_i^\infty \frac{M_{pol}}{M_{solv}} \]  

(3.7)
The latter part of the equation is valid for a binary solvent–polymer solution and \( \gamma_1^\infty \) is the infinite dilution activity coefficient of the solvent.

The weight-based infinite dilution activity coefficient, \( \Omega_1^\infty \), which can be determined experimentally from chromatography, is a very useful quantity for determining good solvents. As mentioned in the previous section, low values (typically below 6) indicate good solvents, while high values (typically above 10) indicate poor solvents according to rules of thumb discussed by several investigators.\(^{28,29}\) The derivation of this rule of thumb is based on the FH model.

This method for solvent selection is particularly useful, because it avoids the need for direct liquid–liquid measurements and it makes use of the existing databases of solvent infinite dilution activity coefficients, which is quite large (e.g., the DEHEMA and DIPPR databases\(^{30,31}\)).

Moreover, in the absence of experimental data, existing thermodynamic models (such as the FH, the Entropic-FV, and the UNIFAC-FV discussed later) can be used to predict the infinite dilution activity coefficient. Since, in the typical case today, existing models perform much better for VLE and activity coefficient calculations than directly for LLE calculations, this method is quite valuable and successful, as shown by sample results in Table 3.1.

This rule of thumb makes use of either experimental or predicted, by a model, infinite dilution activity coefficients. However, the results depend not only on the accuracy of the model, but also on the rule of thumb, which in terms depends on the assumptions of the FH approach. A thermodynamically more correct method is to employ the activity–concentration diagram. The maximum indicates phase split, while a monotonic increase of activity with concentration indicates a single liquid phase (homogeneous solutions).

### 3.2.3 Rule of Thumb Based on the Flory–Huggins Model

The FH model for the activity coefficient, proposed in the early 1940s by Flory and Huggins,\(^{32,33}\) is a famous Gibbs free energy expression for polymer solutions. For binary solvent–polymer solutions and assuming that the parameter of the model, the so-called FH interaction parameter \( \chi_{12} \), is constant, the activity coefficient is given by the equation:

\[
\ln \gamma_1 = \ln \frac{q_1}{x_1} + 1 - \frac{q_1}{x_1} + \chi_{12} q_2^2 = \ln \frac{q_1}{x_1} + \left(1 - \frac{1}{r}\right) q_2 + \chi_{12} q_2^2
\]  \hspace{1cm} (3.8)

where

- \( q_i \) can be volume or segment fractions
- \( r \) is the ratio of the polymer volume to the solvent volume \( V_2/V_1 \) (approximately equal to the degree of polymerization)

Appendix 3.A presents the general expression for the FH model suitable for multicomponent systems.

Using standard thermodynamics and Equation 3.8, it can be shown that for high molecular weight polymer–solvent systems, the polymer critical concentration is close to zero and the interaction parameter has a value equal to 0.5. Thus, a good solvent (polymer soluble in the solvent at all proportions) is obtained if \( \chi_{12} \leq 0.5 \), while values greater than 0.5 indicate poor miscibility. Since the FH model is only an approximate representation of the physical picture and particularly the FH parameter is often not a constant at all, this empirical rule is certainly subject to some uncertainty. Nevertheless, it has found widespread use and its conclusions are often in good agreement with experiment.
### TABLE 3.1
Choice of Suitable Solvents Using the $\omega_1^\ell$-Rule of Thumb for PBMA Systems
(See Section 3.2)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>S/NS</th>
<th>EFV</th>
<th>UFV</th>
<th>GCFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>NS</td>
<td>7.1</td>
<td>7.0</td>
<td>10.7</td>
</tr>
<tr>
<td>$n$-Octane</td>
<td>NS</td>
<td>6.7</td>
<td>6.3</td>
<td>10.4</td>
</tr>
<tr>
<td>$n$-Decane</td>
<td>NS</td>
<td>6.5</td>
<td>6.0</td>
<td>10.7</td>
</tr>
<tr>
<td>$n$-Dodecane</td>
<td>NS</td>
<td>6.6</td>
<td>6.0</td>
<td>11.3</td>
</tr>
<tr>
<td>$n$-Hexadecane</td>
<td>NS</td>
<td>6.8</td>
<td>6.1</td>
<td>13.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>S</td>
<td>3.2</td>
<td>4.4</td>
<td>4.7</td>
</tr>
<tr>
<td>Xylene</td>
<td>S</td>
<td>2.3</td>
<td>3.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Methylene dichloride</td>
<td>S</td>
<td>3.3</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>S</td>
<td>1.9</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>S</td>
<td>2.2</td>
<td>2.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Ethylene dichloride</td>
<td>S</td>
<td>3.5</td>
<td>3.0</td>
<td>—</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>S</td>
<td>2.5</td>
<td>2.9</td>
<td>33.9</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>S</td>
<td>2.5</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>$o$-Dichlorobenzene</td>
<td>S</td>
<td>1.3</td>
<td>2.5</td>
<td>2.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>S</td>
<td>10.9</td>
<td>14.2</td>
<td>11.1</td>
</tr>
<tr>
<td>MEK</td>
<td>S</td>
<td>8.4</td>
<td>10.5</td>
<td>8.2</td>
</tr>
<tr>
<td>MIBK</td>
<td>S</td>
<td>6.3</td>
<td>7.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>S</td>
<td>8.1</td>
<td>9.3</td>
<td>8.6</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>S</td>
<td>6.7</td>
<td>6.7</td>
<td>60.3</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>S</td>
<td>5.3</td>
<td>5.1</td>
<td>31.4</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>S</td>
<td>5.2</td>
<td>5.8</td>
<td>11.6</td>
</tr>
<tr>
<td>THF</td>
<td>S</td>
<td>3.8</td>
<td>4.0</td>
<td>—</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>S</td>
<td>4.1</td>
<td>4.4</td>
<td>159.4</td>
</tr>
<tr>
<td>Methanol</td>
<td>NS</td>
<td>43.7</td>
<td>57.7</td>
<td>35.7</td>
</tr>
<tr>
<td>Ethanol</td>
<td>NS</td>
<td>29.2</td>
<td>31.3</td>
<td>17.3</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>NS</td>
<td>18.1</td>
<td>17.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>NS</td>
<td>24.3</td>
<td>20.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>NS</td>
<td>277.8</td>
<td>—</td>
<td>15,947.0</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>NS</td>
<td>212.6</td>
<td>—</td>
<td>1,879.2</td>
</tr>
<tr>
<td>1,3-Butanediol</td>
<td>NS</td>
<td>158.5</td>
<td>—</td>
<td>525.5</td>
</tr>
<tr>
<td>Glycerol</td>
<td>NS</td>
<td>294.6</td>
<td>—</td>
<td>2,282.4</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>NS</td>
<td>23.4</td>
<td>21.6</td>
<td>10.6</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>S</td>
<td>19.0</td>
<td>17.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>NS</td>
<td>240.1</td>
<td>—</td>
<td>2,470.4</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>NS</td>
<td>127.9</td>
<td>945.7</td>
<td>287.8</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>NS</td>
<td>16.7</td>
<td>17.2</td>
<td>—</td>
</tr>
<tr>
<td>1-Nitropropane</td>
<td>S</td>
<td>4.7</td>
<td>5.2</td>
<td>—</td>
</tr>
<tr>
<td>$N,N$-dimethylformamide</td>
<td>S</td>
<td>3.8</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>


Notes: EFV, Entropic-FV; UFV, UNIFAC-FV; GCFL, GC-Flory; S, solvent; NS, nonsolvent (experimental observation).
There are several, still rather obscure issues about the FH model, which we summarize here together with some recent developments:

1. The FH parameter is typically not a constant and should be estimated from experimental data. Usually, it varies with both temperature and concentration, which renders the FH model useful only for describing experimental data. It cannot be used for predicting phase equilibria for systems for which no data is available. Moreover, when fitted to the critical solution temperature, the FH model cannot yield a good representation of the whole shape of the miscibility curve with a single parameter.

2. Accurate representation of miscibility curves is possible with the FH model using suitable (rather complex) equations for the temperature and the concentration dependence of the FH parameter.

3. In some cases, a reasonable value of the FH parameter can be estimated using solubility parameters via the equation:

\[ \chi_{i2} = \chi_i + \chi_{hi} = 0.35 + \frac{V_i}{RT} (\delta_i - \delta_2)^2 \]  

Equation 3.9, without the empirical 0.35 factor, is derived from the regular solution theory. The constant 0.35 is added for correcting for the deficiencies of the FH combinatorial term. These deficiencies become evident when comparing experimental data for athermal polymer and other asymmetric solutions to the results obtained with the FH model. A systematic underestimation of the data is observed, as discussed extensively in the literature, which is often attributed to the inability of the FH model in accounting for the FV differences between polymers and solvents or between compounds differing significantly in size such as \( n \)-alkanes with very different chain lengths. The term, which contains the “0.35 factor,” corrects in an empirical way for these FV effects. However, and although satisfactory results are obtained in some cases, we cannot generally recommend Equation 3.9 for estimating the FH parameter. Moreover, for many nonpolar systems with compounds having similar solubility parameters, the empirical factor 0.35 should be dropped.

4. Lindvig et al. proposed an extension of the FH equation using the Hansen solubility parameters for estimating activity coefficients of complex polymer solutions.

\[ \ln \gamma_1 = \ln \frac{q_{h1}}{x_1} + 1 - \frac{q_{p1}}{x_1} + \chi_{i2} q_2^2 \]

\[ \chi_{i2} = 0.6 \frac{V_i}{RT} \left[ (\delta_{d1} - \delta_{d2})^2 + 0.25(\delta_{p1} - \delta_{p2})^2 + 0.25(\delta_{h1} - \delta_{h2})^2 \right] \]  

In order to achieve that, Lindvig et al. have, as shown in Equation 3.10, employed a universal correction parameter, which has been estimated from a large number of polymer–solvent VLE data. Very good results are obtained, especially when the volume-based combinatorial term of FH is employed, also for ternary polymer–solvent systems.

5. Based on the FH model, several techniques have been proposed for interpreting and for correlating experimental data for polymer systems, for example, the so-called Schultz–Flory
(SF) plot. Schultz and Flory have developed, starting from the FH model, the following expression, which relates the critical solution temperature (CST), with the theta temperature and the polymer molecular weight:

\[
\frac{1}{\text{CST}} = \frac{1}{\Theta} \left[ 1 + \frac{1}{\psi} \left( \frac{1}{\sqrt{r}} + \frac{1}{2r} \right) \right]
\]

(3.11)

where

\[\psi = ((1/2) - \chi_s)\]

is the entropic parameter of the FH model (Equation 3.9)

\[r\]

is the ratio of molar volumes of the polymer to the solvent

This parameter is evidently dependent on the polymer’s molecular weight. The SF plot can be used for correlating data of critical solution temperatures for the same polymer–solvent system, but at different polymer molecular weights. This can be done, as anticipated from Equation 3.11, because the plot of 1/CST against the quantity in parentheses in Equation 3.11 is linear. The SF plot can also be used for predicting CST for the same system but at different molecular weights than those used for correlation as well as for calculating the theta temperature and the entropic part of the FH parameter. It can be used for correlating CST/molecular weight data for both the UCST and LCST areas. Apparently different coefficients are needed.

### 3.3 FREE-VOLUME ACTIVITY COEFFICIENT MODELS

#### 3.3.1 The Free-Volume Concept

The FH model provides a first approximation for polymer solutions. Both the combinatorial and the energetic terms require substantial improvement. Many authors have replaced the random van-Laar energetic term by a nonrandom local-composition term such as those of the UNIQUAC, NRTL, and UNIFAC models. The combinatorial term should be modified to account for the FV differences between solvents and polymers.

The improvement of the energetic term of FH equation is important. Local-composition terms like those appearing in NRTL, UNIQUAC, and UNIFAC provide a flexibility, which cannot be accounted for by the single-parameter van Laar term of FH. However, the highly pronounced FV effects should always be accounted for in polymer solutions.

The concept of FV is rather loose, but still very important. Elbro demonstrated, using a simple definition for the FV (Equation 3.12), that the FV percentages of solvents and polymers are different. In the typical case, the FV percentage of solvents is greater (40%–50%) than that of polymers (30%–40%). There are two notable exceptions to this rule; water and PDMS: water has lower FV than other solvents and closer to that of most of the polymers, while PDMS has quite a higher FV percentage, closer to that of most solvents. LCST is, as expected, related to the FV differences between polymers and solvents. As shown by Elbro, the larger the FV differences, the lower is the LCST value (the larger the area of immiscibility). For this reason, PDMS solutions have a LCST, which are located at very high temperatures.

Many mathematical expressions have been proposed for the FV. One of the simplest and successful equations is

\[V_f = V - V^* = V - V_e\]

(3.12)

originally proposed by Bondi and later adopted by Elbro et al. and Kontogeorgis et al. in the so-called Entropic-FV model (described later). According to this equation, FV is just
the “empty” volume available to the molecule when the molecules’ own (hard-core or closed-packed \( V^* \)) volume is subtracted.

The FV is not the only concept, which is loosely defined in this discussion. The hard-core volume is also a quantity difficult to define and various approximations are available. Elbro et al.\(^{35} \) suggested using \( V^* = V_w \), that is, equal to the van der Waals volume (\( V_w \)), which is obtained from the group increments of Bondi and is tabulated for almost all existing groups in the UNIFAC tables. Other investigators\(^{41} \) interpreted somewhat differently the physical meaning of the hard-core volume in the development of improved FV expressions for polymer solutions, which employ Equation 3.12 as basis, but with \( V^* \) values higher than \( V_w \) (about 1.2–1.3 \( V_w \)).

### 3.3.2 Entropic-FV Model

The original UNIFAC model does not account for the FV differences between solvents and polymers and, as a consequence of that, it highly underestimates the solvent activities in polymer solutions. One of the most successful and earliest such models for polymers is the UNIFAC-FV by Oishi and Prausnitz.\(^{42} \) The UNIFAC-FV model was developed for solvent activities in polymers, but it cannot be successfully applied to LLE.

A similar to UNIFAC-FV but somewhat simpler approach, which can be readily extended to multicomponent systems and LLE, is the so-called Entropic-FV model proposed by Elbro et al.\(^{35} \) and Kontogeorgis et al.\(^{40} \):

\[
\ln \frac{\gamma_i}{\gamma_i^{UNIFAC}} = \ln \gamma_i^{comb-FV} + \ln \gamma_i^{res}
\]

\[
\ln \gamma_i^{comb-FV} = \ln \frac{\phi_{FV}^i}{x_i} + 1 - \frac{\phi_{FV}^i}{x_i}
\]

\[
\phi_{FV}^i = \frac{x_i V_{i,FV}}{\sum_j x_j V_{j,FV}} = \frac{x_i(V_i - V_{wi})}{\sum_j x_j(V_j - V_{wj})}
\]

\[
\ln \gamma_i^{res} \to UNIFAC
\]

As can be seen from Equation 3.13, the FV definition given by Equation 3.12 is employed. The combinatorial term of Equation 3.13 is very similar to that of FH. However, instead of volume or segment fractions, FV fractions are used. In this way, both combinatorial and FV effects are combined into a single expression. The combinatorial–FV expression of the Entropic-FV model is derived from statistical mechanics, using a suitable form of the generalized van der Waals partition function.

The residual term of Entropic-FV is taken by the so-called new or linear UNIFAC model, which uses a linear-dependent parameter table\(^{43} \):

\[
a_{mn} = a_{mn,1} + a_{mn,2} (T - T_c)
\]

This parameter table has been developed using the combinatorial term of the original UNIFAC model. As with UNIFAC-FV, no parameter re-estimation has been performed. The same group parameters are used in the “linear UNIFAC” and in the Entropic-FV models.

A common feature for both UNIFAC-FV and Entropic-FV is that they require values for the volumes of solvents and polymers (at the different temperatures where application is required). This can be a problem in those cases where the densities are not available experimentally and have to be estimated using a predictive group-contribution or other method, for example, GCVOL\(^{44,45} \) or van Krevelen methods. These two estimation methods perform quite well and often similarly even for low molecular weight compounds or oligomers as plasticizers.
Both UNIFAC-FV and Entropic-FV, especially the former, are rather sensitive to the density values used for the calculations of solvent activities.

As already mentioned, the Entropic-FV model has been derived from the van der Waals partition function. The similarity of the model with the van der Waals equation of state \( P = RT(V - b) - a/V^2 \) becomes apparent if the van der Waals equation of state is written (when the classical van der Waals one fluid mixing and classical combining rules are used) as an activity coefficient model:

\[
\ln \gamma_i = \ln \gamma_i^{\text{comb-FV}} + \ln \gamma_i^{\text{ex}} = \left( \ln \left( \frac{q_i^{FV}}{x_i} + 1 - \frac{q_i^{FV}}{x_i} \right) + \left( \frac{V_i}{RT} \left( \delta_i - \delta_j \right)^2 q_j^2 \right) \right)
\]

\[
q_i^{FV} = \frac{x_i(V_i - b_i)}{\sum_j x_j(V_j - b_j)}
\]

\[
\delta_i = \sqrt{\frac{a_i}{V_i}}
\]

where \( q_i \) is the volume fraction as defined in Equation 3.5. The first term in Equation 3.15 is the same as in Entropic-FV with \( V_u = b \), while the latter term is a regular solution theory or van Laar-type term.

### 3.3.3 Results and Discussion

Table 3.2 presents an overview of the results with Entropic-FV model for different applications together with the corresponding references. Selected results are shown in Tables 3.3 through 3.9 and Figures 3.1 and 3.2.

The most important general conclusions can be summarized as following:

1. Satisfactory predictions are obtained for solvent activities, even at infinite dilution, and for nonpolar, as well as for complex polar and hydrogen bonding systems including solutions of interest to paints and coatings. Rather satisfactory predictions are also achieved when mixed solvents and copolymers are present.

<table>
<thead>
<tr>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>VLE binary solutions</td>
<td>[40,41]</td>
</tr>
<tr>
<td>VLE complex polymers–solvents</td>
<td>[48]</td>
</tr>
<tr>
<td>VLE ternary polymer–solvents</td>
<td>[37]</td>
</tr>
<tr>
<td>Paints</td>
<td>[61]</td>
</tr>
<tr>
<td><strong>Dendrimers</strong></td>
<td></td>
</tr>
<tr>
<td>VLE copolymers</td>
<td>[47]</td>
</tr>
<tr>
<td>VLE athermals systems</td>
<td>[28,35,50,62]</td>
</tr>
<tr>
<td>SLE hydrocarbons</td>
<td>[51,52]</td>
</tr>
<tr>
<td>SLE polymer–solvents</td>
<td>[49]</td>
</tr>
<tr>
<td>Comparison with other models</td>
<td>[40,46,53,60]</td>
</tr>
<tr>
<td>LLE polymer–solvents</td>
<td>[58]</td>
</tr>
<tr>
<td>LLE ternary polymer–mixed solvents</td>
<td>[8]</td>
</tr>
<tr>
<td>Polymer blends</td>
<td>[59]</td>
</tr>
<tr>
<td>EFV + UNIQUAC</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 3.3
Prediction of the Solubility for Characteristic Polymer–Solvent Systems Using the Ω∞∞ Rule of Thumb and Two FV Models for Solvent Selection

<table>
<thead>
<tr>
<th>System</th>
<th>Experiment</th>
<th>Entropic-FV</th>
<th>UNIFAC-FV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBMA/nC_{10}</td>
<td>NS</td>
<td>6.5 (–)</td>
<td>6.1 (–)</td>
</tr>
<tr>
<td>PBMA/xylene</td>
<td>S</td>
<td>2.3 (S)</td>
<td>3.6 (S)</td>
</tr>
<tr>
<td>PBMA/CHCl_{3}</td>
<td>S</td>
<td>1.9 (S)</td>
<td>9.1 (NS)</td>
</tr>
<tr>
<td>PBMA/acetone</td>
<td>S</td>
<td>0.2 (NS)</td>
<td>14.1 (NS)</td>
</tr>
<tr>
<td>PBMA/ethyl acetate</td>
<td>S</td>
<td>6.7 (–)</td>
<td>6.7 (–)</td>
</tr>
<tr>
<td>PBMA/ethyl acetate</td>
<td>NS</td>
<td>29.2 (NS)</td>
<td>31.3 (NS)</td>
</tr>
<tr>
<td>PMMA/acetone</td>
<td>S</td>
<td>10.0 (NS)</td>
<td>16.5 (NS)</td>
</tr>
<tr>
<td>PMMA/ethyl acetate</td>
<td>S</td>
<td>6.6 (–)</td>
<td>8.4 (NS)</td>
</tr>
<tr>
<td>PMMA/butanol</td>
<td>NS</td>
<td>26.8 (NS)</td>
<td>14.4 (NS)</td>
</tr>
<tr>
<td>PEMA/MEK</td>
<td>S</td>
<td>8.1 (NS)</td>
<td>11.7 (NS)</td>
</tr>
<tr>
<td>PEMA/diethyl ether</td>
<td>S</td>
<td>5.8 (S)</td>
<td>7.6 (–)</td>
</tr>
<tr>
<td>PEMA/nitropropane</td>
<td>NS</td>
<td>4.5 (S)</td>
<td>1.4 (S)</td>
</tr>
<tr>
<td>PVAc/hexane</td>
<td>NS</td>
<td>38.7 (NS)</td>
<td>38.6 (NS)</td>
</tr>
<tr>
<td>PVAc/acetone</td>
<td>S</td>
<td>18.9 (NS)</td>
<td>19.4 (NS)</td>
</tr>
<tr>
<td>PVAc/methanol</td>
<td>S</td>
<td>15.2 (NS)</td>
<td>38.9 (NS)</td>
</tr>
<tr>
<td>PVAc/ethyl acetate</td>
<td>S</td>
<td>3.9 (S)</td>
<td>3.8 (S)</td>
</tr>
<tr>
<td>PVAc/THF</td>
<td>S</td>
<td>8.4 (NS)</td>
<td>5.6 (S)</td>
</tr>
</tbody>
</table>

Notes:  S, good solvent; NS, nonsolvent; –, no answer according to the rule of thumb.

TABLE 3.4
Prediction of Infinite Dilution Activity Coefficients for Polyisoprene (PIP) Systems with Two Predictive Group Contribution Models

<table>
<thead>
<tr>
<th>PIP Systems</th>
<th>Exper. Value</th>
<th>Entropic-FV</th>
<th>UNIFAC-FV</th>
</tr>
</thead>
<tbody>
<tr>
<td>+Acetonitrile</td>
<td>68.6</td>
<td>47.7 (31%)</td>
<td>52.3 (24%)</td>
</tr>
<tr>
<td>+Acetic acid</td>
<td>37.9</td>
<td>33.5 (12%)</td>
<td>17.7 (53%)</td>
</tr>
<tr>
<td>+Cyclohexanone</td>
<td>7.32</td>
<td>5.4 (27%)</td>
<td>4.6 (38%)</td>
</tr>
<tr>
<td>+Acetone</td>
<td>17.3</td>
<td>15.9 (8%)</td>
<td>13.4 (23%)</td>
</tr>
<tr>
<td>+MEK</td>
<td>11.4</td>
<td>12.1 (6%)</td>
<td>10.1 (12%)</td>
</tr>
<tr>
<td>+Benzene</td>
<td>4.37</td>
<td>4.5 (2.5%)</td>
<td>4.4 (0%)</td>
</tr>
<tr>
<td>+1,2-Dichloroethane</td>
<td>4.25</td>
<td>5.5 (29%)</td>
<td>6.5 (54%)</td>
</tr>
<tr>
<td>+CCl_{4}</td>
<td>1.77</td>
<td>2.1 (20%)</td>
<td>1.8 (0%)</td>
</tr>
<tr>
<td>+1,4-Dioxane</td>
<td>6.08</td>
<td>6.3 (4%)</td>
<td>5.9 (2%)</td>
</tr>
<tr>
<td>+Tetrahydrofuran</td>
<td>4.38</td>
<td>4.9 (14%)</td>
<td>3.9 (10%)</td>
</tr>
<tr>
<td>+Ethylacetate</td>
<td>7.47</td>
<td>7.3 (2%)</td>
<td>6.6 (11%)</td>
</tr>
<tr>
<td>+n-Hexane</td>
<td>6.36</td>
<td>5.1 (20%)</td>
<td>4.6 (27%)</td>
</tr>
<tr>
<td>+Chloroform</td>
<td>2.13</td>
<td>3.00 (41%)</td>
<td>2.6 (20%)</td>
</tr>
</tbody>
</table>

Experimental values and calculations are at 328.2 K.
### TABLE 3.5

Average Absolute Deviations between Experimental and Calculated Activity Coefficients of Paint-Related Polymer Solutions Using the FH/Hansen Method and Two FV Models

<table>
<thead>
<tr>
<th>Model</th>
<th>% AAD (Systems in Database)</th>
<th>% AAD Araldite 488</th>
<th>% AAD Eponol-55</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH/Hansen, Volume (Equation 3.10)</td>
<td>22</td>
<td>31</td>
<td>28</td>
</tr>
<tr>
<td>Entropic-FV</td>
<td>35</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>UNIFAC-FV</td>
<td>39</td>
<td>119</td>
<td>62</td>
</tr>
</tbody>
</table>

Source: Adapted from Lindvig, Th. et al., *Fluid Phase Equilib.*, 203, 247, 2002.

The second column presents the systems used for optimization of the universal parameter (solutions containing acrylates and acetates). The last two columns show predictions for two epoxy resins.

### TABLE 3.6

Mean Percentage Deviations between Experimental and Calculated Activity Coefficients of Solvents in Various Nearly Athermal Solutions

<table>
<thead>
<tr>
<th>% AAD Infinite Dilution Conditions</th>
<th>Entropic-FV</th>
<th>UNIFAC-FV</th>
<th>Flory-FV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_2^\infty (\Omega_2^\infty$ for Polymers)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short $n$-alkanes/long alkanes</td>
<td>8</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Short branched, cyclic alkanes/long alkanes</td>
<td>10</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>Alkanes/polyethylene</td>
<td>9</td>
<td>23</td>
<td>19</td>
</tr>
<tr>
<td>Alkanes/polyisobutylene</td>
<td>16</td>
<td>12</td>
<td>38</td>
</tr>
<tr>
<td>Organic solvent/PDMS, PS, PVAc</td>
<td>20</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>Overall</td>
<td>13</td>
<td>19</td>
<td>25</td>
</tr>
</tbody>
</table>


### TABLE 3.7

Mean Percentage Deviations between Experimental and Calculated Activity Coefficients of Heavy Alkanes Solutes in Alkane Solvents

<table>
<thead>
<tr>
<th>% AAD infinite dilution conditions, $\gamma_2^\infty$</th>
<th>Entropic-FV</th>
<th>UNIFAC-FV</th>
<th>Flory-FV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric long alkanes/short alkanes</td>
<td>36</td>
<td>47</td>
<td>10</td>
</tr>
<tr>
<td>Medium asymmetric long alkanes/short alkanes</td>
<td>34</td>
<td>48</td>
<td>12</td>
</tr>
<tr>
<td>Asymmetric long alkanes/short alkanes</td>
<td>44</td>
<td>54</td>
<td>37</td>
</tr>
<tr>
<td>Overall</td>
<td>38</td>
<td>50</td>
<td>20</td>
</tr>
</tbody>
</table>

% AAD finite concentrations, $\gamma_2$

<table>
<thead>
<tr>
<th>% AAD finite concentrations, $\gamma_2$</th>
<th>Entropic-FV</th>
<th>UNIFAC-FV</th>
<th>Flory-FV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric long alkanes/short alkanes</td>
<td>14</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>Medium asymmetric long/short alkanes</td>
<td>23</td>
<td>31</td>
<td>11</td>
</tr>
<tr>
<td>Asymmetric long/short alkanes</td>
<td>40</td>
<td>55</td>
<td>16</td>
</tr>
<tr>
<td>Overall</td>
<td>26</td>
<td>34</td>
<td>11</td>
</tr>
</tbody>
</table>

### TABLE 3.8
Average Absolute Logarithmic Percentage Deviations between Experimental and Predicted Equilibrium Pressures and Average Absolute Deviation (×100) between Calculated and Experimental Vapor Phase Compositions (Mole Fractions) for Various Ternary Polymer–Mixed Solvent Systems

<table>
<thead>
<tr>
<th>Sys. No.</th>
<th>Variable</th>
<th>SAFT</th>
<th>EFV/UQ</th>
<th>FH</th>
<th>Pa-Ve</th>
<th>EFV/UN</th>
<th>UFV</th>
<th>GCFL</th>
<th>GCLF</th>
<th>FHHa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P</td>
<td>11</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>2</td>
<td>1</td>
<td>21</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>y</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>P</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3</td>
<td>3</td>
<td>12</td>
<td>5</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>y</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>P</td>
<td>14</td>
<td>16</td>
<td>11</td>
<td>4</td>
<td>17</td>
<td>19</td>
<td>93</td>
<td>5</td>
<td>52</td>
</tr>
<tr>
<td>y</td>
<td>17</td>
<td>17</td>
<td>16</td>
<td>11</td>
<td>17</td>
<td>19</td>
<td>93</td>
<td>5</td>
<td>52</td>
<td></td>
</tr>
</tbody>
</table>


Notes: 1, PS–toluene–ethylbenzene at 303 K; 2, PS–toluene–cyclohexane at 303 K; 3, PVAc–acetone–ethyl acetate at 303 K; 4, PVAc–acetone–methanol at 303 K; 5, PS–chloroform–carbon tetrachloride at 323.15 K.

### TABLE 3.9
Prediction of Liquid–Liquid Equilibria for Polymer–Solvent Systems with Various Thermodynamic Models

<table>
<thead>
<tr>
<th>Polymer System</th>
<th>Molecular Weight</th>
<th>Entropic-FV</th>
<th>N0065w UNIFAC</th>
<th>GC-Flory</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/acetone</td>
<td>4,800</td>
<td>84</td>
<td>21</td>
<td>75</td>
</tr>
<tr>
<td>PS/acetone</td>
<td>10,300</td>
<td>98</td>
<td>8</td>
<td>42</td>
</tr>
<tr>
<td>PS/cyclohexane</td>
<td>20,400</td>
<td>38</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>PS/cyclohexane</td>
<td>37,000</td>
<td>26</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>PS/cyclohexane</td>
<td>43,600</td>
<td>24</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>PS/cyclohexane</td>
<td>89,000</td>
<td>11</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PS/cyclopentane</td>
<td>100,000</td>
<td>15</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>PS/cyclopentane</td>
<td>97,200</td>
<td>27</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>PS/cyclopentane</td>
<td>200,000</td>
<td>12</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>HDPE/n-butyl acetate</td>
<td>13,600</td>
<td>10</td>
<td>82</td>
<td>72</td>
</tr>
<tr>
<td>HDPE/n-butyl acetate</td>
<td>20,000</td>
<td>22</td>
<td>97</td>
<td>70</td>
</tr>
<tr>
<td>HDPE/n-butyl acetate</td>
<td>61,100</td>
<td>29</td>
<td>107</td>
<td>71</td>
</tr>
<tr>
<td>PMMA/1-chloro butane</td>
<td>34,760</td>
<td>53</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PBMA/n-pentane</td>
<td>11,600</td>
<td>Hourglass</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PBMA/n-octane</td>
<td>11,600</td>
<td>155</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Absolute difference between experimental and predicted UCST for several polymer solutions using various models (based on results from Ref. [58]). All results are predictions. The three last models are based on group contributions. The new UNIFAC model is a combination of FH with the UNIFAC residual term.

Notes: PS, polystyrene; HDPE, high-density polyethylene; PMMA, poly(methyl methacrylate); PBMA, poly(butyl methacrylate).
2. Qualitatively correct and occasionally also quantitatively satisfactory representation of LLE for binary and ternary polymer–solvent systems is achieved, especially for the UCST-type phase behavior. A single investigation for SLLE also shows good results.

3. Less satisfactory results are obtained for polymer blends, where FV effects are not as dominant as for polymer solutions.

Some additional observations for specific cases are hereafter presented:

1. Athermal solutions, for example, polyolefins with alkanes offer a way of testing FV terms and numerous such investigations have been presented. FV models perform generally better than those that do not contain volume-dependent terms. Better FV terms than that of
Entropic-FV (Equation 3.13) have been proposed\textsuperscript{41,51,52,57,60} and they may serve as the basis for future developments resulting in even better activity coefficient models for polymer solutions. A rigorous test for newly developed FV expressions is provided by athermal alkane systems, especially the activity coefficients of heavy alkanes in short-chain ones.

2. A difference of 10°–30° should be expected in UCST predictions with Entropic-FV, see Table 3.9.

3. An alternative to Entropic-FV successful approach is the FH/Hansen model presented previously (Equation 3.10). In this case, best results are obtained when the original FH combinatorial rather than a FV term is used together with HSP. It seems that HSP incorporate some FV effects.

### 3.3.4 Correlative Versions of the Entropic-FV Model

Both UNIFAC-FV and Entropic-FV are group contribution models. This renders the models truly predictive, but at the same time with little flexibility if the performance of the models for specific cases is not satisfactory. Two interesting alternative approaches are discussed here, which still maintain the FV terms but use different residual terms.

#### 3.3.4.1 Entropic-FV/UNIQUAC Model

The first approach is to employ the UNIQUAC expression for the residual term. This Entropic-FV/UNIQUAC model has been originally suggested by Elbro et al.\textsuperscript{35} and has shown to give very good results for polymer solutions if the parameters are obtained from VLE data between the solvent and the low molecular weight monomer (or the polymer’s repeating unit).

The Entropic-FV/UNIQUAC model has been recently further developed and extended independently by two research groups.\textsuperscript{55–57} Both VLE and LLE equilibria are considered, but the emphasis is given to LLE. Very satisfactory results are obtained as can be seen for two typical systems in Figures 3.3 and 3.4. It has been demonstrated that the Entropic-FV/UNIQUAC approach can

**FIGURE 3.3** Correlation of liquid–liquid equilibria for the PVAL/water system with the Entropic-FV/UNIQUAC model. (•) Exp. data ($M_n = 140,000$ g/mol); (—) correlation. (From Bogdanic, G. and Vidal, J., *Fluid Phase Equilib.*, 173, 241, 2000. With permission.)
correlate both UCST/LCST and closed-loop behavior and even show the pressure dependency of critical solution temperatures (UCST and LCST).

3.3.4.2 Extension of Free-Volume Models to Gas Solubilities in Elastomers

The second approach proposed by Thorlaksen et al. is based on a combination of the Entropic-FV term with Hildebrand’s regular solution theory and developed a model for estimating gas solubilities in elastomers. The so-called Hildebrand–Entropic-FV model is given by the equation:

\[
\ln\gamma_i = \ln\gamma_i^R + \ln\gamma_i^{C+FV} \tag{3.16}
\]

\[
\ln\gamma_i^R = \frac{V_i^L \cdot (\delta_1 - \delta_2)^2 \cdot \Phi_2^2}{R \cdot T} \tag{3.17}
\]

\[
\ln\gamma_i^{C+FV} = \ln \frac{\Phi_2^{FV}}{x_2} + 1 - \frac{\Phi_2^{FV}}{x_2}
\]

where
- \(\delta_1\) is the solvent solubility parameter
- \(\delta_2\) is the gas solubility parameter
- \(x_2\) is the gas mole fraction in liquid/polymer
- \(\Phi_2\) is the “apparent” volume fraction of solvent, given by

\[
\Phi_2 = \frac{x_2 \cdot V_i^L}{x_1 \cdot V_i^L + x_2 \cdot V_i^L}
\]
\( \Phi_{2}^{FV} \) is the “FV” fraction given by

\[
\Phi_{2}^{FV} = \frac{x_2 \cdot (V_2^{L} - V_2^{VW})}{x_2 \cdot (V_2^{L} - V_2^{VW}) + x_1 \cdot (V_1^{L} - V_1^{VW})}
\]

\( V_2^{L} \) is a hypothetical liquid volume of the (gaseous) solute.

\[
\frac{1}{x_2} = \frac{f_2^{L}}{f_2^{S}} \cdot \exp \left( \frac{V_2^{L} \cdot (\delta_1 - \delta_2)^2 \cdot \Phi_1^2}{R \cdot T} \right)
\]

(3.18)

\( \hat{f}_2^{S} \) is the fugacity of the gas

\( f_2^{L} \) is the fugacity of the hypothetical liquid, which can be estimated from the equation:

\[
\ln \frac{f_2^{L}}{P_c} = 3.54811 - \frac{4.74547}{T_r} + 1.60151 \cdot T_r - 0.87466 \cdot T_r^2 + 0.10971 \cdot T_r^3
\]

(3.19)

Finally, the gas solubility in the polymer is estimated from the equation:

\[
\frac{1}{x_2} = \frac{f_2^{L}}{f_2^{S}} \cdot \exp \left( \frac{V_2^{L} \cdot (\delta_1 - \delta_2)^2 \cdot \Phi_1^2}{R \cdot T} + \ln \left( \frac{\Phi_2^{FV}}{x_2} \right) + 1 - \frac{\Phi_2^{FV}}{x_2} \right)
\]

(3.20)

Calculations showed that the hypothetical gas “liquid” volumes are largely independent to the polymer used, and moreover, for many gases (H\(_2\), O\(_2\), N\(_2\), CO\(_2\) and C\(_2\)H\(_2\)); these are related to the critical volume of the gas by the equation:

\[
V_2^{L} = 1.776V_c - 86.017
\]

(3.21)

Very satisfactory results are obtained as shown in Table 3.10.

A final note for these “classical” activity coefficient models is that, despite the advent of advanced SAFT and other equations of state discussed next (Section 3.4), they are still quite popular and widely used in practical applications. They are also well cited in literature. For example, the historical articles by Flory and Huggins (Refs. [32,33]) are cited 998 (13.5) and 1034 (14) and the citations of the articles by Elbro et al.\( ^{35} \): 164 (6.6), Lindvig et al.\( ^{36} \): 44 (3.4), Kontogeorgis et al.\( ^{40} \): 121 (5.5), and Oishi and Prausnitz\( ^{42} \): 353 (9.5). The citations are per May 2014 and the numbers in parenthesis are citations per year.

### 3.4 SAFT FAMILY OF EQUATIONS OF STATE

#### 3.4.1 INTRODUCTION

“Statistical mechanics is that branch of physics which studies macroscopic systems from a microscopic or molecular point of view. The goal of statistical mechanics is the understanding and prediction of macroscopic phenomena and the calculation of macroscopic properties from the properties of the individual molecules making up the system.”

This is the opening paragraph of “Statistical Mechanics” written by McQuarrie,\(^64\) already in 1976. Attempts to achieve this goal of statistical mechanics have been around for a long time. For example, Wertheim\(^65\) was the first to derive an equation of state for hard-sphere systems. Carnahan and
Starling made an empirical modification to Wertheim’s solution based on molecular simulation data to arrive at what is by now the famous Carnahan–Starling equation of state. As well as being an early attempt to arrive at an engineering model using results from “hard” science (or what we might cynically call “impractical” science), this work also showed the usefulness of using results from molecular simulation. In a sense, molecular simulation fulfills the goal of statistical mechanics, in that it predicts (some) macroscopic properties using only molecular properties as input. However, molecular simulation is system specific, time consuming, and ultimately can only be as successful as the molecular model it is based upon. Thus, while it is certainly a step forward to be able to predict the properties of a system of hard spheres, the hard sphere as a model is itself an incomplete description of a real molecule. Nevertheless, increasing computer power and ever more detailed knowledge of molecular properties, extending even to the quantum level, means that molecular simulation will continue to be an important tool in engineering thermodynamics. See Economou for a review of current industrial applications of molecular simulation.

However, equations of state, too, will be an essential component of chemical engineering theory and practice for the foreseeable future, and as ever, the balance will need to be struck between rigorous theory and engineering applicability. One equation of state, which seems to have done an admirable job of bridging the gap between molecular theory and engineering application, is statistical associating fluid theory (SAFT) and it is with this equation of state and its spin-offs that the remainder of this discussion is concerned.

### TABLE 3.10
Summary of the Performance of the Models Tested at $T = 298 \text{ K}; P = 101.3 \text{ kPa}$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Gas</th>
<th>Michaels/Bixler</th>
<th>Tseng/Lloyd</th>
<th>Hildebrand/Scott</th>
<th>Hildebrand Entropic-FV-1</th>
<th>Hildebrand Entropic-FV-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIP</td>
<td>$N_2$</td>
<td>14.7</td>
<td>73</td>
<td>3.9</td>
<td>−7.9</td>
<td>−4.6</td>
</tr>
<tr>
<td></td>
<td>$O_2$</td>
<td>−16.1</td>
<td>−4</td>
<td>14</td>
<td>10.8</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>$Ar$</td>
<td>−32.5</td>
<td>−23</td>
<td>—</td>
<td>29.4</td>
<td>−22.2</td>
</tr>
<tr>
<td></td>
<td>$CO_2$</td>
<td>−3.2</td>
<td>13</td>
<td>4.5</td>
<td>8.7</td>
<td>4.6</td>
</tr>
<tr>
<td>PIB</td>
<td>$N_2$</td>
<td>−2.5</td>
<td>—</td>
<td>6.8</td>
<td>3.1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>$O_2$</td>
<td>−6.1</td>
<td>—</td>
<td>−1.7</td>
<td>−8.3</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>$Ar$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$CO_2$</td>
<td>32.8</td>
<td>—</td>
<td>−1.9</td>
<td>41.1</td>
<td>35.2</td>
</tr>
<tr>
<td>PBD</td>
<td>$N_2$</td>
<td>22.3</td>
<td>—</td>
<td>8.1</td>
<td>8.1</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>$O_2$</td>
<td>14.9</td>
<td>—</td>
<td>−6</td>
<td>8.7</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>$Ar$</td>
<td>12.1</td>
<td>—</td>
<td>—</td>
<td>111.1</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td>$CO_2$</td>
<td>−9.7</td>
<td>—</td>
<td>−4.6</td>
<td>0.4</td>
<td>−4.0</td>
</tr>
<tr>
<td>PDMB</td>
<td>$N_2$</td>
<td>—</td>
<td>—</td>
<td>−23</td>
<td>−7.5</td>
<td>−3.1</td>
</tr>
<tr>
<td></td>
<td>$O_2$</td>
<td>—</td>
<td>—</td>
<td>−32</td>
<td>−16.8</td>
<td>−15.9</td>
</tr>
<tr>
<td></td>
<td>$Ar$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
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<td>—</td>
<td>—</td>
<td>−24</td>
<td>2.3</td>
<td>−2.2</td>
</tr>
<tr>
<td>PCP</td>
<td>$N_2$</td>
<td>58.1</td>
<td>—</td>
<td>49</td>
<td>−7.0</td>
<td>−4.2</td>
</tr>
<tr>
<td></td>
<td>$O_2$</td>
<td>43.7</td>
<td>—</td>
<td>60</td>
<td>−1.4</td>
<td>−1.4</td>
</tr>
<tr>
<td></td>
<td>$Ar$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$CO_2$</td>
<td>8.8</td>
<td>—</td>
<td>27</td>
<td>−13.3</td>
<td>−17.1</td>
</tr>
<tr>
<td>AAD</td>
<td>—</td>
<td>19.8</td>
<td>28</td>
<td>18</td>
<td>16.8</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Errors associated with models for predicting gas solubilities in polymers.

Hildebrand Entropic-FV-1: The liquid volume of the gas is determined from its relationship with the critical volume, Equation 3.26. Hildebrand Entropic-FV-2: The average hypothetical liquid volume of a gas is used.
3.4.2 SAFT EQUATION OF STATE—HISTORY AND INTRODUCTION

A series of four seminal papers once again written by Wertheim\textsuperscript{68–71} appeared in 1984 and 1986. These papers laid the foundation for the associating theory (or thermodynamic perturbation theory [TPP]), which was to become the key feature in the novel molecular-based equation of state known as SAFT. The theories presented in Wertheim’s papers are highly complex and almost intractable—“essentially incomprehensible,” as one author has put it.\textsuperscript{1} However, in the period 1988–1990 at Cornell University, Chapman and coworkers\textsuperscript{72–75} performed the monumental task of transforming the abstruse theory of Wertheim into workable equations, and finally into an engineering equation of state. SAFT is by no means the only molecular-based equation of state out there—PHSC is another\textsuperscript{76} but it differs from the vast majority of other similar equations of state in one important respect—it is extensively used. In their review of SAFT published in 2001, Müller and Gubbins\textsuperscript{77} estimate that 200 articles dealing with SAFT had appeared. Since that review appeared, a further 70 or so articles have appeared dealing directly with SAFT or one of its variants. Significantly, SAFT is also now available in industrial process simulators such as ASPEN, PRO/II, and ChemCad as well as in the SPECS thermodynamics package of IVC-SEP at the Technical University of Denmark.

One of the drawbacks arising from the extensive use of SAFT is that many versions have appeared, with the result that the literature is complex and can be confusing. Here, we will try to outline the theoretical development in some detail of the original SAFT model (this too is not unambiguous, since “original SAFT” is often used to describe the version due to Huang and Radosz,\textsuperscript{78,79} which is slightly different from that of Chapman), as well as some of its modified versions. We will then summarize some of the more interesting results obtained using SAFT and its variants.

3.4.3 ORIGINAL SAFT\textsuperscript{74}

The foundation for what was to become SAFT was laid in two papers\textsuperscript{72,75} which appeared in the journal \textit{Molecular Physics} in 1988. The first of these papers developed the theory required for associating fluids, while the second focused on chain formation. However, the first paper to contain an equation of state that can realistically be called SAFT appeared in the August, 1990, issue of \textit{Industrial and Engineering Chemistry Research}.\textsuperscript{74} It is interesting that the Huang and Radosz paper appeared in the November issue of the same journal.\textsuperscript{78}

To understand exactly what occurs in SAFT, we refer to Figure 3.5, taken from Fu and Sandler.\textsuperscript{80} Initially, a pure fluid is assumed to consist of equal-sized hard spheres (b). Next a dispersive potential is added to account for attraction between the spheres (c). Typical potentials are the square-well or Lennard–Jones potential. Next each sphere is given two (or more) “sticky” spots, which enables the formation of chains (d). Finally, specific interaction sites are introduced at certain positions in the chain, which enable the chains to associate through some attractive interaction (hydrogen bonding) (e). This interactive energy is often taken to be a square-well potential. The final single molecule is shown in Figure 3.5a. Each of these steps contributes to the Helmholtz energy. The residual Helmholtz energy is given by

\[ a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}} \]  \hspace{1cm} (3.22)

where

- \( a^{\text{res}} \) is the Helmholtz energy of the segment, including both hard-sphere reference and dispersion terms
- \( a^{\text{chain}} \) is the contribution from chain formation
- \( a^{\text{assoc}} \) is the contribution from association
It is this separation of the Helmholtz energy into additive components that is partly responsible for the fact that SAFT has so many variants—each of the contributions can be considered (and modified) separately, or new terms may be added (such as polar, electrostatic, or other contributions). The individual terms may also be used outside of the context of SAFT. Thus, the term that accounts for association has been combined (with minor modification) with the SRK equation to create CPA, an equation of state, which has had remarkable success in a number of applications.\textsuperscript{81}

It is worth noting that both the chain formation and the association term derive from Wertheim's TPT. However, chains (i.e., covalent bonds) are formed in the limit of complete association. It is these two terms that make up the innovative development in SAFT—the first because now we have available a rational method for considering polymer molecules (linear chains with very many bonded segments) and the second because we can now consider associating molecules in a way that more closely resembles the actual physical picture. The calculation of useful thermodynamic properties from $a_{assoc}$ was initially a complex procedure, although Michelsen and Hendriks\textsuperscript{82} simplified the computations considerably by recasting the equations in a simpler, although mathematically equivalent form.

We now consider each of the terms individually. We follow the original notation of Chapman et al.\textsuperscript{74} Each pure component is characterized by a chain length $m$, a size-parameter $\sigma$, and an energy parameter, $\varepsilon$. If the molecule is self-associating, there are two further parameters,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3_5.png}
\caption{Procedure to form a molecule in the SAFT model. (a) The proposed molecule. (b) Initially the fluid is a hard-sphere fluid. (c) Attractive forces are added. (d) Chain sites are added and chain molecules appear. (e) Association sites are added and molecules form association complexes through association sites. (From Fu, Y.-H. and Sandler, S.I., \textit{Ind. Eng. Chem. Res.}, 34, 1897, 1995. With permission.)}
\end{figure}
which characterize the volume ($\kappa^{A,B}$) and energy ($\varepsilon^{A,B}$) of association. The association term is given for mixtures by

$$\frac{a_{\text{assoc}}}{RT} = \sum_i X_i \left[ \sum_{A,B} \ln X_i^A - \frac{X_i^A}{2} + \frac{1}{2} M_i \right]$$

(3.23)

where

$X_i^A$ is the mole fraction of molecules $i$ not bonded at site $A$

$M_i$ is the number of association sites on molecule $i$

We have

$$X_i^A = \left[ 1 + N_{AV} \sum_j \sum_{ij} \rho_j X_j^B \Delta^{A,B} \right]^{-1}$$

(3.24)

where

$N_{AV}$ is the Avogadro's number

$\rho_j$ is the molar density of $j$

$\Delta^{A,B}$ is the association strength given by

$$\Delta^{A,B} = d_{ij}^3 g_{ij}(d_{ij})^{n \sigma} \kappa^{A,B} \left[ \exp \left( \frac{\varepsilon^{A,B}}{kT} \right) - 1 \right]$$

(3.25)

Here $d_{ij}$ is a temperature-dependent size-parameter related to $\sigma_{ij}$ by

$$d = \sigma f \left( \frac{kT}{\varepsilon}, m \right)$$

(3.26)

where

$$f \left( \frac{kT}{\varepsilon}, m \right) = \frac{1 + 0.2977 kT/\varepsilon}{1 + 0.33163 kT/\varepsilon + f(m)(kT/\varepsilon)^2}$$

(3.27)

and

$$f(m) = 0.0010477 + 0.025337 \frac{m-1}{m}$$

(3.28)

This temperature dependence is incorporated to account for the fact that real molecules are not hard spheres, but rather there is some degree of interpenetration between molecules, particularly at high temperatures. Thus, the “effective” hard-sphere diameter of a segment is smaller at higher temperatures. The radial distribution function in Equation 3.25 is given by the mixture version of the Carnahan–Starling equation of state for hard-sphere mixtures:

$$g_{ij}^{\text{res}} (d_{ij}) = g_{ij}^{\text{HS}} (d_{ij}) = \frac{1}{1 - \xi_3} + \frac{d_i d_j}{d_i + d_j} \frac{3 \xi_2}{(1 - \xi_3)^2} + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2 \xi_3^3}{(1 - \xi_3)^3}$$

(3.29)
where

\[ \zeta_i = \frac{\pi N_{AV}}{6} \rho \sum_i X_i m_i d_i^p \] (3.30)

For the chain term in Equation 3.22, we have

\[ \frac{a_{\text{chain}}}{RT} = \sum_i X_i (1 - m_i) \ln (g_a(d_i))_{HS} \] (3.31)

Finally, for the segment term in Equation 3.22, we have

\[ a_{\text{seg}} = a_{0}^{\text{seg}} \sum_i X_i m_i \] (3.32)

where the 0 subscript indicates a nonassociated segment. The segment energy consists of a hard-sphere reference and a dispersion contribution:

\[ a_{0}^{\text{seg}} = a_{0}^{\text{HS}} + a_{0}^{\text{disp}} \] (3.33)

The Carnahan–Starling equation \(^{66}\) is used for both pure components and mixtures to give

\[ \frac{a_{0}^{\text{HS}}}{RT} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \] (3.34)

where for mixtures \( \eta = \zeta_2 \) as defined by Equation 3.30. The dispersion term is given by

\[ a_{0}^{\text{disp}} = \frac{\varepsilon R}{k} \left( a_{01}^{\text{disp}} + \frac{a_{02}^{\text{disp}}}{T_R} \right) \] (3.35)

where

\[ a_{01}^{\text{disp}} = \rho_R \left[ -0.85959 - 4.5424\rho_R - 2.1268\rho_R^2 + 10.285\rho_R^3 \right] \] (3.36)

\[ a_{02}^{\text{disp}} = \rho_R \left[ -1 - 9.075 - 9.9724\rho_R - 22.216\rho_R^2 + 15.904\rho_R^3 \right] \] (3.37)

The reduced quantities are given by \( T_R = kT/(\varepsilon) \) and \( \rho_R = (6/20.5\pi)\eta \).

Most of the results of this initial paper are comparisons with simulation data for chains with various parameters, although pure-component parameters for six hydrocarbons and two associating fluids were fitted. No results for mixtures of real fluids are presented.

### 3.4.4 “Original” SAFT\(^{78}\)

Probably the main contribution of the Huang and Radosz\(^{78}\) version of SAFT was the regression of pure-component parameters for over 100 different fluids. There are also some notational
differences. Thus, instead of a size parameter $\sigma$, they use a volume parameter $v^0_0$, which is related through the equation

$$v^0_0 = \frac{\pi N_A v}{6 \tau}$$

(3.38)

Here $\tau = 0.74048$ is the highest possible packing fraction for a system of pure hard spheres. They also use the notation $u^0$ instead of $\varepsilon$ for the energy parameter, although these terms are completely equivalent.

The rather complex temperature dependence of the hard-sphere diameter given by Equations 3.26 through 3.28 was simplified by Huang and Radosz, following Chen and Kreglewski to

$$d = \sigma \left[ 1 - 0.12 \exp \left( \frac{-3u^0}{kT} \right) \right]$$

(3.39)

The dispersion term is also different from that of Chapman et al. and is given by

$$\frac{D_{ij}^{\text{disp}}}{RT} = \sum_i \sum_j D_{ij} \left( \frac{u}{kT} \right)^i \left( \frac{\eta}{\tau} \right)^j$$

(3.40)

where

- $D_{ij}$ are universal constants
- $u$ is the temperature-dependent energy parameter given by $u = u^0(1 + e/kT)$ and $e/k$ is a constant set to $-10$, with a few exceptions

Another important contribution of Huang and Radosz is the presentation of detailed tables discussing bonding schemes for different associating fluids. These schemes are presented as Tables 3.11 and 3.12 and have been widely adopted in the literature of SAFT and other equations of state for associating fluids.

In their paper on mixture properties, Huang and Radosz also use the full mixture version of the Carnahan–Starling equation for the hard-sphere mixtures reference system:

$$\frac{a_{\text{HS}}}{RT} = \frac{1}{\xi_0} \left[ \frac{3\xi_1\xi_2}{1 - \xi_3} + \frac{\xi_2^3}{\xi_3(1 - \xi_3)^2} + \left( \frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1 - \xi_3) \right]$$

(3.41)

One of the reasons that the Huang and Radosz version of SAFT has been adopted (and is widely referred to as “original” SAFT) is that they undertook an extensive pure-component parameterization for over 100 pure fluids. This meant that their equation of state could be used immediately for real fluids of industrial interest without any intermediate steps. Both Huang and Radosz were employed by Exxon during the development of SAFT. The fact that the model had the backing of a major oil company may also help explain its rapid adoption and use as an engineering tool.

Besides it is interesting to note that the first paper to appear describing PC-SAFT also had pure-component parameters for about 100 species. This fact, coupled with the success of the model, has certainly been partly responsible for the rapid adoption of PC-SAFT in the few years it has been in existence, both in industry and in academia.
### TABLE 3.11
Unbonded Site Fractions $X^A$ for Different Bonding Types

<table>
<thead>
<tr>
<th>Type</th>
<th>$\Delta$ Approximations</th>
<th>$X^A$ Approximations</th>
<th>$X^A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\Delta^{AA} \neq 0$</td>
<td>$X^A = X^B$</td>
<td>$\frac{-1 + (1 + 4\rho\Delta)^{1/2}}{2\rho\Delta}$</td>
</tr>
<tr>
<td>2A</td>
<td>$\Delta^{AA} = \Delta^{BB} \neq 0$</td>
<td>$X^A = X^B$</td>
<td>$\frac{-1 + (1 + 8\rho\Delta)^{1/2}}{4\rho\Delta}$</td>
</tr>
<tr>
<td>2B</td>
<td>$\Delta^{AA} = \Delta^{BB} = 0$</td>
<td>$X^A = X^B$</td>
<td>$\frac{-1 + (1 + 4\rho\Delta)^{1/2}}{2\rho\Delta}$</td>
</tr>
<tr>
<td>3A</td>
<td>$\Delta^{AA} = \Delta^{AB} = \Delta^{AC} = \Delta^{BC} = \Delta^{CC} \neq 0$</td>
<td>$X^A = X^B = X^C$</td>
<td>$\frac{-1 + (1 + 12\rho\Delta)^{1/2}}{6\rho\Delta}$</td>
</tr>
<tr>
<td>3B</td>
<td>$\Delta^{AA} = \Delta^{AB} = \Delta^{BC} = 0$</td>
<td>$X^A = X^B$</td>
<td>$\frac{-1 - 2\rho\Delta + ((1 + \rho\Delta)^2 + 4\rho\Delta)^{1/2}}{6\rho\Delta}$</td>
</tr>
<tr>
<td>4A</td>
<td>$\Delta^{AA} = \Delta^{AB} = \Delta^{AC} = \Delta^{BC} = \Delta^{CC} = \Delta^{AD} = \Delta^{BD} = \Delta^{CD} = \Delta^{DD} \neq 0$</td>
<td>$X^A = X^B = X^C = X^D$</td>
<td>$\frac{-1 + (1 + 16\rho\Delta)^{1/2}}{8\rho\Delta}$</td>
</tr>
<tr>
<td>4B</td>
<td>$\Delta^{AA} = \Delta^{AB} = \Delta^{AC} = \Delta^{BC} = \Delta^{CC} = \Delta^{DD} = 0$</td>
<td>$X^A = X^B = X^C$</td>
<td>$\frac{-1 - 2\rho\Delta + ((1 + 2\rho\Delta)^2 + 4\rho\Delta)^{1/2}}{6\rho\Delta}$</td>
</tr>
<tr>
<td>4C</td>
<td>$\Delta^{AA} = \Delta^{AB} = \Delta^{AC} = \Delta^{BC} = \Delta^{CD} = \Delta^{DD} \neq 0$</td>
<td>$X^A = X^B = X^C = X^D$</td>
<td>$\frac{-1 + (1 + 8\rho\Delta)^{1/2}}{4\rho\Delta}$</td>
</tr>
</tbody>
</table>


### TABLE 3.12
Types of Bonding in Real Associating Fluids

<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>Rigorous Type</th>
<th>Assigned Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>C(\begin{array}{cc}O &amp; H \end{array})O(\begin{array}{c}C\end{array})</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Alkanol</td>
<td>O(\begin{array}{c}A\end{array})(\begin{array}{c}O\end{array})B</td>
<td>3B</td>
<td>2B</td>
</tr>
<tr>
<td>Water</td>
<td>B(\begin{array}{c}O\end{array})A(\begin{array}{c}H\end{array})C(\begin{array}{c}D\end{array})</td>
<td>4C</td>
<td>3B</td>
</tr>
<tr>
<td>Amines</td>
<td>N(\begin{array}{c}A\end{array})</td>
<td>1</td>
<td>Non-self-associating</td>
</tr>
<tr>
<td>Tertiary</td>
<td>A(\begin{array}{c}N\end{array})H</td>
<td>2B</td>
<td>2B</td>
</tr>
<tr>
<td>Secondary</td>
<td>A(\begin{array}{c}N\end{array})H</td>
<td>2B</td>
<td>2B</td>
</tr>
<tr>
<td>Primary</td>
<td>A(\begin{array}{c}N\end{array})H</td>
<td>3B</td>
<td>3B</td>
</tr>
<tr>
<td>Ammonia</td>
<td>A(\begin{array}{c}H\end{array})N(\begin{array}{c}H\end{array})B(\begin{array}{c}D\end{array})</td>
<td>4B</td>
<td>3B</td>
</tr>
</tbody>
</table>

3.4.5 **Simplified SAFT**

The key idea in the work of Fu and Sandler is the simplification of the dispersion term. All other terms from Huang and Radosz are retained. Since the dispersion term given by Huang and Radosz, Equation 3.40, contains 24 constants, it seems reasonable to attempt to simplify this term. For mixtures, the dispersion Helmholtz free energy is

\[
\alpha^{\text{disp}} = mZ_M \ln \left( \frac{v_s}{v_s + \langle v^*_Y \rangle} \right)
\]

(3.42)

where

- “average” chain length \( m = \sum_i x_i m_i \)
- \( Z_M = 36 \) is the maximum coordination number
- \( v_s = 1/\rho m \) is the total molar volume of a segment

\[
\langle v^*_Y \rangle = N_{AV} \frac{\sum_i \sum_j x_i x_j m_i m_j \left( d_{ij}^3 / \sqrt{2} \right) \left[ \exp(u_{ij}/kT) - 1 \right]}{\sum_i \sum_j x_i x_j m_i m_j}
\]

(3.43)

The remaining terms have the same meaning as in Huang and Radosz. Generally, simplified SAFT performs as well as Huang and Radosz SAFT, although it requires refitting all the pure-component parameters. Fu and Sandler provide parameters for 10 nonassociating and 8 associating fluids. Table 3.13 is reproduced from Fu and Sandler. It is interesting because it presents different types of cross-association in some detail. This scheme is completely general and applicable to any equation of state incorporating association. Combining rules for cross-association also need to be introduced, however, and are far from self-evident.

3.4.6 **LJ-SAFT**

The main change in the SAFT version of Kraska and Gubbins is that they use Lennard–Jones (LJ) spheres for the reference term, rather than hard spheres. The remaining terms are unchanged, except that the radial distribution function used in the calculation of the chain and association contributions in Equations 3.25 and 3.31 is the radial distribution function for LJ spheres rather than hard spheres. Thus, an equation of state for LJ spheres is required. The equation used is that of Kolafa and Nezbeda. The Helmholtz energy for the reference (LJ) system is (for a pure fluid)

\[
A_{\text{ref}} = m \left( A_{\text{HS}} + \exp(-\gamma \rho^{*2}) \rho T \Delta B_{2,\text{MBH}} + \sum_{i,j} C_{ij} T^{i/2} \rho^{*j} \right)
\]

(3.44)

where

\[
A_{\text{HS}} = T \left( \frac{5}{3} \ln(1-\eta) + \frac{\eta(34 - 33\eta + 4\eta^2)}{6(1-\eta)^2} \right)
\]

(3.45)

\[
\Delta B_{2,\text{MBH}} = \sum_{i=0}^{0} C_i T^{i/2}
\]

(3.46)
Apart from using a different reference system, the notation in Kraska and Gubbins does not follow the customary SAFT notation, nor are the pure-component parameters defined in the same way (e.g., the energy parameter with units of 1/K is defined inversely as a temperature parameter with units K) and care should be taken in using it. They also incorporate a term to account for dipole–dipole interactions.

### Table 3.13

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Component 1</th>
<th>Component 2</th>
<th>Association Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid–acid</td>
<td>Site A₁</td>
<td>Site A₂</td>
<td>$\varepsilon^{A_i A_j} \neq 0$</td>
</tr>
<tr>
<td>Alcohol–alcohol</td>
<td>Site B₁</td>
<td>Site B₂</td>
<td>$\varepsilon^{B_i B_j} \neq 0$</td>
</tr>
<tr>
<td>Acid–alcohol</td>
<td>Site A₁</td>
<td>Site A₂</td>
<td>$\varepsilon^{A_i A_j} \neq 0$</td>
</tr>
<tr>
<td>Water–acid</td>
<td>Site C₁</td>
<td>Site A₂</td>
<td>$\varepsilon^{A_i C_j} = 0$</td>
</tr>
<tr>
<td>Water–alcohol</td>
<td>Site C₁</td>
<td>Site A₂</td>
<td>$\varepsilon^{A_i C_j} = 0$</td>
</tr>
</tbody>
</table>


$$\rho^* = \frac{mb}{V_m} \quad (3.47)$$

$$\eta = \frac{\pi}{6} \rho^* \sigma_{BH}^3 \quad (3.48)$$

$$\alpha_{BH} = \sum_{i=2}^{1} D_i T^{i/2} + D_{ln} \ln T \quad (3.49)$$
SAFT-VR is the version of SAFT developed by George Jackson and coworkers first at the University of Sheffield and currently at Imperial College (Gil-Vilegas et al.; McCabe et al.). SAFT-VR is identical to the Huang and Radosz version except in the dispersion contribution. This term incorporates attraction in the form of a square-well potential. Thus, in addition to a segment being characterized by a size and an energy parameter, the square-well width ($\lambda$) is also included as a pure-component parameter. Thus, changing the parameter $\lambda$ changes the range of attraction of the segment (hence the name VR for “variable range”). It is the introduction of this extra term that gives SAFT-VR greater flexibility, since we now have an extra pure component to “play with.” Although it is generally desirable to describe pure-component liquid densities and vapor pressure with the minimum number of parameters, the extra variable-range parameter may be necessary for the description of certain anomalous behaviors in systems containing water. The Helmholtz energy for the dispersion energy is given by

$$\alpha^{\text{disp}} = \frac{a_1}{kT} + \frac{a_2}{(kT)^2}$$  \hspace{1cm} (3.50)

where

$$a_1 = -\rho_s \sum_i \sum_j x_{ij} x_{ij} \alpha^{\text{VDW}}_{ij} g^{\HS} \left[ \sigma_{ij} \zeta_{ij}^{\text{eff}} \right]$$  \hspace{1cm} (3.51)

The subscript $s$ refers to segment rather than molecule properties. We have

$$\alpha^{\text{VDW}}_{ij} = \frac{2\pi \varepsilon_{ij} \sigma_{ij}^3 (\lambda_{ij} - 1)}{3}$$  \hspace{1cm} (3.52)

and $g^{\HS}$ is the radial distribution function for hard spheres as before except that the arguments are different:

$$\zeta_{ij}^{\text{eff}} = c_1 \zeta_{ij}^1 + c_2 \zeta_{ij}^2 + c_3 \zeta_{ij}^3$$  \hspace{1cm} (3.53)

$$\alpha_{ij} = \sum_i \sum_j x_{ij} x_{ij} \sigma_{ij}^3$$  \hspace{1cm} (3.54)

$$\zeta_{ij} = \frac{\pi}{6} \rho_s \sigma_{ij}^3$$  \hspace{1cm} (3.55)

The constants $c_j$ in Equation 3.53 are given by

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.66927 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_{ij} \\ \lambda_{ij}^2 \end{pmatrix}$$  \hspace{1cm} (3.56)
The second-order term in Equation 3.50 is given by

\[ a_2 = \sum_{i=1}^{n} \sum_{j=1}^{n} x_{i,j} x_{i,j} \frac{1}{2} K_{HS} \varepsilon_0 \rho_s \frac{\partial a_i}{\partial \rho_s} \]  

(3.57)

where

\[ K_{HS} = \frac{\zeta_0 (1 - \xi_3)^4}{\zeta_0 (1 - \xi_3)^2 + 6 \zeta_5 (1 - \xi_3) + 9 \zeta_2^4} \]  

(3.58)

3.4.8 PC-SAFT

A recent version of SAFT that has appeared is that due to Gross and Sadowski developed at the Technical University of Berlin. Once again, most of the terms in PC-SAFT are the same as those in the Huang and Radosz version. The term that is different is the dispersion term. However, it is not simply a different way of expressing the dispersion attraction between segments, but rather it tries to account for dispersion attraction between whole chains. Referring to Figure 3.5 should make this clear. Instead of adding the dispersion to hard spheres and then forming chains, we first form hard-sphere chains and then add a chain dispersion term, so the route in Figure 3.5 would be (b)–(d)–(c)–(e). To do this, we require interchain rather than intersegment radial distribution functions. These are given by O’Lenick et al. The Helmholtz energy for the dispersion term is given as the sum of a first- and second-order term:

\[ \frac{A_{\text{disp}}}{kT \rho_m} = \frac{A_1}{kT} + \frac{A_2}{kT} \]  

(3.59)

where

\[ A_1 = -2 \pi \rho m^2 \left( \frac{\varepsilon}{kT} \right) \sigma^3 \int_{1}^{\infty} \tilde{u}(x) g^{hc}(m; \frac{\rho \sigma^3}{d}) x^2 dx \]  

(3.60)

\[ A_2 = -\pi \rho m \left( 1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho} \right) m^2 \left( \frac{\varepsilon}{kT} \right)^2 \sigma^3 \frac{\partial}{\partial \rho} \left[ \int_{1}^{\infty} \tilde{u}(x)^2 g^{hc}(m; \frac{\rho \sigma^3}{d}) x^2 dx \right] \]  

(3.61)

where

\[ x = \frac{r}{\sigma} \]

\[ \tilde{u}(x) = u(x)/\varepsilon \] is the reduced intermolecular potential.

The radial distribution function \( g^{hc} \) is now an interchain function rather than a segment function as before. This is a key point in PC-SAFT. The term involving compressibilities is given by

\[ \left( 1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho} \right) = \left( 1 + m \frac{8 \eta - 2 \eta^2}{(1 - \eta)^4} + (1 - m) \frac{20 \eta - 27 \eta^2 + 12 \eta^3 - 2 \eta^4}{((1 - \eta)(2 - \eta))^2} \right) \]  

(3.62)
We still need to solve the integrals in Equations 3.60 and 3.61. Setting

\[ I_1 = \int_1^{\infty} \tilde{u}(x) g_{hc} \left( \frac{m; \frac{x \sigma}{d}}{d} \right) x^2 \, dx \]  
(3.63)

\[ I_2 = \frac{\partial}{\partial \rho} \left[ \rho \int_1^{\infty} \tilde{u}(x)^2 g_{hc} \left( \frac{m; \frac{x \sigma}{d}}{d} \right) x^2 \, dx \right] \]  
(3.64)

we can substitute the Lennard–Jones potential and the radial distribution function of O’Lenick et al.\(^\text{90}\) This was done for the series of \(n\)-alkanes and the integrals were fit as a power series:

\[ I_1 = \sum_{i=0}^{6} a_i \eta^i \]  
(3.65)

\[ I_2 = \sum_{i=0}^{6} b_i \eta^i \]  
(3.66)

with

\[ a_i = a_{0i} + \frac{m-1}{m} a_{1i} + \frac{m-1}{m} \frac{m-2}{m} a_{2i} \]  
(3.67)

\[ b_i = b_{0i} + \frac{m-1}{m} b_{1i} + \frac{m-1}{m} \frac{m-2}{m} b_{2i} \]  
(3.68)

Equations 3.67 and 3.68 require a total of 42 constants, which are adjusted to fit experimental pure-component data of \(n\)-alkanes. This direct fitting to experimental data to some extent accounts for errors in the reference equation of state, the perturbing potential, and the radial distribution function, which appear in the integrals of Equations 3.63 and 3.64. The dispersion potential given by Equations 3.60 and 3.61 is readily extended to mixtures using the van der Waals one-fluid theory.

Since this first PC-SAFT paper appeared, the authors rapidly published a series of further papers applying PC-SAFT to polymers,\(^91,92\) associating fluids\(^93\) and copolymers.\(^94\)

### 3.4.9 Simplified PC-SAFT\(^95\)

Two simplifications to PC-SAFT have been proposed, which simplify phase equilibrium calculations substantially for mixtures. For pure components, this simplified PC-SAFT becomes original PC-SAFT, so the simplifications may be considered as a particular set of mixing rules. The advantage of this is that existing pure-component parameters can be used in simplified PC-SAFT—no refitting is required. The targets of the simplifications are Equations 3.29 and 3.41. In other words, this simplified PC-SAFT targets the hard-sphere reference equation of state. The remaining terms are the same, except as mentioned previously, the simpler radial distribution function will affect both the chain and association terms, since the radial distribution function appears in both of these terms.
By setting \( \eta \equiv \zeta_3 \), Equations 3.29 and 3.40 reduce to

\[
g^{\text{HS}}(d^*) = \frac{1 - \eta/2}{(1 - \eta)^3} \tag{3.69}
\]

and

\[
\tilde{d}^{\text{HS}} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \tag{3.70}
\]

respectively. In the initial paper,\(^{95}\) use of Equation 3.69 only is called modification 1, while use of both Equations 3.69 and 3.70 is called modification 2. This and subsequent work has shown that there is no loss of accuracy using the most simplified version of PC-SAFT, so modification 2 is used throughout and is called “simplified PC-SAFT.” Simplified PC-SAFT has since been applied in our group to several polymer systems including: polymer VLE,\(^{96}\) polymer–solvent binary LLE,\(^{97}\) ternary polymer–solvent and blend systems,\(^{98}\) and high-pressure gas solubility in polymers.\(^{99,100}\)

One of the interesting points about SAFT in general is the ability to extrapolate the properties of higher molecular weight substances from knowledge of similar shorter chain compounds. This is most evident for the \( n \)-alkane series. Pure-component parameters for polyethylene can in principle be predicted by extrapolating from the properties of the \( n \)-alkanes. In practice, this is problematic, since for very long chains, effects such as entanglement of the individual polymer chains start to influence the behavior. Figure 3.6 shows PC-SAFT parameters for the alkanes up to eicosane (C20). The parameters \( m \), \( m\sigma^3 \), and \( m\varepsilon/k \) are all linear with molecular weight. Tables 3.14 and 3.15 show computing times for simplified PC-SAFT compared with original PC-SAFT, as well as with other equations of state.

FIGURE 3.6 The groups \( m \), \( m\sigma^3 \), and \( m\varepsilon/k \) vs. molecular weight for linear alkanes up to eicosane. Points are PC-SAFT parameters, lines are linear fits to these points, excluding methane. (From von Solms, N. et al., Ind. Eng. Chem. Res., 42, 1098, 2003. With permission.)
### 3.4.10 Extensions to SAFT-Type Equations

The additive contributions within SAFT mean that the equation of state is quite versatile—contributions can be added to account for effects not included in the discussion earlier. Thus, papers have appeared accounting for polar,\(^{101}\) quadrupolar,\(^{102}\) and dipolar\(^{103}\) molecules, as well as polarizable dipoles.\(^{104}\)

Versions of SAFT have also appeared, which include an electrostatic contribution, the intention being to develop a version of SAFT suitable for modeling electrolytes.\(^{105,106}\)

Care should be taken when adding very many contributions, since each extra contribution will almost always require one or more pure-component parameters. The actual physical picture should always be borne in mind when considering which contributions to include.

Another recent development is the application of group contribution methods to SAFT (see, e.g., Le Thi et al.\(^{107}\) and references therein). Rather than the addition of extra terms, which then require more pure-component parameters, the use of group contribution methods is an attempt to generalize the parameters in SAFT (extending even to binary interaction parameters). The hope is that in this way SAFT becomes a more predictive tool, relying less on fitting of parameters to experimental data.

---

#### TABLE 3.14
Comparison of Computing Times for 36-Component Phase-Envelope Calculation with PC-SAFT and with Simplified PC-SAFT

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Computing Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase-envelope calculation, 36-component mixture, full PC-SAFT</td>
<td>48</td>
</tr>
<tr>
<td>Phase-envelope calculation, 36-component mixture, PC-SAFT modification 2</td>
<td>32</td>
</tr>
</tbody>
</table>


#### TABLE 3.15
Comparison of Computing Times for Various Models and Mixtures

<table>
<thead>
<tr>
<th>Mixture Model</th>
<th>Computing Time (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fugacity Coefficients Only</td>
</tr>
<tr>
<td>SRK, 6 components</td>
<td>1.9</td>
</tr>
<tr>
<td>SRK, 6 components</td>
<td>3.1</td>
</tr>
<tr>
<td>CPA, 15 components, 0 sites</td>
<td>15</td>
</tr>
<tr>
<td>CPA, 15 components, 2 sites</td>
<td>18.5</td>
</tr>
<tr>
<td>CPA, 15 components, 4 sites</td>
<td>24.4</td>
</tr>
<tr>
<td>CPA, 15 components, 6 sites</td>
<td>32.3</td>
</tr>
<tr>
<td>CPA, 15 components, 8 sites</td>
<td>40.7</td>
</tr>
<tr>
<td>Modification 2, 15 components, 0 sites</td>
<td>15.6</td>
</tr>
<tr>
<td>Modification 2, 15 components, 6 sites</td>
<td>39.1</td>
</tr>
</tbody>
</table>


Number of sites refers to number of association sites on a molecule when employing an equation of state with association.

3.4.11 Applications of SAFT

The remainder of this discussion looks at some polymer applications of SAFT. Figure 3.7 shows the results of using parameters extrapolated based on Figure 3.6. The system is methane–tetratetracontane (C44), where the C44 parameters are obtained by extrapolation of the lines in Figure 3.6. While this is not a polymer system, the method of obtaining parameters by extrapolation is applicable to polymer systems. A more sophisticated method for finding polymer parameters based on extrapolation of the monomer properties and polymer density data has been published recently.108

Figures 3.8 and 3.9 show a comparison of the various modifications and original PC-SAFT for VLE in the systems polystyrene–propyl acetate (Figure 3.8) and polypropylene–diisopropyl ketone (Figure 3.9). In general, PC-SAFT and simplified PC-SAFT performed similarly, as can be seen from Table 3.16, which gives the errors in prediction for a large number of polymer–solvent VLE systems. Figure 3.10 is a pressure–weight fraction diagram (VLE) for the polymer poly(vinyl acetate) in the associating solvent 2-methyl-1-propanol. A small value of the binary interaction parameter correlates the data well.

Figure 3.11 is an illustration of a novel method developed by von Solms et al.97 for finding LLE in polymer systems, known as the method of alternating tangents. This figure shows the Gibbs energy of mixing for two binary systems as a function of the mole fraction of component 1. The method will be illustrated with reference to the system methanol(1)–cyclohexane(2), since this curve clearly shows the existence of two phases. The composition of methanol in each phase is found by locating a single line, which is a tangent to the curve in two places (the common tangent). In Figure 3.11, these compositions are given by $x_{eq1}^{eq1}$ and $x_{eq2}^{eq2}$. In fact the curve for the system PS(1)–acetone(2) also shows the existence of two phases, although this is not visible. The first step in the procedure is to determine whether a spinodal point exists (this is a necessary condition for phase separation). In the figure, the two spinodal points are given by the compositions $x_{sp1}^{sp1}$ and $x_{sp2}^{sp2}$. The spinodal condition is given by $(\partial^2 g_{mix}/\partial x^2) = 0$, that is, an inflection point on the curve. Once a spinodal point has been found (using a Newton–Raphson method), the next step is to find the point of tangent of a
FIGURE 3.8 Vapor pressure curve for the system propyl acetate(1)–polystyrene(2) at \( T = 343.15 \) K. The dashed line is PC-SAFT (the lowest line on the plot), the solid line is modification 1, and the dotted line is modification 2. Points are experimental data. All lines are pure predictions \( (k_{ij} = 0) \). (From von Solms, N. et al., *Ind. Eng. Chem. Res.*, 42, 1098, 2003. With permission.)

FIGURE 3.9 Pressure–weight fraction plot of polypropylene(1)–diisopropyl ketone(2) at \( T = 318 \) K. Polypropylene molecular weight = 20,000. Comparison of experimental data with the predictions of original (solid line) and the simplified version (dotted line) of PC-SAFT. In both curves, the interaction parameter \( k_{ij} = 0 \). (From *Fluid Phase Equilib.*, 215, Kouskoumvekaki, I.A., von Solms, N., Michelsen, M.L., and Kontogeorgis, G.M., Application of a simplified perturbed chain SAFT equation of state to complex polymer systems, 71–78, Copyright 2004, with permission from Elsevier.)
line originating at the spinodal point. In the figure, this is the line connecting $x_{i1}^{sp1}$ and $x_{j}$. This point is just to the left of $x_{i1}^{eq2}$ (i.e., we are not yet quite at the equilibrium concentration after one step). Once the first tangent has been found, the point of tangent opposite is then found in a similar way. This process is repeated until the change in the composition at the tangent point is within a specified tolerance. At this point, the equilibrium values have been calculated.

### TABLE 3.16
Comparison of the Performance of the Simplified against the Original PC-SAFT in Predicting Vapor–Liquid Equilibria of Polymer Solutions ($k_{ij} = 0$ in All Cases)

<table>
<thead>
<tr>
<th>% AAD</th>
<th>PC-SAFT</th>
<th>Simplified Version</th>
<th>Original Version</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cyclic hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS–cyclohexane</td>
<td>13</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>PS–benzene</td>
<td>28</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>PS–ethyl benzene</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>PS–m-xylene</td>
<td>25</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>PS–toluene</td>
<td>18</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>PVAc–benzene</td>
<td>6</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td><strong>Chlorinated hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS–carbon tetrachloride</td>
<td>18</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>PS–chloroform</td>
<td>30</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>PP–dichloromethane</td>
<td>59</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>PP–carbon tetrachloride</td>
<td>55</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td><strong>Esters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS–propyl acetate</td>
<td>5</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>PS–butyl acetate</td>
<td>3</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>PVAc–methyl acetate</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>PVAc–propyl acetate</td>
<td>19</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td><strong>Ketones</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS–acetone</td>
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Average percentage deviation between experimental and predicted equilibrium pressure curves.
FIGURE 3.10 Pressure–weight fraction plot of poly(vinyl acetate)(1)–2-methyl-1-propanol(2) at \( T = 313 \) K. Comparison of experimental data with prediction \((k_{ij} = 0)\) and correlation \((k_{ij} = -0.012)\) results of simplified PC-SAFT. Poly(vinyl acetate) molecular weight = 167,000. (From *Fluid Phase Equilib.*, 215, Kouskoumvekaki, I.A., von Solms, N., Michelsen, M.L., and Kontogeorgis, G.M., Application of a simplified perturbed chain SAFT equation of state to complex polymer systems, 71–78, Copyright 2004, with permission from Elsevier.)

FIGURE 3.11 Illustration of the method of alternating tangents. The solid line is the system methanol(1)–cyclohexane(2). The dotted line is the system PS(1)–acetone. The two spinodal points are indicated by \( x_{1}^{eq1} \) and \( x_{1}^{eq2} \). The equilibrium (binodal) points are indicated by \( x_{1}^{eq1} \) and \( x_{1}^{eq2} \). Starting from a spinodal point, the equilibrium values can be calculated by solving for only one point at a time. (From *Fluid Phase Equilib.*, 222–223, von Solms, N., Kouskoumvekaki, I.A., Lindvig, T., Michelsen, M.L., and Kontogeorgis, G.M., A novel approach to liquid-liquid equilibrium in polymer systems with application to simplified PC-SAFT, 87–93, Copyright 2004, with permission from Elsevier.)
Figures 3.12 through 3.15 are examples of binary LLE for polymer systems. Figure 3.12 shows results for the system polystyrene–methylcyclohexane for different molecular weights of polystyrene. The experimental data are from the classic work of Dobashi et al.\textsuperscript{109} The lines are simplified PC-SAFT correlations with $k_{ij} = 0.0065$ for polystyrene molecular weights 10,200, 46,400 and 719,000 in order of increasing critical solution temperature. The data are reasonably well correlated over a very large range of molecular weight with a single value of the binary interaction parameter, $k_{ij}$. The binary interaction parameter was adjusted to give the correct upper critical solution temperature. However, the correct critical solution concentration is not obtained, although the experimental trends are correctly predicted by the model: The critical solution temperature increases, and the polymer weight fraction at the critical solution temperature decreases with increasing molecular weight.

Figure 3.13 shows results for the system polyisobutylene–diisobutyl ketone at different polymer molecular weights. The experimental data are from Shultz and Flory.\textsuperscript{110} The lines are simplified PC-SAFT correlations. A single binary interaction parameter ($k_{ij} = 0.0053$) was used for all three systems, although it seems that there is a weak dependence of molecular weight on $k_{ij}$. Incorporating a functional dependence of $k_{ij}$ on molecular weight (e.g., a linear fit) would improve the correlation. It should also be noted that these three systems represent a very large range of molecular weights.

Figure 3.14 shows the results for a single molecular weight of HDPE in five different $n$-alkanol solvents from $n$-pentanol up to $n$-nonanol. The results are well correlated using simplified PC-SAFT with a small value of the binary interaction parameter $k_{ij}$. A $k_{ij}$ value of around 0.003 gives a good correlation for all the systems, except HDPE–$n$-pentanol. In the figure, a small value ($k_{ij} = 0.0006$) was used to correlate the data, although the data is also well predicted by simplified PC-SAFT ($k_{ij} = 0$), giving an error in the upper critical solution temperature of 3 K in the case of HDPE–$n$-pentanol.

Figure 3.15 shows the results for the system HDPE–butyl acetate. This system displays both UCST and LCST behaviors. A single binary interaction parameter ($k_{ij} = 0.0156$) was used to correlate the data for both molecular weights shown. The binary interaction parameter was adjusted to

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure312.png}
\caption{Liquid–liquid equilibrium in the system polystyrene–methyl cyclohexane for different molecular weights of polystyrene. The experimental data are from Dobashi et al.\textsuperscript{109} The lines are simplified PC-SAFT correlations with $k_{ij} = 0.0065$ for polystyrene molecular weights 10,200, 46,400 and 719,000 in order of increasing critical solution temperature. (From Fluid Phase Equilib., 222–223, von Solms, N., Kouskoumvekaki, I.A., Lindvig, T., Michelsen, M.L., and Kontogeorgis, G.M., A novel approach to liquid-liquid equilibrium in polymer systems with application to simplified PC-SAFT, 87–93, Copyright 2004, with permission from Elsevier.)}
\end{figure}
FIGURE 3.13  Liquid–liquid equilibrium in the system polyisobutylene–diisobutyl ketone. PC-SAFT parameters for diisobutyl ketone were obtained by fitting to experimental liquid density and vapor pressure data in the temperature range 260–600 K. This data was taken from the DIPPR database. The parameters were: $m = 4.6179$, $\varepsilon/k = 243.72$ K, and $\sigma = 3.7032$ Å. Average percent deviations were 1.03% for vapor pressure and 0.64% for liquid density. Lines are simplified PC-SAFT correlations with $k_{ij} = 0.0053$, the same at all three molecular weights. (From Fluid Phase Equilib., 222–223, von Solms, N., Kouskoumvekaki, I.A., Lindvig, T., Michelsen, M.L., and Kontogeorgis, G.M., A novel approach to liquid–liquid equilibrium in polymer systems with application to simplified PC-SAFT, 87–93, Copyright 2004, with permission from Elsevier.)

FIGURE 3.14  Liquid–liquid equilibrium for HDPE with $n$-alkanols. Lines are simplified PC-SAFT correlations for each of the five solvents (pentanol highest, nonanol lowest). Polymer molecular weight is 20,000. Binary interaction parameters are as follows: pentanol: 0.0006; hexanol: 0.003; heptanol: 0.0025; octanol: 0.0033; and nonanol: 0.0029. (From Fluid Phase Equilib., 222–223, von Solms, N., Kouskoumvekaki, I.A., Lindvig, T., Michelsen, M.L., and Kontogeorgis, G.M., A novel approach to liquid–liquid equilibrium in polymer systems with application to simplified PC-SAFT, 87–93, Copyright 2004, with permission from Elsevier.)
give a good correlation for the UCST curve at the higher molecular weight (64,000). As mentioned earlier, the LCST curve is rather insensitive to $k_{ij}$. Nevertheless, the LCST curve is reasonably well correlated using this value. The prediction ($k_{ij} = 0$) is almost as good for the LCST curve, although the UCST will then be substantially underpredicted.

Figure 3.16 shows a ternary phase diagram for the system polystyrene–acetone–methylcyclohexane. The binary interaction parameters were obtained by fitting to the individual binary systems.
The ternary coexistence curves are predictions. The algorithm for finding ternary LLE in systems containing polymers is an extension of the binary algorithm discussed earlier and was developed by Lindvig et al.\(^98\)

Figure 3.17 from Gross et al.\(^94\) shows high pressure equilibrium for mixtures of poly(ethylene-co-methyl acrylate) (EMA) and propylene for different repeat unit compositions of EMA. As repeat units of methyl acrylate (MA) are added to the polyethylene chain, the demixing pressure at first declines, but then increases as the composition of MA increases. This effect is correctly predicted by PC-SAFT.

Finally, Figure 3.18 shows a comparison of SAFT-VR and simplified PC-SAFT in a recent study\(^100\) where the two models were compared in their ability to model multicomponent phase equilibrium in systems typical of real polyethylene reactors. The system shown here is polyethylene/nitrogen/1-butene. The results of the simplified PC-SAFT and SAFT-VR calculations for this ternary are consistent. From the figure, one can see that as butene in the vapor is replaced by nitrogen, the calculated absorption of butene decreases (not surprisingly—there is less of it to absorb). However, it is also clear that as nitrogen in the vapor is replaced by butene, absorption of nitrogen increases, even though there is less nitrogen to absorb. This suggests that there may be some enhancement/inhibition of absorption effect.

In the time since the previous edition of this work (2008), around 150 articles have appeared applying SAFT to various polymer systems. Certain newer themes become apparent here:

The use of density functional theory combined with equations of state to examine surface and structural properties is a relatively new phenomenon, resulting in equations such as iSAFT.\(^111,112\) For example, Jain et al.\(^111\) used SAFT and density functional theory to probe the structure of tethered polymer chains.

Perhaps the most frequently occurring, relatively new idea is that of group-contribution SAFT, where there has been a great deal of activity.\(^107,113–122\) Part of the motivation for a group-contribution method is the need for an equation that can be readily extended to complex molecules, where pure-component properties may be unavailable, and for which SAFT types of equation are well suited. Examples of complex systems where SAFT has been applied are biopolymers,\(^123\) hyperbranched polymers,\(^124\) and asphaltenes.\(^125\)
FIGURE 3.18 Gas absorptions in amorphous PE calculated with SAFT-VR and simplified-PC-SAFT for a range of vapor compositions of the ternary mixture of (but-1-ene + nitrogen + the reference PE [MW = 12,000 g mol\(^{-1}\)]) at \(T = 80^\circ\text{C}\): (a) 100 vapor mol\% butene (binary mixture); (b) 75% but-1-ene, 25% nitrogen; (c) 50% but-1-ene, 50% nitrogen (with a vertical scale chosen to highlight butene absorption); (d) 50% but-1-ene, 50% nitrogen (with a vertical scale chosen to highlight nitrogen absorption); (e) 20% butene, 80% nitrogen; and (f) 100% nitrogen (binary mixture). In each case, solid curves represent SAFT-VR calculations and dashed curves represent simplified-PC-SAFT calculations. (From Haslam, A.J. et al., Fluid Phase Equilib., 243, 74, 2006. With permission).
Another encouraging feature is the use of SAFT-type models in industrial applications. In addition to the asphaltene example noted earlier,125 work has appeared relevant to refrigeration126,127 and catalytic polymerization processes.128

Finally, it can be mentioned that since the review article by Müller and Gubbins,77 several monographs reviewing various aspects of SAFT have appeared.129–131

3.5 CONCLUDING REMARKS AND FUTURE CHALLENGES

Attempting to summarize in a few words the current status in polymer thermodynamics, we could state

1. Many databases (some available in computer form) and reliable group-contribution methods are available for estimating many pure polymer properties and phase equilibria of polymer solutions such as densities, solubility parameters, glass and melting temperatures, and solvent activity coefficients.

2. Simple group-contribution methods based on UNIFAC, containing corrections for the FV effects, satisfactorily predict the solvent activities and vapor–liquid equilibria for binary and ternary polymer solutions. They are less successful for the prediction of liquid–liquid equilibria if the parameters are based on VLE. They are much more successful if the parameters are based on LLE data. The combination of a simple FV expression such as that employed in the Entropic-FV model and a local-composition energetic term such as that of UNIQUAC seems to be a very promising tool for both VLE and LLE in polymer solutions. We expect that such tools may find widespread use in the future for practical applications.

3. The SAFT model will continue to be a very successful tool for polymer systems. The low-pressure and especially the high-pressure results for systems including solvents and nonpolar polymers (with emphasis to those of interest to the polyolefin industry) are very satisfactory. However, the extension to polar systems represents so far a limitation of the model. In many ways, PC-SAFT has fulfilled the early promise of SAFT—it is reasonably simple to implement (compared with many versions of SAFT), it is relatively undemanding computationally, and it has proved successful in predicting and correlating phase equilibria in many systems containing polymers and/or associating compounds. There is still work to be done, however. One area is in finding parameters for pure polymers. Since polymers are nonvolatile, one cannot use vapor-pressure regression and the energy parameter is relatively insensitive within the range of experimental $P–V–T$ data. Regressing pure-component parameters from binary systems is problematic as this leads to nonunique pure-component parameters—a situation best avoided. Another area where research is needed is in the modeling of water. There was been a great deal of effort in this area, but as yet no satisfactory model, fitting within the existing SAFT framework, has been developed for modeling water-containing systems. Examples of such deficiencies are predicting the density maximum for pure water, as well as modeling water–hydrocarbon mutual solubilities.

4. Most theoretical/modeling studies in polymer thermodynamics are limited to

   a. Organic polymers
   b. Binary systems often involving monodisperse polymers and single solvents
   c. Rather “simple” polymers (polyolefins, polystyrene, PVC, etc.)
   d. Vapor–liquid equilibria and activity coefficients
   e. “Rules of thumb” estimates of miscibility (solubility parameters, theta parameters, etc.)

Some of the future challenges in the area of polymer thermodynamics will involve

1. More emphasis to multicomponent systems including both mixed solvents, blend-solvent systems as well as the effect of polydispersity.

3. Emphasis to high-pressure systems involving both the typical nonpolar and polar polymers as well.

4. New directions such as description of “special materials” including those involving oligomers, copolymers, new structures (star-like and dendrimers), “inorganic” polymers (e.g., tin-based antifouling paints).

5. Proper account for the effects of crystallinity and cross-linking with special attention to swelling phenomena.

6. Closer collaboration with industry, for example, for testing existing theories for polymers having novel structures, for commercial polymers for which so far the structure is not revealed to academic researchers and for many other applications of practical interest. Many industrial systems are much more complex than the ones studied in academia. Closer collaboration in the future between academia and the polymer and paint/adhesives industries may further help the advancements in the area of polymer thermodynamics in the coming years.

3.A APPENDIX

3.A.1 AN EXPRESSION OF THE FH MODEL FOR MULTICOMPONENT MIXTURES

The FH model was originally developed as a model for the entropy of mixing for mixtures containing molecules of different size, but it was soon modified also to account for energetic interactions. The model can be formulated in terms of the excess Gibbs energy as follows (Lindvig et al.37):

$$G^E = G^{E,comb} + G^{E, res}$$

$$\frac{G^{E,comb}}{RT} = \sum_{i=1}^{N} n_i \ln \frac{\psi_i}{x_i}$$

$$\frac{G^{E, res}}{RT} = \sum_{i=1}^{N} \sum_{j=1}^{N} \psi_i \psi_j \sigma_{ij}$$

$$\chi_{ij} = 2 \sigma_{ij} v_i$$

Using basic thermodynamics, the following expression for the activity coefficient is obtained:

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res}$$

where the combinatorial term is given by

$$\ln \gamma_i^{comb} = \ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i}$$

and the residual term is

$$\ln \gamma_i^{res} = 2 v_i \sum_{j=1}^{NC} \psi_j a_{ij} - v_i \sum_{j=1}^{NC} \psi_j \psi_k a_{jk}$$
The aforementioned formulation of the FH model is slightly different from the conventionally used formulation using the FH interaction parameter ($\chi_{12}$), although there is an interrelationship based on the simple equation shown above.

For a binary mixture, the multicomponent equation reduces to the traditional FH residual term:

$$\ln \gamma_i^{res} = \chi_{12} \phi_2^2$$

**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BR</td>
<td>butadiene rubber</td>
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<tr>
<td>CPA</td>
<td>cubic plus association</td>
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<td>CST</td>
<td>critical solution temperature</td>
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<td>EAC</td>
<td>ethyl acetate</td>
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<tr>
<td>EoS</td>
<td>equation of state</td>
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<td>EFV</td>
<td>entropic-free volume</td>
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<td>EMA</td>
<td>poly(ethylene-co-methyl acrylate)</td>
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<tr>
<td>FH</td>
<td>Flory–Huggins (model/equation/interaction parameter)</td>
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<tr>
<td>FV</td>
<td>free-volume</td>
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<tr>
<td>GC</td>
<td>group contribution (method/principle)</td>
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<tr>
<td>GC Fl(ory)</td>
<td>group contribution Flory equation of state</td>
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<tr>
<td>GCVOL</td>
<td>group contribution volume (method for estimating the density)</td>
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<td>HDPE</td>
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<td>LCST</td>
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<td>solid–liquid–liquid equilibria</td>
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<td>SRK</td>
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<tr>
<td>vdW1f</td>
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<tr>
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REFERENCES


